

PH-metry

Probably the greatest fame has been given to electrochemistry due to the possibility of measuring pH via a so-called **glass electrode**. In this case, too, we measure the potential between two half-sheets, i.e. the measuring (indicating) and the reference electrode. In practice, the reference electrode is often built into one body together with the measuring electrode - we speak of a combined pH-metric electrode.

In contrast to the electrochemical cells described above, where the voltage is produced due to the interconnection of different metals (reduction and oxidation), in the glass electrode the voltage is produced due to exchange processes. These take place between the ions 'deposited' in the glass crystal lattice (membrane) and the ions in solution. Ions, mainly hydrogen and alkali metals (e.g. sodium), are bound to the relatively regular silicate crystal lattice of the glass by electrostatic forces. On contact with the solution, a solvated layer forms on the surface in which alkali metal ions (e.g. sodium) and hydrogen ions are exchanged between the solution and the glass. For a glass hydrogen electrode, equation (9) applies:

For more information go to: *Glass electrode*.

$$E = konst + \frac{RT}{F} \cdot \ln(a_{H^+} + K_S \cdot a_{Na^+}) \doteq konst + \frac{RT}{F} \cdot \ln a_{H^+} = konst. - 2,3 \cdot pH \quad (9)$$

where K_S is the selectivity constant, which indicates how selectively the electrode reacts to one or the other ion. If it is sufficiently low, the term in equation (9) that contains it can be neglected and a simplified form used. The term "const." includes the standard reduction potential, the method of preparation of the electrode, the type and composition of the glass, the surface quality, the "age" and the internal charge of the electrode. For simplicity, the decadic logarithm is used in most instruments and the variables are summarised into a single 'constant' numerical value of 2.3 (for a temperature of 25 °C).

At a constant reference electrode potential, the measured voltage is directly proportional to the pH of the solution being analysed over a large part of the entire range of possible pHs. In reality, the theoretical calibration parameters cannot be relied upon and calibration with two or three solutions of known pH values is necessary. Modern instruments calculate the *calibration line directive (slope)* from the measured values, generally for nonlinear electrode sensitivity dependencies, and a correction for temperature is made at the same time. The instrument "remembers" these "calibration parameters" and processes the measured data according to them. The calibration must be repeated periodically, and more often the older the electrode. At the same time, care must be taken to ensure that the calibration takes place under the same conditions as the actual measurement (aqueous environment, non-aqueous environment, alcohol content, etc.). Further inaccuracies to be taken into account are committed by the glass electrode in the acidic and alkaline pH range (*Alkaline (positive) error* - in the strongly alkaline range and *acidic (negative) error* at pH < 1).

An important parameter is also the time constant of the response, usually around 15 to 60 s for glass electrodes. The response time can also be negatively influenced by the composition of the solution - e.g. colloids and the concentration of the measured ion - the equilibrium takes many times longer to settle.

References

Related articles

- PH
- PH of weak acids and bases
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- PH measurement
- Buffers, buffering capacity, oxidation and reduction, electrode processes (1.LF UK, GM)
- PH of urine
- PH of salts