pH SCALE for AQUEOUS SOLUTIONS

Echelle de pH des solutions aqueuses

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pH SCALE for AQUEOUS SOLUTIONS

This Recommendation concerns the pH scale for aqueous solutions, and sets pH values for buffer solutions reproducing this scale in the temperature interval between 0 °C and 95 °C.

The pH value corresponds to the negative logarithm of the ionic activity of hydrogen in the solution, allowing for the non-thermodynamic assumptions mentioned in the Appendix:

$$pH = -\lg a_{H^+}$$

1. The pH scale is based on the reproducible pH values of the following butter solutions:

   — solution of potassium tetraoxalate
$KH_3(C_2O_4)_2 \cdot 2\ H_2O$ - 0.05 mol/kg H_2O ;

   — solution of potassium hydrogen tartrate
$KHC_4H_4O_6$ - saturated at 25 °C ;

   — solution of potassium dihydrogen citrate
$KH_2C_6H_5O7$ - 0.05 mol/kg H_2O ;

   — solution of potassium hydrogen phthalate
$KHC_8H_4O_4$ - 0.05 mol/kg H_2O ;

   — solution of potassium dihydrogen phosphate
KH_2PO_4 - 0.025 mol/kg H_2O

plus disodium hydrogen phosphate
Na_2HPO_4 - 0.025 moi/kg H_2O ;

   — solution of potassium dihydrogen phosphate
KH_2PO_4 - 0.008695 mol/kg H_2O

plus disodium hydrogen phosphate
Na_2HPO_4 - 0.03043 mol/kg H_2O ;

   — solution of sodium tetraborate
$Na_2B_4O_7 \cdot 10\ H_2O$ - 0.01 mol/kg H_2O ;

   — solution of sodium hydrogen carbonate
$NaHCO_3$ - 0.025 mol/kg H_2O

plus sodium carbonate
Na_2CO_3 - 0.025 mol/kg H_2O ;

   — solution of calcium hydroxide
$Ca(OH)_2$ - saturated and filtered at 25 °C.

2. The pH values for buffer solutions are given in Table 1.
These values have been determined by measuring the electromotive force of a hydrogen - silver chloride cell without transference, of the type:

$$Pt \mid H_2 \text{ (gas)} \mid \text{buffer solution, } Cl^- \mid AgCl \mid Ag$$
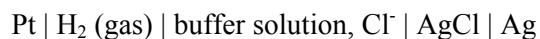
and by calculation.
The method of calculation is described in the Appendix.

The pH values of the indicated solutions may be achieved with an error not exceeding ± 0.01 pH unit.

Table 1 - pH values of buffer solutions

Temperature °C	$KH_3(C_2O_4)\cdot 2H_2O$ 0.05 mol/kg H_2O [1]	$KHC_4H_4O_6$ saturated at 25 °C [1]	$KH_2C_6H_5O_7$ 0.05 mol/kg H_2O [2]	$KHC_8H_4O_4$ 0.05 mol/kg H_2O [1]
0	1.666	--------	3.863	4.003
5	1.668	--------	3.840	3.999
10	1.670	--------	3.820	3.998
15	1.672	--------	3.802	3.999
20	1.675	--------	3.788	4.002
25	1.679	3.557	3.776	4.008
30	1.683	3.552	3.766	4.015
35	1.688	3.549	3.759	4.024
38	1.691	3.548	--------	4.030
40	1.694	3.547	3.753	4.035
45	1.700	3.547	3.750	4.047
50	1.707	3.549	3.749	4.060
55	1.715	3.554	--------	4.075
60	1.723	3.560	--------	4.091
70	1.743	3.580	--------	4.126
80	1.766	3.609	--------	4.164
90	1.792	3.650	--------	4.205
95	1.806	3.674	--------	4.227

Table 1 (cont.) - pH values of buffer solutions

Temper- ature °C	$KH_2 PO_4$ 0.025 mol/kg H_2O + $Na_2H PO_4$ 0.025 mol/kg H_2O [1]	$KH_2 PO_4$ 0.008695 mol/kg H_2O + $Na_2H PO_4$ 0.03043 mol/kg H_2O [1]	$Na_2B_4O_7 \cdot 10 H_2O$ 0.01 mol/kg H_2O [1]	$Na H CO_3$ 0.025 mol/kg H_2O + $Na_2 CO_3$ 0.025 mol/kg H_2O [2]	$Ca (OH)_2$ saturated at 25 °C [1]
0	6.984	7.534	9.464	10.317	13.423
5	6.951	7.500	9.395	10.245	13.207
10	6.923	7.472	9.3.32	10.179	13.003
15	6.900	7.448	9.276	10.118	12.810
20	6.881	7.429	9.225	10.062	12.627
25	6.865	7.413	9.180	10.012	12.454
30	6.853	7.400	9.139	9.966	12.289
35	6.844	7.389	9.102	9.925	12.133
38	6.840	7.384	9.081	--------	12.043
40	6.838	7.380	9.068	9.889	11.984
45	6.834	7.373	9.038	9.856	11.841
50	6.833	7.367	9.011	9.828	11.705
55	6.834	--------	8.985	--------	11.574
60	6.836	--------	8.962	--------	11.449
70	6.845	--------	8.921	--------	--------
80	6.859	--------	8.885	--------	--------
90	6.877	--------	8.850	--------	--------
95	6.886	--------	8.833	--------	--------

APPENDIX

The pH values given in this Recommendation were calculated from the following formula:

$$pH = -\lg a_{H+} \equiv p(a_{H+} \cdot \gamma_{Cl^-})^\circ + \lg \gamma_{Cl^-}$$

The expression $p\,(a_{H+} \cdot \gamma_{Cl^-})^\circ$ was determined by extrapolation to zero chloride ion concentration, by the method of least squares, from at least three values for $p\,(a_{H+} \cdot \gamma_{Cl^-})^\circ$. The latter were calculated from the results of measurement of the electromotive force of a hydrogen-silver chloride cell, in low concentration buffer solutions of sodium or potassium chloride (for example : 0.01 ; 0.015 ; 0.02 mol/kg H_2O).

The values for $p\,(a_{H+} \cdot \gamma_{Cl^-})^\circ$ and $\lg \gamma_{Cl^-}$ were calculated using the following formula :

$$p(a_{H+} \cdot \gamma_{Cl^-}) = \frac{(E - E^\circ) \cdot F}{RT \cdot \ln 10} + \lg m_{Cl^-} \; ;$$

$$\lg \gamma_{Cl^-} = -\frac{A\sqrt{I}}{1 + 1.5\sqrt{I}} \; ;$$

Where:
E — measured electromotive force of the hydrogen-silver chloride cell, V
E° — standard potential of the silver-silver chloride electrode, V
the value of E°, as a function of temperature, is given in Table 2
F — Faraday constant: $F = 96484.56$ C-mol^{-1}
R — gas constant: $R = 8.31441$ J$\cdot$K$^{-1}\cdot$mol^{-1}
T — thermodynamic temperature, K
m_{Cl^-} — molality of chloride ion, mol/kg
A — coefficient the value of which is given, as a function of temperature, in Table 2
I — ionic strength of solution, mol/kg, calculated using the following formula:

$$I = \frac{1}{2}\sum m_i z_i{}^2$$

Where m_t and z_i are respectively the molality and charge number of each type of ion in the solution ; the values of the ionic strength are given in Table 3.

Table 2 - Standard potential $E^\bullet$ and coefficient A as a function of temperature

Temperature °C	E° [3] V	A [1]
0	0.23655	0.4918
5	0.23413	0.4952
10	0.23142	0.4988
15	0.22857	0.5026
20	0.22557	0.5066
25	0.22234	0.5108
30	0.21904	0.5150
35	0.21565	0.5196
38	0.21352	0.5224
40	0.21208	0.5242
45	0.20835	0.5291
50	0.20449	0.5341
55	0.20056	0.5393
60	0.19649	0.5448
70	0.18782	0.5562
80	0.17873	0.5685
90	0.16952	0.5817
95	0.16511	0.5886

Table 3 - Ionic strength *I* of buffer solutions as a function of temperature

Buffer solution	Molality mol/kg	Temperature °C	*I* mol/kg
Potassium tetraoxalate [4]	0.05	0	0.0772
		5	0.0770
		10	0.0767
		15	0.0765
		20	0.0763
		25	0.0760
		30	0.0758
		35	0.0755
		40	0.0753
		45	0.0751
		50	0.0749
		55	0.0747
		60	0.0744
Potassium hydrogen tartrate [5]	solution saturated at 25 °C	25-95	0.04
Potassium dihydrogen citrate [2]	0.05	0	0.0527
		5	0.0526
		10	0.0526
		15	0.0526
		20	0.0526
		25	0.0526
		30	0.0526
		35	0.0525
		40	0.0525
		45	0.0524
		50	0.0524
Potassium hydrogen phthalate [6]	0.05	0-60	0.0535
		65-95	0.053
Potassium dihydrogen phosphate + Disodium hydrogen phosphate [7]	0.025 0.025	0-95	0.1

Table 3 (cont.) - Ionic strength *I* of buffer solutions as a function of temperature

Buffer solution	Molality mol/kg	Temperature °C	*I* mol/kg
Potassium dihydrogen phosphate + Disodium hydrogen phosphate [7]	0.008695 0.03043	0-50	0.1
Sodium tetraborate [7|	0.01	0-95	0.02
Sodium hydrogen carbonate + Sodium carbonate [2]	0.025 0.025	0	0.1
		5	0.1
		10	0.0999
		15	0.0999
		20	0.0999
		25	0.0999
		30	0.0998
		35	0.0998
		40	0.0997
		45	0.0996
		50	0.0995
Calcium hydroxide [8]	solution saturated at 25 °C	0	0.054
		5	0.053
		10	0.051
		15	0.050
		20	0.050
		25	0.049
		30	0.049
		35	0.048
		40	0.048
		45	0.048
		50	0.047
		55	0.047
		60	0.047

REFERENCES

[1]   R.G. BATES, J. Res. Nat. Bur. Stand., **66A** 179 (1962)

[2]   B.R. STAPLES and R.G. BATES, J. Res. Nat. Bur. Stand., **73A** 38 (1969)

[3]   R.G. BATES and V.E. BOWER, J. Res. Nat. Bur. Stand., **53** 283 (1954)

[4]   V.E. BOWER, R.G. BATES and E.R. SMITH, J. Res. Nat. Bur. Stand., **51** 189 (1953)

[5]   R.G. BATES, V.E. BOWER, R.G. MILLER and E.R. SMITH, J. Res. Nat. Bur. Stand., **47** 433 (1951)

[6]   WJ. HAMER, G.D. PINCHING and S.F. ACREE, J. Res. Nat. Bur. Stand., **36** 47 (1946)

[7]   V.E. BOWER and R.G. BATES, J. Res. Nat. Bur. Stand., **59** 263 (1957)

[8]   R.G. BATES: Determination of pH, Wiley, New-York, 1965