

## Piperazine Phosphate as Standard for the Neutral Range of the pH Scale Compared with Some Known Standard Solutions

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When preparing standard solutions for calibration of glass electrodes it is advantageous to use a solution of a salt which forms spontaneously a well defined buffer solution when dissolved in water. The ideal properties required in such a salt are

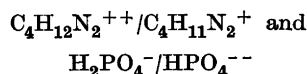
- 1) Good buffer capacity,
- 2) Good crystallization conditions, *i.e.* on crystallization from an aqueous solution which contains an excess of acid or alkaline components, crystals of the proper composition must be formed,
- 3) Moderate solubility at room temperature so that easy purification of the salt can be obtained by recrystallization,
- 4) pH in the solution must show only slight dependence on concentration,
- 5) pH in the solution must show only slight dependence on temperature.

Hitherto three salts are known after thorough testing and examination to have proved satisfactory as standard solutions for the above-mentioned purpose. They are potassium hydrogen tartrate, potassium hydrogen phthalate and sodium borate, the former two representing the acid range of the pH scale, and the last one representing the alkaline range. Potassium hydrogen tartrate satisfies with reasonable tolerance all the above-mentioned conditions. Potassium hydrogen phthalate fails with respect to point (2), but a pure product is easily prepared when certain conditions are observed. Sodium borate fails with respect to point (5).

It is desired to obtain a buffer salt for the neutral range of the pH scale. The possibility has been chosen to find a secondary phosphate of a weak base which possesses as far as possible the mentioned properties. For this purpose piperazine phosphate meets in a very satisfactory way the first four of the mentioned conditions, whereas it fails with regard to temperature dependence, which is of the same direction and order of magnitude as that of sodium borate. As in calibration of glass electrodes a system is most frequently used which besides potassium hydrogen tartrate or potassium hydrogen phthalate, respectively, also includes sodium borate, the dependence on temperature of piperazine phosphate will not prevent its inclusion in such a system.

Piperazine phosphate ( $C_4H_{12}N_2HPO_4 \cdot H_2O$ ; m.wt. 202.16) consists of fine white tabular or platy crystals. It is soluble in 80 parts water of room temperature and in 10 parts boiling water, insoluble in alcohol, ether and chloroform. A saturated solution at room temperature is about 0.065 molar. It may be prepared by crystallization from an aqueous solution of an equimolar mixture of piperazine and phosphoric acid. After one recrystallization it is fit for use. A comparison of pH in solutions of piperazine phosphate prepared in this way at five different laboratories showed an agreement of  $\pm 0.001$  unit.

pH in aqueous solutions depends equally on systems



with the acid dissociation exponents of the orders of magnitude of 5.5 and 7, respectively. The buffer capacity, which is almost linear in the pH 5–7.5 range, is 0.037 for an 0.05 M solution. For purposes of comparison it may be stated that the buffer capacity in a potassium hydrogen phthalate solution of the same molarity is 0.023.

pH in a piperazine phosphate solution is almost independent of concentration. At dilution 1 + 1 an 0.05 M solution showed no measurable change in pH. At dilution 1 + 7 pH was found to be 0.008 unit higher than in the undiluted solution. Thus it is possible to prepare an accurate pH standard by simply shaking an excess of piperazine phosphate with water. Lingane<sup>1</sup> has proposed the same method for potassium hydrogen tartrate.

For calibration of glass electrodes at ordinary room temperatures the values given in the following table are proposed:

*pH Values for Calibration of Glass Electrodes*

	14°C	16°C	18°C	20°C	22°C	24°C	26°C
0.025 M potassium hydrogen tartrate	(3.60)	(3.59)	3.59	3.58	3.58	3.58	3.58
0.05 M piperazine phosphate	6.38	6.36	6.34	6.31	6.29	6.27	6.25
0.05 M sodium borate	9.28	9.26	9.25	9.23	9.21	9.19	9.17

Parenthesized values are for a saturated solution at the pertinent temperature

The values stated for piperazine phosphate are obtained on the basis of glass electrode measurements by graphic interpolation between a total of 28 determinations in the interval 14°C—25°C. At 18°C hydrogen electrode measurements were made as well, and the value 6.337 was found, which is in agreement with the value of the table.

The values stated for potassium hydrogen tartrate are obtained by extrapolation or interpolation from those stated by Bates and others<sup>2</sup>.

As points of departure for obtaining the borate values are used those stated by Hitchcock and Taylor<sup>3</sup> and accepted by British Standard<sup>4</sup>, viz. pH at 25°C = 9.18 and pH at 38°C = 9.07. The values given in the table were obtained by graphic extrapolation from the two values, the temperature dependence being assumed to take a course parallel to those applying to lower ionic strengths, which are known from a paper by Manov, DeLollis and Acree<sup>5</sup>. The position of the two above-mentioned values at 25°C and 38°C in

relation to the latter values justifies the assumption.

The experimental part of this investigation has been carried out in accordance with British Standard. Similarly the same principles — now accepted by British Standard — have been applied in the quoted literature<sup>1-5</sup>. With respect to potassium hydrogen phthalate these principles involve a pH value of 4.005 at 25°C in an 0.05 M solution. At calibration of glass electrodes of Corning 015 glass or glass of a corresponding composition on the basis of the above table, values are ob-

tained in the interval pH 2—9 for diluted aqueous solutions which with good approximation represent the negative logarithm of the hydrogen ion activity. The present values are 0.02 to 0.04 units higher than those obtained on the basis of the original system stated by S. P. L. Sørensen<sup>6</sup>.

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