pH SCALE FOR AQUEOUS SOLUTIONS

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A Working Party of IUPAC, after extensive considerations over five years, has recently produced a report (1) which sets pH firmly within the International System of Units (SI). A summary of these important developments is given below.

The concept of pH is unique amongst the commonly encountered physicochemical quantities in that, in terms of its definition,

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

it involves a single ion quantity, the activity of the hydrogen ion, which is immeasurable by any thermodynamically valid method and requires a convention for its evaluation.

pH was originally defined by Sørensen (2) in terms of the concentration of hydrogen ions (in modern nomenclature) as $\mathrm{pH} = -\lg (c_{\mathrm{H}}/c^{\mathrm{o}})$ where c_{H} is the hydrogen ion concentration in mol dm^{-3}, and $c^{\mathrm{o}} = 1$ mol dm^{-3} is the standard amount concentration. Subsequently (3), it was accepted as more satisfactory to define pH in terms of the relative activity of hydrogen ions in solution

$$\mathrm{pH} = -\lg a_{\mathrm{H}} = -\lg (m_{\mathrm{H}}\gamma_{\mathrm{H}}/m^{\mathrm{o}}) \qquad (2)$$

where a_{H} is the relative (molality basis) activity and γ_{H} is the molal activity coefficient of the hydrogen ion H^+ at the molality m_{H} , and m^{o} the standard molality. The quantity pH is intended to be a measure of the activity of hydrogen ions in solution. However, since it is defined in terms of a quantity that cannot be measured by a thermodynamically valid method, eqn.(2) can only be considered a *notional definition* of pH.

pH being a single ion quantity, it is not determinable in terms of a fundamental (or base) unit of any measurement system, and there is difficulty providing a proper basis for the traceability of pH measurements. A satisfactory approach is now available in that pH determinations can be incorporated into the International System (SI) if they can be traced to measurements made using a method that fulfils the definition of a 'primary method of measurement' (4).

The essential feature of a primary method is that it must operate according to a well-defined measurement equation in which all of the variables can be determined experimentally in terms of SI units. Any limitation in the determination of the experimental variables, or in the theory, must be included within the estimated uncertainty of the method if traceability to the SI is to be established. If a convention were used without an estimate of its uncertainty, true traceability to SI would not be established. The electrochemical cell without liquid junction, known as the Harned cell (5), fulfils the definition of a primary method for the measurement of the acidity function, $\mathrm{p}(a_{\mathrm{H}}\gamma_{\mathrm{Cl}})$, and subsequently of the pH of buffer solutions.

The Harned cell is written as

$$\mathrm{Pt} \mid \mathrm{H_2} \mid \text{buffer S}, \mathrm{Cl^-} \mid \mathrm{AgCl} \mid \mathrm{Ag} \qquad \text{Cell I}$$

and contains a standard buffer, S, with chloride ions, as potassium or sodium chloride, added in order to use the silver-silver chloride electrode as reference electrode. The application of the Nernst equation to the spontaneous cell reaction of Cell I:

$$^1/_2\ \mathrm{H_2} + \mathrm{AgCl} \rightarrow \mathrm{Ag(s)} + \mathrm{H^+} + \mathrm{Cl^-}$$

yields the potential difference E_{I} of the cell (corrected to 1 atm (101.325 kPa), the partial pressure of hydrogen gas used in electrochemistry in preference to 100 kPa) as

$$E_{\mathrm{I}} = E^{\mathrm{o}} - (RT/F)\ln 10 \lg [(m_{\mathrm{H}}\gamma_{\mathrm{H}}/m^{\mathrm{o}})(m_{\mathrm{Cl}}\gamma_{\mathrm{Cl}}/m^{\mathrm{o}})] \qquad (3)$$

which can be rearranged, since $a_{\mathrm{H}} = m_{\mathrm{H}}\gamma_{\mathrm{H}}/m^{\mathrm{o}}$, to give the acidity function

$$\mathrm{p}(a_{\mathrm{H}}\,\gamma_{\mathrm{Cl}}) = -\lg(a_{\mathrm{H}}\gamma_{\mathrm{Cl}}) = (E_{\mathrm{I}} - E^{\mathrm{o}})/[(RT/F)\ln 10] + \lg(m_{\mathrm{Cl}}/m^{\mathrm{o}}) \qquad (4)$$

where E^{o} is the standard potential difference of the cell, and hence of the silver-silver chloride electrode, and γ_{Cl} is the activity coefficient of the chloride ion.

The standard potential difference of the silver/silver chloride electrode, E^{o}, is determined from a Harned cell in which only HCl is present at a fixed molality (e.g. $m = 0.01$ mol kg^{-1})

$$\mathrm{Pt} \mid \mathrm{H_2} \mid \mathrm{HCl}\ (m) \mid \mathrm{AgCl} \mid \mathrm{Ag} \qquad \text{Cell Ia}$$

The application of the Nernst equation to the HCl cell (Ia) gives

$$E_{\mathrm{Ia}} = E^{\mathrm{o}} - (2RT/F)\ln 10 \lg[(m_{\mathrm{HCl}}/m^{\mathrm{o}})(\gamma_{\pm\mathrm{HCl}})] \qquad (5)$$

where E_{Ia} has been corrected to 1 atmosphere partial pressure of hydrogen gas (101.325 kPa) and $\gamma_{\pm\mathrm{HCl}}$ is the mean ionic activity coefficient of HCl.

Values of the activity coefficient ($\gamma_{\pm\mathrm{HCl}}$) at molality 0.01 mol kg^{-1} and various temperatures were given by Bates and Robinson (6). The standard potential difference depends on the method of preparation of the electrodes, but individual determinations of the activity coefficient of HCl at 0.01 mol kg^{-1} are more uniform than values of E^{o}. Hence the practical determination of the potential difference of the cell with HCl at 0.01 mol kg^{-1} is recommended at 298.15 K at which the mean ionic activity coefficient is 0.904. (It is unnecessary to repeat the measurement of E^{o} at other temperatures but simply to correct published smoothed values by the observed difference in E^0 at 298.15 K)

In national metrology institutes (NMIs), measurements of Cells I and Ia are often done simultaneously in a thermostat bath. Subtracting eqn.(5) from (3) gives

$$\Delta E = E_{\mathrm{I}} - E_{\mathrm{Ia}} = -(RT/F)\ln 10\{\lg[(m_{\mathrm{H}}\gamma_{\mathrm{H}}/m^{\mathrm{o}})(m_{\mathrm{Cl}}\gamma_{\mathrm{Cl}}/m^{\mathrm{o}})] - \lg[(m_{\mathrm{HCl}}/m^{\mathrm{o}})^2\gamma^2_{\pm\mathrm{HCl}}]\} \qquad (6)$$

which is independent of the standard potential difference. Therefore, the subsequently calculated pH does not depend on the standard potential difference and hence does not depend on the assumption that the standard potential of the hydrogen electrode is zero at all temperatures. Therefore, the Harned cell gives an exact comparison between hydrogen ion activities at different temperatures.

The quantity $\mathrm{p}(a_{\mathrm{H}}\gamma_{\mathrm{Cl}}) = -\lg (a_{\mathrm{H}}\gamma_{\mathrm{Cl}})$, on the left hand side of (4), is called the acidity function (5). To obtain the quantity pH according to eqn. (2) from the acidity function, it is necessary to evaluate $\lg \gamma_{\mathrm{Cl}}$ independently. This is done in two steps: (i) the

value of lg ($a_H\gamma_{Cl}$) at zero chloride molality, lg ($a_H\gamma_{Cl}$)°, is evaluated and (ii) a value for the activity of the chloride ion γ^o_{Cl}, at zero chloride molality (sometimes referred to as the limiting or 'trace' activity coefficient) is calculated using the Bates-Guggenheim convention (7). The value of lg ($a_H\gamma_{Cl}$)° corresponding to zero chloride molality is determined by linear extrapolation of measurements using Harned cells with at least three added molalities of sodium or potassium chloride (I < 0.1 mol kg^{-1}).

The value of lg ($a_H\gamma_{Cl}$)° corresponding to zero chloride molality is determined by linear extrapolation of measurements using Harned cells with at least three added molalities of sodium or potassium chloride (I < 0.1 mol kg^{-1}) in accord with eqn. (7):

$$-\lg (a_H\gamma_{Cl}) = -\lg (a_H\gamma_{Cl})^o + Sm_{Cl} \quad (7)$$

where S is an empirical, temperature dependent, constant.

The Bates-Guggenheim convention (7) assumes that the trace activity coefficient of the chloride ion γ^o_{Cl} is given by

$$\lg \gamma^o_{Cl} = -A\, I^{1/2} / (1 + Ba\, I^{1/2}) \quad (8)$$

where A is the Debye-Hückel temperature dependent constant (limiting slope), a is the *mean* distance of closest approach of the ions (ion size parameter), Ba is set equal to 1.5 (mol kg^{-1})$^{-1/2}$ at all temperatures in the range 5-50 °C, and I is the ionic strength of the buffer (which for its evaluation requires knowledge of appropriate acid dissociation constants).

The various stages in the assignment of primary standard pH values are combined in eqn. (9), which is derived from eqns. (4), (5) and (8)

$$\mathrm{pH(PS)} = \lim m_{Cl\to 0} \{(E_I - E^o)/[(RT/F)\ln 10] + \lg (m_{Cl}/m^o)\} - AI^{1/2}/[1 + 1.5\,(I/m^o)^{1/2}] \quad (9)$$

In order for a particular buffer solution to be considered a primary buffer solution, it must be of the "highest metrological" quality (4) in accordance with the definition of a primary standard. It is recommended that it have the following attributes (9):

1. High buffer value in the range 0.016-0.07 (mol OH^-)/pH.
2. Small dilution value at half concentration (change in pH with change in buffer concentration) in the range 0.01-0.20.
3. Small dependence of pH on temperature less than ± 0.01 K^{-1}.
4. Low residual liquid junction potential < 0.01 in pH.
5. Ionic strength ≤0.1 mol kg^{-1} to permit applicability of Bates-Guggenheim convention.
6. NMI certificate for specific batch.
7. Reproducible purity of preparation (lot to lot differences of |ΔpH(PS)| < 0.003).
8. Long term stability of stored solid material.

Values for the above and other important parameters for the primary and secondary buffer materials are given in Table 1.

Primary Standard Buffers

As there can be significant variations in the purity of samples of a buffer of the same nominal chemical composition, it is essential that the primary buffer material used has been certified with values that have been measured with Cell I. The Harned cell is used by many national metrological institutes for accurate measurements of pH of buffer solutions.

Typical values of the pH(PS) of the seven solutions from the six accepted primary standard reference buffers, which meet the conditions stated above, are listed in Table 2. Batch-to-batch variations in purity can result in changes in the pH value of samples of at most 0.003. The typical values in Table 2 should not be used in place of the certified value (from a Harned cell measurement) for a specific batch of buffer material.

The required attributes listed above effectively limit the range of primary buffers available to between pH 3 and 10 (at 25 °C). Calcium hydroxide and potassium tetraoxalate are excluded because the contribution of hydroxide or hydrogen ions to the ionic strength is significant. Also excluded are the nitrogen bases of the type BH^+ (such as tris(hydroxymethyl)aminomethane and piperazine phosphate) and the zwitterionic buffers (e.g. HEPES and MOPS (10)). These do not comply because either the Bates-Guggenheim convention is not applicable, or the liquid junction potentials are high. This means the choice of primary standards is restricted to buffers derived from oxy-carbon, -phosphorus, -boron and mono, di- and tri-protic carboxylic acids. The uncertainties (11) associated with Harned cell measurements are calculated (1) to be 0.004 in pH at NMIs, with typical variation between batches of primary standard buffers of 0.003.

Secondary Standards

Substances that do not fulfil all the criteria for primary standards, but to which pH values can be assigned using Cell I are considered to be secondary standards (Table 3). Reasons for their exclusion as primary standards include difficulties in achieving consistent and suitable chemical quality (e.g. acetic acid is a liquid), suspected high liquid junction potential, or inappropriateness of the Bates-Guggenheim convention (e.g. other charge-type buffers). The uncertainty is higher (e.g. 0.01) for biological buffers. Certain other substances, which cannot be used in cells containing hydrogen gas electrodes, are also classed as secondary standards.

Calibration Procedures

(a) One-point calibration

A single point calibration is insufficient to determine both slope and one-point parameters. The theoretical value for the slope can be assumed but the practical slope may be up to 5% lower. Alternatively, a value for the practical slope can be assumed from the manufacturer's prior calibration. The one-point calibration therefore yields only an estimate of pH(X). Since both parameters may change with age of the electrodes, this is not a reliable procedure.

(b) Two-point calibration [target uncertainty: 0.02-0.03 at 25 °C]

In the majority of practical applications, glass electrodes cells are calibrated by a two-point calibration, or bracketing, procedure using two standard buffer solutions, with pH values, pH(S_1) and pH(S_2), bracketing the unknown pH(X). Bracketing is often taken to mean that the pH(S_1) and pH(S_2) buffers selected from Table 2 should be those that are immediately above and below pH(X). This may not be appropriate in all situations and choice of a wider range may be better.

(c) Multi-point calibration [target uncertainty: 0.01-0.03 at 25 °C].
Multi-point calibration is carried out using up to five standard buffers . The use of more than five points yields no significant improvement in the statistical information obtainable.
Details of uncertainty computations (11) have been given (1).

Measurement of pH and choice of pH Standard Solutions

1a) If pH is not required to better than ±0.05 any pH standard solution may be selected.
1b) If pH is required to ±0.002 and interpretation in terms of hydrogen ion concentration or activity is desired, choose a standard solution, pH(PS), to match X as closely as possible in terms of pH, composition and ionic strength.
2) Alternatively, a bracketing procedure may be adopted whereby two standard solutions are chosen whose pH values, pH(S1), pH(S2) are on either side of pH(X). Then if the corresponding potential difference measurements are E(S1), E(S2), E(X), then pH(X) is obtained from

$$\mathrm{pH(X)} = \mathrm{pH(S1)} + [E(\mathrm{X}) - E(\mathrm{S1})]/\ \%k$$

where $\%k = 100[E(\mathrm{S2}) - E(\mathrm{S1})]/[\mathrm{pH(S2)} - \mathrm{pH(S1)}]$ is the apparent percentage slope. This procedure is very easily done on some pH meters simply by adjusting downwards the slope factor control with the electrodes in S2. 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)

The standard solutions selected for calibration of the pH meter system should be reported with the measurement as follows:

System calibrated with pH(S) = ... at ...K.

System calibrated with two primary standards, pH(PS1) =.... and pH(PS2) =....at ....K.

System calibrated with *n* standards, pH(S1) =.... , pH(S2) =.... etc. at....K.

Interpretation of pH(X) in terms of hydrogen ion concentration

The defined pH has no simple interpretation in terms of hydrogen ion concentration but the mean ionic activity coefficient of a typical 1:1 electrolyte can be used to obtain hydrogen ion concentration subject to an uncertainty of 3.9% in concentration, corresponding to 0.02 in pH.

References

1. Buck, R.P., Rondinini, S., Covington, A.K., Baucke, F.G.K., Brett, C.M.A., Camoes, M.F.C., Milton, M.J.T., Mussini, T., Naumann, R., Pratt, K.W., Spitzer, P., and Wilson, G.S. *Pure Appl. Chem.,* 74, 2105, 2002.
2. Sørensen, S.P.L. *Comp. Rend.Trav. Lab. Carlsberg,* 8**,** 1, 1909.
3. Sørensen, S.P.L., and Linderstrøm-Lang, K.L., *Comp. Rend. Trav. Lab. Carlsberg*, 15**,** 1924.
4. BIPM, *Com. Cons. Quantité de Matière* 4, 1998. See also M.J.T. Milton and T.J. Quinn, *Metrologia* 38, 289, 2001.
5. Harned H.S., and Owen, B.B., *The Physical Chemistry of Electrolytic Solutions*, Ch 14, Reinhold, New York, 1958.
6. Bates R.G., and Robinson, R.A., *J. Soln. Chem*. 9, 455, 1980.
7. Bates R.G., and Guggenheim, E.A., *Pure Appl. Chem.* 1, 163, 1960.
8. *International Vocabulary of Basic and General Terms in Metrology* (VIM), Beuth, Berlin, 2nd. Edn. 1994.
9. Bates, R.G. *Determination of pH*, Wiley, New York, 1973.
10. Good, N.E. et al., *Biochem. J.* 5, 467, 1966.
11. *Guide to the Expression of Uncertainty* (GUM), BIPM, IEC, IFCC, ISO, IUPAC, IUPAP, OIML, 1993.

TABLE 1. Summary of Useful Properties of Some Primary and Secondary Standard Buffer Substances and Solutions

Salt or solid substance	Formula	Molality/ mol kg^{-1}	Molar mass/ g mol^{-1}	Density/ g/mL	Amount conc. at 20°C/ mol dm^{-3}	Mass/g to make 1 dm^3	Dilution value $\Delta pH_{1/2}$	Buffer value (β)/ mol OH$^-$ dm^{-3}	pH Temperature coefficient/ K^{-1}
Potassium tetroxalate dihydrate	$KH_3C_4O_8{\cdot}2H_2O$	0.1	254.191	1.0091	0.09875	25.101			
Potassium tetraoxalate dihydrate	$KH_3C_4O_8{\cdot}2H_2O$	0.05	254.191	1.0032	0.04965	12.620	0.186	0.070	0.001
Potassium hydrogen tartrate (sat at 25°C)	$KHC_4H_4O_6$	0.0341	188.18	1.0036	0.034	6.4	0.049	0.027	- 0.0014
Potassium dihydrogen citrate	$KH_2C_6H_5O_7$	0.05	230.22	1.0029	0.04958	11.41	0.024	0.034	- 0.022
Potassium hydrogen phthalate	$KHC_8H_4O_4$	0.05	204.44	1.0017	0.04958	10.12	0.052	0.016	0.00012
Disodium hydrogen orthophosphate +	Na_2HPO_4	0.025	141.958	1.0038	0.02492	3.5379	0.080	0.029	- 0.0028

Salt or solid substance	Formula	Molality/ mol kg^{-1}	Molar mass/ g mol^{-1}	Density/ g/mL	Amount conc. at 20°C/ mol dm^{-3}	Mass/g to make 1 dm^3	Dilution value $\Delta pH_{1/2}$	Buffer value (β)/ mol OH$^-$ dm^{-3}	pH Temperature coefficient/ K^{-1}
potassium dihydrogen orthophosphate	KH_2PO_4	0.025	136.085			3.3912			
Disodium hydrogen orthophosphate +	Na_2HPO_4	0.03043	141.959	1.0020	0.08665	4.302	0.07	0.016	- 0.0028
potassium dihydrogen orthophosphate	KH_2PO_4	0.00869	136.085		0.03032	1.179			
Disodium tetraborate decahydrate	$Na_2B_4O_7{\cdot}10H_2O$	0.05	381.367	1.0075	0.04985	19.012			
Disodium tetraborate decahydrate	$Na_2B_4O_7{\cdot}10H_2O$	0.01	381.367	1.0001	0.00998	3.806	0.01	0.020	- 0.0082
Sodium hydrogen carbonate +	$NaHCO_3$	0.025	84.01	1.0013	0.02492	2.092	0.079	0.029	-0.0096
sodium carbonate	Na_2CO_3	0.025	105.99			2.640			
Calcium hydroxide (sat. at 25°C)	$Ca(OH)_2$	0.0203	74.09	0.9991	0.02025	1.5	-0.28	0.09	-0.033

TABLE 2. Typical Values of pH(PS) for Primary Standards at 0–50°C

	Temperature in °C										
Primary standards (PS)	0	5	10	15	20	25	30	35	37	40	50
Sat. potassium hydrogen tartrate (at 25°C)						3.557	3.552	3.549	3.548	3.547	3.549
0.05 mol kg^{-1} 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
0.05 mol kg^{-1} potassium hydrogen phthalate	4.000	3.998	3.997	3.998	4.000	4.005	4.011	4.018	4.022	4.027	4.050
0.025 mol kg^{-1} disodium hydrogen phosphate + 0.025 mol kg^{-1} 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
0.03043 mol kg^{-1} disodium hydrogen phosphate + 0.008695 mol kg^{-1} 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^{-1} disodium tetraborate	9.464	9.395	9.332	9.276	9.225	9.180	9.139	9.102	9.088	9.068	9.011
0.025 mol kg^{-1} sodium hydrogen carbonate + 0.025 mol kg^{-1} sodium carbonate	10.317	10.245	10.179	10.118	10.062	10.012	9.966	9.926	9.910	9.889	9.828

TABLE 3. Values of pH(SS) of Some Secondary Standards from Harned Cell I Measurements

	Temperature in °C									
Secondary standards	**0**	**5**	**10**	**15**	**20**	**25**	**30**	**37**	**40**	**50**
0.05 mol kg^{-1} potassium tetroxalate[a]	1.67	1.67	1.67	1.67	1.68	1.68	1.68	1.69	1.69	1.71
0.05 mol kg^{-1} sodium hydrogen diglycolate[b]		3.47	3.47	3.48	3.48	3.49	3.50	3.52	3.53	3.56
0.1 mol dm^{-3} acetic acid + 0.1 mol dm^{-3} sodium acetate	4.68	4.67	4.67	4.66	4.66	4.65	4.65	4.66	4.66	4.68
mol dm^{-3} acetic acid + 0.1 mol dm^{-3} sodium acetate	4.74	4.73	4.73	4.72	4.72	4.72	4.72	4.73	4.73	4.75
0.02 mol kg^{-1} piperazine phosphate [c]	6.58	6.51	6.45	6.39	6.34	6.29	6.24	6.16	6.14	6.06
0.05 mol kg^{-1} tris hydrochloride + 0.01667 mol kg^{-1} tris [c]	8.47	8.30	8.14	7.99	7.84	7.70	7.56	7.38	7.31	7.07
0.05 mol kg^{-1} disodium tetraborate	9.51	9.43	9.36	9.30	9.25	9.19	9.15	9.09	9.07	9.01
Saturated (at 25 °C) calcium hydroxide	13.42	13.21	13.00	12.81	12.63	12.45	12.29	12.07	11.98	11.71

[a] Potassium trihydrogen dioxalate ($KH_3C_4O_8$)
[b] Sodium hydrogen 2,2'-oxydiacetate
[c] 2-Amino-2-(hydroxymethyl)-1,3 propanediol or tris(hydroxymethyl)aminomethane