

INTERNATIONAL UNION OF PURE
AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION
COMMISSION ON ELECTROANALYTICAL CHEMISTRY*

**REFERENCE VALUE STANDARDS
AND PRIMARY STANDARDS FOR
pH MEASUREMENTS**
**in Organic Solvents and Water + Organic
Solvent Mixtures of Moderate to High
Permittivities**

Prepared for publication by

S. RONDININI, P. R. MUSSINI AND T. MUSSINI

Department of Physical Chemistry and Electrochemistry,
University of Milan, I-20133 Milano, Italy

* Membership of the Commission during 1983–85 when the report was prepared was as follows:

Chairman: J. Jordan (USA); *Secretary:* K. Izutsu (Japan); *Titular Members:* A. K. Covington (UK); J. Juillard (France); R. C. Kapoor (India); E. Pungor (Hungary); *Associate Members:* W. Davison (UK); R. A. Durst (USA); M. Gross (France); K. M. Kadish (USA); R. Kalvoda (Czechoslovakia); H. Kao (China); Y. Marcus (Israel); T. Mussini (Italy); H. W. Nürnberg (FRG); M. Senda (Japan); N. Tanaka (Japan); K. Tóth (Hungary); *National Representatives:* D. D. Perrin (Australia); B. Gilbert (Belgium); W. C. Purdy (Canada); A. A. Vlček (Czechoslovakia); H. Monien (FRG); M. L'Her (France); Gy. Farsang (Hungary); H. C. Gaur (India); W. F. Smyth (Ireland); E. Grushka (Israel); S. R. Cavallari (Italy); W. Frankvoort (Netherlands); Z. Galus (Poland); G. Johansson (Sweden); J. Buffle (Switzerland); H. Thompson (UK); J. G. Osteryoung (USA); I. Piljac (Yugoslavia).

Republication of this report is permitted without the need for formal IUPAC permission on condition that an acknowledgement, with full reference together with IUPAC copyright symbol (© 1987 IUPAC), is printed. Publication of a translation into another language is subject to the additional condition of prior approval from the relevant IUPAC National Adhering Organization.

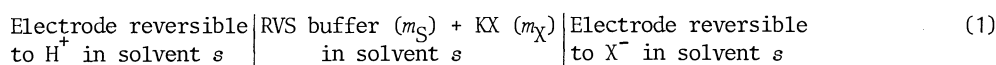
Reference value standards and primary standards for pH measurements in organic solvents and water + organic solvent mixtures of moderate to high permittivities

Following the recent report on the criteria for standardization of pH measurements in aqueous organic solvent mixtures [*Pure Appl. Chem.* 57, 865-876 (1985)], the present report concerns the re-examination of reference value standards (pH_{RVS}) and primary standards (pH_{S}) determined prior to 1985, the aggregation of new standards freshly determined in the light of IUPAC rules and procedures, and the compilation of recommended data. The pH_{RVS} data (the RVS material is the 0.05 m potassium hydrogenphthalate buffer) now available cover the following solvents and/or their mixtures with water: methanol, ethanol, 2-propanol, 1,4-dioxane, acetonitrile, dimethylsulphoxide, and heavy water (D_2O); the various pH_{S} now available cover methanol, ethanol, dimethylsulphoxide and D_2O .

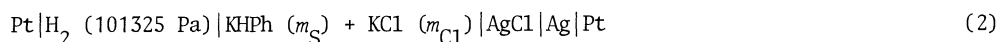
1. INTRODUCTION

Rules and procedures for the determination of Reference Value Standards (pH_{RVS}) and Primary Standards (pH_{S}) for pH measurements in organic solvents and binary aqueous organic solvent mixtures of moderate to high permittivities (approximately $\epsilon > 30$) have been recently endorsed by IUPAC (ref. 1).

In terms of the above rules, the pH of the buffer solution of potassium hydrogenphthalate (KHP) of molality 0.05 mol/kg is recognized as the reference value standard in the given (single or mixed) solvent s and at the given temperature. The procedure for the determination of pH_{RVS} requires measuring the electromotive force (e.m.f.) E of the reversible cell:



which for most aquo-organic mixed solvents (and also for several 100%-pure nonaqueous solvents) s takes the simpler and familiar form:



where m_{S} is fixed (0.05 mol/kg) and m_{Cl} is varied.

From the e.m.f. expression:

$$(E - E^\circ)/k = \text{p}(\alpha_{\text{H}}\gamma_{\text{Cl}}) + \text{p}m_{\text{Cl}} = \text{pH} + \text{p}\gamma_{\text{Cl}} + \text{p}m_{\text{Cl}} \quad (3)$$

where E° is the standard e.m.f. of cell (2), $k = (1n10)RT/F$, and the subscript ions are henceforth indicated without charge to simplify printing, it is clear that:

(i) knowledge of accurate E° values is essential; and

(ii) an extrathermodynamic assumption, *i.e.* a Debye-Hückel equation of the type:

$$\text{p}\gamma_{\text{Cl}} = A I^{\frac{1}{2}} / (1 + a_0 B I^{\frac{1}{2}}) \quad (4)$$

is necessary to compute the single-Cl⁻-ion activity coefficient γ_{Cl} in order to obtain the non-thermodynamic quantity pH from the thermodynamic quantity $\text{p}(\alpha_{\text{H}}\gamma_{\text{Cl}})$.

The equation (4), where I is the total ionic strength of the mixed electrolyte KHP+KCl, introduces two further features:

- (iii) one can write $I = I_S + m_{\text{Cl}}$, where I_S is the ionic strength of KHP alone, but $I_S \neq m_S$ depending on the ionisation constants of the *o*-phthalic acid H_2Ph : this implies iterative calculations procedures, whose steps have been described earlier (ref. 1), to obtain I_S , I and ultimately γ_{Cl} ; and
- (iv) the ion-size parameter α_0 is assigned a value fixed by the Bates-Guggenheim convention extended to the general solvent s (refs. 1,2):

$$({}^s\alpha_0 {}^sB)_T = 1.5 \left\{ \frac{{}^w\epsilon {}^s\rho}{{}^s\epsilon {}^w\rho} \right\}_T^{\frac{1}{2}} \quad (5)$$

where sB is the classical Debye-Hückel constant of eq. (4), appropriate to the general (single or mixed) solvent s , ${}^w\epsilon$ and ${}^s\epsilon$ are the relative permittivities of pure water (superscript w) and of the solvent (superscript s), and ${}^w\rho$ and ${}^s\rho$ are the corresponding densities (ref. 1). If s is water itself, eq. (5) reduces to $\alpha_0B = 1.5$, which is the form of the Bates-Guggenheim convention which was introduced originally for pH standardisation in pure water (ref. 2).

The equations (3) to (5) are combined into a special extrapolation function Φ to determine pH_{RVS} as intercept at $m_{\text{Cl}} = 0$ of a linear regression plot of Φ vs. m_{Cl} , with optimization of pH_{RVS} through iterative calculation cycles (ref. 1). In this context, another important point must be outlined:

- (v) the above determination and optimization of pH_{RVS} must be carried out at *each* distinct composition of the solvent s , such a composition being usually expressed by the mole fraction x of the *nonaqueous* component. In fact, an even minimal change in x causes a change in the standard state "*hyp. m = 1*" for the H^+ ion (*primary medium effect* upon H^+ , refs. 1,3) and also a change in both the pH scale and its position relative to the familiar aqueous pH scale. Therefore, each pH_{RVS} so determined in a solvent s is only valid for the pH scale in *that* solvent. Now, it was recently shown (refs. 4-7) that the above determination and optimization of pH_{RVS} at each composition x of the solvent can be rigorously inserted in, and carried out by, a procedure of single-stage multilinear regression of E as a function of m_{Cl} , x , and temperature T , giving the final, smoothed, recommended values. This is a very important feature because there might be various independent E sets from different authors with obvious problems of overlapping and of extracting therefrom the unified set (best values) for any related quantity. The same applies for the determination of the standard e.m.f. E° of cell (2), required by eq. (3), which is currently carried out by the classical method of extrapolating to $I = 0$ a suitable function of the e.m.f. of the cell:



Thus, the interconnection of problems emphasized by the above points (i) to (v) for different solvents s can be summarized by the scheme in Figure 1, which is the basic scheme of the present report. Of course, this scheme is valid for both pH_{RVS} and pH_S determinations.

The IUPAC document mentioned above (ref. 1) also underlines how the above multilinear regression method permits an appropriate analysis of the internal consistency of pH_{RVS} data relevant to the various solvents.

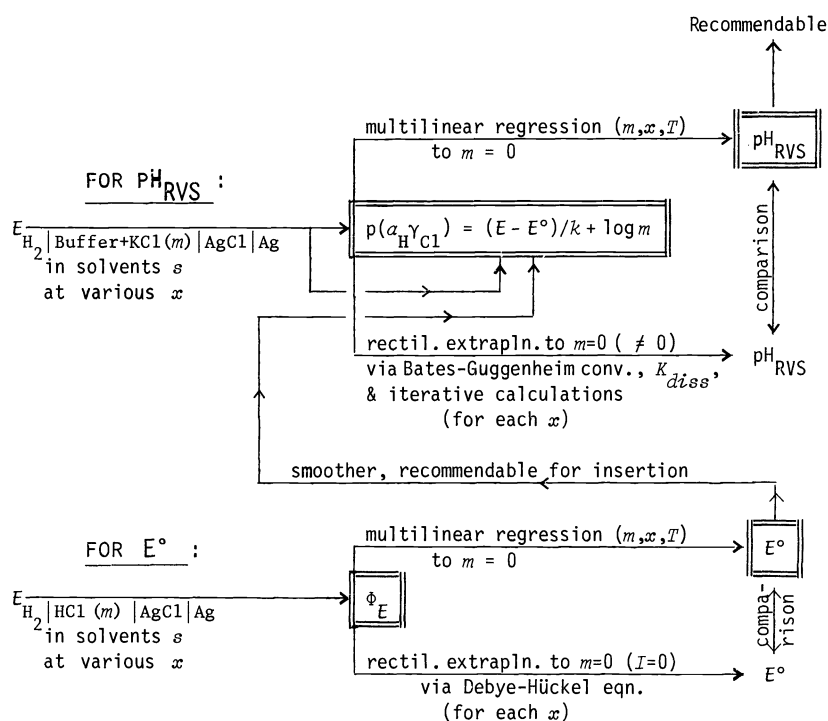


FIGURE 1
Connections between interrelated quantities and their treatments for determining pH_{RVS} values.

2. PRESENTATION OF DATA AND DISCUSSION

All the reference value standards (pH_{RVS}) and primary standards (pH_{S}) determined up to date have been re-examined to ensure compliance with the above IUPAC rules and to provide sets of recommended data. These have been grouped in three Tables, of which Table 1 reports the data (pH_{RVS}) which are relevant to the RVS buffer (the 0.05 *m* potassium hydrogenphthalate buffer) in various aqueous organic solvent mixtures (refs. 4-11). Table 2 reports those (pD_{RVS}) that pertain to the special case of the RVS buffer (the 0.05 *m* potassium deuteriumphthalate buffer (KDPh) for *pD* in heavy water D_2O (ref. 12), and Table 3 collects those for such other buffers as acetate, oxalate, carbonate, succinate, phosphate, *TRIS* + *TRISHCl*, and so on, in different (single or mixed) solvents (including heavy water, D_2O) and at various temperatures (refs. 11, 13-24): in the case of ethanol/water and dimethylsulphoxide/water mixtures, the temperature range extends to include also a subzero strip.

The domain of *ethanol/water* mixtures has required special attention for various reasons. Firstly, till recently, pH_{RVS} data were unavailable, and they have consequently been freshly determined in these Laboratories (ref. 8,8a) in compliance with the recent IUPAC document (ref. 1).

Secondly, pH_{S} data at 25 °C for such buffers as oxalate, succinate, salicylate, and diethylbarbiturate were proposed by De Ligny and associates as early as in 1958-1964 (refs. 13-15), namely, much before the issue of the present IUPAC rules.

Thirdly, the available values of the standard e.m.f. E^0 of the cell (2), which are essential for the determination of the pH standards (pH_{RVS} or pH_{S}) as shown by eq. (3), were insufficient and scattered at the time of the very valuable work on pH_{S} determinations by De Ligny, Luykx, Rehbach and Wienecke (ref. 13) and Gelsema (ref. 14), but new E^0 values (even covering down to -10 °C) have appeared in the literature since then.

TABLE 1 - Values of pH-metric Reference Value Standards (pH_{RVS}) for the 0.05 m Potassium Hydrogenphthalate (KHPH) buffer in various aqueous organic solvent mixtures at different temperatures $t/^\circ\text{C}$, with overall estimated uncertainties δ .

| | | Weight percent of the nonaqueous solvent in admixture with water | | | | | | | | | |
|---------------------|---------------------------------|--|-------------|--------|-------------|-------------|-------------|-------------|--------|-------------|--------|
| | | 5 | 10 | 15 | 20 | 30 | 40 | 50 | 64 | 70 | 84.2 |
| METHANOL | $t/^\circ\text{C}$ ^x | | 0.0588 | | 0.1232 | | | 0.3599 | 0.4999 | | 0.7498 |
| | 10 | | 4.254 | | 4.490 | | | 5.151 | 5.488 | | 6.254 |
| | 25 | | 4.243 | | 4.468 | | | 5.125 | 5.472 | | 6.232 |
| | 40 | | 4.257 | | 4.472 | | | 5.127 | 5.482 | | 6.237 |
| | δ | | ± 0.003 | | | | | | | | |
| Refs. | | 4,7 | | | | | | | | | |
| ETHANOL | x | | 0.0416 | | 0.0891 | | 0.2068 | | | 0.4771 | |
| | -5 | | 4.266 | | 4.570 | | 5.112 | | | 5.527 | |
| | 0 | | 4.249 | | 4.544 | | 5.076 | | | 5.500 | |
| | 10 | | 4.235 | | 4.513 | | 5.026 | | | 5.469 | |
| | 25 | | 4.236 | | 4.508 | | 4.976 | | | 5.472 | |
| | 40 | | 4.260 | | 4.534 | | 4.978 | | | 5.493 | |
| | δ | | ± 0.002 | | ± 0.003 | | ± 0.002 | | | ± 0.002 | |
| Refs. | | 8,8a | | | | | | | | | |
| 2-PROPANOL | x | | 0.0322 | | | 0.1138 | | 0.2305 | | 0.4115 | |
| | 15 | | 4.238 | | | 4.889 | | 5.217 | | 5.514 | |
| | 25 | | 4.242 | | | 4.849 | | 5.186 | | 5.499 | |
| | 35 | | 4.251 | | | 4.836 | | 5.204 | | 5.541 | |
| | 45 | | 4.274 | | | 4.830 | | 5.191 | | 5.587 | |
| | δ | | ± 0.005 | | | ± 0.002 | | ± 0.006 | | ± 0.013 | |
| Refs. | | 7,9 | | | | | | | | | |
| ACETONITRILE | x | 0.0226 | | 0.0719 | | 0.1583 | | 0.3050 | | 0.5059 | |
| | 15 | 4.163 | | 4.533 | | 5.001 | | 5.456 | | 6.159 | |
| | 25 | 4.166 | | 4.533 | | 5.000 | | 5.461 | | 6.194 | |
| | 35 | 4.178 | | 4.542 | | 5.008 | | 5.475 | | 6.236 | |
| | δ | | ± 0.005 | | | | | | | | |
| Refs. | | 6,7,10 | | | | | | | | | |
| 1,4-DIOXANE | x | | 0.0222 | | | 0.0806 | | 0.1697 | | | |
| | 15 | | 4.330 | | | 5.034 | | 5.779 | | | |
| | 25 | | 4.329 | | | 5.015 | | 5.782 | | | |
| | 35 | | 4.337 | | | 5.007 | | 5.783 | | | |
| | 45 | | 4.355 | | | 5.008 | | 5.783 | | | |
| | δ | | ± 0.002 | | | | | | | | |
| Refs. | | 5,7 | | | | | | | | | |
| DIMETHYL-SULPHOXIDE | x | | | | 0.0545 | 0.0899 | | | | | |
| | -12 | | | | | 4.870 | | | | | |
| | 25 | | | | 4.471 | 4.761 | | | | | |
| | δ | | ± 0.002 | | | | | | | | |
| Refs. | | 7,11 | | | | | | | | | |

TABLE 2 - Values of pD-metric Reference Value Standards (pD_{RVS}) for the 0.05 m Potassium Deuteriophthalate (KDPh) buffer in Deuterium Oxide (D_2O) at various temperatures $t/^\circ\text{C}$, with overall estimated uncertainty δ .

| $t/^\circ\text{C}$ | 5 | 10 | 15 | 20 | 25 | 30 | 35 | 40 | 45 | 50 |
|--------------------|-------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| pD_{RVS} | 4.546 | 4.534 | 4.529 | 4.522 | 4.521 | 4.523 | 4.528 | 4.532 | 4.542 | 4.552 |
| δ | ± 0.007 | | | | | | | | | |
| Ref. | 12 | | | | | | | | | |

Therefore, both in view of the recent determinations of pH_{RVS} (ref. 8,8a) and for a possible revision of the pH_S values determined by De Ligny and associates, the available E° data have been re-analysed (ref. 8a,25) through the multiregression method described recently (refs. 25-27). A set of smoothed E° data was thus derived covering the temperature range from -10 to $+40$ °C for the ethanol/water mixtures up to 70 wt % of ethanol, as reported in Table 4 ,

TABLE 3 - Values of primary standards (pH_S) for pH measurements in different solvents or aqueous organic solvent mixtures at various temperatures, taken or recalculated from the given references. Values not fully complying with the IUPAC criteria (ref.1) are quoted in parentheses (); values not satisfying F-tests are quoted in braces {}. All % values for solvents mixed with water are by weight.

| METHANOL 50 % | | | | | | | | | | OXALATE ^g | SUCCINATE ^h | OXALATE ^j | SUCCINATE ^k | | |
|----------------------|----------------------|------------------------|------------------------|---------------------------|---------------------------|----------|-------------------|------------------|-------------------------|--------------------------|------------------------|----------------------|------------------------|--|--|
| $t/^\circ C$ | ACETATE ^a | SUCCINATE ^b | PHOSPHATE ^c | TRIS+TRISHCl ^d | AmPy+AmPyHCl ^e | wt % | METHANOL at 25 °C | ETHANOL at 25 °C | | | | | | | |
| 10 | (5.518) | (5.720) | (7.937) | 8.436 | 9.116 | 0 | {2.145} | {4.119} | 2.146 | 4.113 | | | | | |
| 15 | (5.506) | (5.697) | (7.916) | 8.277 | 8.968 | 30 | | | 2.312 | 4.691 | | | | | |
| 20 | (5.498) | (5.680) | (7.898) | 8.128 | 8.829 | 39.14 | {2.374} | | | | | | | | |
| 25 | (5.493) | (5.666) | (7.884) | 7.985 | 8.695 | 43.30 | | 4.938 | | | | | | | |
| 30 | (5.493) | (5.656) | (7.872) | 7.850 | 8.570 | 50 | | | 2.506 | 5.073 | | | | | |
| 35 | (5.496) | (5.650) | (7.863) | 7.720 | 8.446 | 64 | | {5.398} | | | | | | | |
| 40 | (5.502) | (5.648) | (7.858) | 7.599 | 8.332 | 70 | {2.771} | | | | | | | | |
| | | | | | | 71.89 | | | 2.985 | 5.713 | | | | | |
| Refs. | 21,22,23 | | | 18 | 19 | 84.20 | 3.358 | | | | | | | | |
| | | | | | | 84.40 | | {6.289} | | | | | | | |
| | | | | | | 90 | {3.729} | | SALICYLATE ⁱ | BARBITURATE ^j | | | | | |
| | | | | | | 94.20 | {7.147} | | | | | | | | |
| | | | | | | 94.29 | 4.133 | | | | | | | | |
| | | | | | | 100 | (5.79) | (8.75) | (8.31) | (13.23) | | | | | |
| Refs. | 13,15,20 | | | | | | | 14,15 | | | | | | | |
| ACETATE ^k | | | | | | | | | | PHOSPHATE ^l | | | | | |
| $t/^\circ C$ | ETHANOL | | | $t/^\circ C$ | ETHANOL | | | | | | | | | | |
| | H ₂ O | 10% | 20% | 40% | H ₂ O | 10% | 20% | 40% | | | | | | | |
| -10 | | | 5.075 | 5.498 | -10 | | 7.376 | 7.638 | | | | | | | |
| -5 | | 4.881 | 5.044 | 5.470 | -5 | | 7.315 | 7.569 | | | | | | | |
| 0 | 4.687 | 4.861 | 5.021 | 5.445 | 0 | 6.984 | 7.263 | 7.508 | | | | | | | |
| 25 | 4.670 | 4.822 | 4.967 | 5.395 | 25 | 6.865 | 7.104 | 7.310 | 7.597 | | | | | | |
| Refs. | 16,23 | | | | | | | 16,23 | | | | | | | |
| CITRATE ⁿ | | | PHOSPHATE ^o | CARBONATE ^p | PHOSPHATE ^l | | | | | | | | | | |
| $t/^\circ C$ | D ₂ O | D ₂ O | D ₂ O | $t/^\circ C$ | H ₂ O | DMSO 20% | DMSO 30% | | | | | | | | |
| | | | | 25 | 6.865 | 7.407 | 7.710 | | | | | | | | |
| | | | | Refs. | 24 | 11 | | | | | | | | | |
| 5 | 4.378 | 7.539 | 10.998 | PHOSPHATE ^m | | | | | | | | | | | |
| 10 | 4.352 | 7.504 | 10.924 | $t/^\circ C$ | H ₂ O | DMSO 20% | DMSO 30% | | | | | | | | |
| 15 | 4.329 | 7.475 | 10.855 | 25 | 7.413 | 7.959 | 8.266 | | | | | | | | |
| 20 | 4.310 | 7.449 | 10.793 | Refs. | 24 | 11 | | | | | | | | | |
| 25 | 4.293 | 7.428 | 10.736 | TES+NaTES ^q | | | | | | | | | | | |
| 30 | 4.279 | 7.411 | 10.685 | $t/^\circ C$ | H ₂ O | DMSO 20% | DMSO 30% | | | | | | | | |
| 35 | 4.268 | 7.397 | 10.638 | 12 | | | 8.210 | | | | | | | | |
| 40 | 4.260 | 7.387 | 10.597 | -5.5 | | 7.889 | | | | | | | | | |
| 45 | 4.253 | 7.381 | 10.560 | 0 | 7.558 | 7.649 | 7.860 | | | | | | | | |
| 50 | 4.250 | 7.377 | 10.527 | 25 | 7.026 | 7.106 | 7.128 | | | | | | | | |
| Refs. | 17,23 | | | | | | | 11 | | | | | | | |

^l: KH₂PO₄ (0.025m) + Na₂HPO₄ (0.025m); ^m: KH₂PO₄ (0.008695m) + Na₂HPO₄ (0.03043m);
ⁿ: K₂C₂O₄ (0.05m); ^o: K₂PO₄ (0.025m) + Na₂DPO₄ (0.025m); ^p: Na₂CO₃ (0.025m) + Na₂CO₃ (0.025m); ^q: TES = N-tris(hydroxymethyl)methyl-2-aminoethane sulphonic acid (0.070m) + NaTES = Sodium salt of TES (0.030m).
 For the buffers ^a, ^b, ^c, ^d, ^e the original works give pH_S values from 0.005, 0.005, 0.002, 0.01, 0.02 *m* to 0.05, 0.05, 0.02, 0.02, 0.10, 0.10 *m* at 0.005, 0.005, 0.002, 0.01, 0.02 intervals, respectively.
 * The standard values in heavy water (D₂O) are in terms of pD_S .

TABLE 4 - Values of the standard e.m.f.'s E_2° and (in *italics*) E_7° of the cells (2) and (7), respectively, used for the revision of pH_{RYS} and pH_S at various temperatures and compositions of aqueous organic solvent mixtures.

| wt % of + in mixture with H ₂ O | METHANOL | | | ETHANOL | | | | | ACETONITRILE | | | 2-PROPANOL | | | | | | | |
|--|----------------|--------|--------|----------------|--------|--------|--------|--------|---------------------------------------|--------|----------|----------------|--------|--------|--------|--------|--------|--------|--------|
| | E_2°/mV | | | E_2°/mV | | | | | E_2°/mV and $\{E_7^\circ/mV\}$ | | | E_2°/mV | | | | | | | |
| | 10°C | 25°C | 40°C | -5°C | 0°C | 10°C | 25°C | 40°C | x | 15°C | 25°C | 35°C | x | 15°C | 25°C | 35°C | 45°C | | |
| 0 | 0.0000 | 231.35 | 222.48 | 212.01 | 0.0000 | 236.70 | 231.40 | 222.36 | 212.08 | 0.0000 | 228.41 | 222.32 | 215.82 | 0.0000 | 228.34 | 222.23 | 215.54 | 208.30 | |
| 5 | | | | | | | | | | 0.0226 | 224.66 | 217.92 | 210.78 | | | | | | |
| 10 | 0.0588 | 223.38 | 215.21 | 205.43 | 0.0416 | 227.12 | 225.90 | 222.46 | 214.94 | 204.70 | 0.0719 | 217.90 | 209.94 | 201.59 | 0.0323 | 219.68 | 214.25 | 207.79 | 200.33 |
| 15 | | | | | | | | | | | | | | | | | | | |
| 20 | 0.1232 | 216.57 | 208.56 | 198.92 | 0.0891 | 218.44 | 217.66 | 214.88 | 207.76 | 197.26 | | | | | | | | | |
| 30 | | | | | 0.1435 | 213.48 | 212.28 | 208.77 | 200.76 | 189.61 | 0.1583 | 207.73 | 198.04 | 188.14 | 0.1138 | 202.29 | 196.66 | 189.58 | 181.10 |
| 39.14 | 0.2656 | 206.20 | 196.75 | 185.69 | | | | | | | | | | | | | | | |
| 40 | | | | | 0.2068 | 212.04 | 209.58 | 203.93 | 193.68 | 181.41 | | | | | | | | | |
| 43.30 | 0.3004 | 204.17 | 194.08 | 182.39 | | | | | | | | | | | | | | | |
| 50 | 0.3599 | 200.72 | 189.38 | 176.43 | 0.2811 | 212.48 | 208.16 | 199.37 | 185.82 | 171.84 | 0.3050 | 179.35 | 167.15 | 155.99 | 0.2306 | 183.73 | 174.92 | 165.05 | 154.16 |
| 64 | 0.4999 | 190.66 | 175.90 | 159.53 | | | | | | | | | | | | | | | |
| 70 | 0.5675 | 183.63 | 167.22 | 149.20 | 0.4771 | 190.20 | 185.53 | 175.41 | 158.36 | 139.19 | 0.5059 | 157.53 | 148.68 | 139.84 | 0.4115 | 150.48 | 137.21 | 122.60 | 106.70 |
| 71.89 | | | | | 0.5000 | | | | 150.9** | | | | | | | | | | |
| 84.20 | 0.7498 | 151.90 | 132.13 | 110.75 | | | | | | | | | | | | | | | |
| 84.40 | 0.7526 | 151.22 | 131.42 | 110.01 | | | | | | | | | | | | | | | |
| 90 | 0.8350 | 128.24 | 107.92 | 85.98 | | | | | | | | | | | | | | | |
| 94.20 | 0.9013 | 104.87 | 84.77 | 63.06 | | | | | | | | | | | | | | | |
| 94.29 | 0.9028 | 104.29 | 84.20 | 62.50 | | | | | | | | | | | | | | | |
| 100 | 1.0000 | *-9.90 | | | | | | | -81.38*** | | | | | | | | | | |
| Refs. | | 26 | | | 25 | | | | | | 10, {40} | | | | | | | 44 | |

* Ref. 42; ** Ref. 41; *** Ref. 43.

and used for the pH_{RVS} determination (ref. 8,8a). In addition, the value $E^\circ = 150.9$ mV at 25 °C for the 71.89 wt % ethanol/water mixtures was adopted and used in connection with Gelsema's results (ref. 14). In fact, the range of ethanol/water mixtures studied by Gelsema covered up to 71.89 wt % ethanol for the oxalate and succinate buffers, whereas pH_{S} values for the oxalate and succinate buffers concern the 100 wt % ethanol only, and occurrence of some ionic association in mixtures from 71.89 wt % upwards was explored. It is worthwhile noting that Gelsema (but also De Ligny and associates in the case of methanol/water mixtures) used the extended-terms equation of Gronvall, La Mer and Sandved (ref.28) *in lieu* of the simpler equation (4) for the calculation of γ_{Cl} . Now, almost the whole range of ethanol/water mixtures (up to ≈ 86 wt % ethanol) at ordinary temperature is characterized by relative permittivities higher than 30, therefore they are practically entirely covered by the aforementioned IUPAC document (ref. 1) which implies no correction for ion association in the above ϵ range. Considering certain values of dissociation constants of HCl and LiCl in 71.89 to 100 wt % ethanol (refs. 29-31) Gelsema assumed some ionic association to occur even down to 71 wt % ethanol (with $\epsilon \approx 37$) and estimated corrections which would, however, not exceed 0.004 in pH in the latter solvent mixture.

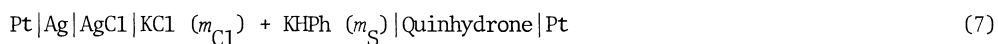
Therefore, for the time being, and pending the final approval of the procedure for the determination of the standard e.m.f. E° of cell (2) in (single or mixed) solvents of relative permittivities lower than 30 (ref. 32) by the next General Assembly of IUPAC (Boston, 1987), Gelsema's data have here been re-examined in strict terms of the aforementioned IUPAC document (ref. 1) ignoring ion association, also on account of the related minimal errors estimated by the author. Moreover, as the pH_{S} data for the salicylate and diethylbarbiturate buffers in 100 wt % ethanol were obtained from e.m.f. measurements of cells where the buffer molality was not constant, they could not be processed in terms of the IUPAC procedure; they are, however, very useful at least as orientative data and they have been, therefore, quoted in parentheses in Table 3. (Clearly, new and extended measurements of cell (2), and new and extended determinations of related E° values in ethanol/water mixtures at 70 to 100 % ethanol and over the temperature range from -10 to +40 °C are badly needed to give the long-overdue completion and systematisation to this matter). The same applies also to the pH_{S} values for the acetate, succinate, and phosphate buffers in 50 wt % methanol/water mixtures obtained by Paabo, Robinson and Bates (refs. 21,22), because these values relate to solutions of buffer substances each of which contains added equimolar NaCl and are not susceptible of the prescribed extrapolation to $m_{\text{Cl}} = 0$ at fixed molality m_{S} of the buffer substance. Finally, the statistical test of significance (F-test) has been performed on each pH vs. m_{Cl} straight line (whose extrapolation to $m_{\text{Cl}} = 0$ leads to the pH_{S} value, as explained above) at each methanol/water and ethanol/water composition x . The dependence of pH on m_{Cl} was found to be not significant for the oxalate buffer at 0, 39.14, 70 and 90 wt % methanol, and for the succinate buffer at 0, 64.0 and 84.4 wt % methanol, in agreement with the analysis of significance performed by De Ligny and associates (ref. 13) on the $\text{p}(\alpha_{\text{H}}\gamma_{\text{Cl}})$ vs. m_{Cl} characteristics. Hence the pH_{S} values corresponding to the above cases of non-significance have been quoted in braces in Table 3. It is worthwhile noting that the differences between each of the above values in braces and the respective original datum does not exceed 0.01 in pH. The three pH_{S} values

at 25 °C reported by Popa and associates for the 0.01 *m* borax buffer in 10, 20 and 40 wt % methanol, respectively (ref. 33), and the single pH_S value for the 0.01 *m* potassium hydrogenphthalate (ref. 34) were obtained from eq. (3) using E° values from the literature (ref. 35) and calculating the γ_{Cl} term through an adaptation of the Maronny-Valensi convention (refs. 36-39). Recalculation of Popa's results in terms of the IUPAC-endorsed extended Bates-Guggenheim convention (refs. 1,2) would be possible; however, the design adopted for the hydrogen electrode and the cell (2) e.m.f. measurements made with the silver chloride electrode not properly separated from the hydrogen electrode compartment but rather in contact with the solution saturated by the hydrogen gas bubbling through, raises serious doubts about the reliability of the measured e.m.f. values, and errors greater than 0.1 in pH must be expected. Therefore, these data have not been accepted for insertion in Table 3.

Looking over the buffers quoted in this Table, and taking also into account the abnormally large residual liquid junction potentials that in operational cells for pH measurements can be caused by certain buffers such as the TRIS + TRISHCl (refs. 18,24), the following overall uncertainties in pH_S values can be estimated: ± 0.01 , 0.01, 0.01, 0.05, 0.05, 0.02, 0.02, 0.02, 0.07, 0.12, 0.002, 0.002, 0.002, 0.002, 0.002, 0.002, and 0.05 for the buffers marked in alphabetical order from *a* to *q*, respectively, in Table 3.

When stocks of pH_{RVS} or pH_S buffer solutions in alcohols, glycols and glycerols (and in their mixtures with water) have been prepared for long-duration service or conservation, it is recommended to store them at freezer temperatures (≈ -15 °C) to prevent any undesired esterification.

As for the reference value standards in Table 1, all original pH_{RVS} results for KHPH in solvent mixtures published prior to 1985 have been revised to make all of them in line with the procedural sequence with $\text{p}\gamma_{\text{Cl}}$ calculation through eq. (3), subsequent linear regression of pH values *vs.* m_{Cl} and extrapolation to $m_{\text{Cl}} = 0$ giving pH_{RVS} . In the case of acetonitrile/water mixtures, two separate sets of pH_{RVS} values were determined: one (ref. 6) working with the cell (2) at 5 to 30 wt % acetonitrile, and one (ref. 10) working at 30 to 70 wt % acetonitrile with the cell:



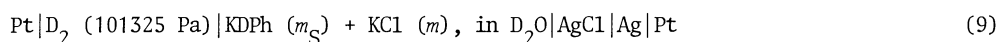
where the quinhydrone electrode replaces the hydrogen electrode. (Of course, this implies the additional determination of the standard e.m.f. E_7° of the cell (7) by extrapolating to $m = 0$ the appropriate function of the measured e.m.f. of the analogous cell:



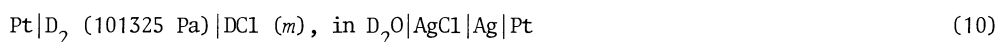
The E_7° values found are collected in Table 4). The two sets of pH_{RVS} values have thus been unified by the multilinear regression method, and the final values are quoted in the Table 1. For the user's convenience, in Table 4 are found the refined E_2° values for cell (2), as resulting from the multilinear regression procedure mentioned above, which were used for the revision of the pH_{RVS} and pH_S values (according to the scheme in Figure 1) for methanol/water, ethanol/water, acetonitrile/water and 2-propanol/water solvent mixtures. The E_2° values for 1,4-dioxane/water mixtures could not be refined because it was, unfortunately, impossible to

obtain the bulk of the original data (ref. 45) of the measured e.m.f. of cell (6). In the case of dimethylsulphoxide (DMSO)/water mixtures, there are only three E_2° values available for each of the two solvent mixtures explored, and the multilinear regression procedure would not be advantageously applied. Now, in *pure* DMSO the hydrogen electrode does not show proper thermodynamic behaviour but displays rather a steady state potential because of poisoning of the platinum sheet as well as some reduction of DMSO by hydrogen; also the silver/silver-chloride electrode may be affected by formation of some dihalogenocomplexes of silver. However, in *water-rich* DMSO mixtures the above drawbacks virtually vanish working with careful design of cell and electrodes (particularly working with light platinising of the platinum sheet and avoiding unnecessary prolonged exposures of the latter to the solution, and using low Cl^- molalities as in cell (2)), thus significant, stable and reproducible, e.m.f.'s are obtained. Moreover, Taylor used the same electrode pair under the same conditions both in cell (6) for the determination of E° (ref. 46) and in cell (2) for the determination of pH (ref. 11), so that the difference $E - E^\circ$ is unaffected in each solvent mixture, and the accuracy of the pH_{RVS} values derived therefrom for the DMSO/water mixtures considered is not impaired; but, obviously, such E° values for the above DMSO/water mixtures could not in themselves be recommended.

Quite recently, Wu and Koch (ref. 12) have determined the pD_{RVS} for the 0.05 *m* potassium deuteriumphthalate (KDPh) buffer in D_2O at temperatures from 5 to 50 °C by measuring the e.m.f. of the reversible cell:



analogously to cell (2), and eq. (3) is applicable with pH obviously replaced by pD. Their procedure is, however, quite different from that endorsed by IUPAC in that it requires working with various molalities m_{S} of the KDPh buffer and the ion-size parameter is fixed as $\alpha_0 = 0.41 \text{ nm}$ throughout. They have also in parallel carried out an accurate determination of the standard e.m.f. E_9° of the cell (9) for insertion into eq. (3), from e.m.f. measurements of the reversible cell:



using the same electrodes as in cell (9). Since these E_9° values are in excellent agreement with those determined in 1963 (equally under the N.B.S. aegis) by Gary, Bates and Robinson (ref. 47), they have been used here without any further refinement to recalculate the pD_{RVS} results for KDPh in terms of the IUPAC procedure based on the Bates-Guggenheim convention (eq. (4)), with the ion-size parameter α_0 assigned the values given by eq. (5); namely, $\alpha_0 = 0.456 \text{ nm}$ at 25 °C. The resulting pD_{RVS} values are slightly higher (by 0.005 on average) than those published (ref. 12), and are collected in Table 2. The relevant F-coefficients, however, turn out to be lower than desirable, mainly due to the fact that there are only three m_{KCl} values at constant $m_{\text{KDPh}} = 0.04986 \text{ mol/kg}$ (rounded off to 0.05 mol/kg). A comparison of pD_{RVS} for the above KDPh buffer in D_2O with the parallel pH_{RVS} for KHPH in H_2O (ref. 24), and a similar comparison of pD_{S} for the 0.025 *m* $\text{KD}_2\text{PO}_4 + \text{Na}_2\text{DPO}_4$ buffer in D_2O (Table 3, refs. 17,23) with the parallel pH_{S} for 0.025 *m* $\text{KH}_2\text{PO}_4 + \text{Na}_2\text{HPO}_4$ in H_2O (ref. 24) can be made, with

result that the difference $\Delta = \text{pD}_{\text{RVS}} - \text{pH}_{\text{RVS}}$ runs perfectly parallel to the difference $\Delta' = \text{pD}_{\text{S}} - \text{pH}_{\text{S}}$, as a function of temperature, and Δ and Δ' are similar (namely, ≈ 0.55 ; cf. also ref. 23), which confirms the consistency and usefulness of the above data and obviously relates to the different standard states involved (*hyp.* $m_{\text{H}^+} = 1$ in H_2O , and *hyp.* $m_{\text{D}^+} = 1$ in D_2O , respectively).

3. CONCLUSIONS

It is evident that in terms of pH_{S} electrochemists have concentrated their efforts almost exclusively on methanol, ethanol and their aqueous mixtures (refs. 13-24,48-50).

The situation is now better in the case of pH_{RVS} where, however, acquisition of fresh data for higher alcohols, glycols, amides and the respective mixtures with water is highly desirable and overdue. Accumulation of such important data is awaited.

REFERENCES

1. T. Mussini, A.K. Covington & S. Rondinini, *Pure Appl. Chem.*, **57**, 865 (1985).
2. R.G. Bates & E.A. Guggenheim, *Pure Appl. Chem.*, **1**, 163 (1960).
3. B.B. Owen, *J. Amer. Chem. Soc.*, **54**, 1756 (1932).
4. T. Mussini, A.K. Covington, F. Dal Pozzo, P. Longhi, S. Rondinini & Zi-Ya Zou, *Electrochim. Acta*, **28**, 1593 (1983).
5. T. Mussini, A.K. Covington, M. Cicognini, P. Longhi & S. Rondinini, *Anal. Chim. Acta*, **162**, 103 (1984).
6. T. Mussini, A.K. Covington, P. Longhi, S. Rondinini & M. Tettamanti, *Anal. Chim. Acta*, **174**, 331 (1985).
7. P. Longhi, T. Mussini & S. Rondinini, *Anal. Chem.*, **58**, 2290 (1986).
8. P.R. Mussini, Thesis, University of Milan, 1986.
- 8a. P. Longhi, P.R. Mussini, T. Mussini & S. Rondinini, submitted to *J. Solution Chem.*
9. M. Pozzi, Thesis, University of Milan, 1985.
10. S. Rondinini & A. Nese, unpublished data.
11. M.J. Taylor, *J. Chem. Eng. Data*, **24**, 230 (1979).
12. Yung Chi Wu & W.F. Koch, *J. Solution Chem.*, **15**, 481 (1986).
13. C.L. De Ligny & P.F.M. Luykx, *Rec. Trav. Chim.*, **77**, 154 (1958); C.L. De Ligny, P.F.M. Luykx, M. Rehbach & A.A. Wienecke, *Rec. Trav. Chim.*, **79**, 699, 713 (1960).
14. W.J. Gelsema, Thesis, University of Utrecht, 1964.
15. R.G. Bates, *Determination of pH - Theory and Practice*, 2nd edn., Wiley, New York, 1973, pp. 244-248.
16. R.G. Bates, H.P. Bennetto & M. Sankar, *Anal. Chem.*, **52**, 1598 (1980).
17. M. Paabo & R.G. Bates, *Anal. Chem.*, **41**, 283 (1969).
18. M. Woodhead, M. Paabo, R.A. Robinson & R.G. Bates, *Anal. Chem.*, **37**, 1291 (1965).
19. M. Paabo, R.A. Robinson & R.G. Bates, *Anal. Chem.*, **38**, 1572 (1966).
20. M. Alfenaar & C.L. De Ligny, *Rec. Trav. Chim.*, **86**, 1185 (1967).
21. M. Paabo, R.A. Robinson & R.G. Bates, *J. Amer. Chem. Soc.*, **87**, 415 (1965).
22. R.G. Bates, *Pure Appl. Chem.*, **18**, 421 (1969).
23. R.G. Bates, Ref. 15, pp. 249-253.
24. A.K. Covington, R.G. Bates & R.A. Durst, *Pure Appl. Chem.*, **57**, 531 (1985).

25. P.R.Mussini, T.Mussini & S.Rondinini, *Ann. Chim. (Rome)*, 76, 333 (1986).
26. A.K.Covington & Zi-Ya Zou, *Electrochim. Acta*, 28, 1587 (1983).
27. P.Longhi, T.Mussini, F.Penotti & S.Rondinini, *J. Chem. Thermodyn.*, 17, 355 (1985).
28. T.H.Gronvall, V.K.La Mer & K.Sandved, *Physik. Z.*, 29, 358 (1928).
29. E.F.Sieckmann & E.Grunwald, *J. Amer. Chem. Soc.*, 76, 3855 (1954).
30. I.I.Bezman & F.H.Verhoek, *J. Amer. Chem. Soc.*, 67, 1330 (1945).
31. J.R.Graham, G.S.Kell & A.R.Gordon, *J. Amer. Chem. Soc.*, 79, 2353 (1957).
32. Y.Marcus & T.Mussini, *The Extrapolation of E.M.F. Data to Infinite Dilution in Non-Aqueous and Mixed Solvents*, Report to Electrochemical and Electroanalytical Commissions of IUPAC, 33rd General IUPAC Assembly, Lyon, 1985.
33. G.Popa, O.Enea & C.Luca, *Z. physik. Chem. (Leipzig)*, 230, 271 (1965).
34. G.Popa, C.Luca & O.Enea, *Z. physik. Chem. (Leipzig)*, 230, 262 (1965).
35. M.Laloi-Diard, *Bull. Soc. Chim. France*, p. 1663 (1961).
36. G.Maronny & G.Valensi, *J. Chim. Phys.*, 49, C91 (1952).
37. G.Maronny, *Electrochim. Acta*, 2, 326 (1960).
38. G.Valensi, *Compt. Rend. 3^e Réunion Com.Int.Thermodyn.Cinét.Electrochim.*, Berne, 1951, p.3 .
39. R.G.Bates, Ref. 15, p.39 .
40. S.Rondinini, C.Confalonieri, P.Longhi & T.Mussini, *Electrochim. Acta*, 30, 981 (1985).
41. W.J.Gelsema, Ref. 14, p.15 .
42. D.J.G.Ives & G.J.Janz, *Reference Electrodes*, Academic Press, New York, 1961, p.197 .
43. H.Taniguchi & G.J.Janz, *J. Phys. Chem.*, 61, 688 (1957).
44. R.N.Roy & A.Bothwell, *J. Chem. Eng. Data*, 15, 548 (1970); C.A.Vega, B.Perez & C.Torres, *J. Chem. Eng. Data*, 29, 129 (1984); R.L.Moore & W.L.Felsing, *J. Amer. Chem. Soc.*, 69, 1076 (1947); H.S.Harned & C.Calmon, *J. Amer. Chem. Soc.*, 61, 1491 (1939); K.Bose, K.Das, A.K.Das & K.K.Kundu, *J. Chem. Soc., Faraday Trans. I*, 74, 1051 (1978).
45. M.M.Elsemongy & A.S.Fouda, *J. Chem. Soc., Faraday Trans. I*, 77, 1157 (1981).
46. M.J.Taylor, *J. Chem. Eng. Data*, 23, 308 (1978).
47. R.Gary, R.G.Bates & R.A.Robinson, *J. Phys. Chem.*, 68, 1186 (1964).
48. D.D.Perrin & B.Dempsey, *Buffers for pH and Metal Ion Control*, Chapman & Hall, London, 1974, pp. 77-93 .
49. N.A.Izmailov, *Elektrokhimiya Rastvorov (Electrochemistry of Solutions)*, 3rd. edn., Khimiya Press, Moscow, 1976, Chapter IX.
50. V.V.Aleksandrov, *Kislotnost Nevodnykh Rastvorov (Acidity of Non-Aqueous Solutions)*, Vishcha Shkola Press, Kharkov, 1981.