

The background of pH measurement and hints for your daily work

1 A bit of history

It all began with food. Food is truly of the essence, and good food is highly valued but too rarely found. In earlier years people used to *taste* the food in order to establish the quality of a product. Working for the food industry could be a hard job.

Little did they know at the time that the **pH** of food / drinks can often yield information about its state such as whether fruit is fresh, or not or whether wine will taste sweet or bitter.

Some of them were lucky to work with pleasant products like wine or juices and they were happy. However some of them were a bit less lucky (vinegar?) and they must have been sad. Not only to make the sad ones happy but to make the happy ones even happier, science had to think up something called **potentiometry**, which then enabled people to directly *measure* the pH instead of tasting.

Not only was this the birth of proper quality control in the food industry but in conjunction with further developments allowed many other industries to grow.

2 The magic term "pH" ...

Is a liquid (or solid for that matter) acidic like lemon juice or is it basic (sometimes also termed alkaline, although this actually refers to the presence of alkali ions) like bleach?

How do we know? How do we measure? Does anyone care?

Whether a substance is acidic or basic all depends on a single ion: **H₃O⁺**, the **hydronium ion**.

If the hydronium ion is present at a concentration higher than 0.0000001 mol/l (10^{-7} mol/l) we are talking about an acidic solution. The higher the concentration of the hydronium ion the more acidic the solution is.



On the other hand concentrations below 10^{-7} mol/l H₃O⁺ lead to a basic solution.

Well, these numbers are terribly long and difficult to handle, which is probably what Mr. Sørensen 1909 thought when he

devised the pH term and pH scale. **pH** simply stands for the negative logarithm of the hydronium ion concentration. So a concentration of 10^{-7} mol/l H_3O^+ means a pH value of 7. Likewise, a H_3O^+ concentration of 0.1 mol/l would give a pH of 1. A difference of 1 in pH therefore means that the hydronium ion concentration has changed by a factor of ten! A solution at pH 6 has ten times more hydronium ions than one at pH 7.

Don't forget: a solution is

- **acidic** if the pH value is below 7;
- **basic** if the pH value is above 7;
- **neutral** if the pH value is exactly 7.

3 Modern pH measurement

3.1 The method: potentiometry

Did that word scare you? Don't let it. All potentiometry does is to measure (meter) the **voltage** (potential) caused by our friend, the hydronium ion: H_3O^+ .

However this new method gave **accuracy**, **reliability** and **faster** results than the taste of any human being. It also saved some people from early death and gave the rest of the chemical industry a chance to prosper. Finally, scientists all over the world could measure things which were previously unmeasurable.

3.2 Tools for measuring pH

As mentioned, potentiometry is a measurement of voltage. The tools used for this are:

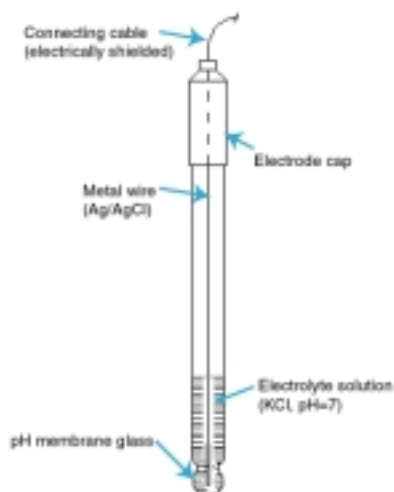
- a **pH meter** (to accurately measure and transform the voltage caused by our hydronium ion into a pH value);
- a **pH electrode** (to sense all the hydronium ions and to produce a potential);
- a **reference electrode** (to give a constant potential no matter what the concentration of our hydronium ion is).

3.2.1 The pH meter

Basically, a pH meter measures the potential between our pH electrode (which is sensitive to the hydronium ions) and the reference electrode (which doesn't care what's in the solution).

3.2.2 The pH electrode

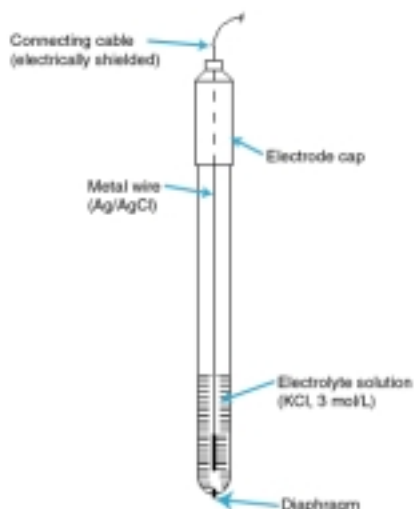
The **pH electrode's potential changes with the H_3O^+ ion concentration** in the solution. A pH electrode is built as follows:



The clever bit is that the pH electrode only senses the hydronium ions. This means that any voltage produced is from hydronium ions only. This way we can relate the potential directly to the hydronium concentration. Pretty neat.

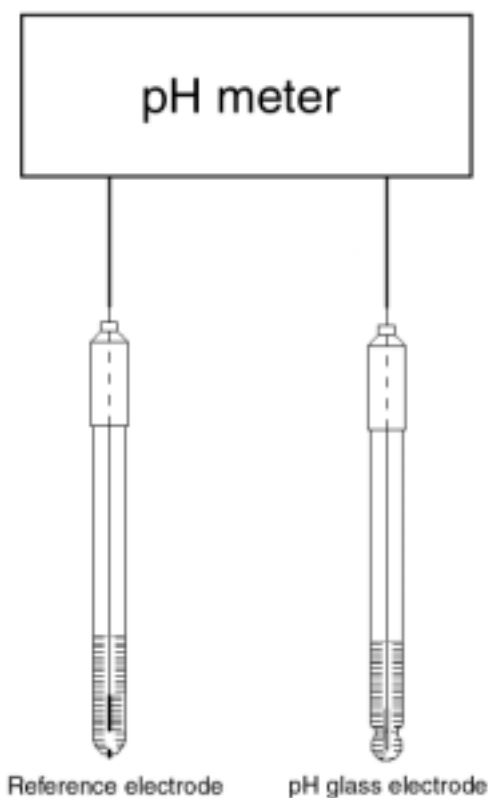
3.2.3 The reference electrode

The **reference electrode supplies a “constant” value** against which we measure the potential of the pH electrode. That's the funny thing about potentials, they have to be in pairs to produce a voltage. A reference electrode is built as follows:



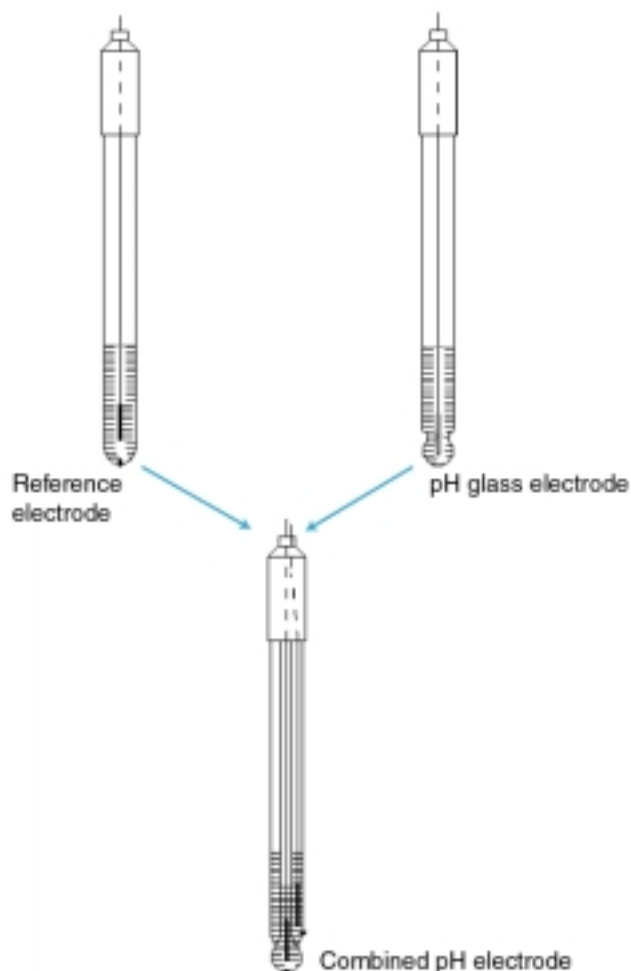
3.2.4 The classical set-up

The classical set-up for measuring pH consisted of a pH meter, a pH electrode and a reference electrode:



3.2.5 The modern set-up

Although you can perfectly measure pH using the "classical" set-up, it was soon realised that the two electrodes could be built into the same probe (although there still are two totally separate electrodes). This is nowadays called the **combined pH electrode**, which is, of course, much more practical (see following page):



3.3 The magical formula for pH calculation

From the above we know that in order to measure pH we measure potential differences. But how do we get a pH value from a millivolt value (1 mV = one thousandth of a volt – the unit used to define potentials)?

Fret not, we have the answer. And the answer is: **Nernst**.

What's Nernst? Before we can answer that, you must first ask the right question. It's not WHAT is Nernst, it should be WHO is (or was) Nernst?

Walther Hermann Nernst was a clever guy. He studied the relation between the mV (millivolt) reading produced by a pH electrode against a **standard hydrogen electrode** and the pH (using the scale devised by that other clever guy Sørensen) of the measuring solutions.

Now, a standard hydrogen electrode is a rather complicated and ugly piece of equipment which you're better off knowing little about. Suffice to say that it gives very well defined and reproducible mV readings over a wide range of pH values and strictly responds only to hydronium ions.

After much calculation and probably lots of weekends alone in his laboratory he came to the conclusion that the relation (**Nernst equation**) looks like this:

$$U = U_0 + \frac{2.303RT}{z_i F} \lg[\text{H}_3\text{O}^+]$$

Where:

U potential measured between indicator and reference electrode (this part we've already introduced)

U₀ standard potential of the electrode assembly, depends on its construction (well made electrodes give 0 mV with pH 7 – neutral solution)

R gas constant (8.31441 J K⁻¹ mol⁻¹) (forget this one, it's a number some other guy calculated – clever lot these scientists!)

T absolute temperature in K (273.15 + t in °C) (oh well ... scientists are not only smart, they're also very awkward. Instead of measuring temperatures in degrees Celsius (or Fahrenheit if you're American) they use Kelvin. The temperature in Kelvin is simply the temperature in degrees Celsius plus 273.15)

z_i charge of the hydronium ion (1+) (each ion carries a single positive charge with it)

F Faraday constant (96 484.56 C * mol⁻¹) (yet another clever number from another smart guy – his name was Faraday).

The pH meter basically uses this equation to calculate the pH value. However, all the individual parts within the equation have to be known (not everything is constant). The potential is measured by the electrodes, and the temperature (T) needs to be measured as well and if there isn't any temperature sensor connected to the meter, the temperature (T) value has to be entered.

You will see that the **temperature plays a key role** (please check also under 3.4.3).

3.4 What pH measurement REALLY is all about

3.4.1 Be real!

A direct pH measurement, without calibration is as bad as a blatant lie. Why's that?

In theory a pH electrode is so constructed that its potential in buffer pH = 7 equals 0 mV. (A buffer is a solution which keeps a given concentration of hydronium ions and therefore a given pH). This potential is called the **zero potential** of a pH electrode (you would never guess why!). This is one of the two main characteristics of a pH electrode.

The second characteristic is the **electrode slope**. The slope of an electrode gives the change of potential measured between two buffers with a pH difference of 1 in comparison to what is expected by theory (from Nernst). Nernst calculated this value as 59.16 mV/pH at 25 degrees Celsius (or of course 293.15 Kelvin).

But this is just theory and as we all know the practice always looks a little different. In practice the zero point as well as the slope of the electrode differ from what they should be.

This difference has to be known so that the meter can compensate for any changes in electrode response. This way you get "true" results. Determining the deviation of the zero point and the slope from their theoretical values and saving these values into the meter (it works automatically) is called **calibration**.

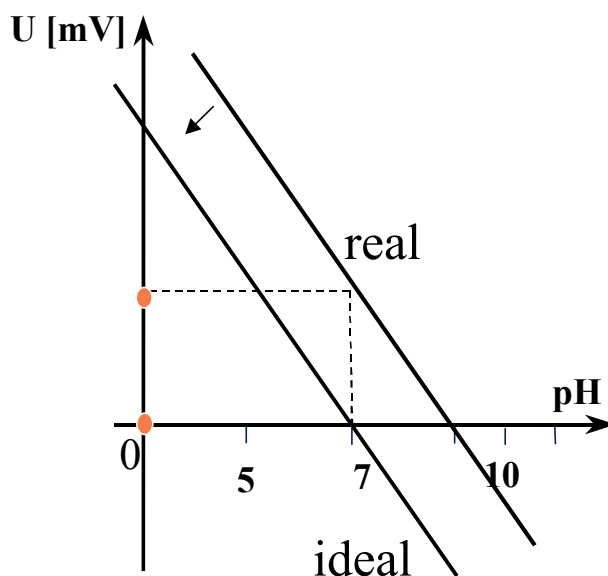
3.4.2 How to calibrate your pH meter

How do you perform a calibration? You do it as follows:

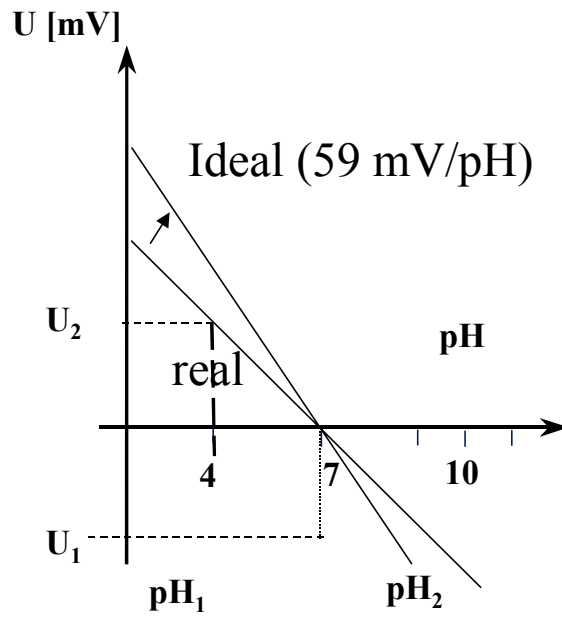
1. Take the pH electrode and connect it to the meter. Remove the storage vessel and rinse the sensing area thoroughly with distilled water. Dab the electrode with a soft paper tissue to remove the rest of water (don't rub the electrode surface).
2. Dip the electrode into buffer pH = 7, so that the diaphragm of the electrode is well immersed. If the pH electrode doesn't have an integrated temperature sensor, connect a separate temperature sensor to the meter and dip it also into the buffer solution. If you don't have a temperature sensor which you can connect to the meter, use a conventional sensor and enter the temperature into the meter when required.

- Start the calibration on the meter (check instructions for use of the meter). You will notice that the temperature is measured first and then a mV reading is taken, which should be around 0 mV. The difference to 0 mV will be registered by the meter and taken into account during later measurements:

Adjustment of the „zero point“



- Rinse the sensors thoroughly with distilled water and dab the electrode with a soft paper tissue to remove the rest of water (don't rub the electrode surface). Dip in buffer pH = 4 and repeat the procedure.
- Having two mV readings, this and the previous one, the meter can establish a linear function $U = f(\text{pH})$ and also calculate the slope of the electrode. The real value differs again from the theory of 59.16 mV/pH. The meter saves the difference and takes it into account during later measurement (please see following page):



Here is a typical calibration report:

```

713 pH Meter           0E2/101 713.0021
date 1999-05-20 time 09:56:40 2
pH      pH      electr.id    60234100
pH calibration
meas.input           1
temperature           23.3 °C
c.dat. 1999-05-20 09:56
cal.interval         24 h
buffer type          Metrohm
                    pH      U/mV
buffer 2      7.007      -2.9
buffer 1      3.997      172.8

```

The calibration plot shows potential U [mV] on the y-axis (ranging from -50 to 200) versus pH on the x-axis (ranging from 4 to 8). Two data points are plotted: (3.997, 172.8) and (7.007, -2.9). A solid line represents the linear fit through these points. The x-axis has tick marks at 4, 5, 6, 7, and 8. The y-axis has tick marks at -50, 0, 50, 100, 150, and 200.

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slope           0.992
pH(as)         6.957

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pH(as) expresses here the zero point of the electrode (the little as on the right hand side differentiates this value from normal pH values). A pH(as) of 6.957 means that the electrode which is dipped into a buffer pH = 7.0 reads a pH value of 6.957. The difference of 0.043 pH is registered by the meter and its taken into account during the measurement.

A slope of 0.992 means that the *real* slope of the electrode is 99.2 % of the theoretical slope (59.16 mV/pH = 100%), in other words the real slope of the electrode is 58.7 mV/pH.

Please remember:

Generally **slopes between 96% and 102% are OK**. Slopes over 102% are known, but usually indicate problems with either the electrodes or the calibration.

It is of extreme importance to know that only pH values measured with a calibrated system can be relied upon. Don't trust any pH measurement performed with a non-calibrated system.

Practical hints for successful calibration:

- Always use fresh buffer solutions!
- A two-point calibration is recommended for normal use.

Also: Calibrating with buffers that lie within your pH measuring range increases the accuracy of the measurement.

Stirring during the calibration process also plays a big role. Very important: The stirring speed during the calibration process should be identical with the stirring speed during the pH measurement.

When stirring during the pH measurement is not required or not possible (penetration measurements for example), the calibration should also be carried out without stirring.

3.4.3 When you need temperature compensation

Temperature plays a key role in pH measurement. There are two reasons for this:

- the pH value of the solution changes with the temperature;
- the slope (theoretical slope) of the electrode changes with the temperature.

That last point won't bother you any longer:

The METROHM 713 pH Meter as well as the 704 and the 744 pH Meter together with all METROSENSOR electrodes can handle this problem. These meters easily compensate the error caused by the dependence of the Nernstian slope on the temperature.

However you will still have to cope with the pH change of your sample with the temperature! It is the nature of all things to change their characteristics with the temperature. And one of them is the pH value!

Clear and simple: pH measurement should *always* be performed together with temperature measurement because only pH values measured at the same temperature can be compared!

The exception to the rule...

Of course there is one exception which confirms the rule above. This is when you calibrate. In this case both problems mentioned above are eliminated.

The reason for this is the **cleverness of METROHM meters**. These meters know the temperature dependence of several buffer solutions such as NIST, DIN, METROHM, Fisher etc.

So all you need to do is to let the meter know what temperature you're calibrating at and the compensation will be done automatically. No need to thermostat the buffer solutions any longer.

Important: This can not be said when you measure the sample. No meter knows the temperature dependence of your sample so therefore it can't be compensated. This is why (the sentence above needs to be repeated here): only pH values taken at the same temperature can be compared to each other!

4 Summary

There are many factors which influence pH measurement. Compensation for or elimination of these factors is the key to accurate and precise pH measurement.

Don't forget **quality pH measurement**:

Quality pH measurement means: **Long life of your investment**

Quality measurement pH means: **Ease to use**

Quality measurement pH means: **Service for many years**

Quality measurement pH means: **Reliable results**

Quality measurement pH means: **Help in applications**

Quality measurement pH means: **Being there**

Quality measurement pH means: **METROHM**

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