

THE UNIVERSAL pH-SCALE FOR SOLUTIONS AT DIFFERENT TEMPERATURES AND IN DIFFERENT SOLVENTS

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A universal acidity scale, holding for solutions at any temperature and in any solvent, is developed. It is based on the operational pH-definition and relates the measured pH-values to the change in chemical potential on transferring a proton from solution X to a hypothetical solution of unit proton activity at 25° in water.

This acidity scale is an extension of the universal pH-scale for methanol-water mixtures at 25° proposed by the authors¹ and is closely related to the universal acidity scale for water at different temperatures, proposed by *Aleksandrov and Lebed'*.² The disadvantage of the latter is that it does not lead to a simple, or easily applicable, physical significance of the measured acidities.

We suggest that the measure for the acidity of any solution be termed "pH" and that it be defined operationally, analogous to the definition of the isothermal pH-scales in aqueous solutions. This operational pH-definition is based on the electrometric method of pH-determination, developed by the *National Bureau of Standards*³ and is almost universally used today. In the general case considered here, the procedure is as follows. The emf of the two cells given below is measured:

indicator electrode	solution of unknown acidity (X)	salt bridge	reference electrode
indicator electrode	standard solution at the same temperature and in the same solvent (St)	salt bridge	reference electrode

Generally, the indicator electrode is a glass electrode, the salt bridge a saturated KCl-solution in water at room temperature and the reference electrode a saturated calomel electrode, also in water at room temperature.

The operational pH-definition is:

$$\text{pH}_X \equiv \frac{E_X - E_{St}}{2.3026 RT/F} + \text{pH}_{St} \quad (1a)$$

or:

$$2.3026 RT \text{ pH}_X \equiv F(E_X - E_{St}) + 2.3026 RT \text{ pH}_{St} \quad (1b)$$

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¹ M. Alfenaar and C. L. de Ligny, *Rec. Trav. Chim.* **86**, 1185 (1967).

² V. V. Aleksandrov and V. I. Lebed', *Zhur. Fiz. Khim.* **40**, 646 (1966).

³ R. G. Bates, "Determination of pH", John Wiley and Sons, Inc., New York (1964).

Provided the electrolyte compositions of the solutions X and St do not differ too widely the pH so defined has a certain amount of physical significance. In this case, namely, the liquid-junction potentials between the salt bridge on the one hand and the solutions X and St on the other are nearly equal, so that:

$$F(E_X - E_{St}) \approx 2.3026 RT (\log a_{H,St} - \log a_{H,X}) = \Delta \mu_{H,St-X} \quad (2)$$

where $\Delta \mu_{H,St-X}$ is the change in chemical potential on transferring a proton from solution X to solution St. From (1b) and (2) it follows that:

$$2.3026 RTpH_X \approx \Delta \mu_{H,St-X} + 2.3026 RTpH_{St} \quad (3)$$

The logical consequence of (3) for establishing a universal pH-scale is that $2.3026 RTpH_{St}$, for standard solutions at any temperature and in any solvent, equals the change in chemical potential on transferring a proton from solution St to a single primary standard solution St° , for which the hypothetical solution of unit proton activity (on the molality scale) at 25° in water can be chosen. In this case the following equation holds:

$$2.3026 RTpH_X \approx \Delta \mu_{H,St-X} + \Delta \mu_{H,St^\circ-St} = \Delta \mu_{H,St^\circ-X} \quad (4)$$

that is, $2.3026 RTpH_X$ equals the change in chemical potential on transferring a proton from solution X to the primary standard solution St° .

So we have the condition:

$$2.3026 RTpH_{St} = \Delta \mu_{H,St^\circ-St} = \mu_{H,St^\circ} - \mu_{H,St} \quad * \quad (5)$$

in which:

$$\mu_{H,St^\circ} = \mu_{H,298.2}^\circ \quad (6)$$

and:

$$\mu_{H,St} = \mu_{H,T}^\circ + 2.3026 RT \log m_H \gamma^* \gamma_H^\circ \quad (7)$$

where μ° = standard chemical potential (solvent independent)

$2.3026 RT \log \gamma^*$ = salt effect (accounting for the transfer from the ideal to the real solution)

- The corresponding equation of *Aleksandrov and Lebed'* reads:

$$pA_T = \frac{-\Delta \mu_{H^+}}{2.3026 R \cdot 298}$$

or, in our symbols:

$$pH_{St} = \frac{\Delta \mu_{H,St^\circ-St}}{2.3026 R \cdot 298}$$

This would yield, however, instead of (4):

$$2.3026 RTpH_X \approx \Delta \mu_{H,St-X} + \frac{T}{298} \Delta \mu_{H,St^\circ-St}$$

which does not lead to a simple or easily applicable physical significance of pH_X .

$2.3026 RT \log \gamma^\circ$ = medium effect (accounting for the transfer from water to the solvent under consideration)

so that:

$$\begin{aligned} \text{pH}_{\text{st}} &= \frac{\mu^\circ_{\text{H}, 298.2} - \mu^\circ_{\text{H}, \text{T}}}{2.3026 RT} - \log m_{\text{H}} \gamma^*_{\text{H}} \gamma^\circ_{\text{H}} = \\ &= \frac{\mu^\circ_{\text{H}, 298.2} - \mu^\circ_{\text{H}, \text{T}}}{2.3026 RT} + \text{pH}^*_{\text{st}} - \log \gamma^\circ_{\text{H}} \end{aligned} \quad (8)$$

where pH^*_{st} is the pH of the standard solution on the solvent and temperature dependent pH-scale.

pH^*_{st} -values have been tabulated for buffer solutions in water at a range of temperatures³ and for buffer solutions in methanol-water mixtures and methanol and in ethanol-water mixtures and ethanol at 25°.^{4, 5}

Values of $-\log \gamma^\circ_{\text{H}}$ have been tabulated for methanol-water mixtures at 25°.¹

Values of $\mu^\circ_{\text{H}, 298.2} - \mu^\circ_{\text{H}, \text{T}}$ have been tabulated from 0 to 100°.² From these values, the correction term $(\mu^\circ_{\text{H}, 298.2} - \mu^\circ_{\text{H}, \text{T}})/2.3026 RT$ which must be added to the pH^*_{st} values of the standard solutions on the solvent and temperature dependent pH-scales to obtain the pH_{st} -values on the universal pH-scale, can be calculated to be:

Table I

temperature (°C)	$(\mu^\circ_{\text{H}, 298.2} - \mu^\circ_{\text{H}, \text{T}}) / 2.3026 RT$
0	+ 0.43
10	+ 0.25
25	0
40	- 0.24
60	- 0.55
80	- 0.85
100	- 1.13

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⁴ C. L. de Ligny, P. F. M. Luykx, M. Rehbach and A. A. Wieneke, *Rec. Trav. Chim.* **79**, 713 (1960).

⁵ W. J. Gelsema, C. L. de Ligny and G. F. Visserman, *ibid.* **84**, 1129 (1965).