1.13 Determination of pH

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A value characteristic of an aqueous solution is its pH value, which represents conventionally its acidity or alkalinity.

The pH of a solution is the negative logarithm of the hydrogen ion activity, which may be measured potentiometrically. Formerly, pH was regarded as the negative logarithm of the hydrogen ion concentration. As it is known that not all hydrogen ions are necessarily equally active, this concentration may be different from the hydrogen ion activity. However, if the activity coefficient is close to 1, as is true in dilute solutions, the values of hydrogen ion activity and hydrogen ion concentration become nearly identical.

The determination of the pH value is carried out by measurement of the potential difference between electrodes immersed in standard and test solutions. The standard solutions used are assigned a definite pH value by convention.

In the measurement of pH, glass electrode finds wide applicability as it shows an immediate response to rapid changes of hydrogen ion concentrations even in poorly buffered solutions. Since the mechanism of this electrode involves no electron exchange it is the only electrode sensitive to hydrogen ions that is not disturbed by oxidizing or reducing agents.

The pH values of solutions or suspensions that are only partially aqueous and that can be considered only as "apparent pH values" can also be measured by using the proper electrode and by suitably standardizing the pH-meter.

As pH values are dependent on temperature, the measurements are carried out at selected constant temperatures.

Solutions used in determinations of pH are prepared with carbon-dioxide-free water R.

pH scale

The difference in pH between two solutions, *X* and *S,* at the same temperature may be defined operationally as follows:

The electromotive force E_x, of the cell

Pt | H_2 | solution *X* | 3.5 mol/l KCl | reference electrode

and the electromotive force, E_s, of the cell

Pt | H_2 | solution *S* | 3.5 mol/l KCl | reference electrode

are measured, both cells being at the same temperature throughout and the reference electrodes and bridge solutions being identical in the two cells.

The pH of solution *X,* denoted by pH (*X*), is then related to the pH of solution *S*, denoted by pH (*S*), by the equation:

$$pH(X) = pH(S) + \frac{E_x - E_s}{2.3026\ RT/F}$$

where *R* denotes the gas constant, *T* the thermodynamic temperature (in K), and *F* the Faraday constant. Thus defined, the quantity pH is a dimensionless number.

Numerical values of the factor 2.3026 *RT/F* at several temperatures are given below:

Temperature (in °C)	*2.3026 RT/F* (mV)
10	56.18
15	57.17
20	58.17
25	59.16
30	60.15

Potentiometric determination of pH

For the practical determination of pH, a potentiometric method is usually employed. When glass electrodes are used they should be stored in a suitable liquid, usually water.

It is often found more convenient to measure pH by means of a glass electrode instead of the hydrogen electrode. In some solutions, especially those containing oxidizing agents, the glass electrode can be used when the hydrogen electrode cannot. The accuracy and reproducibility of ± 0.005 usually obtainable with the hydrogen electrode are, however, rarely obtainable with the glass electrode, and never outside the pH range 2–10.

When the glass electrode is used, the best accuracy is obtained by assuming that over a short range of pH there is a linear

relation between pH and measured electromotive force, but that the proportionality factor relating them is not necessarily exactly 2.3026 *RF/T*. This method of using the glass electrode necessitates calibration by means of two solutions of known pH, near to, and preferably bracketing, the pH to be measured. There are at present various suitable solutions, the pH values of which are reliably known to an accuracy of ± 0.005 (see Table 3).

TABLE 3. Standard buffer solutions and their pH values

Standard buffer solutions	pH values at various temperatures				
	20 °C	25 °C	30 °C	35 °C	40 °C
Potassium tetraoxalate standard TS	1.675	1.679	1.683	1.688	1.694
Potassium hydrogen tartrate standard TS	–	3.557	3.552	3.549	3.547
Potassium hydrogen phthalate standard TS	4.002	4.008	4.015	4.024	4.035
Phosphate standard buffer, pH 6.8, TS	6.881	6.865	6.853	6.844	6.838
Phosphate standard buffer, pH 7.4, TS	7.429	7.413	7.400	7.389	7.380
Sodium tetraborate standard TS	9.225	9.180	9.139	9.102	9.068
Sodium carbonate standard TS	10.062	10.012	9.966	9.925	9.889

Calibration of apparatus

The apparatus is calibrated with standard buffer solutions to check the linearity of the response of the electrode at different pH values and to detect a faulty glass electrode. The standardization of the apparatus with only a single solution may be completely erroneous and therefore at least two standard buffer solutions should be used for calibration. The presence of a faulty electrode will be detected by failure to obtain a reasonably correct value (± 0.04 unit) for the pH of the second standard solution when the apparatus has been standardized in terms of the first standard. A cracked electrode will yield pH values that are essentially the same for both solutions. If the difference between the known and the observed pH values for the second solution exceeds ± 0.04, another glass electrode should be substituted. If the difference persists, fresh standard solutions should be prepared.

Recommended procedure

After the apparatus has been calibrated, thoroughly wash the electrodes and the cup. Fill the cup with a portion of the solution to be tested and obtain a preliminary value for the pH. In general, this value will drift and is regarded as an approximation. Subsequent readings taken on additional portions of the same solution will yield successively more constant pH values. In the case of solutions that are well buffered, 3 portions may be sufficient to yield pH values that are reproducible to ± 0.04 units and that show drifts of less than ± 0.04 units in 1 or 2 minutes. In the case of very dilute or unbuffered solutions, as many as 6 portions of the test solution may be required, and the pH values may continue to drift and be reproducible to only ± 0.05 units.

If a precision greater than 0.1 pH unit is desired, the temperature of the standard solutions, the indicator and reference electrodes and the test solutions must be within 2 °C of one another, and the electrodes, standard solutions, test solutions and wash water must be kept at the temperature of measurement for at least 2 hours prior to making the measurement in order to reduce to a negligible value the effects of thermal or electrical hysteresis of the electrodes.

Standard buffer solutions

Standard buffer solutions are used in the determination of pH values. They are prepared with carbon-dioxide-free water R. They should be stored in bottles of chemically-resistant glass or in bottles made of polyethylene.

Unless otherwise specified, standard buffer solutions should not be used later than 3 months after preparation. If growth of microorganisms starts in the solutions they should immediately be discarded and the bottles thoroughly cleaned and sterilized before refilling.