

**INTERNATIONAL UNION OF PURE
AND APPLIED CHEMISTRY**

PHYSICAL CHEMISTRY DIVISION

COMMISSION ON PHYSICOCHEMICAL MEASUREMENTS AND STANDARDS

**SUBCOMMITTEE ON CALIBRATION
AND TEST MATERIALS**

**RECOMMENDED REFERENCE
MATERIALS FOR REALIZATION OF
PHYSICOCHEMICAL PROPERTIES**

Recommendations (1976)

EDITOR: E. F. G. HERINGTON

**SECTION: POTENTIOMETRIC ION
ACTIVITIES**

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INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

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RECOMMENDED REFERENCE MATERIALS FOR REALIZATION OF
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EDITOR: E. F. G. HERINGTON

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INTRODUCTION

Since single ion activities cannot be measured experimentally, it is a recognized fact that the pH value is an inexact physical quantity. In order that the measured pH be endowed with as much precise significance as possible, a conventional $p\alpha_{\text{H}}$ scale has been adopted which is defined by reference solutions with assigned values of pH and ionic strengths less than 0.1 mol dm⁻³. Equation (1) has achieved nearly universal acceptance as the operational definition of the pH value (Ref. 1).

$$\text{pH}(X) = \text{pH}(S) - [(E_x - E_s) F/RT \ln 10] \quad (1)$$

where E_s is the electromotive force of the cell:

reference electrode | KCl(≥ 3.5 mol/l) || Solution S | H₂(g) | Pt

and E_x is the electromotive force of the same cell when the reference buffer solution S [$p\alpha_{\text{H}} = \text{pH}(S)$] is replaced by the sample solution X; F is the faraday, 96,487 C mol⁻¹; R is the gas constant, 8.3143 J K⁻¹ mol⁻¹; T is the thermodynamic temperature in kelvins, $T/K = \theta/^\circ\text{C} + 273.15$; both cells being at the same temperature throughout and the reference electrodes and bridge solutions being identical in the two cells. The use of equation (1) obviously requires one or more reference solutions with assigned values of pH. Whatever the method of assignment of $\text{pH}(S)$, the definition of pH given in equation (1) furnishes a set of reproducible pH values and thus fulfills the most important requirement of a measurement scale.

The acceptance of several reference solutions allows the use of an alternative definition of pH:

$$\text{pH}(X) = \text{pH}(S_1) - [E_x - E_{S1}] [\text{pH}(S_2) - \text{pH}(S_1)] / (E_{S2} - E_{S1}) \quad (2)$$

where E_{S1} and E_{S2} are the cell potentials measured when the sample solution X is replaced in the cell by the reference solutions S_1 and S_2 such that the values E_{S1} and E_{S2} are on either side of, and as near as possible to E_x . Equation (2) assumes linearity of the pH vs E response between the two reference solutions, whereas equation (1) assumes both linearity and Nernstian response of the pH electrode. A two-point calibration procedure is especially recommended when the hydrogen-ion-responsive electrode being calibrated is a glass electrode (Ref. 1).

1.1 *Measurement scales*

1.1 (a) *pH scales*. The United Kingdom (Ref. 2) and Japanese (Ref. 3) scales use a 0.05 mol dm⁻³ solution of potassium hydrogen phthalate and obtain other pH values by the use of equation (1). The pH(S) of this solution is defined as having the value 4 exactly at 15 °C. At other temperatures, its pH is given by the formula:

$$\text{pH(S)} = 4.000 + 0.5 [(\theta/^\circ\text{C} - 15)/100]^2 \quad (3)$$

when $\theta/^\circ\text{C}$ is between 0 and 55, and

$$\text{pH(S)} = 4.000 + 0.5 [(\theta/^\circ\text{C} - 15)/100]^2 - (\theta/^\circ\text{C} - 55)/500 \quad (4)$$

when $\theta/^\circ\text{C}$ is between 55 and 95. The Japanese scale uses only equation (3) and applies this equation to the temperature range between 0 and 60 °C. Other calibrating solutions are recommended for checking the response of glass electrodes.

The United States National Bureau of Standards (Ref. 4) has adopted a pH scale based on the series of primary and secondary reference solutions listed in Table 1.

Table 1. U.S. National Bureau of Standards pH reference solutions

Solution composition (molality)	pH(S) at 25 °C
Primary reference solutions:	
KH tartrate (satd at 25 °C)	3.557
0.05m KH ₂ citrate*	3.776
0.05m KH phthalate	4.004
0.025m KH ₂ PO ₄ + 0.025m Na ₂ HPO ₄	6.863
0.008695m KH ₂ PO ₄ + 0.03043m Na ₂ HPO ₄	7.415
0.01m Na ₂ B ₄ O ₇ · 10 H ₂ O	9.183
0.025m NaHCO ₃ + 0.025m Na ₂ CO ₃	10.014
Secondary reference solutions:	
0.05m K tetroxalate · 2H ₂ O	1.679
0.01667m Tris + 0.05m Tris · HCl	7.699
Ca(OH) ₂ * (satd at 25 °C)	12.454

* pH values have been assigned but batches of this Reference Material are not available for purchase.

The 1973 edition of the IUPAC Manual (Ref. 1) lists a series of pH(S) values for five reference solutions given in Table 2.

Table 2. Values of pH(S) for five reference solutions

$\theta/^\circ\text{C}$	A	B	C	D	E
0		4.003	6.984	7.534	9.464
5		3.999	6.951	7.500	9.395
10		3.998	6.923	7.472	9.332
15		3.999	6.900	7.448	9.276
20		4.002	6.881	7.429	9.225
25	3.557	4.008	6.865	7.413	9.180
30	3.552	4.015	6.853	7.400	9.139
35	3.549	4.024	6.844	7.389	9.102
38	3.548	4.030	6.840	7.384	9.081
40	3.547	4.035	6.838	7.380	9.068
45	3.547	4.047	6.834	7.373	9.038
50	3.549	4.060	6.833	7.367	9.011
55	3.554	4.075	6.834		8.985
60	3.560	4.091	6.836		8.962
70	3.580	4.126	6.845		8.921
80	3.609	4.164	6.859		8.885
90	3.650	4.205	6.877		8.850
95	3.674	4.227	6.886		8.833

The compositions of these solutions are:

- A: KH tartrate (saturated at 25 °C)
 B: KH phthalate, $m = 0.05 \text{ mol kg}^{-1}$
 C: KH_2PO_4 , $m = 0.025 \text{ mol kg}^{-1}$;
 Na_2HPO_4 , $m = 0.025 \text{ mol kg}^{-1}$;
 D: KH_2PO_4 , $m = 0.008695 \text{ mol kg}^{-1}$
 Na_2HPO_4 , $m = 0.03043 \text{ mol kg}^{-1}$
 E: $\text{Na}_2\text{B}_4\text{O}_7$, $m = 0.01 \text{ mol kg}^{-1}$

where m denotes molality and the solvent is water.

The values of pH obtained by measurement when a glass electrode is used may be slightly dependent on which reference solution is used, but such variations are usually too small to be of practical significance. Deviations in the measured values may be caused by imperfections in the response of the pH glass electrode and/or by variations in the liquid-junction potentials resulting from the different ionic compositions and mobilities in the various solutions and from differences in the geometry of the liquid-junction boundary.

Since only minor differences exist between the various national pH scales, it is to be hoped that a single unified scale, such as the one recommended in the 1973 IUPAC Manual (Ref. 1), will soon be adopted in all countries. As discussed by Bates (Ref. 5), and by Bates and Guggenheim (Ref. 6), the basis for an international pH scale should include the following recommendations: (a) that the symbol pH denote the experimental practical pH value and that reference values based on a conventional hydrogen ion activity be denoted pH(S) or $\text{p}a_{\text{H}}$, (b) that the operational definition of pH given by equation (1) be adopted, (c) that the activity coefficient

of the chloride ion at ionic strengths (I) not exceeding 0.1 mol dm^{-3} be defined conventionally by equation (5) with $B_a^0 = 1.5$ (Ref. 6):

$$\log \gamma_{\text{Cl}} = A I^{\frac{1}{2}} / (1 + B_a^0 I^{\frac{1}{2}}) \quad (5)$$

and (d) that the pH scale be fixed by one or more solutions.

The data sheets in this report identify the reference materials in use in Germany, Hungary, Japan, Poland, Rumania, Union of Soviet Socialist Republics, United Kingdom and the United States of America to realize the pH scales presently being employed in those countries.

1.1(b) *pD scale*. The two reference solutions defining a practical scale of pD in deuterium oxide (heavy water) are listed in section 2.9 and are recommended for the realization of an acidity scale in this solvent. They have been certified at the National Bureau of Standards using a procedure analogous to the assignment of pH values in ordinary water except the deuterium gas electrode was used as the deuterium ion indicator electrode (Ref. 7).

1.1(c) *Ionic activity scales*. The first requirement for ionic activity reference materials for the calibration of ion-selective electrodes is the establishment of a conventional scale of ionic activity. One approach used to achieve a self-consistent scale of individual ionic activities is described in an IUPAC report (Ref. 8) and is based on the hydration theory due to Stokes and Robinson. Although this approach is still under investigation and may be subject to future modification, it is already capable of bringing some order to this rapidly advancing field of research and technology. The National Bureau of Standards has adopted this method for the certification of ionic activity standards for Na^+ , K^+ , Cl^- and F^- as listed in section 3.0. While it is perhaps premature to recommend a scale of single ionic activities for ions other than hydrogen, these reference materials will be adaptable to whatever scale is ultimately adopted.

1.2 Summary

The purpose of establishing a consistent set of pH reference materials is two-fold; first, to provide a common basis for all pH measurements in order that the pH values obtained will be truly reproducible and second, through assignment of suitable pH values, to permit the measured pH to assume as much quantitative meaning in terms of chemical equilibria as possible. In accordance with the recommendations stated above, an operational pH scale is achieved for the most practical purposes. In most respects, only minor differences exist between the procedures and scales adopted by the various nations included in this report.

The following provisos apply to the information on reference materials: (a) the recommended materials have not been independently checked by IUPAC; (b) the quality of the material may change with time; (c) the cited sources of supply may not be exclusive sources; (d) the IUPAC does not guarantee any of the materials recommended in this report.

It is the intention of the Subcommittee to revise periodically the information given in this report, and users are invited to send suggestions for improvements and extensions of the recommendations to the Secretary of Commission I.4.

REFERENCES

1. *Manual of Symbols and Terminology for Physicochemical Quantities and Units*, 1973 Edition, International Union of Pure and Applied Chemistry (1975).
2. *Specification for pH Scale*, British Standard 1647, British Standards Institution, London (1961).
3. S. Ishizaka, Standard buffer solutions for pH measurements, *Keisoku* 6, 579 (1956); also Japanese Industrial Standard Z8802.
4. R. A. Durst, *Standard Reference Materials: Standardization of pH Measurements*, NBS Special Publication 260-53 U.S. Govt. Printing Office, Washington, D.C. (December 1975).
5. R. G. Bates, *Chimia* 14, 111 (1960); see also *Determination of pH, Theory and Practice*, 2nd ed, J. Wiley, New York (1973).
6. R. G. Bates and E. A. Guggenheim, *Pure Appl. Chem.* 1, 163 (1960).
7. R. G. Bates, *Anal. Chem.* 40 (6), 28A (1968).
8. R. G. Bates and R. A. Robinson, *Pure Appl. Chem.* 37, 575 (1974).

2. NATIONAL pH SCALES AND MATERIALS

2.1 pH Scale of Germany

Contributor: F. G. K. Baucke

A series of reference materials define (Ref.1) the DIN (German Industrial Standards) pH scale which is based on conventional ion activity and uses solutions which contain a defined weight of salt in 1000 ml of solution. The DIN scale is identical with the NBS scale except for slight differences in the compositions of the solutions.

Solid samples of the reference materials can be obtained from supplier (C).

2.1(a) *Potassium tetroxalate dihydrate*. The use of a solution containing 12.61 g of the salt in 1000 ml of solution at 25 °C is recommended. Values of pH(S) for the temperature range 0-95 °C are:

$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)
0	1.666	30	1.683	60	1.723
5	1.668	35	1.688	70	1.743
10	1.670	40	1.694	80	1.766
15	1.672	45	1.700	90	1.792
20	1.675	50	1.707	95	1.806
25	1.679	55	1.715		

2.1(b) *Potassium hydrogen tartrate*. The use of the solution saturated at 25 °C is recommended. Values of pH(S) for the temperature range 25-95 °C are:

$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)
25	3.557	45	3.547	70	3.580
30	3.552	50	3.549	80	3.609
35	3.549	55	3.554	90	3.650
40	3.547	60	3.560	95	3.674

2.1(c) *Potassium dihydrogen citrate*. The use of a solution containing 11.41 g of the salt in 1000 ml of solution at 25 °C is recommended. Values of pH(S) for the temperature range 0-50 °C are (Ref. 2):

$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)
0	3.863	20	3.788	40	3.753
5	3.840	25	3.776	45	3.750
10	3.820	30	3.766	50	3.749
15	3.802	35	3.759		

2.1(d) *Potassium hydrogen phthalate*. The use of a solution containing 10.21 g of the salt in 1000 ml of solution at 25 °C is recommended. Values of pH(S) for the temperature range 0-95 °C are:

$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)
0	4.003	30	4.015	60	4.091
5	3.999	35	4.024	70	4.126
10	3.998	40	4.035	80	4.164
15	3.999	45	4.047	90	4.205
20	4.002	50	4.060	95	4.227
25	4.008	55	4.075		

2.1(e) *Potassium dihydrogen phosphate and disodium hydrogen phosphate*. Data are given for two solutions. The use of a solution containing 3.38g KH_2PO_4 plus 3.53g Na_2HPO_4 in 1000 ml of solution at 25 °C is recommended. Values of pH(S) for the temperature range 0-95 °C are:

$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)
0	6.984	30	6.853	60	6.836
5	6.951	35	6.844	70	6.845
10	6.923	40	6.838	80	6.859
15	6.900	45	6.834	90	6.877
20	6.881	50	6.833	95	6.886
25	6.865	55	6.834		

Also recommended is a 'physiological pH' solution containing 1.179g KH_2PO_4 plus 4.30g Na_2HPO_4 in 1000 ml of solution at 25 °C. Values of pH(S) for the temperature range 0-50 °C are:

$\theta/^{\circ}\text{C}$	pH(S)	$\theta/^{\circ}\text{C}$	pH(S)	$\theta/^{\circ}\text{C}$	pH(S)
0	7.534	20	7.429	38	7.384
5	7.500	25	7.413	40	7.380
10	7.472	30	7.400	45	7.373
15	7.448	35	7.389	50	7.367

2.1(f) *Sodium tetraborate decahydrate (borax)*. The use of a solution containing 3.814g of the salt in 1000 ml of solution at 25 °C is recommended. Values of pH(S) for temperature range 0-95 °C are:

$\theta/^{\circ}\text{C}$	pH(S)	$\theta/^{\circ}\text{C}$	pH(S)	$\theta/^{\circ}\text{C}$	pH(S)
0	9.464	30	9.139	60	8.962
5	9.395	35	9.102	70	8.921
10	9.332	40	9.068	80	8.885
15	9.276	45	9.038	90	8.850
20	9.225	50	9.011	95	8.833
25	9.180	55	8.985		

2.1(g) *Sodium carbonate and sodium hydrogen carbonate*. The use of a solution containing 2.640g of Na_2CO_3 plus 2.092g NaHCO_3 in 1000 ml of solution at 25 °C is recommended. Values of pH(S) for the temperature range 0-50 °C are (Ref. 2):

$\theta/^{\circ}\text{C}$	pH(S)	$\theta/^{\circ}\text{C}$	pH(S)	$\theta/^{\circ}\text{C}$	pH(S)
0	10.317	20	10.062	40	9.889
5	10.245	25	10.012	45	9.856
10	10.179	30	9.966	50	9.828
15	10.118	35	9.925		

2.1(h) *Calcium hydroxide*. The use of a saturated solution at 25 °C is recommended. Values of pH(S) for the temperature range 0-60 °C are:

$\theta/^{\circ}\text{C}$	pH(S)	$\theta/^{\circ}\text{C}$	pH(S)	$\theta/^{\circ}\text{C}$	pH(S)
0	13.423	25	12.454	50	11.705
5	13.207	30	12.289	55	11.574
10	13.003	35	12.133	60	11.449
15	12.810	40	11.984		
20	12.627	45	11.841		

REFERENCES

1. DIN 19 266, *pH Measurement; Standard Buffer Solutions* (October 1971).

2. B.R. Staples and R.G. Bates, *J. Res. Nat. Bur. Std.* 73A, 37 (1969).

2.2 pH Scale of Hungary

Contributor: P. Honti

A series of reference materials defines the Hungarian pH scale which is based on conventional hydrogen ion activity. The pH(S) values given below correspond to $\log(1/a_{\text{H}})$ where a_{H} is a conventional activity of the hydrogen ion referred to the standard state on the scale of molality (Refs. 1,2). The values quoted are derived from emf measurements on cells without liquid junction by a method of calculation that has been described (Ref. 3).

All these reference materials are sold as solids and may be obtained from supplier (D) with instructions for drying the salts and for the preparation of the required solutions. All the solutions, which should be protected against evaporation and contamination by mould should be replaced at frequent intervals and whenever mould appears. Solutions of materials (d), (e) and (f) should be protected against atmospheric carbon dioxide.

2.2.(a) *Potassium tetroxalate*. The 0.05 molal solution has a pH(S) value of 1.68 at 25 °C with an uncertainty estimated not to exceed ± 0.01 .

2.2(b) *Potassium hydrogen tartrate*. The saturated solution at 25 °C has a pH(S) value of 3.55 at 25 °C with an uncertainty estimated not to exceed ± 0.01 .

2.2(c) *Potassium hydrogen phthalate*. The 0.05 molal solution at 25 °C has a pH(S) value of 4.01 with an uncertainty estimated not to exceed ± 0.01 .

2.2(d) *Potassium dihydrogen phosphate and disodium hydrogen phosphate*. Two solutions are used for the calibration of pH equipment: 0.025m KH_2PO_4 + 0.025m Na_2HPO_4 which at 25 °C has a pH(S) value of 6.86, and 0.008695m KH_2PO_4 + 0.03043m Na_2HPO_4 which at 25°C has a pH(S) value of 7.41. The uncertainty in these values is estimated not to exceed ± 0.01 .

2.2(e) *Sodium tetraborate decahydrate (borax)*. The 0.01 molal solution at 25 °C has a pH(S) value of 9.18 with an uncertainty estimated not to exceed ± 0.01 .

2.2(f) *Sodium carbonate and sodium hydrogen carbonate*. The 0.025m Na_2CO_3 + 0.025m NaHCO_3 solution at 25 °C has a pH(S) value of 10.01 with an uncertainty estimated not to exceed ± 0.01 .

REFERENCES

1. E. Deák and E. Juhász, *Mérésügyi Közlemények* 9, 73 (1970).
2. R.G. Bates, *Determination of pH, Theory and Practice*, 2nd ed. J. Wiley, New York (1973).
3. *Trudi-institutov Comiteta* 68, 128, Standartgis, Moscow(1963).

2.3 pH Scale of Japan

A solution containing 0.05 mole of potassium hydrogen phthalate per litre defines (Refs 1,2) the Japanese pH scale and the values of pH(S) for this solution are defined by the equation:

$$\text{pH(S)} = 4.000 + 0.5[(\theta/^{\circ}\text{C}-15)/100]^2 \quad (1)$$

when $\theta/^{\circ}\text{C}$ is between 0 and 60.

In addition to this phthalate solution, four other reference solutions are recommended for the determination of pH with the glass electrode. These reference solutions and their methods of preparation and preservation are described in reference (1).

Solid samples of these reference materials which satisfy the specifications of the corresponding Japanese Industrial Standard are obtainable from suppliers (B) and (H).

2.3(a) *Potassium hydrogen phthalate*. The pH(S) values for a 0.05 mol/l solution of potassium hydrogen phthalate for the temperature range 0-60 $^{\circ}\text{C}$ are:

$\theta/^{\circ}\text{C}$	pH(S)	$\theta/^{\circ}\text{C}$	pH(S)
0	4.01	35	4.02
5	4.01	40	4.03
10	4.00	45	4.04
15	4.00	50	4.06
20	4.00	55	4.08
25	4.01	60	4.10
30	4.01		

The maximum impurities and assay for the salt used in this reference solution are (Ref. 3):

Total chloride	0.003%
Total sulphur	0.002%
Ammonium	0.003%
Heavy metals	0.0005%
Iron	0.001%
Sodium	passes test
Drying loss (110 $^{\circ}\text{C}$)	0.05%
Assay	99.9%

2.3(b) *Potassium tetroxalate dihydrate*. The pH(S) values for a 0.05 mol/l solution of potassium tetroxalate for the temperature range 0-60 $^{\circ}\text{C}$ are:

$\theta/^{\circ}\text{C}$	pH(S)	$\theta/^{\circ}\text{C}$	pH(S)
0	1.67	35	1.69
5	1.67	40	1.70
10	1.67	45	1.70
15	1.67	50	1.71
20	1.68	55	1.72
25	1.68	60	1.73
30	1.69		

The pH values of this solution agree within ± 0.02 with the values determined by the definition given in equation (1). The specifications for this salt are given in *Japanese Industrial Standard K 8474 Potassium Tetroxalate for pH Measurement*.

2.3(c) *Potassium dihydrogen phosphate and disodium hydrogen phosphate*. The pH(S) values for a 0.025 mol/l potassium dihydrogen phosphate plus 0.025 mol/l disodium hydrogen phosphate solution for the temperature range 0–60 °C are:

$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)
0	6.98	35	6.84
5	6.95	40	6.84
10	6.92	45	6.83
15	6.90	50	6.83
20	6.88	55	6.84
25	6.86	60	6.84
30	6.85		

The pH value of this solution agree within ± 0.02 with the values determined by the definition given in equation (1). The specifications for these salts are given in *Japanese Industrial Standard K 9007 Potassium Phosphate, Monobasic for pH Measurement* and *Japanese Industrial Standard K 9020 Sodium Phosphate, Dibasic Anhydrous for pH Measurement*.

2.3(d) *Sodium tetraborate (borax)*. The pH(S) values for a 0.01 mol/l solution of sodium tetraborate for the temperature range 0–60 °C are:

$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)
0	9.46	35	9.10
5	9.39	40	9.07
10	9.33	45	9.04
15	9.27	50	9.01
20	9.22	55	8.99
25	9.18	60	8.96
30	9.14		

The pH values of this solution agree within ± 0.02 with the values determined by the definition given in equation (1). The specifications for this salt are given in *Japanese Industrial Standard K 8866 Sodium Borate (Borax) for pH Measurement*.

2.3(e) *Sodium hydrogen carbonate and sodium carbonate*. The pH(S) values for a 0.025 mol/l sodium hydrogen carbonate plus 0.025 mol/l sodium carbonate solution for the temperature range 0–38 °C are:

$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)
0	10.32	25	10.02
5	10.25	30	9.97
10	10.18	35	9.93
15	10.12	38	9.91
20	10.07		

The pH values of this solution agree within ± 0.02 with the values determined by the definition given in equation (1). The specifications for these salts are given in *Japanese Industrial Standard K 8622 Sodium Bicarbonate for pH Measurement* and *Japanese Industrial Standard K 8625 Sodium Carbonate, Anhydrous for pH Measurement*.

REFERENCES

1. *Method for Determination of pH*, Japanese Industrial Standard Z 8802-1958, Japanese Standards Association, Tokyo.
2. S. Ishizaka, *Standard Buffer Solutions for pH Measurements*, *Keisoku* **6**, 579 (1956).
3. *Potassium Hydrogen Phthalate for pH Measurement*, Japanese Industrial Standard K 8809, Japanese Standards Association, Tokyo.

2.4 pH Scale of Poland

Contributor: T. Plebanski

Investigations of reference materials for this scale are carried out for supplier (F) by J. Bulawa. The following details of reference substances are provided.

2.4(a) *Potassium tetroxalate*. The following pH(S) values for the temperature range 0-95 °C refer to a 0.05m solution:

$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)
0	1.67	30	1.68	55	1.72
5	1.67	35	1.69	60	1.72
10	1.67	38	1.69	70	1.74
15	1.67	40	1.69	80	1.77
20	1.68	45	1.70	90	1.79
25	1.68	50	1.71	95	1.81

The uncertainty in these values is ± 0.02 at the 99% confidence level.

2.4(b) *Potassium hydrogen tartrate*. The following pH(S) values for the temperature range 25-95 °C refer to a saturated solution at 25 °C:

$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)
25	3.56	55	3.55
30	3.55	60	3.56
35	3.55	70	3.58
40	3.55	80	3.61
45	3.55	90	3.65
50	3.55	95	3.67

The uncertainty in these values is ± 0.02 at the 95% confidence level.

2.4(c) *Potassium hydrogen phthalate*. The following pH(S) values for the temperature range 0–95 °C refer to a 0.05*m* solution:

$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)
0	4.00	40	4.04
5	4.00	45	4.05
10	4.00	50	4.06
15	4.00	55	4.08
20	4.00	60	4.09
25	4.01	70	4.13
30	4.02	80	4.16
35	4.02	90	4.20
		95	4.23

The uncertainty in these values is ± 0.02 at the 99% confidence level.

2.4(d) *Potassium dihydrogen phosphate and disodium hydrogen phosphate*. The following pH(S) values for the temperature range 0–95 °C refer to a solution which is 0.025*m* in potassium dihydrogen phosphate and 0.025*m* in disodium hydrogen phosphate.

$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)
0	6.98	45	6.83
5	6.95	50	6.83
10	6.92	55	6.83
15	6.90	60	6.84
20	6.88	70	6.84
25	6.86	80	6.86
30	6.85	90	6.88
35	6.84	95	6.89
40	6.84		

The uncertainty in these values is ± 0.02 at the 99% confidence level.

The following pH(S) values for the temperature range 0–50 °C refer to a solution which is 0.008695*m* in potassium dihydrogen phosphate and 0.03043*m* in disodium hydrogen phosphate:

$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)
0	7.53	30	7.40
5	7.50	35	7.39
10	7.47	38	7.38
15	7.45	40	7.38
20	7.43	45	7.37
25	7.41	50	7.37

The uncertainty in these values is ± 0.02 at the 99% confidence limit.

2.4 (e) *Sodium tetraborate decahydrate*. The following pH(S) values for the temperature range 0–95°C refer to a 0.01*m* solution:

$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)
0	9.46	45	9.04
5	9.40	50	9.01
10	9.33	55	8.98
15	9.28	60	8.96
20	9.22	70	8.92
25	9.18	80	8.88
30	9.14	90	8.85
35	9.10	95	8.83
40	9.07		

The uncertainty in these values is ± 0.02 at the 99% confidence limit.

2.4(f) *Calcium hydroxide*. The following pH(S) values for the temperature range 0–60 °C refer to a saturated solution at 25 °C:

$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)
0	13.42	35	12.13
5	13.21	40	11.98
10	13.00	45	11.84
15	12.81	50	11.70
20	12.63	55	11.57
25	12.45	60	11.45
30	12.29		

The uncertainty in these values is ± 0.01 at the 95% confidence limit.

REFERENCE

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

2.5 pH Scale of Rumania

Contributor: I. Iscrulescu

A series of reference solutions are produced by supplier (I), and these solutions define the Rumanian pH scale:

2.5(a) *Potassium hydrogen tartrate* (saturated at 25 °C);

2.5(b) 0.05m *Potassium hydrogen phthalate*;

2.5(c) 0.025m *Potassium dihydrogen phosphate* + 0.025m *disodium hydrogen phosphate*;

2.5(d) 0.008695m *Potassium dihydrogen phosphate* + 0.03043m *disodium hydrogen phosphate*;

2.5(e) 0.01m *Borax*.

The properties and conditions of these reference solutions are similar to those promulgated by the U.S. National Bureau of Standards (Ref. 1).

REFERENCE

1. R.A. Durst, *Standard Reference Materials: Standardization of pH Measurements*, NBS Spec. Publ. 260-53, U.S. Govt. Printing Office, Washington (Dec. 1975).

2.6 pH Scale of the Union of Soviet Socialist Republics

A series of reference materials defines this pH scale which is based on conventional hydrogen ion activity. The pH(S) values given below correspond to $\log(1/a_{\text{H}})$ where a_{H} is a conventional hydrogen ion activity referred to the standard state on the molal scale (Ref. 1). The values of pH(S) are derived from emf measurements on cells without transference and the maximum deviation of the pH(S) values is ± 0.005 over the temperature range 0–60 °C and ± 0.008 from 60 to 95 °C.

2.6.(a) *Potassium tetroxalate dihydrate*. The pH(S) values for a 0.05m solution of this salt are:

$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)
0	1.666	30	1.683	55	1.715
5	1.668	35	1.688	60	1.723
10	1.670	38	1.691	70	1.743
15	1.672	40	1.694	80	1.766
20	1.675	45	1.700	90	1.792
25	1.679	50	1.707	95	1.806

2.6(b) *Potassium hydrogen tartrate*. The pH(S) values for a solution of this salt saturated at 25 °C are:

$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)
25	3.557	50	3.549
30	3.552	55	3.554
35	3.549	60	3.560
38	3.548	70	3.580
40	3.547	80	3.609
45	3.547	90	3.650
		95	3.674

2.6(c) *Potassium hydrogen phthalate*. The pH(S) values for a 0.05m solution of this salt are:

$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)
0	4.003	30	4.015	55	4.075
5	3.999	35	4.024	60	4.091
10	3.998	38	4.030	70	4.126
15	3.999	40	4.035	80	4.164
20	4.002	45	4.047	90	4.205
25	4.008	50	4.060	95	4.227

2.6(d) *Potassium dihydrogen phosphate and disodium hydrogen phosphate*. The pH(S) values for a solution 0.025m in each of these salts are:

$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)
0	6.984	30	6.853	55	6.834
5	6.951	35	6.844	60	6.836
10	6.923	38	6.840	70	6.845
15	6.900	40	6.838	80	6.859
20	6.881	45	6.834	90	6.877
25	6.865	50	6.833	95	6.886

The pH(S) values for a solution 0.008695*m* in potassium dihydrogen phosphate and 0.03043 in disodium hydrogen phosphate are:

$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)
0	7.534	35	7.389
5	7.500	38	7.384
10	7.472	40	7.380
15	7.448	45	7.373
20	7.429	50	7.367
25	7.413		
30	7.400		

2.6(e) *Sodium tetraborate decahydrate*. The pH(S) values for a 0.01*m* solution of this salt are:

$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)
0	9.464	30	9.139	55	8.985
5	9.395	35	9.102	60	8.962
10	9.332	38	9.081	70	8.921
15	9.276	40	9.068	80	8.885
20	9.225	45	9.038	90	8.850
25	9.180	50	9.011	95	8.833

2.6(f) *Calcium hydroxide*. The pH(S) values for a solution of calcium hydroxide saturated at 25 $^\circ\text{C}$ are:

$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)
0	13.423	35	12.133
5	13.207	38	12.043
10	13.003	40	11.984
15	12.810	45	11.841
20	12.627	50	11.705
25	12.454	55	11.574
30	12.289	60	11.449

REFERENCE

1. *pH Scale for Aqueous Solutions*, USSR GOST 8,134-74, GOSSTANDART, Moscow.

2.7 *pH Scale of the United Kingdom*

Contributor: A. J. Head

Potassium hydrogen phthalate defines the British pH scale (Ref. 1). The pH of a 0.05 mol dm⁻³ solution of pure potassium hydrogen phthalate is defined as having the value 4 exactly at 15 °C. At any other temperature ($\theta/^\circ\text{C}$) between 0 and 95, the pH(S) of this solution is defined by:

$$\begin{aligned} \text{pH(S)} &= 4.000 + 0.5[(\theta/^\circ\text{C}-15)/100]^2 & (0 < \theta/^\circ\text{C} \leq 55) \\ \text{pH(S)} &= 4.000 + 0.5[(\theta/^\circ\text{C}-15)/100]^2 + (\theta/^\circ\text{C}-55)/500 & (55 < \theta/^\circ\text{C} \leq 95) \end{aligned}$$

The accuracy in the assigned pH(S) value is ± 0.005 . The criteria of purity are not rigorously defined and a batch of potassium hydrogen phthalate intended for use as a pH standard is examined by comparing the pH of a 0.05 mol dm⁻³ solution with the pH of a 0.05 mol dm⁻³ solution prepared from potassium hydrogen phthalate of high purity. Emf measurements are made at several temperatures on a cell (with liquid junction) consisting of a hydrogen electrode (in the solution under examination) and a saturated calomel electrode with a 3.5 mol dm⁻³ (or greater) potassium chloride bridge solution (Ref. 2).

Solid samples of potassium hydrogen phthalate certified by the National Physical Laboratory, UK, as conforming (within ± 0.005) to the British Standard (Ref. 1), are available from supplier (A). To prepare the reference solution, 10.21g of pure potassium hydrogen phthalate, dried by heating to 110 °C for 2 h, are dissolved in freshly distilled water (or water of at least equal purity) with a carbon dioxide content not exceeding that in air-equilibrated water, and diluted to 1 dm³.

For accurate measurements of pH by means of a glass electrode, it is recommended (Ref. 1) that calibration be performed using two reference solutions, near to, and preferably bracketing, the pH to be measured. The pH values of calibrating solutions other than the potassium hydrogen phthalate solution are obtained by determinations relative to that solution by the use of a hydrogen electrode, in a cell with liquid junction, and the operational definition of pH, equation (1).

The pH(S) values for other reference solutions, determined according to the British Standard (Ref. 1) and reliably known to an accuracy of ± 0.005 , are given below with specifications for the chemicals.

2.7(a) *Potassium hydrogen phthalate*. Values of pH(S) of the 0.05 mol dm⁻³ solution of potassium hydrogen phthalate calculated for selected temperatures by equations (3) and (4) are:

$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)
0	4.011	50	4.061
5	4.005	55	4.080
10	4.001	60	4.091
15	4.000	65	4.105
20	4.001	70	4.121
25	4.005	75	4.140
30	4.011	80	4.161
35	4.020	85	4.185
40	4.031	90	4.211
45	4.045	95	4.240

Note. The third decimal place is not significant, but is included to facilitate smooth interpolation (Ref. 1).

Maximum limits of impurities:

Chloride	0.001 %
Sulphate	0.01 %
Loss on drying at 110 °C	0.1%
Sodium	0.05%
Assay	not less than 99.9 % and not more than 100.1 %.

2.7(b) *Potassium tetroxalate dihydrate*. The pH(S) values for a 0.1 mol dm⁻³ solution of this salt are:

$\theta/^\circ\text{C}$	pH(S)
25	1.48
38	1.50

Maximum limits of impurities:

Chloride	0.002 %
Sulphate	0.01 %
Calcium	0.005 %
Sodium	0.05 %
Assay	not less than 99.9 % and not more than 100.1 %.

2.7(c) *Hydrochloric acid + potassium chloride*. The pH(S) values for a 0.01 mol dm⁻³ HCl + 0.09 mol dm⁻³ KCl solution are:

$\theta/^\circ\text{C}$	pH(S)
25	2.07
38	2.08

Maximum limits of impurities:

HCl	Non-volatile matter	0.0015 %
	Free chlorine	0.0002 %
	Sulphate	0.003 %

KCl	Free acid	5 μmol per 100g
	Free alkali	5 μmol per 100g
	Ammonia	0.001 %
	Sodium	0.05 %
	Loss on drying at 150 °C	0.3 %
	Assay (on dry material)	not less than 99.8 % and and not more than 100.2 %.

2.7(d) *Acetic acid + sodium acetate*. The pH(S) values for a 0.1 mol dm⁻³ acetic acid + 0.1 mol dm⁻³ sodium acetate solution are:

$\theta/^\circ\text{C}$	pH(S)
12	4.65
25	4.64
38	4.65

The pH(S) values for a 0.01 mol dm⁻³ acetic acid + 0.01 mol dm⁻³ sodium acetate solution are:

$\theta/^\circ\text{C}$	pH(S)
12	4.71
25	4.70
38	4.72

The solution is prepared from pure acetic acid, diluted and half neutralized with sodium hydroxide; it should not be prepared from sodium acetate (Ref. 1).

Maximum limits of impurities in glacial acetic acid:

Non-volatile matter	0.001 %
Chloride	0.0002 %
Sulphate	0.004 %
Assay	not less than 99.5 %.

2.7(e) *Potassium dihydrogen phosphate + disodium hydrogen phosphate*. The pH(S) values for a 0.025 mol dm⁻³ KH₂PO₄ + 0.025 mol dm⁻³ Na₂HPO₄ solution are:

$\theta/^\circ\text{C}$	pH(S)
25	6.85
38	6.84

Maximum limits of impurities in KH₂PO₄:

Chloride	0.0005 %
Sulphate	0.01 %
Ammonia	0.001 %
Sodium	0.05 %
Loss on drying 110 °C	0.1 %
Assay (on dry material)	not less than 99.5 % and not more than 100.5 %

Drying Heat for 2 h at 110 °C
and allow to cool in a
desiccator, before use.

Maximum limits of impurities in Na₂HPO₄:

Chloride	0.006 %
Sulphate	0.03 %
Potassium	0.05 %
Loss on drying at 120 °C	0.2 %
Assay (on dry material)	not less than 99.5% and not more than 100.5 %
Drying	Heat for 2 h at 120 °C, and allow to cool in a desiccator, before use.

2.7(f) *Sodium tetraborate decahydrate (borax)*. The pH(S) values for a 0.05 mol dm⁻³ solution of this salt are:

$\theta/^\circ\text{C}$	pH(S)
25	9.18
38	9.07

Maximum limits of impurities in sodium tetraborate decahydrate:

Carbonate	0.05 %
Chloride	0.001 %
Sulphate	0.005%
Calcium	0.01 %
Assay	not less than 99.5% and not more than 100.5 %.

2.7(g) *Sodium hydrogen carbonate + sodium carbonate*. The pH(S) value for a 0.025 mol dm⁻³ NaHCO₃+ 0.025 mol dm⁻³ Na₂CO₃ solution is 10.00 at 25 °C.

Maximum limits of impurities in NaHCO₃:

Chloride	0.005 %
Sulphate	0.005 %
Potassium	0.02 %
Assay	not less than 99.5 %.

Maximum limits of impurities in Na₂CO₃:

Chloride	0.005 %
Sulphate	0.005 %
Potassium	0.01 %
Loss at 300 °C	1.0 %
Assay (on dry material)	not less than 99.9 %.

The British pH scale is under revision.

REFERENCES

1. *Specification for pH Scale*, British Standard 1647, British Standards Institution, London (1961)

2. D.J. Alner, J.J. Greczek and A.G. Smeeth, *J. Chem. Soc. A*, 1205 (1967).

2.8 *pH Scale of the United States of America*

Contributors: Richard A. Durst and J. Paul Cali

The National Bureau of Standards, Washington, D.C. (NBS) has adopted (Refs. 1,2) a pH scale based on ten reference solutions, details of eight of which are given on the accompanying data sheets. Two solutions (*viz.* 0.05*m* potassium dihydrogen citrate and a saturated solution at 25 °C of calcium hydroxide) have been assigned pH(S) values, but certified reference samples are not available. The ten solutions defining the NBS pH scale are divided into two series, three reference materials (0.05*m* potassium tetroxalate; 0.01667*m* Tris plus 0.05*m* Tris hydrochloride; and a saturated solution of calcium hydroxide at 25 °C) are regarded as providing secondary reference points, the other seven are considered to provide primary reference points on the NBS pH scale.

The distinction between primary and secondary buffer solutions is based on recognition that the liquid-junction potential of the common pH cell displays considerably greater variability outside the pH range 2.5–11.5. In spite of these liquid-junction potential uncertainties, which could result in pH differences of several hundredths, it is nevertheless desirable to affirm the proper functioning of the glass electrode outside this pH range. For this purpose, secondary pH reference materials have been designated: potassium tetroxalate of pH(S) = 1.68 at 25°C and a saturated solution of calcium hydroxide of pH(S) = 12.45 at 25°C. Even within the pH range 2.4–11.5, secondary reference materials may have certain advantages over the primary reference materials. The Tris buffer was selected as a physiological pH reference material because of its freedom from undesirable side reactions in biological fluids and the similarity of its pH temperature coefficient to that of blood. However, because of anomalous liquid-junction potentials, this buffer may exhibit operational pH values which differ from the assigned pH(S) values by as much as several hundredths (Ref. 1). All of the primary pH reference solutions have demonstrated an internal consistency to better than 0.01 when compared using cells having a properly designed liquid junction (Ref. 2).

The NBS pH scale is based on a conventional hydrogen ion activity (Ref. 3). The values of pH(S) listed correspond to values of $\log(1/a_{\text{H}})$, where a_{H} is the conventional activity of the hydrogen (hydronium) ion referenced to the standard state on the scale of molality. There are four steps in the assignment of the pH(S) values to the reference materials (Ref. 4): (a) determination of the acidity function $p(a_{\text{H}}\gamma_{\text{Cl}})$; (b) evaluation of the limiting acidity function $p(a_{\text{H}}\gamma_{\text{Cl}})^{\circ}$; (c) computation of $p\alpha_{\text{H}}$ from $p(a_{\text{H}}\gamma_{\text{Cl}})^{\circ}$; and (d) identification of $p\alpha_{\text{H}}$ with pH(S). Emf measurements are made on a cell without transference consisting of a hydrogen electrode and a silver/silver chloride electrode (Ref. 5). The measurements are made at various temperatures and concentrations of chloride ion, and values of pH(S) are derived by the method of calculation described in reference (5).

Samples of reference materials for the NBS pH scale are available from supplier (E). Directions for drying the materials (if necessary) and preparation of the buffer solutions are given on the NBS Standard Reference Materials Certificates accompanying the materials.

2.8(a) *Potassium tetroxalate dihydrate*. Each batch of this salt, issued as SRM 189, is prepared to ensure high purity and uniformity and to assay close to 100 %. However, this reference material is certified only with respect to pH(S) values, not as a pure substance.

Directions are given for the preparation of a 0.05 molal solution which is recommended for the realization of a secondary reference point with the values given below. The uncertainty in the values of pH(S) is estimated not to exceed ± 0.005 from 0 to 60 °C and ± 0.01 from 60 to 95 °C.

$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)
0	1.666	30	1.683	55	1.715
5	1.668	35	1.688	60	1.723
10	1.670	38	1.691	70	1.743
15	1.672	40	1.694	80	1.766
20	1.675	45	1.700	90	1.792
25	1.679	50	1.707	95	1.806

The liquid-junction potential of many pH cells show considerable variability in solutions of low pH and as a result, measured pH values with this reference solution may differ by 0.02-0.05 from the pH(S) values listed. For this reason, while solutions of potassium tetroxalate are useful as secondary standards and for confirmatory purposes, they are not recommended as primary standards of pH except in cases where a liquid junction is not involved.

2.8(b) *Potassium hydrogen tartrate*. Each batch of this salt, issued as SRM 188, is prepared to ensure high purity and uniformity and to assay close to 100 %. However, samples of this material should not be considered as entirely free from impurities such as traces of free acid or alkali, occluded water, chlorides, sulfur compounds and heavy metals. Directions are given for the preparation of saturated and 0.01 molal solutions. Tartrate reference solutions should be prepared fresh each day because solutions of this material are very susceptible to growth of mould which is usually accompanied by an increase of a few hundredths in the pH value. The distilled water used in the preparation of these solutions should have a conductivity not greater than $2 \times 10^{-4} \text{ S cm}^{-1}$ at 25 °C, but dissolved carbon dioxide need not be removed.

A solution saturated with potassium hydrogen tartrate near 25 °C is recommended for the calibration of pH equipment by the use of the following values of pH(S) in the temperature range 25-95 °C:

$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)
25	3.557	45	3.547	70	3.580
30	3.552	50	3.549	80	3.609
35	3.549	55	3.554	90	3.650
38	3.548	60	3.560	95	3.674
40	3.547				

The 0.01 molal solution is also recommended as a reference solution for the temperature range 0-60 °C with the following values of pH(S):

$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)
0	3.711	20	3.647	40	3.632
5	3.689	25	3.639	45	3.635
10	3.671	30	3.635	50	3.639
15	3.657	35	3.632	55	3.644
		38	3.631	60	3.651

The uncertainty in the pH values of these solutions is estimated not to exceed ± 0.005 for 0-60 $^\circ\text{C}$.

2.8(c) *Potassium hydrogen phthalate*. Each batch of salt, issued as SRM 185, is prepared to ensure high purity and uniformity. Samples meet the specifications of the American Chemical Society for reagent-grade material, but should not be considered as entirely free from impurities such as traces of occluded water, free acid or alkali, chlorides, sulfur compounds, and heavy metals. Directions are given for drying the solid and for the preparation of a 0.05 molal solution which should be protected against evaporation and contamination by mould. The solution should be replaced at frequent intervals and whenever mould is apparent.

The pH(S) values for a 0.05m solution prepared from SRM 185e for the temperature range 0-95 $^\circ\text{C}$ are:

$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)
0	4.003	25	4.004	45	4.042	70	4.12
5	3.998	30	4.011	50	4.055	80	4.16
10	3.996	35	4.020	55	4.070	90	4.19
15	3.996	40	4.030	60	4.085	95	4.21
20	3.999						

The uncertainty in these values is estimated to be ± 0.005 for 0-60 $^\circ\text{C}$ and ± 0.01 for 60-95 $^\circ\text{C}$.

2.8(d) *Potassium dihydrogen phosphate and disodium hydrogen phosphate*. Batches of potassium dihydrogen phosphate (SRM 186-I) and disodium hydrogen phosphate (SRM 186-II) are prepared to ensure high purity and uniformity. Samples meet the specifications of the American Chemical Society for reagent-grade materials, but should not be considered to be entirely free from impurities such as traces of water, free acid or alkali, carbon dioxide, chlorides, sulfur compounds and heavy metals. Directions are given for drying the salts and for preparation of the equimolal and the physiological buffer solutions. The solutions should be replaced after a few weeks or sooner if mould or sediment appears or if they have been exposed repeatedly to air containing carbon dioxide. The physiological buffer solution is more sensitive to contamination with carbon dioxide than is the equimolal solution and if the solution is to maintain the assigned pH(S) value for a few weeks, exclusion of carbon dioxide may be essential.

The solution 0.025 molal with respect to each salt is recommended for the calibration of pH equipment. The pH(S) values for the equimolal solution prepared from SRM 186-I-c and SRM 186-II-c for the temperature range 0-50 $^\circ\text{C}$ are:

$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)
0	6.982	20	6.878	37	6.839
5	6.949	25	6.863	40	6.836
10	6.921	30	6.851	45	6.832
15	6.898	35	6.842	50	6.831

The uncertainty in the pH(S) value is estimated not to exceed ± 0.005 .

For pH measurements in the physiological range (pH 7-8) a solution 0.008695 molal in KH_2PO_4 (SRM 186-I-c) and 0.03043 molal in Na_2HPO_4 (SRM 186-II-c) is useful. The pH(S) values for the physiologic buffer solution (Ref. 6) for the temperature range 0-50 $^\circ\text{C}$ are:

$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)
0	7.534	20	7.430	37	7.392
5	7.501	25	7.415	40	7.388
10	7.472	30	7.403	45	7.385
15	7.449	35	7.394	50	7.384

The uncertainty of the assigned values of pH(S) is estimated not to exceed ± 0.005 . The values listed apply only to the batches here certified and minor variations in the values of pH(S), of the order of a few thousandths, may be expected to occur between different batches.

2.8(e) *Tris(hydroxymethyl)aminomethane and Tris(hydroxymethyl)aminomethane hydrochloride.* Batches of these reference materials (Tris, SRM 922, and Tris·HCl, SRM 923) are prepared to ensure high purity and uniformity. However, they are certified only with respect to values of pH(S), not as pure substances. Directions are given for preparation of the reference solution. This buffer was selected as a physiological pH reference solution because of its freedom from undesirable side reactions in biological fluids and the similarity of its pH temperature coefficient to that of blood. However, this solution should not be regarded as a primary reference material except in cases where a liquid junction is not involved (Refs. 7,8).

The solution containing 0.0167 molal Tris and 0.0500 molal Tris·HCl is recommended for use as a physiological pH reference material with the following pH(S) values for the temperature range 0-50 $^\circ\text{C}$ (Refs. 9,10):

$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)
0	8.471	20	7.840	37	7.382
5	8.303	25	7.699	40	7.307
10	8.142	30	7.563	45	7.186
15	7.988	35	7.433	50	7.070

The uncertainty in the pH(S) values is estimated not to exceed ± 0.005 .

2.8(f) *Sodium tetraborate decahydrate.* Each batch of this salt (SRM 187) is prepared to ensure high purity and uniformity. Samples meet the specifications of the American Chemical

Society for reagent-grade material. The water content of this salt, stored under ordinary conditions, is less than the formula content ($\text{Na}_2\text{B}_4\text{O}_7 : 10 \text{H}_2\text{O}$). This does not affect the use of this salt as a pH(S) reference material, but could lead to erroneous results were the partially dehydrated salt used as a boron or volumetric standard. Directions are given for the preparation of a 0.01 molal solution. The solution must be protected from contamination by atmospheric carbon dioxide.

The values of pH(S) for the 0.01*m* solution prepared from SRM 187b for the temperature range 0-50 °C are:

$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)
0	9.460	20	9.227	37	9.093
5	9.392	25	9.183	40	9.074
10	9.331	30	9.143	45	9.044
15	9.276	35	9.107	50	9.017

The uncertainty in the pH(S) values is estimated not to exceed ± 0.005 .

2.8(g) *Sodium bicarbonate and sodium carbonate*. Batches of sodium bicarbonate (SRM 191) and sodium carbonate (SRM 192) are prepared to ensure high purity and uniformity. Samples meet the specifications of the American Chemical Society for reagent-grade materials but should not be considered as entirely free from impurities such as traces of water, free alkali, silica, chlorides, sulfur compounds and heavy metals.

Directions are given for the preparation of the solution 0.025 molal with respect to each salt. Although elaborate precautions to prevent contamination of the solution with atmospheric carbon dioxide are usually unnecessary, the container should be kept tightly stoppered at all times when a sample is not actually being removed.

The pH(S) values for the solution 0.025 molal with respect to both NaHCO_3 and Na_2CO_3 for the temperature range 0-50 °C are:

$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)	$\theta/^\circ\text{C}$	pH(S)
0	10.321	20	10.064	40	9.891
5	10.248	25	10.014	45	9.859
10	10.181	30	9.968	50	9.831
15	10.120	35	9.928		

The uncertainty in the assigned values of pH(S) is estimated not to exceed ± 0.005 .

The values of pH(S) listed apply only to the batches here certified and minor variations in the pH(S) value, of the order of a few thousandths, may be expected to occur between different batches.

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2.9 pD Scale of the United States of America

Contributors: R. A. Durst and J. P. Cali

The National Bureau of Standards, Washington, D.C. (NBS) has adopted (Refs. 1-3) a pD scale based on deuterium ion activity. The pD(S) values listed correspond to values of $\log(1/a_D)$, where a_D is the conventional activity of the deuterium ion referred to the standard state on the scale of molality. These reference materials have been certified at NBS using a procedure strictly analogous to the assignment of pH(S) values for ordinary water except a deuterium gas electrode was used as the deuterium ion indicator electrode (Ref. 4). There are four steps in the assignment of the pD(S) values to reference materials (a) determination (Ref. 5) of the acidity function $p(a_D\gamma_{Cl})$; (b) evaluation of the limiting acidity function $p(a_D\gamma_{Cl})^0$; (c) computation of pa_D from $p(a_D\gamma_{Cl})^0$; and (d) identification of pa_D with pD(S). Emf measurements are made on a cell without transference consisting of the deuterium gas electrode and silver/silver chloride electrode (Ref. 6). Emf measurements on the buffer solutions are made on cells without liquid junction at various temperatures and concentrations of chloride ion and the pD(S) values are derived by a method of calculation (Ref. 6) analogous to that described for the assignment of pH(S) values. These solutions are recommended for the calibration of pH meters to be used for the measurement of pD in deuterium oxide.

Samples of reference materials for the NBS pD scale are available from supplier (E).

2.9(a) *Potassium dihydrogen phosphate and disodium hydrogen phosphate*. Batches of potassium dihydrogen phosphate (SRM 2186-I) and disodium hydrogen phosphate (SRM 2186-II) are prepared to the same purity specifications as stated for reference material 2.8(d).

Directions are given for drying the salts and the preparation of a solution 0.025 molal with respect to both KD_2PO_4 and Na_2DPO_4 . These components are prepared *in situ* by hydrogen-deuterium exchange between the protium salts and the deuterium oxide solvent. Although elaborate precautions to prevent contamination of the buffer solution by atmospheric carbon dioxide are usually unnecessary, the container should be kept tightly stoppered at all times when a sample is not actually being removed. The pD(S) values for this solution for the temperature range 0-50 °C are:

$\theta/^\circ\text{C}$	pD(S)	$\theta/^\circ\text{C}$	pD(S)	$\theta/^\circ\text{C}$	pD(S)
5	7.539	25	7.428	40	7.387
10	7.504	30	7.411	45	7.381
15	7.475	35	7.397	50	7.377
20	7.449				

The uncertainty in the assigned values of pD(S) is estimated not to exceed ± 0.01 . The values listed apply only to the batches here certified and minor variations of the pD(S) values, of the order of a few thousandths, may be expected to occur between batches.

2.9(b) *Sodium bicarbonate and sodium carbonate.* Batches of sodium bicarbonate (SRM 2191) and sodium carbonate (SRM 2192) are prepared to the same purity specifications as stated for reference material 2.8(g).

Directions are given for the preparation of a solution 0.025 molal with respect to each salt. The NaDCO_3 is prepared *in situ* by the hydrogen-deuterium exchange between the protium salt and the deuterium oxide solvent. Although elaborate precautions to prevent contamination of the buffer solution with atmospheric carbon dioxide are usually unnecessary, the container should be kept tightly stoppered at all times when a sample is not actually being removed. The pD(S) values for this solution for the temperature range 5–50 $^\circ\text{C}$ are:

$\theta/^\circ\text{C}$	pD(S)	$\theta/^\circ\text{C}$	pD(S)	$\theta/^\circ\text{C}$	pD(S)
5	10.998	25	10.736	40	10.597
10	10.923	30	10.685	45	10.559
15	10.855	35	10.638	50	10.527
20	10.793				

The uncertainty in the assigned values of pD(S) is estimated not to exceed ± 0.01 . The values listed apply only to the batches here certified and minor variations of the pD(S) values, of the order of a few thousandths, may be expected to occur between different batches.

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3.1 IONIC ACTIVITY SCALES OF THE UNITED STATES OF AMERICA

Contributors: R.A. Durst and J.P. Cali

The National Bureau of Standards, Washington, D.C. (NBS) certifies samples of potassium chloride, sodium chloride and potassium fluoride as ionic activity reference materials for K^+ , Na^+ , Cl^- , and F^- . These three materials are intended for use in the calibration of ion-selective electrodes.

The NBS has adopted the convention (Refs. 1,2) for single ion activities based on the hydration theory due to Stokes and Robinson (Ref. 3). The details of this activity scale have been reviewed (Ref. 4). Briefly, the single ion activity coefficients are calculated from experimental values of the mean molal activity coefficient (γ_{MX}), the osmotic coefficient (ϕ), and an assigned hydration number (h). For univalent electrolytes the defining equations are:

$$\log \gamma_M^+ = \log \gamma_{MX} + 0.00782 (h_M - h_X)m\phi$$

$$\log \gamma_X^- = \log \gamma_{MX} + 0.00782 (h_X - h_M)m\phi.$$

As in the case of the pH scale, it is necessary to make certain extra-thermodynamic assumptions. The 'conventional' step in the treatment is the assignment of hydration numbers to the individual ionic species. The hydration numbers are calculated from smoothed values of γ_{MX} and ϕ using the Stokes-Robinson hydration theory. The hydration number for the electrolyte is then 'split' between the cation and anion by assigning a hydration value to one of the ions. For the present scale, the hydration number for the chloride ion was taken to be zero, and the other ionic hydration numbers are referred to this convention (Ref. 3). Ionic activity for unassociated electrolytes derived on the basis of this hydration convention have been found to be consistent with the observed responses of ion-selective electrodes.

This treatment has been used to compute single ion activity coefficients for the ions K^+ , Na^+ , Cl^- and F^- for these three reference solutions. The pK, pNa, pCl and pF values listed correspond to $\log(1/a_i)$ where $i = K^+$, Na^+ , Cl^- or F^- and where a_i is the conventional activity of the ions referred to the standard state on the scale of molality.

It is recommended that the reference solutions be used at a concentration similar to that of the sample to minimize liquid junction potential errors. Use of a bracketing technique (two reference solutions which bracket the sample solution concentration) will minimize errors due to non-Nernstian response of the electrodes and will increase the reliability of measurements.

Samples of reference materials for the NBS ionic activity scale are available from supplier (E).

3.1(a) *Potassium chloride*. Batches of potassium chloride (SRM 2202) meet the specifications of the American Chemical Society for reagent-grade material but should not be considered to be entirely free from impurities such as occluded water and traces of bromide and heavy metals. Directions are given for drying the salt and for the preparation of a 0.1 and 1.0 molal solution which is then used to prepare other reference solutions by dilution.

The certified values for these solutions at 25 °C are:

Molality	mol/l	γ_{K^+}	γ_{Cl^-}	pK	pCl
0.001	0.000997	0.965	0.965	3.016	3.016
0.01	0.00997	0.901	0.901	2.045	2.045
0.1	0.0994	0.772	0.768	1.112	1.115
0.2	0.1983	0.723	0.713	0.841	0.846
0.3	0.2967	0.693	0.680	0.682	0.690
0.5	0.4916	0.659	0.639	0.482	0.495
1.0	0.9692	0.623	0.586	0.206	0.232
1.5	1.4329	0.611	0.558	0.0376	0.078
2.0	1.8827	0.609	0.539		

The uncertainties in the assigned values of pK and pCl are estimated not to exceed ± 0.01 .

3.1(b) *Sodium chloride*. Batches of sodium chloride (SRM 2201) meet the specifications of the American Chemical Society for reagent-grade material but should not be considered entirely free from impurities such as occluded water and traces of bromide and heavy metals.

Directions are given for drying the salt and for the preparation of 0.1 and 1.0 molal solutions which are then used to prepare other reference solutions by dilution. The certified values for these solutions at 25 °C are:

Molality	mol/l	γ_{Na^+}	γ_{Cl^-}	pNa	pCl
0.001	0.000997	0.965	0.965	3.015	3.015
0.01	0.00997	0.903	0.902	2.044	2.045
0.1	0.0995	0.783	0.773	1.106	1.112
0.2	0.1987	0.744	0.727	0.828	0.838
0.3	0.2975	0.721	0.697	0.664	0.680
0.5	0.4941	0.701	0.662	0.455	0.480
1.0	0.9789	0.696	0.620	0.157	0.208
1.5	1.4543	0.718	0.602		
2.0	1.9200	0.752	0.593		

The uncertainties in the assigned values of pNa and pCl are estimated not to exceed ± 0.01 .

3.1(c) *Potassium fluoride*. Batches of potassium fluoride (SRM 2203) are of analytical reagent-grade purity but should not be considered entirely free of traces of chloride, fluosilicate and heavy metals. Directions are given for drying the salt and for the preparation of a 0.1 and 1.0 molal solution which is then used to prepare other reference solutions by dilution.

The values certified for these solutions at 25 °C are:

Molality	mol/l	Activity coefficient ($\gamma_{\text{F}^-} = \gamma_{\text{K}^+} = \gamma_{\pm}$)	pF
0.0001	0.0000997	0.988	4.00 ₅
0.0005	0.000499	0.975	3.31 ₂
0.001	0.000997	0.965	3.01 ₆
0.005	0.00498	0.927	2.33 ₄
0.01	0.00997	0.902	2.04 ₅
0.05	0.0498	0.818	1.38 ₈
0.1	0.0996	0.773	1.11 ₂
0.2	0.1990	0.726	0.83 ₈
0.3	0.2982	0.699	0.67 ₈
0.5	0.4961	0.670	0.47 ₅
0.75	0.7424	0.652	0.31 ₁
1.0	0.9873	0.645	0.19 ₀
1.5	1.4729	0.646	+0.01 ₄
2.0	1.9523	0.658	-0.11 ₉

The uncertainty in the assigned value of pF is estimated not to exceed ± 0.01 .

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