

3.4 pH and related terms

3.4.1 Introduction

Much discussion has centered around the standardization of pH, with earlier recommendations in Great Britain, the United States, and Japan. Although general agreement was achieved between the three approaches, there were important differences in the recommendations of primary standards to be used. IUPAC discussions led to a 5 reference solution system based on NBS values. In order to accommodate the wide interests of chemists, biologists and engineers in pH measurements, a special IUPAC-sponsored conference on 'Harmonization of pH Scale Recommendations' took place in 1980. The decision of the conference to support the resolution that 'A single primary standard pH scale should replace the existing IUPAC multiple primary scale' fell short of a consensus of expert opinion. It was reported to the joint commission meeting in Leuven in August 1981. There, a third joint meeting of Commissions I.3 and V.5 voted to adopt a compromise proposal that embraces both NBS and British Standard approaches.

3.4.2 Symbols

There already exists international agreement that pH should be written and printed on line in Roman type. We recommend that the operator p (printed in Roman) should denote $-\log_{10}$ or $-\lg$. With the introduction of numerous ion selective electrodes responding to the solution activities of cations and anions, the symbolism p(ion) and related definitions can now be extended to these cases.

3.4.3 Definitions

Notional definition

The *concept of pH* first introduced as

$$\text{pH} = -\lg c_{\text{H}} \quad 3.11$$

where c_{H} is the hydrogen ion concentration (in mol dm^{-3}), was subsequently modified to

$$\text{pH} = -\lg a_{\text{H}} = -\lg m_{\text{H}}\gamma_{\text{m,H}} \quad 3.12$$

where a_{H} is the hydrogen ion activity. This can only be a notional definition, for pH involves a single ion activity which is immeasurable.

pH is a dimensionless quantity. It is not correct to write, in isolation, the logarithm of a quantity other than a dimensionless number, and the full form of the last equation is either

$$\text{pH} = -\lg (m_{\text{H}}\gamma_{\text{m,H}} / \text{m}^{\circ}) \quad 3.13$$

or

$$\text{pH} = -\lg (c_{\text{H}}\gamma_{\text{H}} / c^{\circ}) \quad 3.14$$

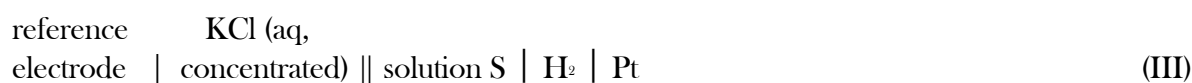
where m° and c° are arbitrary constants, representing the standard state condition, numerically equal to either 1 mol kg^{-1} or 1 mol dm^{-3} , respectively, m_{H} is the molality of hydrogen ions, c_{H} is the amount-of-substance concentration of hydrogen ion and $\gamma_{m,\text{H}}$ and $\gamma_{c,\text{H}}$ are the single ion activity coefficients of hydrogen ion on the two scales, respectively. For most purposes, the difference between the two scales for dilute aqueous solutions can be ignored; it depends on the density of water, and is about 0.001 at 298.15 K rising to 0.02 at 398.15 K. The normal range of pH is determined by the ionic product or autoprotolysis constant of water, $K_w \approx 10^{-14}$ at 298.15 K (see 3.2.3.5).

Operational definition

It is universally agreed that the definition of **pH difference** is an operational one. The electromotive force E_x of the cell:



is measured and likewise the electromotive force, E_s of the cell:



both cells being at the same temperature throughout and the reference electrodes and bridge solutions being identical in the two cells. The pH of the solution X, denoted by $\text{pH}(\text{X})$, is then related to the pH of the *standard reference solution* S, denoted by $\text{pH}(\text{S})$, by the definition:

$$\text{pH}_x = \text{pH}_s - (E_x - E_s)/k \quad 3.15$$

where $k = (RT/F)\ln 10$ and R denotes the gas constant, T the thermodynamic temperature, and F the Faraday constant, ignoring a term $\Delta E_j = E_x - E_s$, which is called the *residual liquid junction potential*.

To a good approximation, the hydrogen electrodes in both cells may be replaced by other hydrogen-ion-responsive electrodes, e.g., quinhydrone or glass. In most measurements, a single glass electrode replaces the hydrogen electrode and along with the reference electrode, is transferred between cells. The two bridge solutions may be any molality of potassium chloride, not less than 3.5 mol kg^{-1} , provided they are the same.

3.4.4 Standard reference solutions

The difference between the pH of two solutions having been defined as above, the definition of

pH must be completed by assigning a value of pH at each temperature to one or more chosen solutions designated as *standard reference solutions*.

Reference value pH standard

The useful qualities of potassium hydrogen phthalate, the most studied of all the pH reference materials, are well recognized, and so it has been designated as the *reference value pH standard* (RVS) at the specified molality of 0.05 mol kg⁻¹. The reference value is obtained from the cell without liquid junction (Cell IV).



The best values of pH_{RVS} for temperatures 0 - 95°C are given in Table 3.4.1. Values for CRM (*certified reference material*) samples (Section 3.4.6) may differ slightly. Values are determined as follows from the e.m.f. of cell (IV):

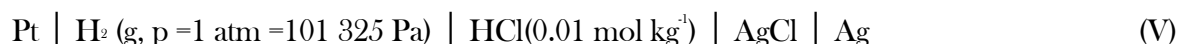
$$E = E^\circ - k \lg [m_{\text{H}^+} m_{\text{Cl}^-} \gamma_{\text{H}^+} \gamma_{\text{Cl}^-} / (m^\circ)^2] \quad 3.16$$

where m signifies the molality and γ the activity coefficient of the subscripted species, E° is the standard e.m.f., $m^\circ = 1 \text{ mol kg}^{-1}$.

The last equation can be rearranged to

$$-\lg (m_{\text{H}^+} \gamma_{\text{H}^+} \gamma_{\text{Cl}^-} / m^\circ) = (E - E^\circ) / k + \lg (m_{\text{Cl}^-} / m^\circ) \quad 3.17$$

The standard e.m.f. is derived from measurements on the cell:



and calculated from equation 3.16 with $\gamma_{\text{H}^+} \gamma_{\text{Cl}^-} = \gamma_\pm^2$, where γ_\pm is the mean ionic activity coefficient of HCl at 0.01 mol kg⁻¹.

The value of $-\lg (m_{\text{H}^+} \gamma_{\text{H}^+} \gamma_{\text{Cl}^-} / m^\circ)$ is calculated from measured E values for several molalities m_{Cl^-} of chloride ion, plotted against m_{Cl^-} and extrapolated to $m_{\text{Cl}^-} = 0$. Then, pH(RVS) is calculated from

$$\text{pH}_{\text{RVS}} = [-\lg (m_{\text{H}^+} \gamma_{\text{H}^+} \gamma_{\text{Cl}^-} / m^\circ)]_{m_{\text{Cl}^-} \rightarrow 0} + \lg \gamma_{\text{Cl}^-} \quad 3.18$$

where γ_{Cl^-} is obtained from the Bates-Guggenheim convention ($I \leq 0.1 \text{ mol kg}^{-1}$) (see equation 3.09), where

$$\lg \gamma_{\text{Cl}^-} = -A(I/m^\circ)^{1/2} / [1 + 1.5(I/m^\circ)^{1/2}]; \quad 3.19$$

A is the Debye-Hückel (temperature dependent) constant and I the ionic strength. Values of A , γ_\pm at 0.01 mol kg⁻¹, and E° are available.

Note: In 1981, the IUPAC Thermodynamics Commission I.2 recommended a change from 1 atm to 1 bar (10^5 Pa) for the standard state pressure. Since all standard electrode potentials are related to the standard hydrogen electrode, this recommendation requires a change, which amounts to -0.169 mV at 298.15 K, to be made to all existing tabulated standard electrode potentials. The existing tabulated data for the silver-silver chloride electrode refer to 1 atm = 101 325 Pa and so do published data on cells V and VI see below. Since the cell pairs (V)-(IV) or (VI)-(IV) are involved in these calculations of the data in Tables 3.4.1 and 3.4.2, differences in standard electrode potentials consequent upon the recommended change in standard state pressure cancel out. Therefore, the standard state condition of 1 atm in cells IV, V and VI is retained here.

TABLE 3.4.1 Values of pH_{RVS} for the Reference Value Standard of 0.05 mol kg^{-1} potassium hydrogenphthalate at various temperatures

$t/^{\circ}\text{C}$	pH_{RVS}	$t/^{\circ}\text{C}$	pH_{RVS}	$t/^{\circ}\text{C}$	pH_{RVS}
0	4.000	35	4.018	65	4.097
5	3.998	37	4.022	70	4.116
10	3.997	40	4.027	75	4.137
15	3.998	45	4.038	80	4.159
20	4.001	50	4.050	85	4.183
25	4.005	55	4.064	90	4.21
30	4.011	60	4.060	95	4.24

Primary pH standards

Certain substances which meet the criteria of:

- (i) reproducible preparation in a highly pure state, and availability as a *certified reference material* (CRM) - see Section 3.4.6;
- (ii) stability of solution over a reasonable period of time;
- (iii) having a low value of the *residual liquid junction potential* - see section 3.4.5;
- (iv) having pH between 3 and 11,

are designated as *primary reference standards* (PS) in aqueous solution of specified concentration.

The number of such standards may be revised from time to time, but for the present is restricted to 7, including the reference value pH standard. The pH_{PS} values assigned to these primary

standards are derived from measurements on cells without liquid junction:



Values of pH^{rs} for temperatures 0 - 95°C are given in Table 3.4.2 and have been assigned by the same method as that used for the reference value solution. These are best values: values for CRMs (see Section 3.4.6) may differ slightly.

If the definition of pH given above is adhered to, then the pH^{x} of a solution using cells I and II (see Section 3.4.3) may be slightly dependent on which standard solution is used. The deviations are due to

- (i) the Bates-Guggenheim convention (see Section 3.4.5) adopted for the single ion activity coefficient of the chloride ion (in order to obtain pH^{rs} values from the analysis of measurements on the cell without transference), being applied to all seven standard reference solutions;
- (ii) variations in the liquid junctions resulting from the different ionic compositions and mobilities of the several standards and from differences in the geometry of the liquid-liquid boundary in these standards. In fact, such variations in measured pH^{x} are usually at the 0.02 level and are too small to be of practical significance for most measurements.

Operational pH standards (OS)

To minimize variation in pH^{x} , *operational standards* are defined, traceable directly to pH^{rvs} . Operational standards are in no way to be regarded as inferior to, but on a par with, primary standards for the purpose of pH measurement with Cell III. Certain substances which meet the criteria of

- (i) reproducible preparation in highly pure state
- (ii) stability of solution over a reasonable period of time,

are designated as operational standards in aqueous solution of specified concentration. Their number is in principle unlimited, but values are available now for 15 solutions. The values of pH^{os} are assigned by comparison with the pH^{rvs} in cells with liquid junction, where the liquid junctions are formed within vertical 1 mm capillary tubes (Cell VII). Consequently, the pH^{os} values include a liquid-junction factor for this particular junction geometry, thereby partially compensating the liquid junction potential of the operational cell (III) which may have different construction, e.g., fiberwick, ground sleeve, ceramic plug, etc.



Values of $\text{pH}(\text{OS})$ for 0 - 95°C are given in Table 3.4.3.

TABLE 3.4.2 Values of pH^{ps} for Primary Standard Reference Solutions

Primary Reference Standard	$t/^{\circ}\text{C}$															
	0	5	10	15	20	25	30	35	37	40	50	60	70	80	90	95
Saturated (at 25°C) Potassium Hydrogen Tartrate	-	-	-	-	-	3.557	3.552	3.549	3.548	3.547	3.549	3.560	3.580	3.610	3.650	3.674
0.1 mol/kg Potassium Dihydrogen Citrate	3.863	3.840	3.820	3.802	3.788	3.776	3.759	3.756	3.754	3.749	-	-	-	-	-	-
0.025 mol/kg Disodium Hydrogen Phosphate +0.025 mol/kg Potassium Dihydrogen Phosphate	6.984	6.951	6.923	6.900	6.881	6.865	6.853	6.844	6.841	6.838	6.833	6.863	6.845	6.859	6.876	6.886
0.03043 mol/kg Disodium Hydrogen Phosphate +0.008695 mol/kg Potassium Dihydrogen Phosphate	7.534	7.500	7.472	7.448	7.429	7.413	7.400	7.389	7.386	7.380	7.367	-	-	-	-	-
0.01 mol/kg Sodium Tetraborate	9.464	9.395	9.332	9.276	9.225	9.180	9.139	9.102	9.088	9.068	9.011	8.962	8.921	8.884	8.850	8.833
0.025 mol/kg Sodium Hydrogen Carbonate +0.025 mol/kg Sodium Carbonate	10.317	10.245	10.179	10.118	10.012	9.966	9.926	9.910	9.889	9.828	-	-	-	-	-	-

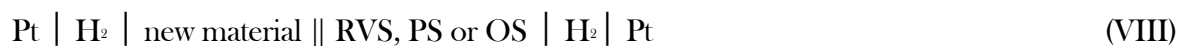
3.4.5 Conventional residual liquid junction potential

The difference $\text{pH}(\text{PS})-\text{pH}(\text{OS})$ is a measure of the *conventional residual liquid junction potential* for a given solution and construction of the liquid junction. This difference is called a conventional value because the method of assigning pH^{ps} values is based on the Bates-Guggenheim convention for the single ion activity coefficient of the chloride ion (See section 3.4.4). Values given in terms of $10^3 \Delta\text{pH}$ for free diffusion junctions formed in a capillary tube are given in Table 3.4.3 (the second row of each entry).

pH^{os} values obtained using another of the Primary Standards in Cell VII will be slightly different from those obtained with the RVS because of slight inconsistencies between the assigned pH^{ps} values. Correction can be made to RVS based values with knowledge of *conventional residual liquid junction potential* values between the PS or RVS and KCl. It is not possible to make this correction unless the liquid junction has been formed within a capillary tube. Only then is the geometry of the liquid junction sufficiently defined and the value reproducible. Most commercial designs for formation of liquid junctions are of ill-defined geometry and hence provide poor reproducibility.

3.4.6 Certified reference materials (CRM) for pH

National Standards Organizations and Metrological Laboratories are encouraged to make available *certified reference materials*. It is desirable that criteria established for the purity of these materials be based on non-electrometric methods. But until such time as these are developed, purity can be assessed by measurements on cells IV or VI, or by comparison with a known quality material in cell VII or in the simpler cell VIII



where \parallel is a sintered glass disc of porosity grade 4.

TABLE 3.4.3 pH_{os} Values for Operational Standard Reference Solutions

Operational Standard Reference Solution	t/°C														
	0	5	10	15	20	25	30	37	40	50	60	70	80	90	95
0.1 mol/kg Potassium Tetraoxalate	-	-	-	-	1.475	1.479	1.483	1.490	1.493	1.503	1.513	1.52	1.53	1.53	1.53
0.05 mol/kg Potassium Tetraoxalate	-	-	1.683	1.642	1.644	1.646	1.648	1.649	1.650	1.653	1.660	1.671	1.689	1.72	1.73
			32	30	31	30	35	42	44	54	63	73	77	72	76
0.05 mol/kg Sodium Hydrogen Diglycolate	-	3.466	3.470	3.476	3.484	3.492	3.502	3.519	3.527	3.558	3.595	-	-	-	-
		9	11	13	15	17	18	18	21	22	24				
Saturated (at 25°C) Potassium Hydrogen Tartrate	-	-	-	-	-	3.556	3.549	3.544	3.542	3.544	3.553	3.570	3.596	3.627	3.649
						1	3	4	5	5	7	10	13	33	25
0.05 mol/kg Potassium Hydrogen Phthalate (RVS)	4.000	3.998	3.997	3.998	4.000	4.005	4.011	4.022	4.027	4.050	4.080	4.115	4.159	4.21	4.24
0.1 mol/dm ³ Acetic Acid + 0.1 mol/dm ³ Sodium Acetate	4.664	4.657	4.652	4.647	4.645	4.644	4.643	4.647	4.650	4.663	4.684	4.713	4.75	4.80	4.83
	18	16	13	9	11	10	11	11	11	12					
0.1 mol/dm ³ Acetic Acid + 0.01 mol/dm ³ Sodium Acetate	4.729	4.722	4.717	4.714	4.712	4.713	4.715	4.722	4.726	4.743	4.768	4.800	4.839	4.88	4.91
	8	8	8	8	8	7	7	5	4	2					
0.02 mol/kg Piperazine Phosphate	-	6.477	6.419	6.364	6.310	6.259	6.209	6.143	6.116	6.030	5.952	-	-	-	-
		38	34	30	28	25	25	24	24	28					
0.025 mol/kg Disodium Hydrogen Phosphate + 0.025 mol/kg Potassium Dihydrogen Phosphate	6.961	6.935	6.912	6.891	6.873	6.857	6.843	6.828	6.823	6.814	6.817	6.830	6.85	6.90	6.92
	23	16	11	9	8	8	10	13	15	19	19	15	0	-23	-34

TABLE 3.4.3 (continued)

Operational Standard Reference Solution	t/°C														
	0	5	10	15	20	25	30	37	40	50	60	70	80	90	95
0.03043 mol/kg Disodium Hydrogen Phosphate + 0.008695 mol/kg Potassium Dihydrogen Phosphate	7.056 23	7.482 18	7.460 12	7.441 7	7.423 6	7.406 7	7.390 10	7.369 16	-	-	-	-	-	-	-
0.04 mol/kg Disodium Hydrogen Phosphate + 0.01 mol/kg Potassium Dihydrogen Phosphate	-	7.512	7.448	7.466	7.445	7.428	7.414	7.404	-	-	-	-	-	-	-
0.05 mol/kg TRIS Hydrochloride + 0.01667 mol/kg TRIS	8.399 72	8.238 65	8.083 58	7.933 55	7.788 52	7.648 52	7.513 50	7.332 50	7.527 52	7.018 52	6.794	-	-	-	-
0.05 mol/kg Sodium Tetraborate	9.475 35	9.409 23	9.347 17	9.288 15	9.233 12	9.182 12	9.134 15	9.074 19	9.051 20	8.983 26	8.932 24	8.898	8.88	8.84	8.89
0.01 mol/kg Sodium Tetraborate	9.451 13	9.388 7	9.329 3	9.275 1	9.225 0	9.179 1	9.138 1	9.066 2	9.066 2	9.009 2	8.698 -3	8.932 -11	8.91	8.90	8.89
0.025 mol/kg Sodium Hydrogen Carbonate + 0.025 mol/kg Sodium Carbonate	10.273 54	10.212 33	10.154 25	10.098 20	10.045 17	9.995 17	9.948 18	9.889 14	9.866 23	9.800 28	9.753	9.728	9.725	9.75	9.77
Saturated (at 20°C) Calcium Hydroxide	13.360 63	13.159 48	12.965 38	12.780 30	12.602 25	12.431 23	12.267 22	12.049 23	11.959 25	11.678 27	11.423 26	11.192	10.984	10.80	10.71

3.4.7 Measurement of pH_x

Choice of standard reference solution

The following extreme cases can be identified: (a) pH_x is required to not better than ± 0.05 . Choose any standard reference solution. (b) pH_x is required to ± 0.002 and interpretation in terms of hydrogen ion concentration or activity is desired. Choose a primary standard to match X as closely as possible in pH, composition and ionic strength. Even so, the uncertainty in hydrogen ion concentration is ± 0.02 in pH_x . Alternatively choose an operational standard on the same criteria. The uncertainty in hydrogen ion concentration will be of the same order but will additionally include the liquid junction contribution between RVS and KCl. The evidence is that this is small. (c) pH_x is required for quality control purposes. Choose an operational standard appropriately in the range 0 - 14 pH or devise a working standard using cell VI specially for the purpose.

Bracketing procedure

Alternatively, a *bracketing procedure* may be adopted as follows: The electromotive force E_x is measured, and likewise the electromotive forces E_{S1} and E_{S2} of two similar cells with the solution X replaced by the standard solutions S_1 and S_2 such that the E_{S1} and E_{S2} values are on either side of, and as near as possible to, E_x . The pH of solution X is then obtained by assuming linearity between pH and E, that is:

$$\frac{\text{pH}_x - \text{pH}_{S1}}{\text{pH}_{S2} - \text{pH}_{S1}} = \frac{E_x - E_{S1}}{E_{S2} - E_{S1}} \quad 3.20$$

Using this procedure, it will not be possible to select both standard reference buffers to match in pH, composition and ionic strength. The purpose of the bracketing procedure is to compensate for deficiencies in the electrodes and measuring system.

Information to be given about the measurement of pH_x

Workers measuring pH_x values should provide the following information about the measurements: (a) Manufacturer and type of glass electrode and reference electrode. Method of forming the liquid junction of the reference electrode. (b) Manufacturer and level of discrimination of pH meter. (c) Method adopted to calibrate the pH meter system, for example:

System calibrated with phthalate buffer
 $\text{pH}_{\text{RVS}} = \dots$ at \dots K

System calibrated with two primary standards
 $\text{pH}_{\text{PS}} = \dots$ and $\text{pH}_{\text{PS}} = \dots$ at \dots K,

practical slope factor =

System calibrated with operational standard

pH_{os} = .. at .. K

Errors of glass electrodes

The criterion of perfect behavior of an hydrogen-ion responsive glass electrode is that the e.m.f of the cell



should be constant independent of solution composition. Departure from this behavior, or error, is indicated by the difference between the e.m.f. values obtained with two different solutions.

For practical reasons the following glass (G) and hydrogen (H) cells are set up, which correspond to the invariant cell (IX) if the solution used is identical:



Denoting the e.m.f of cell IX when a reference solution R is employed by E_{IX}^R , then

$$E_{IX}^R = E_H^R - E_G^R \quad 3.21$$

where E_H^R, E_G^R are the e.m.f.'s of cells H and G, respectively, with a reference solution R. Replacing solution R, in which the glass electrode is assumed to be error-free, by another solution (T) of different pH gives, in general, new values E_{IX}^T, E_H^T, E_G^T so that

$$E_{IX}^T = E_H^T - E_G^T \quad 3.22$$

The *error of the glass electrode* ΔE is defined by

$$\begin{aligned} \Delta E &= E_{IX}^T - E_{IX}^R \\ &= (E_H^T - E_G^T) - (E_H^R - E_G^R) \\ &= (E_H^T - E_H^R) - (E_G^T - E_G^R) \end{aligned} \quad 3.23$$

Thus the error of a glass electrode, relative to a solution where it is assumed to be error-free, can be obtained by subtracting the difference between the two values obtained for cell G from the corresponding two values for cell H, which have been determined for specially devised buffer solutions.

For testing pH responsive glass electrodes at 25, 37, 65 and 85°C and for the determination of alkaline errors up to 1 mol dm⁻³ Na⁺, K⁺, Li⁺, detailed procedures are given in the paper: PAC,

3.4.8 Interpretation of pH in terms of hydrogen ion concentration

The quantity pH as defined in Section 3.4.3 has no easy interpretation. However, in the restricted range of dilute aqueous solutions (of total ionic strength not exceeding 0.1 mol kg^{-1}) in the pH range 2-12, that is for solutions closely matching the concentrations and compositions of the primary and operational standard buffers, the definition is such that

$$\text{pH} = -\lg (c_{\text{H}^+}\gamma_{\pm}/c^{\circ}) \pm 0.02 \quad 3.24$$

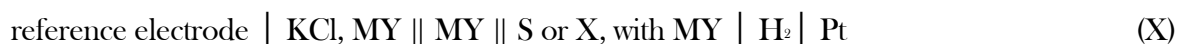
or

$$\text{pH} = -\lg (m_{\text{H}^+}\gamma_{\pm}/m^{\circ}) \pm 0.02 \quad 3.25$$

where γ_{\pm} or γ_{\pm}° denotes the mean ionic activity coefficient of a typical 1:1 electrolyte in solution. The uncertainty of 0.02 in pH corresponds to an uncertainty of $\pm 4.7\%$ in hydrogen ion concentration.

3.4.9 Determination of $\text{pH}^{\circ} = -\lg (c_{\text{H}^+}/c^{\circ})$ in solutions of constant ionic strength

At constant ionic strength, the mean activity coefficient γ_{\pm} may be assumed to be approximately constant, and therefore the difference in using the activity, $\text{pH} = -\lg (c_{\text{H}^+}\gamma_{\pm}/c^{\circ})$, and the concentration, $\text{pH}^{\circ} = -\lg (c_{\text{H}^+}/c^{\circ})$, is constant. If the standardization of the cell VIII normally used in such cases,



has been done with solutions containing a known hydrogen ion concentration in MY, where Y is the anion of a strong acid HY (e.g., dilute HClO_4 in NaClO_4), then e.m.f. measurements with the cell allow the determination of pH° , where

$$\text{pH}_x^{\circ} = \text{pH}_s^{\circ} - (E_x - E_s)/k \quad 3.26$$

and hence of the concentration of the hydrogen ion in the test solution. All solutions used should be identical in composition with respect to the inert salt MY, and the other components of the solutions (S or X) should be present in negligible concentrations with respect to that of MY.

This procedure is mostly used in the investigations of protonation and complex formation equilibria where, for practical reasons, a glass electrode often replaces the hydrogen gas electrode.

3.4.10 Determination of pH in waters of various compositions

pH is the most commonly measured chemical quantity in natural waters and knowledge of pH is a prerequisite for the understanding of the distribution of trace elements and also organic substances in their various forms in natural waters. The designation 'natural waters' includes fresh waters of low ionic strengths, estuarine and seawater, and also some highly saline waters (salinity of > 35‰). The errors in observed pH values on calculated equilibrium or kinetic parameters may cause surprisingly large effects.

To carry out measurements in various types of natural waters, consultation of the following papers is recommended: *Recommendations for the determination of pH in low ionic strength fresh waters*, PAC, **57**(6) 877-886 (1985); *Recommendations for the determination of pH in seawater and estuarine waters*, PAC, **60**(6) 865-870 (1988); *Determination of pH in highly saline waters*, PAC, **61**(6) 1133-1138 (1989).

3.4.11 Determination of pH in blood and body fluids

For pH determinations of biological fluids the hydrogen electrode is unsuitable, thus the reference method must be based on the glass electrode.

For some fundamental aspects see the following papers: *Physico-chemical quantities and units in clinical chemistry (with special emphasis on activities and activity coefficients)*, PAC, **56**(5) 567-594 (1984). *IFCC Reference methods for measurement of pH, gases and electrolytes in blood: reference materials*, Eur. J. Clin. Chem. Clin. Biochem., **29** 253-261 (1991).

3.4.12 Glossary

Asymmetry potential of a glass electrode

This is the measured potential difference of a symmetrical cell with identical solutions and reference electrodes on each side of the glass membrane. There is rarely the need, nor the possibility, of measuring the asymmetry potential of commercial glass electrodes. Drifts in glass electrode potentials with time and day-to-day variations in the potential measured in a standard buffer may be attributed to changes in asymmetry potential.

Bridge solution (of a double junction reference electrode)

A solution of high concentration of inert salt, preferably comprising cations and anions of equal mobility, optionally interposed between the *reference electrode filling* and both the test and standard solution, when the test solution and *filling solution* are chemically incompatible. This procedure introduces into the operational cell a second liquid junction formed in a similar way to

the first.

Filling solution (of a reference electrode)

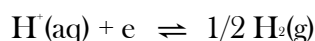
A solution containing the anion to which the reference electrode of the operational pH cell is reversible, e.g., chloride for a silver-silver chloride electrode. In the absence of a *bridge solution*, a high concentration of filling solution comprising cations and anions of almost equal mobility is employed as a means of maintaining the liquid junction potential small and approximately constant on substitution of test solution for standard solution(s).

Glass electrode error

Deviation of a glass electrode from the hydrogen-ion response function. An example often encountered is the error due to sodium ions at alkaline pH values, which by convention is regarded as positive.

Hydrogen gas electrode

A thin foil of platinum electrolytically coated with a finely divided deposit of platinum or palladium metal, which catalyzes the electrode reaction:



in solutions saturated with hydrogen gas.

Internal filling solution (of a glass electrode)

An aqueous electrolyte solution, which may be gelled, containing a fixed concentration of hydrogen ions, e.g., HCl or a buffer solution, and a fixed concentration of the ion to which the inner reference electrode is reversible, e.g., chloride ion in the case of silver-silver chloride, or calomel electrodes.

Internal reference electrode (of a glass electrode)

An electrode, e.g., silver-silver chloride, electrically connected to the screened input cable to the pH meter, and in contact with the *internal filling solution*.

Liquid junction

Any junction between two electrolyte solutions that have different compositions. Across such a

junction there arises a potential difference, called the liquid junction potential. In the operational pH cell, the junction is between the test, or pH standard, solution and the *filling solution* or the *bridge solution* of the reference electrode.

Operational pH cell

An electrochemical cell which is the basis of practical pH measurements. It consists of a hydrogen ion-responsive electrode (hydrogen gas, or glass) and a reference electrode immersed in the test solution.

Operational pH standards

Solutions with pH_{os} values assigned by the operational cell method, with reference to values of the reference value pH standard at each temperature.

pH Glass electrode

A hydrogen-ion responsive electrode usually consisting of a bulb, or other suitable form, of a special glass attached to a stem of high resistance glass complete with internal reference electrode and internal filling solution system. Other geometrical forms may be appropriate for special applications, e.g., capillary electrode for measurement of blood pH.

Primary pH standards

Aqueous solutions of selected reference buffer solutions to which pH_{ts} values have been assigned over the temperature range 0 - 95°C from measurements on cells without liquid junction.

Reference electrode

External electrode system which comprises an inner element, usually mercury-mercury(I) chloride (calomel), silver-silver chloride or thallium amalgam-thallium(I) chloride, a chamber containing the appropriate *filling solution* and a device for forming a *liquid junction*, e.g., capillary, ceramic plug, fritted disc or ground glass sleeve.

Reference value pH standard

Aqueous solution of 0.05 mol potassium hydrogen phthalate per kg water, which is the reference value for the definition of pH_{rvs} values in the temperature range 0 - 95°C.

Residual liquid junction (potential) error

Error arising from breakdown in the assumption that the liquid junction potential remains constant when solution X is substituted for solution S in the operational cell.

Zero point (of a glass electrode)

Value of the pH of a solution, which in combination with a stated outer reference electrode, gives zero e.m.f. from the operational cell.