

The Operational Definition of pH

The operational definition of pH endorsed by the National Institute of Standards and Technology (NIST), similar organizations in other countries, and the IUPAC is based on the direct calibration of the meter with carefully prescribed standard buffers followed by potentiometric determination of the pH of unknown solutions.

and we can write

$$\text{pH}_S = \frac{E_S - K}{0.0592}$$

where E_S is the cell potential when the electrodes are immersed in the buffer. Similarly, if the cell potential is E_U when the electrodes are immersed in a solution of unknown pH, we have

$$\text{pH}_U = \frac{E_U - K}{0.0592}$$

It should be emphasized that the strength of the operational definition of pH is that it provides a coherent scale for the determination of acidity or alkalinity. Measured pH values cannot be expected to yield a detailed picture of solution composition that is entirely consistent with solution theory, however. This uncertainty stems from our fundamental inability to measure single-ion activities. That is, the operational definition of pH does not yield the exact pH as defined by the equation

$$\text{pH} = -\log \gamma_{\text{H}^+} [\text{H}^+]$$

By subtracting the first equation from the second and solving for pH_{U} ,

$$\text{pH}_{\text{U}} = \text{pH}_{\text{S}} - \frac{(E_{\text{U}} - E_{\text{S}})}{0.0592}$$

ERRORS

1) Alkaline error

In basic solutions:

glass electrode respond to alkali metal ions (Na^+) in addition to H^+

observed pH < actual pH

- Occur above ~ pH 9

2) Acid error

observed pH > actual pH

- pH < ~ 0.5
- Reasons are not well understood.

Glass electrodes for other cations:

- Na⁺, Li⁺, K⁺, Cs⁺, Rb⁺, Ag⁺, NH⁴⁺ have been developed.

3) Dehydration may cause erratic behavior.

4) Variation in junction potential.

A fundamental source of uncertainty that for which a correction can not be applied, which

results due to differences in concentration of standards and samples.

5) Errors in the pH of standard buffer.

Any error in the preparation or any change in the composition or during storage of buffers can cause error.

e.g. Action of bacteria on organic buffer.

6) Errors in low ionic strength solutions.

e.g. Lake or stream water.

Non reproducible junction potential due to partial clogging of fitted plug between salt bridge and analyte solution.

Electrodes with **FFJ (Free Flow Junction)** are used for these types of application.