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pH SCALE for AQUEOUS SOLUTIONS

Echelle de pH des solutions aqueuses

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## Foreword

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## Introduction

Determination of the hydrogen pH is the most common method for controlling the composition of liquid media, since the activity of hydrogen ions pH is one of the most important physicochemical (acid-base characteristics) properties of aqueous solutions.

Technological processes in the production of chemical reagents, fertilizers, agricultural and food products, household chemicals are carried out with constantly monitoring of pH. That is why, the vast majority of analytical laboratories in the world are equipped with various types of pH measuring instruments. The modern development of the chemical industry, nuclear energy, microelectronics, robotics, medicine and biotechnology, increasing demands on the effectiveness of environmental control and environmental protection measures require increasing the accuracy of determining pH values. This fact necessitates reliable measuring instruments that are traceable to the National primary standard of pH. And, the National primary standard of pH need to have the highest measurement accuracy for pH in the country and providing maintenance and reproducing of the pH scale.

However, the pH scale indicated in the OIML R 54 Recommendation “pH Scale for Aqueous solutions”, which has been in force since 1981, has some discrepancies with the results of more recent studies pointed in the joint publication of the experts in 2002 [1]. Thus, the revision of the Recommendation has become relevant since 2002. Over the years, the pH scale has been repeatedly verified and defined more precisely in key comparisons within the framework of the Working Group on Electrochemical Analysis (EAWG) of the Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology (CCQM) of the International Committee for Weights and Measures (CIPM) of the International Bureau of Weights and Measures (BIPM).

This Recommendation is a revised version of OIML Recommendation R 54 “pH Scale for Aqueous solutions” (1981) taking into account international comparisons between the leading metrology institutes in this area. The Recommendation is harmonized with the International Recommendation IUPAC “Measurement of pH. Definition, standards, and procedures, IUPAC Recommendations 2002” [1], and takes into consideration Recommendations of some international standards [2-5].

The pH values of the scale have been specified by the primary measurement method of pH.

The primary method of measuring pH is applied in the electrochemical Harned cell, using a platinum/palladium coated platinum foil electrode, hydrogen gas and silver-silver chloride electrodes, in the pH range 3.5 – 10.3 in the temperature range 278.15 – 323.15 K.

The Recommendation provides the primary pH standards of the OIML state-members with the pH scale for metrological control.

## pH scale for aqueous solutions

### 1. Scope

- 1.1 This Recommendation cites the pH values Scale for primary pH standards reproducing this scale in the temperature interval between 278.15 – 323.15 K.
- 1.2 The pH values of the Scale have been specified by the primary method of pH measurement.
- 1.3 The Scale is used for the calibration and verification of pH measuring equipment.
- 1.4 The Scale are appropriate for aqueous and dilute ionic strength ( $\leq 0.1 \text{ mol}\cdot\text{kg}^{-1}$ ) solutions.

### 2. Terms and definition [1]

#### 2.1. pH, a single ion quantity,

is negative decimal logarithm of hydrogen ion relative activity  $a_H$  of solution:

$$\text{pH} = -\lg a_H = -\lg(m_H \gamma_H / m^0)$$

where  $a_H$  is the relative (molality basis) activity and  $\gamma_H$  is the molal activity coefficient of the hydrogen ion  $\text{H}^+$  at the molality  $m_H$ , and  $m^0$  is the molality standard state exhibiting infinitely diluted behaviour.

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

*Note. 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, the equation can be only a notional definition of pH [1].*

#### 2.2. primary method of pH measurement [2, 6, 7],

- a primary method of measurement is a method having the highest metrological qualities, whose operation can be completely described and understood, for which a complete uncertainty statement can be written down in terms of SI units;
- a primary direct method measures the value of an unknown without reference to a standard of the same quantity;
- a primary ratio method measures the value of a ratio of an unknown to a standard of the same quantity; its operation must be completely described by a measurement equation.

#### 2.3. primary pH standards,

aqueous solutions of selected reference buffer solutions to which pH(PS) values have been assigned over the temperature range 278,15–323,15 K from measurements on cells without transference, called Harned cells, by use of the Bates–Guggenheim convention [1]. These primary standards have good reproducibility and low uncertainty.

### 3. Instrumental (conventional) definition of pH [1]

#### 3.1. The primary method of pH measurement, Harned cell

The pH value can be determined from electrochemical data from the cell without transference using the hydrogen gas electrode, known as the electrochemical Harned cell:



and containing certified standard buffer and chloride ions, which are added in order to use the silver-silver chloride electrode.

3.2. These following six buffer solutions are recommended as references

- Solution of potassium hydrogen tartrate  $\text{KHC}_4\text{H}_4\text{O}_6$  - saturated at 298.15 K;
- Solution of potassium hydrogen phthalate  $\text{KHC}_8\text{H}_4\text{O}_4$  - 0.050 mol·kg<sup>-1</sup>;
- Solution of potassium dihydrogen phosphate and of sodium hydrogen phosphate  $\text{KH}_2\text{PO}_4 + \text{Na}_2\text{HPO}_4$  - 0.025 + 0.025 mol·kg<sup>-1</sup>;
- Solution of potassium dihydrogen phosphate and of sodium hydrogen phosphate  $\text{KH}_2\text{PO}_4 + \text{Na}_2\text{HPO}_4$  - 0.009 + 0.030 mol·kg<sup>-1</sup>;
- Solution of disodium tetraborate decahydrate  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  - 0.01 mol·kg<sup>-1</sup>;
- Solution of sodium hydrogen carbonate and of disodium carbonate  $\text{NaHCO}_3 + \text{Na}_2\text{CO}_3$  - 0.025 + 0.025 mol·kg<sup>-1</sup>.

3.3. Typical values of pH for the primary pH standards (buffer solutions) obtained using Harned cell in the temperature range 278.15 – 323.15 K are given on the Table 1.

3.4. The technical characteristics of the primary pH standards (buffer solutions) are shown in the Appendix A.

3.5. The Primary pH method is described in the Appendix B.

**Table 1 - Typical values of pH for the primary buffer solutions in the temperature range 278.15 – 323.15 K [1]**

Temperature, K	Potassium hydrogen tartrate $\text{KHC}_4\text{H}_4\text{O}_6$ - saturated at 298.15 K	Potassium hydrogen phthalate $\text{KHC}_8\text{H}_4\text{O}_4$ - $0.050 \text{ mol}\cdot\text{kg}^{-1}$	Potassium dihydrogen phosphate and of sodium hydrogen phosphate $\text{KH}_2\text{PO}_4 + \text{Na}_2\text{HPO}_4$ - $0.025 + 0.025 \text{ mol}\cdot\text{kg}^{-1}$	Potassium dihydrogen phosphate and of sodium hydrogen phosphate $\text{KH}_2\text{PO}_4 + \text{Na}_2\text{HPO}_4$ - $0.009 + 0.030 \text{ mol}\cdot\text{kg}^{-1}$	Disodium tetraborate decahydrate $\text{Na}_2\text{B}_4\text{O}_7\cdot 10\text{H}_2\text{O}$ - $0.01$ $\text{mol}\cdot\text{kg}^{-1}$	Sodium hydrogen carbonate and of disodium carbonate $\text{NaHCO}_3 + \text{Na}_2\text{CO}_3$ - $0.025 + 0.025 \text{ mol}\cdot\text{kg}^{-1}$
278.15	-	3.998	6.951	7.500	9.395	10.245
283.15	-	3.997	6.923	7.472	9.332	10.179
288.15	-	3.998	6.900	7.448	9.276	10.118
293.15	-	4	6.881	7.429	9.225	10.062
298.15	3.557	4.005	6.865	7.413	9.180	10.012
303.15	3.552	4.011	6.853	7.400	9.139	9.966
308.15	3.549	4.018	6.844	7.389	9.102	9.926
310.15	3.548	4.022	6.841	7.386	9.088	9.910
313.15	3.547	4.027	6.838	7.380	9.068	9.889
323.15	3.549	4.050	6.833	7.367	9.011	9.828

Note 1. Since there can be significant variations in the purity of samples of the same nominal chemical composition, batch-to-batch variations of  $0.003 \div 0.004$  pH units are typical.

Note 2. Tabulated pH values are given as examples and it is recommended that actual pH values be taken from certificates, which are to accompany each batch of certified reference material.

Note 3. Recommended target uncertainties of pH measurement are in the order of  $U(\text{pH}) \leq 0.003$  ( $k = 2$ ) at 298.15 K. In the temperature range 278.15 – 323.15 K (except 298.15 K) the target expanded uncertainty of pH measurement is 0.005.



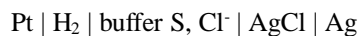
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**APPENDIX A**
**Table 2 - Technical characteristics of the primary pH standards**

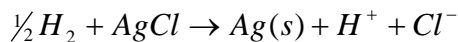
Name of chemical substances, included in the composition of standard-titers	Chemical formulations of substances	Mass to make 1 l volume at 293.15 K, g	Molality, mol·kg <sup>-1</sup>	Reproducible pH value at the temperature of 298.15 K, measured in the Harned cell
Potassium hydrogen tartrate	KHC <sub>4</sub> H <sub>4</sub> O <sub>6</sub>	9.5000	Saturated at 298,15 K	3.557
Potassium hydrogen phthalate	KHC <sub>8</sub> H <sub>4</sub> O <sub>4</sub>	10.1200	0.050	4.005
Potassium dihydrogen orthophosphate	KH <sub>2</sub> PO <sub>4</sub>	3.3880	0.025	6.865
Disodium hydrogen orthophosphate	Na <sub>2</sub> HPO <sub>4</sub>	3.5330	0.025	
Potassium dihydrogen orthophosphate	KH <sub>2</sub> PO <sub>4</sub>	1.1790	0.009	7.413
Disodium hydrogen orthophosphate	Na <sub>2</sub> HPO <sub>4</sub>	4	0.030	
Disodium tetraborate decahydrate	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O	3	0.010	9.180
Disodium carbonate	Na <sub>2</sub> CO <sub>3</sub>	2.6428	0.025	10.012
Sodium hydrogen carbonate	NaHCO <sub>3</sub>	2.0947	0.025	

## APPENDIX B

Primary pH method is based on measurements of the potential difference of the Harned cell:



The application of Nernst equation to the spontaneous cell reaction:



yields the potential difference of the cell (corrected to 1 atm) as:

$$E_1 = E^0 - k \cdot \lg \left[ \left( \frac{m_{\text{H}} \gamma_{\text{H}}}{m^0} \right) \left( \frac{m_{\text{Cl}} \gamma_{\text{Cl}}}{m^0} \right) \right], \quad (1)$$

which can be rearranged to give the acidity function:

$$p(a_{\text{H}} \gamma_{\text{Cl}}) = -\lg(a_{\text{H}} \gamma_{\text{Cl}}) = \frac{E_1 - E^0}{k} + \lg \left( \frac{m_{\text{Cl}}}{m^0} \right), \quad (2)$$

where  $E^0$  is the standard potential (table B2) of ,  $k=(RT/F)\ln 10$  is the Nernst slope,  $\gamma_{\text{Cl}}$  is the activity coefficient of the chloride ion at the molality  $m_{\text{Cl}}$ ;  $T$  – thermodynamic temperature, K;  $R$  – gas constant:  $R = 8.314\,4626\,(18)\,\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ;  $F$  – Faraday constant:  $F = 96485.33\,212\,(33)\,\text{C}\cdot\text{mol}^{-1}$  [8].

The standard potential of the silver-silver chloride electrode is obtained from the potential difference of the Harned cell in which only HCl is present at a fixed molality (e.g.,  $m_{\text{HCl}} = 0.01\,\text{mol}\cdot\text{kg}^{-1}$ ). The application of the Nernst equation to HCl cell:



gives

$$E_2 = E^0 - 2k \cdot \lg \left( \frac{m_{\text{HCl}} \gamma_{\pm\text{HCl}}}{m^0} \right), \quad (3)$$

where  $E_2$  is the corrected to 1 atmosphere partial pressure of hydrogen gas potential difference of the cell and  $\gamma_{\pm\text{HCl}}$  is the mean ionic activity coefficient of HCl at the molality  $m_{\text{HCl}}$  [9].

The effect of the chloride on the electromotive force of Harned cell is eliminated by using at least three buffer solutions with varying chloride contents  $m_{\text{Cl}}$  and by linear extrapolation to zero chloride, yielding the empirical function:

$$-\lg(a_{\text{H}} \gamma_{\text{Cl}}) = -\lg(a_{\text{H}} \gamma_{\text{Cl}})^0 + S \cdot m_{\text{Cl}}, \quad (4)$$

where  $p(a_{\text{H}} \gamma_{\text{Cl}})^0$  is the limiting acidity function and  $S$  is the experimental, temperature-dependent constant.

Primary standard pH value of certified buffer is calculated from the following formula:

$$\text{pH}(PS) = -\lg a_{\text{H}} \equiv -\lg(a_{\text{H}} \gamma_{\text{Cl}})^0 + \lg \gamma_{\text{Cl}}^0, \quad (5)$$

using the trace activity coefficient of the chloride ion  $\lg \gamma_{\text{Cl}}^0$ . The latter (like the activity coefficient of the hydrogen ion) is an immeasurable quantity, but can be calculated adopting the Bates-Guggenheim convention [10]:

$$\lg \gamma_{Cl}^0 = -AI^{1/2} / (1 + 1.5)I^{1/2}, \quad (6)$$

where  $A$  is the Debye-Hückel temperature-dependent constant (Table B2) and  $I$  is ionic strength of the buffer.

Although the resulting pH value is a conventional quantity it can be incorporated into the SI system at condition to take into account of pH uncertainty the uncertainties of mean ionic activity coefficient of HCl and of trace activity coefficient of the chloride ion.

**Table B2 – Standard potential  $E^\circ$  and coefficient  $A$  as a function of temperature**

Temperature K	$E^\circ$	$A$
278.15	0.23413	0.4952
283.15	0.23142	0.4988
288.15	0.22857	0.5026
293.15	0.22557	0.5066
298.15	0.22234	0.5108
303.15	0.21904	0.5150
308.15	0.21565	0.5196
313.15	0.21208	0.5242
323.15	0.20449	0.5341

**Table B3 – Ionic strength  $I$  of buffer solutions as a function of temperature**

Buffer solution	Molality mol/kg	Temperature K	$I$ mol/kg
Potassium tetraoxalate	0.05		
Potassium hydrogen citrate	solution saturated at 298.15 K	298.15-368.15	0.04
Potassium dihydrogen citrate	0.05		0.0526 0.0526 0.0526 0.0526 0.0526 0.0526 0.0525 0.0525 0.0524 0.0524
Potassium hydrogen phthalate	0.05	273.15-333.15	0.0535
Potassium dihydrogen phosphate + Disodium hydrogen phosphate	0.025  0.025	278.15-323.15	0.1

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

Buffer solution	Molality mol/kg	Temperature K	$I$ mol/kg
Potassium dihydrogen phosphate + Disodium hydrogen phosphate	0.008695  0.03043	278.15-323.15	0.1
Sodium tetraborate	0.01	278.15-323.15	.02
Sodium hydrogen carbonate + Sodium carbonate	0.025  0.025		0.1 0.0999 0.0999 0.0999 0.0999 0.0998 0.0998 0.0997 0.0996 0.0995
Calcium hydroxide	solution saturated at 298.15 K		0.053 0.051 0.050 0.050 0.049 0.049 0.048 0.048 0.048 0.047

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