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COMMISSION ON PHYSICO-CHEMICAL SYMBOLS AND TERMINOLOGY

REPORT ON THE STANDARDIZATION OF pH AND RELATED TERMINOLOGY*

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The standardization of pH has been achieved in Great Britain[1], in the United States[2-5], and recently also in Japan[6]. In their essential elements, the three standards are in agreement; only differences of detail exist. It is the object of this report to summarize, for the information of all national groups interested in pH, the extent of standardization already achieved and to indicate how this area of agreement could perhaps be extended to other conceptions related to pH.

1. SYMBOLS

There already exists international agreement that pH should be written and printed on line in roman type. We recommend that, with the unique exception of pH, the operator p (printed in roman) should denote $-\log_{10}$. For example

$$\mathrm{p}m_\mathrm{H} \qquad \text{means} \qquad -\log_{10}m_\mathrm{H}$$

$$\mathrm{p}m_\mathrm{H}\gamma_{\mathrm{H,Cl}} \qquad \text{means} \qquad -\log_{10}(m_\mathrm{H}\gamma_{\mathrm{H,Cl}})$$

$$\mathrm{p}m_\mathrm{H}\gamma_{\mathrm{H,Cl}}^2 \qquad \text{means} \qquad -\log_{10}(m_\mathrm{H}\gamma_{\mathrm{H,Cl}}^2)$$

where m denotes molality and γ denotes mean activity coefficient (molality scale).

2. DEFINITION OF pH

In all three existing national standards the definition of pH is an operational one. The electromotive force E_X of the cell

Pt,H_2 | solution X | concentrated KCl solution | reference electrode

is measured and likewise the electromotive force E_S of the cell

Pt,H_2 | solution S | concentrated KCl solution | reference electrode

both cells being at the same temperature throughout and the reference electrodes and bridge solutions being identical in the two cells. The pH of the solution X, here denoted by pH(X), is then related to the pH of the solution S, here denoted by pH(S), by the definition

$$pH(X) - pH(S) = \frac{E_X - E_S}{(RT \ln 10)/F}$$

where R denotes the gas constant, T the absolute temperature, and F the faraday. In this equation the numerator and denominator must be expressed in the same units so that the pH difference here defined is a pure number.

The hydrogen electrodes in both cells may be replaced by identical hydrogen-ion-responsive electrodes, $e.g.$, glass or quinhydrone.

The two bridge solutions may be of any molality not less than about 3·5, provided they are the same.

3. STANDARDS

The difference between the pH of two solutions having been defined as above, the definition of pH can be completed by assigning a value of pH at each temperature to one chosen solution called the primary standard. In the British and Japanese Standards this is the definition of pH, the primary standard being a one-twentieth molar solution of pure potassium hydrogen phthalate. The pH of this solution is defined as having the value 4 exactly at 15°C. At any other temperature t°C between 0°C and 60°C its pH is defined by

$$pH = 4 \cdot 00 + \frac{1}{2} \left(\frac{t-15}{100} \right)^2$$

This formula is for all practical purposes equivalent to one given elsewhere[7]. The question how this formula might be extended to temperatures higher than 60°C has been raised but not yet formally answered. The American Standard described below is in practically complete agreement with

$$pH = 4 \cdot 00 + \frac{1}{2} \left(\frac{t-15}{100} \right)^2 \qquad 0 \leqslant t \leqslant 55$$

$$pH = 4 \cdot 00 + \frac{1}{2} \left(\frac{t-15}{100} \right)^2 - \frac{t-55}{500} \qquad 55 \leqslant t \leqslant 95$$

The American Standard specifies four standard solutions with pH values specified at each temperature covering the range of pH from 2 to 12. These are given in *Table 1*[8].

There is a proposal to add as secondary standards 0·05 molar potassium tetroxalate (pH $\simeq$ 1·7) and saturated calcium hydroxide (pH $\simeq$ 12).

Table 1*

t (°C)	KH tartrate (satd at 25°C)	0·05 KH phthalate	0·025 KH_2PO_4 + 0·025 Na_2HPO_4	0·01 Borax
0	—	4·01	6·98	9·46
5	—	4·01	6·95	9·39
10	—	4·00	6·92	9·33
15	—	4·00	6·90	9·27
20	—	4·00	6·88	9·22
25	3·56	4·01	6·86	9·18
30	3·55	4·01	6·85	9·14
35	3·55	4·02	6·84	9·10
40	3·54	4·03	6·84	9·07
45	3·55	4·04	6·83	9·04
50	3·55	4·06	6·83	9·01
55	3·56	4·07	6·84	8·99
60	3·56	4·09	6·84	8·96
70	3·58	4·12	6·85	8·93
80	3·61	4·16	6·86	8·89
90	3·65	4·20	6·88	8·85
95	3·68	4·23	6·89	8·83

* All concentrations are quoted in moles/litre of solution.

If the definition of pH in section **2** is adhered to strictly, then the pH of a solution might be slightly dependent on which standard solution was used. In fact any such variation is too small to be of practical significance. Moreover the American acceptance of several standards allows the use of the following alternative definition of pH. The electromotive force E_X of the cell

Pt,H_2| solution X | concentrated KCl solution | reference electrode

is measured, and likewise the electromotive forces E_1 and E_2 of two similar cells with the solution X replaced by the standard solutions S_1 and S_2 such that the E_1 and E_2 values are on either side of, and as near as possible to, E_X. The pH of solution X is then obtained by assuming linearity between pH and E, that is to say

$$\frac{pH(X) - pH(S_1)}{pH(S_2) - pH(S_1)} = \frac{E_X - E_1}{E_2 - E_1}$$

This procedure is in fact useful and especially recommended when the hydrogen-ion-responsive electrode is a glass electrode.

This completes our report on the definition and measurement of the experimental quantity pH, of which the value depends on molalities, activity coefficients and transference numbers of the ions present.

The rest of this report is concerned with the interpretation of pH values as approximations to thermodynamical quantities.

4. IONIC ACTIVITY COEFFICIENTS

As a prelude to our discussion of the interpretation of pH it is expedient to say something about ionic activity coefficients. For the sake of brevity we shall restrict our detailed discussion to solutions containing only 1–1 electrolytes. The extension of the discussion to the more general case would require more complicated formulae without any new physical principles.

Electromotive force measurements on cells without liquid–liquid junctions (or other less direct experimental techniques) lead to experimental values of mean activity coefficients of an electrolyte but not to ionic activity coefficients. In particular the electromotive force of the cells

$$H_2,Pt \ \left| \ \begin{array}{c} \text{solution containing} \\ \text{H}^+ \text{ and Cl}^- \end{array} \right| \ AgCl \ \left| \ Ag \right.$$
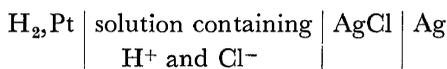
leads directly to the value of $m_H m_{Cl} \gamma_{H,Cl}^2$ and, if the value of m_{Cl} is known, indirectly to that of $m_H \gamma_{HCl}^2$.

It is permissible, and often convenient, to write conventionally

$$\gamma_{H,Cl}^2 = \gamma_H \gamma_{Cl}$$
$$\gamma_{Na,Cl}^2 = \gamma_{Na} \gamma_{Cl}$$
$$\gamma_{K,Cl}^2 = \gamma_K \gamma_{Cl}$$

and so on, but the values of the ionic activity coefficients γ_H, γ_{Na}, γ_K, γ_{Cl} are not uniquely defined. In each solution an arbitrary value may be assigned to the γ of any one chosen ionic species. This does not mean that one convention may not be more convenient than another. In particular all 1–1 electrolytes present in a solution of total molality less than 0·01 have, to an accuracy sufficient for most purposes, equal mean activity coefficients. Under these conditions it is natural to equate the ionic activity coefficients to the common mean activity coefficient; in fact any other convention would be far-fetched.

At higher molalities different electrolytes in the same solution have different mean activity coefficients and consequently the convention must be less simple. The following convention was described by one of us many years ago[9]. If we use M to denote a cation and X an anion, then

$$\frac{\gamma_H}{\gamma_M} \equiv \frac{\gamma_H \gamma_X}{\gamma_M \gamma_X} \equiv \frac{\gamma_{H,X}^2}{\gamma_{M,X}^2}$$

is thermodynamically well defined as is, of course, $\gamma_M \gamma_X \equiv \gamma_{M,X}^2$. The convention for defining γ_H is

$$\ln \gamma_H = \frac{\Sigma_M m_M \ln(\gamma_H/\gamma_M) + \Sigma_X m_X \ln(\gamma_H \gamma_X)}{\Sigma_M m_M + \Sigma_X m_X}$$

with the analogous definition for a typical anion, say Br⁻:

$$\ln \gamma_{Br} = \frac{\Sigma_M m_M \ln(\gamma_M \gamma_{Br}) + \Sigma_X m_X \ln(\gamma_{Br}/\gamma_X)}{\Sigma_M m_M + \Sigma_X m_X}$$

These conventional relations automatically satisfy the thermodynamic requirement

$$\ln\gamma_H + \ln\gamma_{Br} = 2\ln\gamma_{H,Br}$$

When there is only a single electrolyte present, say HBr, these conventions reduce to

$$\ln\gamma_H = \ln\gamma_{Br} = \ln\gamma_{H,Br}$$

This convention is the simplest possible which treats all ionic species on a par. It is, in our opinion, aesthetically satisfying, but it has little practical utility because the values of all the mean activity coefficients of the several electrolytes present are usually not known. (In the more general case of ions with various charges the formulae are more complicated.)

We are therefore driven to using a much simpler, though less symmetrical convention. One that has proved especially useful is to define the activity coefficient of the *chloride* ion, at an ionic strength I not exceeding 0·1, by

$$\log\gamma_{Cl} = -\frac{AI^{\frac{1}{2}}}{1 + \rho I^{\frac{1}{2}}}$$

where A has at each temperature the value given by the theory of Debye and Hückel and ρ has a specified value; that recommended is $\rho = 1\cdot5$ mole$^{-\frac{1}{2}}$ kg$^{\frac{1}{2}}$.

Once the value of the activity coefficient of the chloride ion has been conventionally defined, this value may be combined with the value of $m_H\gamma_{H,Cl}^2 = m_H\gamma_H\gamma_{Cl}$ to obtain a value of $m_H\gamma_H$ or of $pm_H\gamma_H = -\log_{10}m_H\gamma_H$.

5. pH OF STANDARD SOLUTIONS

We have stated that pH values have been assigned to four standard solutions in the American Standard and to one of these in the British and Japanese standards. We have as yet said nothing of how these values were chosen. They are in fact defined for each standard solution S by

$$\mathrm{pH(S)} = pm_H\gamma_H$$

where the quantity on the right is determined according to the convention of section **4**.

6. APPROXIMATE INTERPRETATION OF pH

As a consequence of the relation

$$\mathrm{pH} = pm_H\gamma_H$$

defining the pH of standard solutions, it can be verified that this same relation holds with an accuracy of $\pm0\cdot02$ or better for all aqueous solutions of total ionic strength not exceeding 0·1, provided the pH lies between 2 and 12. Outside this pH range a more complicated recipe would be needed in any attempt to correlate pH with $pm_H\gamma_H$.

7. THE ABBREVIATION pa_H

Some people may wish to abbreviate $pm_H\gamma_H$ (as conventionally defined in section 4) to pa_H. Other people have strong objections to this notation because it may revive controversies of the days before the nature of pH was properly understood.

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References

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