

FAST FACTS

FAST FACTS is a quick reminder of the key points in the theory and measurement of **ELECTROCHEMISTRY**.

Should you require more in-depth information or would like to arrange a training session, please do not hesitate to contact us.

FAST FACTS

pH MEASUREMENT

What is pH?

The pH of a solution is a measure of its acidity or alkalinity.

What are the characteristics of a solution that make it acid or alkaline?

In an aqueous solution the level of acidity or alkalinity is determined by the balance between the H^+ and OH^- ions present. $H_2O \rightleftharpoons H^+ + OH^-$

How does this relate to a solution that is neither acidic or alkaline?

As the ionic product of water, K_w remains constant at 10^{-14} regardless of how the acid/alkaline balance shifts, then $H_2O = [H^+][OH^-] = 10^{-14}$ mol/l. In pure water at equilibrium then $H^+ = OH^- = 10^{-7}$ mol/l

How can we compare the relative strengths of acid and alkaline solutions?

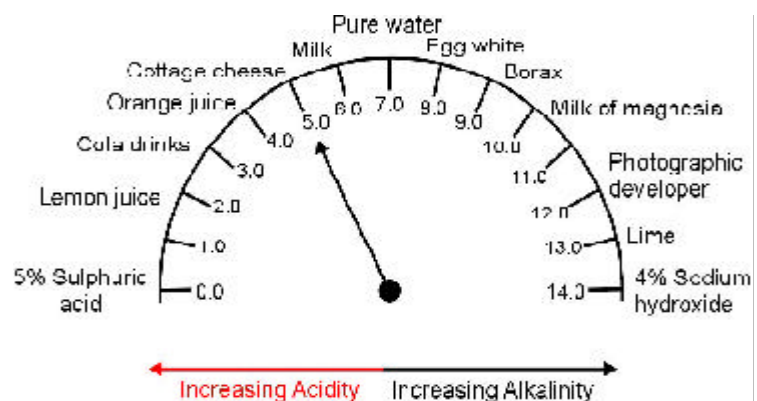
The pH scale is defined by the Sorensen equation:

$$pH = -\log H^+$$

Substituting the above values at equilibrium ($H^+ = 10^{-7}$) then $pH = 7$ for a neutral solution.

What are typical pH values for some common substances?

Acidic solutions have a $pH < 7$
Alkaline solutions have a $pH > 7$
Neutral solutions have a $pH = 7$



Common substances related to the pH scale.

How is pH measured in practice?

The most commonly used method for measuring pH is the glass electrode which generates a voltage proportional to the hydrogen ion concentration in a solution. The glass electrode must be used with a reference electrode to make a measuring system. When the glass electrode and reference electrode are combined into one body, this is referred to as a combination electrode.

Do electrodes work in all types of solution?

There are many and various general purpose and specialised pH electrodes. Selecting the correct one for specific applications will ensure consistent and reliable results and an extended working life.

How is the output from the electrode converted to a pH reading on the meter?

The response of all glass pH electrodes is defined by the Nernst equation:

$$E = E_0 + 2.3 \frac{RT}{nF} \log H^+$$

where E is the mV output
E₀ is the zero offset constant for the electrode
R is the gas constant
F is the Faraday constant
T is the temperature in °K
n is the ionic charge (+1 for Hydrogen)

What is the actual output at different pH levels?

Solving the Nernst equation for consecutive pH values shows that an ideal electrode has a change in output of 59.16mV per pH unit @ 25°C. This is the ideal slope value.

pH Electrode Output @ 25°C

0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
+414.12	+354.96	+295.80	+236.64	+177.48	+118.32	+59.16	0	-59.16	-118.32	-177.48	-236.64	-295.80	-354.96	-414.12

How does this theory relate to electrodes in general use?

In practical situations the E_o and slope values can be used to describe the performance of an electrode. The E_o value should be between +30 and -30mV and the slope value greater than 45mV. The slope value is often referred to as a % of the ideal value.

How are these variations corrected when making readings?

All pH measuring systems must be calibrated against standard solutions (pH buffers). These are available at values across the complete pH range and are formulated to various national and international standards. All buffers are temperature dependant and care should be taken to calibrate to the **temperature corrected** value and not the normal value.

What else affects the output of a pH electrode?

As shown by the Nernst equation the output of the glass electrodes varies with temperature. In practice, this temperature effect is more significant the further measurements are made from 7pH or the true isopotential value. Most modern pH meters enable manual or automatic temperature compensation (ATC) to correct this variation.

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CONDUCTIVITY MEASUREMENT

What is Conductivity?

More correctly, this should be called 'electrolytic conductivity', which is the ability of a solution to pass an electric current.

How does a solution pass an electric current?

Compounds dissolved in water will take up an ionised state. These electrically charged ions enable the passage of current through the solution.

Can conductivity be used to determine the concentration of a compound dissolved in water?

In general, conductivity is used to determine the purity of a solution or to indicate the total concentration of all the various ions in that solution.
If the solution consists of a single compound dissolved in pure water then the conductivity level can be referred to standard tables or graphs that convert this to a concentration.

What unit is conductivity measured in?

The unit of measurement for conductivity is the Siemen/cm. This is a very high conductivity level so, in practice, millisiemens (mS/cm) and microsiemens ($\mu\text{S/cm}$) are the practical levels reported. Resistivity is the reciprocal of conductivity and is often used for pure water measurement when results are reported in mega ohms ($\text{M}\Omega/\text{cm}$).

What are typical conductivity values?

Typical Conductivity Values

	Conductivity	Resistivity
Pure Water	0.055 $\mu\text{S/cm}$	18.3 $\text{M}\Omega\text{-cm}$
Distilled Water	0.05 $\mu\text{S/cm}$	2.0 $\text{M}\Omega\text{-cm}$
Power Plant Boiler Water	1.0 $\mu\text{S/cm}$	1.0 $\text{M}\Omega\text{-cm}$
Pure Mountain Stream	10 $\mu\text{S/cm}$	100 $\text{K}\Omega\text{-cm}$
Good Tap Water	50 $\mu\text{S/cm}$	rarely used
0.001 N Potassium Chloride Solution	1409 $\mu\text{S/cm}$	
Maximum for Potable Water	1500 $\mu\text{S/cm}$	
Sea Water	53 mS/cm	
10% Sodium Hydroxide	355 mS/cm	
10% Sulphuric Acid	432 mS/cm	

How is conductivity measured?

The theoretically ideal conductivity cell measures the ability of current to flow through a trapped volume of solution between two plates 1cm square, and separated by 1cm.

How do practical conductivity cells vary from this ideal?

The practical implementation of the ideal conductivity cell is very difficult. Modern cells are typically built into insertion probes fabricated in glass or plastic tubes where the plates may be curved and separated by varying distances.

How are variations in cell geometry corrected for in measurement?

In practice the conductivity (C) is calculated from the actual conductance (G), measured between the plates, multiplied by the cell constant (K). Any cell, however irregular, can be represented by an equivalent cell with square and parallel plates and in this case the formula can be expanded to:

$$C = G \frac{L}{A}$$

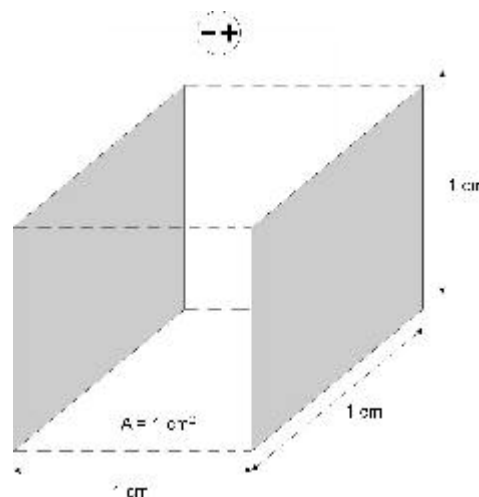
where C = Conductivity (S/cm)

G = Conductance (S)

L = Distance between plates (cm)

A = Area of plates (cm²)

A precise cell constant or K factor, to 2 decimal places, may be given to a cell during manufacture by direct comparison to a standard cell.



What is the typical range of available cell constants?

To improve the resolution of measurements made in low conductivity samples, the plates can be placed closer together (L is reduced) to give cell constants of 0.1. Similarly, in high conductivity samples the upper limits of the measuring range can be extended by cells where L is increased to give cell constants of 10 or more. In general, the actual K factor quoted for a cell should be within 10% of its nominal value.

How is electrolysis of the sample avoided when measurements are made?

If a d.c. voltage is applied to the plates, as in the theoretical cell, then polarisation and electrolysis will occur. This will cause bubbles to form on the plates and the conductivity to decrease rapidly. To overcome this problem an a.c. voltage is applied to the plates which are also coated with a black platinised coating that will absorb the products of electrolysis on alternative half cycles.

What maintenance and care is required for conductivity cells?

If a conductivity cell has become fouled with residue from adhering samples this should be removed using a suitable solvent (check it is compatible with the materials used in the probe assembly). It should then be thoroughly rinsed with deionised water. The platinised surfaces of the plates should not be touched as any scratches or marks on these will alter the effective surface area and hence the K factor specified. In this case the K factor will need to be re-calculated using accurate standard solutions and temperature control.

How is the current flow measured by the cell converted to a conductivity reading?

Most modern meters can be calibrated for use with a specific cell by simply entering the K factor, either digitally or by using a rotary control. The problem with this system occurs when the plates become damaged and the K factor is no longer valid. In this case a good meter will have additional functions allowing automatic and/or manual calibration against standard solutions.

What effect does sample temperature have on the readings?

Temperature is very critical in conductivity measurement. All conductivity measurements are reported at a Reference Temperature. Various national and international standards have stipulated this to be either 18°C, 20°C or 25°C. Currently, the most commonly used is the SI standard at 25°C, but having a meter with all the options available ensures maximum flexibility.

Conductivity is dependent on the total ion concentration of a sample. As the activity of these ions changes with temperature so will the conductivity. Where only one ionic species is present this can be accurately compensated for by adjustment of the Temperature Coefficient to the value applicable to that ion.

Most ions will fall in the range of 1% to 4% change in conductivity per degree Celcius.

Where a solution is a mixture of ions the typical coefficient will be 2%/°C.

Table of Coefficients

Substance at 25°C	Concentration	Alpha (α)
HCl	10 wt%	1.56
KCl	10 wt%	1.88
H ₂ SO ₄	50 wt%	1.93
NaCl	10 wt%	2.14

How can conductivity measurements be compared?

Conductivity results must always be reported with the Reference Temperature, the Actual Sample Temperature and the temperature coefficient used. For maximum accuracy in laboratory situations, the Temperature Coefficient should be set to zero and the samples/calibrants maintained at the reference temperature by use of a thermostatic water bath.

What is TDS measurement?

TDS refers to the Total Dissolved Solids in solutions and is based on the weight of solid material remaining after complete evaporation. There are a number of standards for this, the most common ones relating to the concentration of KCl and CaCO_3 in solution. For most accurate measurements calibration should be made against the relevant standard. Many meters offer a variable factor (EC Ratio) that will calculate an equivalent TDS value based on the conductivity reading.

How is Salinity measured on a conductivity meter?

The measurement of Salinity by a conductivity meter is a common application. A conductivity reading can be converted to a Salinity concentration by the use of 'look up tables' in the meter's memory, or by use of equations built into the software, or variable factors as in TDS measurement. It must be remembered, however, that such conversion is dependent on the samples conductivity being entirely due to Salinity with no other ions present.

FAST FACTS

DISSOLVED OXYGEN MEASUREMENT

Why is dissolved oxygen measured?

Dissolved oxygen is critical in the aquatic environment, supporting plants, fish life and the numerous biological and biochemical processes therein. It is important in determining the quality of potable waters and in monitoring the performance of water processing plants. It has gained in popularity as a simple method for monitoring sewage and effluent treatment prior to discharge, as well as being the basis for the standard BOD₅ methodology.

What methods are used to measure dissolved oxygen?

Historically, a complex iodometric titration was used for dissolved oxygen measurement. A number of variations of this were developed to counter the significant interferences found in the wide range of samples being measured. The most popular of these was the Winkler method.

With the advent of membrane sensor technology direct measurement in samples became possible in the laboratory and in the field. Two types of probe are available – the galvanic probe and the polarographic probe.

What are the differences between galvanic and polarographic probes?

In both types of probe dissolved oxygen diffuses across a permeable membrane and is reduced in a reaction with a fill solution generating a current flow between cathode and anode. This current flow is proportional to the amount of oxygen that crosses the membrane.

In the galvanic probe the voltage difference between the anode and cathode, required for this reduction, is generated by the choice of anode and cathode material and the fill solution. In principle, this works much like a battery and similarly will have a finite life.

In the polarographic probe the anode and cathode are made from noble metals (silver and gold) and the voltage required for the reduction of oxygen at the cathode is accurately and consistently supplied from the meter. This probe has an infinite life (subject to usage and care) with only the membrane and solution requiring replacement.

Do these probes suffer from any interferences like the titration methods?

The key interferences are sample flow rate, temperature, atmospheric pressure and salinity. The probes can also be affected by samples that deposit a coating on the membrane, but this can generally be countered by good maintenance and care.

How does sample flow rate affect results?

As the dissolved oxygen diffuses across the membrane it is consumed by reduction at the cathode. This means that in a static sample the area close to the membrane gradually becomes oxygen depleted and results will slowly drift downwards. This will not be a problem when testing flowing surface water. In static water such as wells or ponds the probe should be gently moved in a circular motion and in laboratory analysis a stirrer should be used.

How does temperature affect results?

When measuring dissolved oxygen as % saturation the only effect temperature has is to change the permeability of the membrane. This is usually compensated for by an integral Automatic Temperature Compensation (ATC) element built into the probe body.

When measuring dissolved oxygen as a concentration in mg/l then compensation also has to be made for the change in solubility of oxygen with temperature. This is often carried out by a second temperature sensing element in the probe. More modern meters use the same sensor to make the relevant corrections through software functions.

How does atmospheric pressure affect results?

The polarographic and galvanic cells respond to the partial pressure of oxygen in solutions. If the atmospheric pressure increases then the partial pressure of oxygen will increase by the same percentages, even though the oxygen will still represent the same proportion of the total. In this case, the meter will give an incorrectly high reading. If the meter is calibrated at the same atmospheric pressure as the samples are measured at then no compensation is required. Where samples are measured at a different atmospheric pressure, as when working at varying depths or altitudes, then correction must be made.

How does salinity affect results?

A sample's ability to dissolve oxygen is reduced by the salinity of that sample. Correction must be made for this effect. This is usually made possible by the entry of the salinity or the conductivity level.