

Principles of potentiometric pH and Redox measuring techniques

General

Accurate measurement and control of the pH and Redox values is the most important factor in processing techniques for water treatment.

The pH value is defined in DIN specification 19260 as follows

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

aH^+ being the hydrogen ion activity of the test solution. The pH value is defined as the negative common logarithm of hydrogen ion activity. When the concentration of H^+ ions changes by one power of ten, the pH value changes by one. The effective pH scale of measurement is referenced to standardised buffer solutions, the composition of which is accurately stated and to which pH values are ascribed.

In the potentiometric method the pH value is measured with the aid of a glass electrode. The measured value is here

$$pH = pH_s - \frac{U - U_s}{U_N}$$

where pH_s is the pH value of the standard buffer solution, U_s is the potential with the test electrode immersed in the standard buffer solution; U is the potential with the test electrode immersed in the solution being tested; U_N is the theoretical electrode slope, also known as Nernst voltage.

The equation here is:

$$U_N = \frac{R \cdot T}{F} \ln 10$$

- T = abs. temperature (T = 273.15 K)
- R = Gas constant (8.31349 JK⁻¹ mol⁻¹)
- F = Faraday constant (9.648456 · 10⁴ Mol⁻¹)

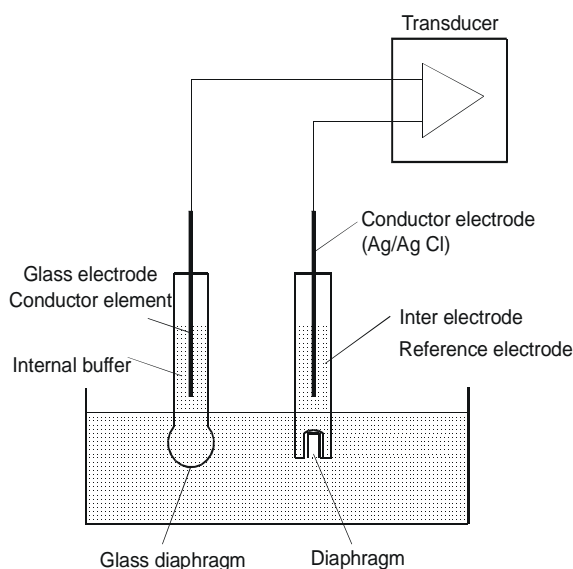
In the following table the correlation between temperature and electrode slope is given.

Correlation of temperature/Nernst voltage:

Temperature	U_N	Temperature	U_N	Temperature	U_N
° C	mV	° V	mV	° V	mV
0	54.20	35	61.14	70	68.08
5	55.19	40	62.13	75	69.08
10	56.18	45	63.12	80	70.07
15	57.17	50	64.12	85	71.06
20	58.16	55	65.11	90	72.05
25	59.16	60	66.10	95	73.04
30	60.15	65	67.09	100	74.04

pH measuring equipment

The pH measuring equipment used for determining the pH value by the potentiometric method consists of a glass electrode, the reference electrode and the transducer.



The glass electrode

The glass pH electrode builds up an expanding layer on the inside of the glass diaphragm. This expanding layer is in contact with a certain buffer solution (internal buffer). Since the glass electrode has an internal buffer with constant pH value, the potential on the inside of the electrode remains constant throughout the measurement. When a glass pH electrode is immersed in an aqueous solution, an expanding layer also builds up on the outside of the delicate glass diaphragm. Depending on the nature of the measuring liquid, the H^+ ions diffuse either into or out of this expanding layer. If the solution is alkaline, the H^+ ions diffuse outwards and a negative voltage builds up on the outside of the expanding layer. The total potential of the diaphragm is consequently equal to the difference between the internal and external charge.

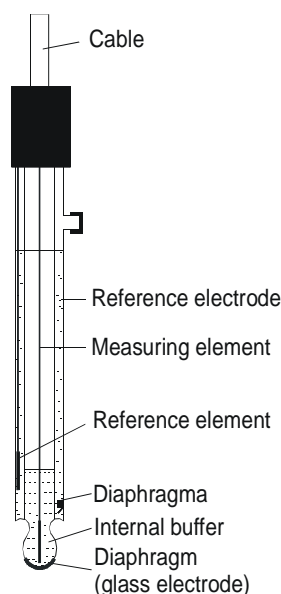
The reference electrode

The function of the reference electrode is to produce a constant comparison or derived potential for the measuring electrode. The reference electrode comprises a reference element which is similarly immersed in a defined electrolyte. This electrolyte must be in contact with the measuring liquid, usually via a porous ceramic diaphragm. Silver/silver chloride is usually used for the reference system.

The potential of the reference system is determined by the reference electrolyte and the reference element. The reference electrolyte must have a high and constant ion concentration in order to ensure low electrical resistance and a constant potential.

Combination electrode

The glass electrode and the reference electrode are installed either in separate shafts or in a single shaft. They are referred to as a combination electrode when installed in a single shaft.



pH measuring system

pH values can only be measured reliably if the correct electrodes are used and suitable reagents are available for calibration and verification. A pH electrode is characterized by its zero point and its steepness. The response of a pH electrode is determined by the **Nernst equation**.

When measuring hydrogen ions, the steepness factor at 25 °C yields a value of 59.16 mV. This represents the *ideal steepness value*. This consequently means that if the value changes by one pH unit, the voltage at the glass electrode must change by 59.16 mV.

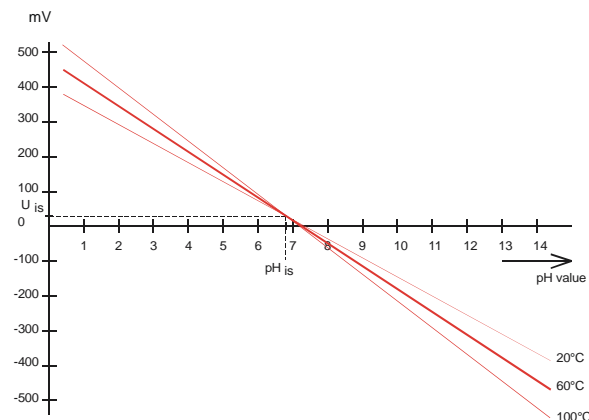
If the steepness of the pH electrode drops below 50 mV/pH unit or if the deviation at the zero point exceeds ± 30 mV, it may be necessary to thoroughly clean or replace the pH electrode in order to ensure accurate measurement of the pH value.

The isothermal point of intersection is defined as the common point of intersection of the slope lines as a function of temperature. The coordinates pertaining to them on the pH axis and mV axis respectively are pH_{is} and U_{is} .

The potential of an electrode measurement chain for the arbitrary pH value pH x is therefore:

$$dU / U = (pH_{is} - pH_x) + U_{is} dpH$$

With symmetrical measurement chains the zero point in the chain is largely identical with the isothermal point of intersection.



For industrial pH test procedures, pH single bar measurement chains are almost universally adopted. Many errors in pH measurement at industrial level are due to faults in reference electrodes. The membrane may fail as a result of impurities, causing the electrolyte contact with the test solution to be interrupted, either wholly or partially. The remedy to be applied is chemical or mechanical cleaning.

Measurement of Redox potential

All electrochemical processes in which chemical reactions are involved can be related to oxidation or reduction. Active oxidising substances pick up electrons - active reducing substances give off electrons - and they continue to do so until an equilibrium is established. Oxidation or reduction cannot occur in a system unless another oxidation or reduction at the expense of the previous one.

Measuring the pH value makes it possible to establish whether a system is „acid“, „alkaline“ or neutral. The redox potential is similarly used to establish whether the system has an „oxidizing“ or „reducing“ effect.

The redox potential can be measured with a redox electrode. Since the redox electrode can also absorb or liberate electrons, metals are used here provided that they do not react chemically with the measuring solution.

If a non-attackable electrode is immersed in a solution containing ions in oxidised and reduced form, it will take on a potential that is a function of the interrelationship of the ion activities.

The practically current less determination of the potential marginally changes the chemical composition of the measuring solution and prevents undesirable polarization phenomena at the redox electrode. During formation of the redox potential, electrons flow from the redox electrode to the redox system or vice versa. Charge separation causes a potential to build up on the metal surface which counteracts the transport of electrons. In a state of equilibrium, the electrochemical power (voltage) and chemical power (oxidizing or reducing power) cancel one another out. For this reason, the measuring solution becomes increasingly positive with increasing oxidation.

A reference electrode is required for every potentiometric measurement. The reference electrodes of the redox measuring system are the same as the reference electrode for pH measurement.

Only the system potential between the reference electrode and the redox electrode can be measured potentiometrically. Relevant statements are only possible when using a standardized reference electrode to which all measurements are referred.

Nernst's equation for redox potential is based on thermodynamic laws. The oxidizing power and the reducing power of a solution are directly related to the redox potential.

Example:

- The rate at which Coli bacteria are killed off in swimming pools is determined by the magnitude of the redox potential.
- Open and closed-loop control of the detoxification of effluent containing cyanide, chromate or nitrite.

Redox measuring electrodes

For industrial applications gold or platinum are used as electrode materials. The use of gold is preferable for solutions of high oxidising power, whereas platinum is used for oxidising solutions containing chlorine and in the case of reduction processes. Preferably the silver/silver chloride reference electrode should be employed as the reference element.

When platinum electrodes are used in highly oxidising solutions, oxygen occupies the surface of the electrode, and when they are used in oxidising solutions it is hydrogen that collects. As a consequence, operation is sluggish and takes a long time in the electrode measuring chain. In order to counter this passivation of the system it is necessary to introduce an electrochemical "auxiliary grid current electrode cleaning" system, or to use electrodes that are mechanically cleaned automatically.

Since H^+ ions also play a part in the creation of Redox voltage potential, it necessarily follows that the Redox potential measurement is a function of the pH value of a solution. For this reason, for measurement of the Redox potential, the pH value must always be retained.

The measuring transformer

The measuring transformer must be able to measure the pH-related electrode potential supplied by the electrode system with as little power as possible. In other words, it must have a very high input impedance. DIN 19265 stipulates that this value must equal at least 5×10^{11} ohm. In addition, pH transducers can be adjusted in order to bring the transducer into line with the individual properties of a measuring system, i.e. adjustment of the steepness and zero point.

Modern pH transducers can compensate the temperature-dependent system potential. Either the temperature of the measured medium can be set on the transducer or it features an automatic compensation mechanism in which the temperature of the measured medium is determined by a platinum resistance thermometer and forwarded to the measuring amplifier.

pH transducers with a correspondingly modified measuring range are used to measure the redox potential. Like the pH electrode potential, the redox potential is consequently measured with zero current.

The insulation of the lines connecting the combined measuring and reference electrodes and the measuring transducers must meet very high standards. Due to the high impedance of the measuring circuit, particular precautions must be taken to prevent electrical interference signals. In other words, the measuring lines must be shielded and they must have high-impedance insulation against ground.