Pure & Appl. Chem., Vol. 57, No. 3, pp. 531–542, 1985.
Printed in Great Britain.

INTERNATIONAL UNION OF PURE
AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION
COMMISSION ON ELECTROANALYTICAL CHEMISTRY*

and

PHYSICAL CHEMISTRY DIVISION
COMMISSION ON ELECTROCHEMISTRY†

DEFINITION OF pH SCALES, STANDARD REFERENCE VALUES, MEASUREMENT OF pH AND RELATED TERMINOLOGY

(Recommendations 1984)

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Definition of pH scales, standard reference values, measurement of pH and related terminology (Recommendations 1984)

This document deals with definitions, procedures and terminology for the quantity pH which is of wide interest for chemists, biologists and engineers. It is the result of discussions since 1977 within IUPAC and related discussions in other international bodies. It constitutes in the definition of pH scales a compromise which recognises the advantages of both the previously endorsed multistandard approach and that based on the definition of a single standard with associated operational standards.

INTRODUCTION

The concept (ref. 1) of pH is unique amongst physicochemical quantities accorded a Section in the IUPAC *Manual of Symbols and Terminology for Physicochemical Quantities and Units* (ref. 2) in that, in terms of its (notional) definition

$$\mathrm{pH} = -\lg a_{\mathrm{H}}$$

involving as it does a single ion activity, it is immeasurable. It is therefore defined *operationally* in terms of the *operation* or method used to measure it, that is, by means of the cell or variants of it:

$$\text{reference electrode} \mid \mathrm{KCl}\ (\geq 3.5\ \mathrm{mol\ kg^{-1}}) \parallel \text{Solution} \mid \mathrm{H_2} \mid \mathrm{Pt}$$

called the operational cell (see Section 1.2). The cell is standardized by solution(s) of assigned pH value. Such standard reference solutions are buffer solutions whose pH values are assigned from measurements on cells without liquid junction. With the use of several standard reference solutions, this constitutes the multi-primary standard approach pioneered by work (ref. 3) at the US National Bureau of Standards (NBS) during 1943-1969. Most national pH scale recommendations have been based on this multistandard system. The situation has recently been reviewed (ref. 4) by IUPAC Commission I 4 and this revealed differences in the number of primary reference standards recommended and pH values assigned. The British Standard pH scale (ref. 5), in contrast, recommends only one primary standard (potassium hydrogen phthalate) determined by the cell without liquid junction and a number of secondary standards determined by the operational cell. The basis of this different approach is the argument that to define the pH scale (i.e. to define the line of operational cell electromotive force *vs.* pH) only one point, or primary reference standard, is required, the other parameter being the theoretical slope (59.159 mV at 298.15 K). It must be emphasized that the definition of pH scale is quite distinct from the measurement of pH with glass-reference electrode-pH meter assemblies where several standards are used in order to take into account possible deficiencies in the electrode and meter performance.

The present IUPAC recommendation (ref. 2) is 5 primary reference standards based on NBS values. A joint meeting of IUPAC Commissions I.3 and V.5 first discussed pH scale recommendations in Warsaw in 1977. A sub-committee consisting of R. G. Bates (Florida), A. K. Covington (Newcastle) and R. A. Durst (Washington) was charged with reporting back to a second joint meeting of the two Commissions in Davos in 1979 and as a result a conference of pH experts was convened to discuss the matter. This meeting took place (ref. 6) as a IUPAC-sponsored conference on 'Harmonization of pH Scale Recommendations' in Lisbon in June 1980.

The decision of the conference in support of 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 and 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 which recognizes the validity of both NBS and British Standard approaches. It is the purpose of this report to describe this proposal which is intended to replace the existing IUPAC definition of the quantity pH (ref. 2). Further details of the background to these discussions and arguments can be found in two recent reviews (refs. 7,8).

1. DEFINITIONS

1.1 Notional definition. The concept of pH first introduced (ref. 1) as

$$\mathrm{pH} = -\lg c_{\mathrm{H}} \qquad (1)$$

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

$$\mathrm{pH} = -\lg a_{\mathrm{H}} \qquad (2)$$

where a_{H} is the (relative) hydrogen ion activity. This can only be a notional definition, for pH involves a single ion activity which is immeasurable. Equation (2) is often written as

$$\mathrm{pH} = -\lg m_{\mathrm{H}}\gamma_{\mathrm{H}} \quad \text{or} \quad \mathrm{pH} = -\lg c_{\mathrm{H}}y_{\mathrm{H}} \qquad (3)$$

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 forms of equation (3) are either

$$\mathrm{pH} = -\lg (m_{\mathrm{H}}\gamma_{\mathrm{H}}/m^{\ominus}) \qquad (4)$$

or

$$\mathrm{pH} = -\lg (c_{\mathrm{H}}y_{\mathrm{H}}/c^{\ominus}) \qquad (5)$$

where $m^{\ominus}$ and $c^{\ominus}$ 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 γ_{H}, y_{H} are 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 393.15 K.

1.2 Operational definition. It is universally agreed that the definition of pH difference is an operational one. The electromotive force E(X) of the cell:

reference electrode | KCl(aq,concentrated) ¦¦ solution X | H_2 | Pt   I

is measured and likewise the electromotive force (e.m.f.) E(S) of the cell:

reference electrode | KCl(aq,concentrated) ¦¦ solution S | H_2 | Pt   II

both cells being at the same temperature throughout and the hydrogen gas pressures and the reference electrode being identical in the two 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 (ref. 9). The pH of solution X, denoted by pH(X), is then related to the pH of the standard reference solution S, denoted by pH(S), by the definition:

$$\mathrm{pH(X)} = \mathrm{pH(S)} + \frac{E(\mathrm{S}) - E(\mathrm{X})}{(RT/F)\ \ln 10} \qquad (6)$$

where R denotes the gas constant, T the thermodynamic temperature, and F the Faraday constant.

To a good approximation, the hydrogen electrodes in both cells may be replaced by other hydrogen-ion-responsive electrodes, e.g. quinhydrone; in particular, in most measurements a single glass electrode, transferred between the cells, replaces the two hydrogen electrodes.

2. 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.

2.1 Reference Value pH Standard. The qualities of potassium hydrogen phthalate as the most studied (refs. 10-14) of all the pH reference materials are recognised and so it is designated as the reference value pH standard (RVS) at specified molality of 0.05 mol kg^{-1}. The reference value method is the cell without liquid junction (Cell III).

$$\mathrm{Pt(Pd)}\ |\ \mathrm{H_2}\ (\mathrm{g},\ p = 1\ \mathrm{atm} = 101\ 325\ \mathrm{Pa})\ |\ \mathrm{RVS,\ Cl^-}\ |\ \mathrm{AgCl}\ |\ \mathrm{Ag} \qquad \mathrm{(III)}^*$$

Best values of pH(RVS) for temperatures 0 - 95 °C are given in Table 1. Values for CRM samples (Section 4) may differ slightly (± 0.005 in pH). Values are determined as follows:-

TABLE 1. Values of pH(RVS) for the reference value standard of 0.05 mol kg^{-1} potassium hydrogen phthalate at various temperatures

t/°C	pH(RVS)	t/°C	pH(RVS)	t/°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	4.080	95	4.24

The e.m.f. of cell (III) is given by

$$E = E^\ominus - k\ \lg\ [m_\mathrm{H}\ m_\mathrm{Cl}\gamma_\mathrm{H}\gamma_\mathrm{Cl}/(m^\ominus)^2] \qquad (7)$$

where m signifies molality and γ activity coefficient of the subscripted species, $E^\ominus$ is the standard e.m.f., $m^\ominus = 1\ \mathrm{mol\ kg^{-1}}$ and $k = RT(\ln 10)/F$.

Equation (7) can be rearranged to

$$-\lg\ (m_\mathrm{H}\gamma_\mathrm{H}\gamma_\mathrm{Cl}/m^\ominus) = (E - E^\ominus)/k + \lg\ (m_\mathrm{Cl}/m^\ominus) \qquad (8)$$

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

$$\mathrm{Pt}\ |\ \mathrm{H_2}\ (g,\ p = 1\ \mathrm{atm} = 101\ 325\ \mathrm{Pa})\ |\ \mathrm{HCl(0.01\ mol\ kg^{-1})}\ |\ \mathrm{AgCl}\ |\ \mathrm{Ag} \qquad \mathrm{(IV)}^*$$

and calculated from equation (7) with $\gamma_\mathrm{H}\gamma_\mathrm{Cl} = \gamma_\pm^2$, where $\gamma_\pm$ is the mean ionic activity coefficient of HCl at 0.01 mol kg^{-1}.

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

$$\mathrm{pH(RVS)} = [-\lg\ (m_\mathrm{H}\gamma_\mathrm{H}\gamma_\mathrm{Cl}/m^\ominus)]_{m_\mathrm{Cl} \to 0} + \lg\ \gamma_\mathrm{Cl} \qquad (9)$$

where γ_Cl is obtained from the Bates-Guggenheim convention

$$\lg\ \gamma_\mathrm{Cl} = -\mathrm{A}(I)^{\frac{1}{2}}/[1 + 1.5(I/(m^\ominus)^{\frac{1}{2}}] \ ;\ (I \leqslant 0.1\ \mathrm{mol\ kg^{-1}}) \qquad (10)$$

and A is the Debye-Hückel (temperature dependent) limiting slope and I the ionic strength. Values of A, $\gamma_\pm$ at 0.01 mol kg^{-1}, and $E^\ominus$ are available (refs. 15,16).

2.2 Primary pH Standards. Certain substances which meet the criteria of: (i) preparation in highly pure state reproducibly, and availability as certified reference material (CRM) - see Section 4; (ii) stability of solution over a reasonable period of time; (iii) having low value of the residual liquid junction potential - see Section 3; (iv) having pH value between 3 and 11, shall be designated as primary reference standards (PS) in aqueous solution of specified concentration. Their number shall be reviewed from time to time but for the present shall be 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

$$\mathrm{Pt}\ |\ \mathrm{H_2}\ (g,\ p = 1\ \mathrm{atm} = 101\ 325\ \mathrm{Pa})\ |\ \mathrm{PS,\ Cl^-}\ |\ \mathrm{AgCl}\ |\ \mathrm{Ag} \qquad \mathrm{(V)}^*$$

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* See NOTE at end of this paper.

TABLE 2. Values of pH(PS) for Primary Standard Reference Solutions (ref. 15)

Primary Reference Standard	t/°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	3.766	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	6.836	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 Disodium 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	10.062	10.012	9.966	9.926	9.910	9.889	9.828	-	-	-	-	-

Note: Based on an uncertainty of $\pm$ 0.2 mV in determined (E-E$^{\ominus}$), the uncertainty is $\pm$ 0.003 in pH in the range 0-50 °C (15).

Values of pH(PS) for temperatures 0 - 95 °C are given in Table 2 (ref. 15) and have been assigned by the same method as that used for the reference value solution. These are best values i.e. mean of a large number of determinations: values for CRM (see Section 4) may differ slightly (+ 0.005 in pH).

If the definition of pH given above is adhered to, then the pH(X) of a solution using cells I and II (see Section 1.2) may be slightly dependent on which standard solution is used. These deviations are due to (i) the Bates-Guggenheim convention (see Section 3 and equation (10)) adopted for the single ion activity coefficient of the chloride ion (in order to obtain, from the analysis of measurements on the cell without liquid junction, pH(PS) values) being applied to all seven standard reference solutions; and (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 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.

To avoid variation in pH(X) with choice of primary reference standard, essentially a problem of overdefinition, operational standards are defined, traceable directly to pH(RVS), as described in Section 2.3. 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 II.

2.3 Operational pH Standards (OS). Certain substances which meet the criteria of (i) preparation in highly pure state reproducibly; (ii) stability of solution over a reasonable period of time shall be 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, the operational cells, where the liquid junctions are formed within vertical 1 mm capillary tubes.

$$\mathrm{Pt}\ |\ \mathrm{H_2}\ |\ \mathrm{OS}\ ||\ \mathrm{KCl}\ \geqslant 3.5\ \mathrm{mol\ dm^{-3}}\ ||\ \mathrm{RVS}\ |\ \mathrm{H_2}\ |\ \mathrm{Pt(Pd)} \qquad \mathrm{(VI)}$$

Values of pH(OS) for 0 - 95 °C are given in Table 3 (ref. 8).

3. CONVENTIONAL RESIDUAL LIQUID JUNCTION POTENTIAL

The difference pH(PS)-pH(OS) is a measure of the conventional residual liquid junction potential for a given solution. This difference is called a conventional value because the method of assigning pH(PS) values is based on the Bates-Guggenheim (ref. 9) convention for the single ion activity coefficient of the chloride ion (equation 10). Values are given in terms of $10^3\ \Delta\mathrm{pH}$ in italics for free diffusion junctions formed in a capillary tube (ref. 8) in Table 3.

pH(OS) values obtained using another of the Primary Standards in cell VI 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 (ref. 8). 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 poor reproducibility.

4. CERTIFIED REFERENCE MATERIALS (CRM) FOR pH

National Standards Organisations and Metrological Laboratories shall be encouraged to continue to make available certified reference materials. It is desirable that criteria be established for the purity of these materials based on non-electrometric methods, but until such time as these are developed, purity can be assessed by measurements on cells III or V, or by comparison with known quality material in cell VI or in the simpler cell VII (ref. 17)

$$\mathrm{Pt}\ |\ \mathrm{H_2}\ |\ \text{new material}\ ||\ \mathrm{RVS,\ PS\ or\ OS}\ |\ \mathrm{H_2}\ |\ \mathrm{Pt} \qquad \mathrm{(VII)}$$

where || is a sintered glass disc of porosity grade 4.

5. MEASUREMENT OF pH(X)

5.1 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 will correspond to ± 0.02 in pH(X). Alternatively, choose an operational standard on the

TABLE 3. pH(OS) values for Operational Standard Reference Solutions (ref. 8).

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[a]	-	-	-	-	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[a]	-	-	1.638 *32*	1.642 *30*	1.644 *31*	1.646 *33*	1.648 *35*	1.649 *42*	1.650 *44*	1.653 *54*	1.660 *63*	1.671 *72*	1.689 *77*	1.72 *72*	1.73 *76*
0.05 mol/kg Sodium hydrogen diglycolate[b]	-	3.466 *9*	3.470 *11*	3.476 *13*	3.484 *15*	3.492 *17*	3.502 *18*	3.519 *18*	3.527 *21*	3.558 *22*	3.595 *24*	-	-	-	-
Saturated (at 25 °C) Potassium hydrogen tartrate	-	-	-	-	-	3.556 *1*	3.549 *3*	3.544 *4*	3.542 *5*	3.544 *5*	3.553 *7*	3.570 *10*	3.596 *13*	3.627 *23*	3.649 *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 *19*	4.657 *16*	4.652 *13*	4.647 *9*	4.645 *11*	4.644 *10*	4.643 *11*	4.647 *11*	4.650 *11*	4.663 *12*	4.684	4.713	4.75	4.80	4.83
0.01 mol/dm^3 Acetic acid + 0.01 mol/dm^3 Sodium acetate	4.729 *8*	4.722 *8*	4.717 *8*	4.714 *8*	4.712 *8*	4.713 *7*	4.715 *7*	4.722 *5*	4.726 *4*	4.743 *2*	4.768	4.800	4.839	4.88	4.91
0.02 mol/kg Piperazine phosphate[c]	-	6.477 *38*	6.419 *34*	6.364 *30*	6.310 *28*	6.259 *25*	6.209 *25*	6.143 *24*	6.116 *24*	6.030 *28*	5.952	-	-	-	-
0.025 mol/kg Disodium hydrogen phosphate + 0.025 mol/kg Potassium dihydrogen phosphate	6.961 *23*	6.935 *16*	6.912 *11*	6.891 *9*	6.873 *8*	6.857 *8*	6.843 *10*	6.828 *13*	6.823 *15*	6.814 *19*	6.817 *19*	6.830 *15*	6.85 *0*	6.90 *-23*	6.92 *-34*
0.03043 mol/kg Disodium hydrogen phosphate + 0.008695 mol/kg Potassium dihydrogen phosphate	7.506 *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	7.488	7.466	7.445	7.428	7.414	7.404	-	-	-	-	-	-	-
0.05 mol/kg Tris Hydrochloride + 0.01667 mol/kg Tris[d]	8.399 *72*	8.238 *65*	8.083 *58*	7.933 *55*	7.788 *52*	7.648 *52*	7.513 *50*	7.332 *50*	7.257 *52*	7.018 *52*	6.794	-	-	-	-
0.05 mol/kg Disodium tetraborate ($Na_2B_4O_7$)	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 *25*	8.932 *24*	8.898	8.88	8.84	8.89
0.01 mol/kg Disodium tetraborate ($Na_2B_4O_7$)	9.451 *13*	9.388 *7*	9.329 *3*	9.275 *1*	9.225 *0*	9.179 *1*	9.138 *1*	9.086 *2*	9.066 *2*	9.009 *2*	8.965 *-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	13.159	12.965	12.780	12.602 *38*	12.431 *39*	12.267 *43*	12.049	11.959	11.678	11.423	11.192	10.984	10.80	10.71

Note: Uncertainty is ± 0.003 in pH between 0 and 60 °C rising to ± 0.01 above 70 °C.

[a] potassium trihydrogen dioxalate ($KH_3C_4O_8$); [b] sodium hydrogen 2,2'oxydiacetate; [c] $C_4H_{10}N_2 \cdot H_3PO_4$; [d] 2-amino-2-(hydroxymethyl)-1,3-propanediol or tris(hydroxymethyl)aminomethane

same criteria so that the residual liquid junction potential is small. The uncertainty in hydrogen ion concentration will correspond to ± 0.02 in pH(X) but will additionally include the liquid junction contribution between RVS and KCl; the evidence is (ref. 8) that this is small. (c) pH(X) is required for quality control purposes. Choose an operational standard appropriately in the pH range 0 - 14 or devise a working standard using cell VI specially for the purpose.

5.2 Bracketting Procedure. Alternatively, a bracketting procedure may be adopted as follows: the electromotive force $E(\mathrm{X})$ is measured, and likewise the electromotive forces $E(\mathrm{S}_1)$ and $E(\mathrm{S}_2)$ of two cells II with standard solutions S_1 and S_2 such that the $E(\mathrm{S}_1)$ and $E(\mathrm{S}_2)$ values are on either side of, and as near as possible to, $E(\mathrm{X})$. The pH of solution X is then obtained by assuming linearity between pH and E, that is to say:

$$\frac{\mathrm{pH(X)} - \mathrm{pH}(\mathrm{S}_1)}{\mathrm{pH}(\mathrm{S}_2) - \mathrm{pH}(\mathrm{S}_1)} = \frac{E(\mathrm{X}) - E(\mathrm{S}_1)}{E(\mathrm{S}_2) - E(\mathrm{S}_1)} \qquad (11)$$

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 bracketting procedure is to compensate for deficiencies in the electrodes and measuring system.

5.3 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 type and discrimination of pH meter. (c) Method adopted to calibrate the pH meter system, for example:

System calibrated with phthalate buffer
pH(RVS) = .. at .. K

System calibrated with two primary standards
pH(PS) = .. and pH(PS) = .. at .. K,
practical slope = ... mV

System calibrated with operational standard
pH(OS) = .. at .. K

For general discussions of the problems of defining pH and making pH measurements see refs. 15,7,8.

6. INTERPRETATION OF pH IN TERMS OF HYDROGEN ION CONCENTRATION

The quantity pH as defined in Section 1.2 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

$$\mathrm{pH} = -\lg(c_{\mathrm{H}}y_{\pm}/c^{\ominus}) \pm 0.02 \qquad (12)$$

or

$$\mathrm{pH} = -\lg(m_{\mathrm{H}}\gamma_{\pm}/m^{\ominus}) \pm 0.02 \qquad (13)$$

where $y_{\pm}$ or $\gamma_{\pm}$ denote 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 ± 3.9% in concentration.

7. DETERMINATION OF $\mathrm{pH}_c = -\lg(c_{\mathrm{H}}/c^{\ominus})$ IN SOLUTIONS OF CONSTANT IONIC STRENGTH

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

$$\text{reference electrode} \mid \mathrm{KCl,\ MY} \parallel \mathrm{MY} \parallel \mathrm{S\ or\ X,\ with\ MY} \mid \mathrm{H}_2 \mid \mathrm{Pt} \qquad (\mathrm{VIII})$$

has been done with solutions containing a known hydrogen ion concentration, e.g. dilute $\mathrm{HClO_4}$ in MY, where Y is the anion of a strong acid HY, then e.m.f. measurements with the cell allow the determination of pH_c where

$$\mathrm{pH}_c(\mathrm{X}) = \mathrm{pH}_c(\mathrm{S}) + \{E(\mathrm{S}) - E(\mathrm{X})\}F/(RT\ \ln 10) \qquad (13)$$

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 (e.g. KCl, $NaClO_4$, KNO_3, $NaNO_3$).

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.

8. DETERMINATION OF pH IN BLOOD AND BODY FLUIDS

It is not intended that the foregoing recommendations should apply to determination of pH in blood plasma, blood serum, whole blood or urine, where the 0.025 mol kg^{-1} equimolal phosphate buffer is used as standard reference solution by the International Federation of Clinical Chemistry (IFCC) Expert Panel on pH and Blood Gases and provisional (ref. 18) and draft IFCC/IUPAC documents should be referred to for further details. The choice of phosphate buffer is more appropriate for these measurements in view of the fact that its ionic strength (0.1 mol kg^{-1}) is closer to the ionic strength of body fluids (0.16 mol kg^{-1}) and closer in pH than the RVS. These requirements justify the definition of a separate pH scale for clinical measurements as is also needed for sea water measurements (ref. 19) where the ionic strength is even higher (0.7 mol kg^{-1}).

9. GLOSSARY

9.1 Operational pH cell. Electrochemical cell which is the basis of practical pH measurements consisting of a hydrogen ion-responsive electrode (hydrogen gas, or glass) and a reference electrode (9.11) immersed in the test solution.

9.2 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.

9.3 Primary pH Standards. Aqueous solutions of six selected reference buffer solutions to which pH(PS) values have been assigned over the temperature range 0 - 95 °C from measurements on cells without liquid junction.

9.4 Operational pH Standards. Solutions with pH(OS) values assigned by the operational cell method with reference to values of the reference value pH standard (9.2) at each temperature.

9.5 pH glass electrode. Hydrogen-ion responsive electrode usually consisting of a bulb, or other suitable form, of special glass attached to a stem of high resistance glass complete with internal reference electrode (9.6) and internal filling solution system (9.7). Other geometrical forms may be appropriate for special applications e.g. capillary electrode for measurement of blood pH.

9.6 Internal reference electrode (of a glass electrode). 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.

9.7 Internal filling solution (of a glass electrode). Aqueous electrolyte solution, which may be gelled, containing 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.

9.8 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.

9.9 Asymmetry potential of a glass electrode. 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 variations from day-to-day in the potential measured in a standard buffer may be attributed to changes in asymmetry potential.

9.10 Hydrogen gas electrode. A thin foil of platinum electrolytically coated with finely divided deposit of platinum or palladium metal, which catalyses the electrode reaction:-

$$H^+ + e \rightleftharpoons \tfrac{1}{2}H_2$$

in solutions saturated with hydrogen gas.

9.11 Reference electrode. External electrode system which comprises an inner element, usually calomel, silver-silver chloride or thallium amalgam-thallous chloride, a chamber containing the appropriate filling solution (9.14) and a device for forming a liquid junction (9.12), e.g. capillary, ceramic plug, fritted disc or ground glass sleeve.

9.12 Liquid junction. Any junction between two electrolyte solutions of different composition. 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 (9.15) of the reference electrode.

9.13 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.

9.14 Filling solution (of a reference electrode). Solution containing the anion to which the reference electrode of the operational pH cell is reversible, e.g. chloride for silver-silver chloride electrode. In the absence of a bridge solution (9.15) 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).

9.15 Bridge solution (of a double junction reference electrode). Solution of high concentration of inert salt, preferably comprising cations and anions of equal mobility, optionally interposed between the reference electrode filling (9.14) 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 usually in a similar way to the first.

9.16 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.

10. SUMMARY

The compromise recommendation described above recognises that pH experts are divided and IUPAC is unable to recommend, unreservedly, on scientific grounds, one or other of the two approaches to pH scale definition.

In permitting the validity of either approach, with the proviso that results are properly reported, indicating which system and standards have been used, it is hoped that there will be greater realisation of the problems of pH measurement by the scientific community. Further research is needed to establish the respective merits of the two approaches and only then can a thermodynamically significant and metrologically sound pH scale be recommended.

* Note: In 1981, IUPAC Commission I.2 Thermodynamics recommended (ref. 20) 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, be made to all existing tabulated standard electrode potentials. The existing tabulated data for the silver-silver chloride electrode (15,16) refer to 1 atm = 101 325 Pa and so do published data on cells IV and V. Since the cell pairs IV-III or (V)-(III) are involved in these calculations of the data in Tables 1 and 2, the difference in standard electrode potential consequent upon the recommended change in standard state pressure cancels out. Therefore, the standard state condition of 1 atm in cells III, IV and V is retained here.

REFERENCES

1. S. P. L. Sorensen, *Biochem. Z.*, 21, 131, 201 (1909); *C. R. Trav. Lab. Carlsberg*, 8, 1 (1909).

2. 'Manual of Symbols and Terminology for Physicochemical Quantities and Units', 2nd rev., *Pure Appl. Chem.*, 51, 1 (1979).

3. R. A. Durst, Standard Reference Materials; Standardization of pH Measurements, NBS Spec. Publ., 260-53, Washington D.C. U.S. Gov. Printing Office (1975).

4. R. A. Durst and J. P. Cali, *Pure Appl. Chem.*, 50, 1485 (1978).

5. British Standards Institution, Specification for pH Scale BS1647 (1961).

6. *Chem. Internat.* No. 6, 23 (1980).

7. R. G. Bates, *Crit. Rev. Anal. Chem.*, 10, 247 (1981).

8. A. K. Covington, *Anal. Chim. Acta*, 127, 1 (1981).

9. R. G. Bates and E. A. Guggenheim, *Pure Appl. Chem.*, 1, 163 (1960).

10. W. J. Hamer and S. F. Acree, *J. Res. Nat. Bur. Stand.*, 32, 215 (1944).

11. W. J. Hamer, G. D. Pinching and S. F. Acree, *J. Res. Nat. Bur. Stand.* 36, 47 (1946).

12. H. B. Hetzer, R. A. Durst, R. A. Robinson and R. G. Bates, *J. Res. Nat. Bur. Stand.*, 81A, 21 (1977).

13. E. Etz, unpublished work (1973) quoted in ref. 14.

14. H. P. Bütikofer and A. K. Covington, *Anal. Chim. Acta*, 108, 179 (1979).

15. R. G. Bates, *Determination of pH. Theory and Practice*, 2nd edn., Wiley, New York (1973).

16. R. G. Bates and R. A. Robinson, *J. Soln. Chem.*, 9, 455 (1980).

17. F. G. K. Baucke, Chem. Ing. Tech., 41, 739 (1977); Further details to be published.

18. *J. Clin. Chem. Clin. Biochem.*, 18, 829 (1980).

19. R. G. Bates, *Pure Appl. Chem.*, 54, 229 (1982).

20. *Pure Appl. Chem.*, 54, 1239 (1982); R. D. Freeman, *Bull. Chem. Thermodyn.* 25, 523 (1982).