THE SODIUM PHOSPHATE STANDARDS OF ACIDITY

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During a recent investigation into the hydrogen ion concentration $[H^+]$ of phosphate solutions by the hydrogen electrode method¹, certain relations were discovered between these and the second and third dissociation constants of phosphoric acid. These constants, K_2 and K_3 , allow of an easy calculation of $[H^+]$ over the range most required in the case of N/10 sodium phosphate solutions. The experience gained in the experimental work has led to certain conclusions as to the advantages and disadvantages of making up such solutions from standard NaOH and H_3PO_4 , rather than from mixtures of mono- di- and tri-sodium phosphate², or from mixtures of other salts³.

To eliminate the diffusion potential between the solutions, saturated potassium chloride was used in most of the measurements. A few comparisons with the liquid potential eliminator used by Salm, i.e., the addition of N/8 or N/10 sodium chloride to all solutions, showed that the same E.M.F. is obtained with either method, a fact which considerably strengthens the probability that both methods do really attain the desired object.

The normal H_3PO_4 was made from Merck's purest acid (density = 1.73) which was found free from nitrate, chloride, sulphate, and HPO_3 , and carefully analysed by conversion into $Mg_2P_2O_7$.

The NaOH was made from the sticks (pure by alcohol) dissolved in CO_2 free water, and analysed as sodium chloride.

All the decinormal solutions referred to can, of course, be rapidly prepared from these two stocks.

As will be seen from the enclosed table, all solutions up to the neutral point give values of $[H^+]$ closely agreeing with those obtained by Salm from various mixtures of N/10 NaH_2PO_4 and N/10 Na_2HPO_4 , and with those calculated by the formula mentioned below. No special care need be taken even to secure alkali or water free from CO_2 , since the solutions weighed in Jena glass flasks can be boiled for a few minutes after making

1. *Journ. Chem. Soc.*, p. 2224, June, 1911.

2. Salm, *Zeitsch. physikal. Chem.*, LVII, p. 492, 1907; Friedenthal, *Zeitsch. Elektrochem.*, X, p. 113, 1904.

3. See Walpole.

up, then brought to the original weight with the required volume of water.

As will be seen from the enclosed curve the $[\text{H}^+] = 1 \times 10^{-4}$ to $[\text{H}^+] = 1 \times 10^{-6}$ varies rather rapidly with the relative proportions of NaOH and H_3PO_4 . In this part, therefore, the ratios given in the table should be accurately observed, a difference of 1 per cent. in amount of NaOH added making a difference of about 0.5 in the exponent of $[\text{H}^+]$. Since, however, the normal solutions can easily be standardised within one per cent., and excess of CO_2 can be driven off as described above, the standards are easily reproducible in practice.

Even less accuracy is required in the preparation of solutions from $[\text{H}^+] = 1 \times 10^{-6}$ to the neutral point, since here the curve is quite flat, and the unavoidable errors of the hydrogen electrode will be far larger than any accruing from possible excess or defect of alkali. And from $[\text{H}^+] = 1 \times 10^{-7}$ to $[\text{H}^+] = 1 \times 10^{-8}$ the solutions are still easy to reproduce with sufficient accuracy, although, since they are on the alkaline side of the neutral point, CO_2 must be more carefully guarded against.

From this point onwards, however, the third dissociation constant begins to have an increasing effect, and the curve shows a rapid decrease of $[\text{H}^+]$ with added NaOH, until at $[\text{H}^+] = 1 \times 10^{-9}$, which corresponds almost exactly to the composition Na_2HPO_4 , an error of 1 per cent. in the composition of the mixture makes a difference of 0.25 in the exponent of $[\text{H}^+]$ on the acid side of 1×10^{-9} , and 0.37 on the alkaline side. It was actually found that deviations of about this order occurred in the measured $[\text{H}^+]$ of synthetic solutions of this composition, the cause being almost certainly the presence of small and varying quantities of CO_2 . The effect of CO_2 may easily be observed by leaving a solution coloured with phenolphthalein exposed to the air. It was measured in the following way. A solution giving by the hydrogen electrode a value of $[\text{H}^+] = 1.6 \times 10^{-11}$ was exposed for an hour to a current of CO_2 . The $[\text{H}^+]$ again measured was found to have risen to 7.0×10^{-9} . This is an extreme case, of course, but serves to illustrate the care required.

The reproducibility of Na_2HPO_4 standard from crystalline salt was next studied. The salt must, of course, be re-crystallized, since crude specimens may give $[\text{H}^+]$ as far from the true value as 1×10^{-11} . In view of the required accuracy of the ratio $\frac{\text{NaOH}}{\text{H}_3\text{PO}_4}$ the conditions of crystallisation would appear not unimportant, in order to ensure that

traces of Na_3PO_4 , or NaH_2PO_4 are absent. A solution of the crystalline salt is made slightly acid to phenolphthalein with phosphoric acid, and evaporated down to beyond the point where crystallisation should commence, a high degree of supersaturation being possible. The solution may be slightly pink when hot. To this, normal NaOH is added, drop by drop, from a burette, until, at a certain point crystallisation takes place, the mass of fine crystals being then rapidly sucked dry and washed on a Buchner funnel.

This preparation gave a value of $[\text{H}^+] = 1.3 \times 10^{-9}$ approximating very closely to that of Salm (1.5×10^{-9}) and to the value depending on the dissociation constants (1×10^{-9}).

Slightly on the alkaline side of $[\text{H}^+] = 1 \times 10^{-10}$ the errors in stoichiometrical proportions of NaOH and H_3PO_4 and the presence of CO_2 again become relatively unimportant compared to those of the hydrogen electrode, and this statement holds true up to Na_3PO_4 .

In conclusion it may be stated that solutions from $[\text{H}^+] = 1 \times 10^{-4}$ to $[\text{H}^+] = 1 \times 10^{-8}$ and 1×10^{-11} to 1×10^{-12} may be prepared, either from mixtures of the NaOH and H_3PO_4 or solutions prepared from the crystalline sodium phosphates, the former method being perhaps preferable as requiring only two standard solutions and analytical controls. For solutions in the neighbourhood of $[\text{H}^+] = 1 \times 10^{-9}$, however, it seems better to use the re-crystallised salt Na_2HPO_4 .

As far as an easily attainable analytical accuracy is concerned, the exponent of $[\text{H}^+]$ is actually determined for each solution to about 0.1 of a unit in the flat parts of the curve. Unfortunately the $[\text{H}^+]$ cannot be measured with anything like this accuracy. By using, however, a large number of measurements and finding an equation to the whole curve, it is considered that the numerical value $[\text{H}^+]$ has been determined with a much greater probability than could be attained by any individual measurement. The constants K_2 K_3 of this equation have been found to be 2.0×10^{-7} and 3.0×10^{-12} , the former being practically identical with the second dissociation constant of H_3PO_4 found by Abbott and Bray¹, using a different method; that of distribution ratios and conductivities.

A simplified equation which permits of a rapid calculation of the ratio $\frac{\text{NaOH}}{\text{H}_3\text{PO}_4}$ required for any given value of $[\text{H}^+]$; the solution being always $\frac{1}{10}$ molecular with respect to the latter, is as follows² :—

1. *Journ. Amer. Chem. Soc.*, XXXI, p. 730, 1909.

2. The deduction of this may be found in the preceding communication already referred to—*Journ. Chem. Soc.*, p. 2224, June, 1911.

$$\frac{\text{NaOH}}{\text{H}_3\text{PO}_4} = \frac{2 + \frac{a_1 [\text{H}^+]}{a_2 K_2} + \frac{3a_1 K_3}{a_3 [\text{H}^+]}}{1 + \frac{a_1 [\text{H}^+]}{a_2 K_2} + \frac{a_1 K_3}{a_3 [\text{H}^+]}}$$

α_1 , α_2 , α_3 , the degrees of dissociation of Na_2HPO_4 , NaH_2PO_4 and Na_3PO_4 were found to be 0.06, 0.077, 0.05 by Abbott and Bray¹.

Putting in K_2 , K_3 as above:—

$$\frac{\text{NaOH}}{\text{H}_3\text{PO}_4} = \frac{2 + 0.39 \times 10^7 [\text{H}^+] + \frac{10.8 \times 10^{-12}}{[\text{H}^+]}}{1 + 0.39 \times 10^7 [\text{H}^+] + \frac{3.6 \times 10^{-12}}{[\text{H}^+]}}$$

This calculation may be used from $[\text{H}^+] = 1 \times 10^{-5}$ to $[\text{H}^+] = 1 \times 10^{-11}$. From 1×10^{-5} to $1 \times 10^{-7.5}$ the K_3 term is negligible and the equation reduces to:—

$$\frac{\text{c.c. } \frac{\text{N}}{\text{NaOH}}}{\text{c.c. } \frac{\text{N}}{\text{H}_3\text{PO}_4}} = \frac{2 + 0.39 \times 10^7 [\text{H}^+]}{1 + 0.39 \times 10^7 [\text{H}^+]}$$

The table gives some observed values for comparison with those calculated by this equation.

Molecules NaOH to 10 Molecules H_3PO_4	$[\text{H}^+]$ found	$[\text{H}^+]$ calculated
10.0 (NaH_2PO_4)	9.3×10^{-5} (Salm)	1.2×10^{-4} *
"	1.5×10^{-4} (Prideaux)	
10.6		1.0×10^{-5}
11.05	1.7×10^{-6} (P.)	
11.5	9.7×10^{-7} (S.)	
12.05		1.0×10^{-6}
14.45	2.6×10^{-7} (P.)	
14.45		3.2×10^{-7}
15.50	1.5×10^{-7} (S.)	
15.50	2.0×10^{-7} (P.)	
17.2		1.0×10^{-7}
17.7 (Neutral point)		0.73×10^{-7}
17.6	0.76×10^{-7} (P.)	
19.5	1.0×10^{-8} (S.)	
19.6		1.0×10^{-8}
20.0 (Na_2HPO_4)	1.3×10^{-9} (S.)	1.0×10^{-9}
"	1.5×10^{-9} (P.)	
20.04		1.0×10^{-10}
20.3	9.8×10^{-11} (S.)	
20.5	5.9×10^{-11} (P.)	
21.4	1.3×10^{-11} (S.)	
21.6	2.0×10^{-11} (P.)	
22.2	1.2×10^{-11} (P.)	
22.6		1.0×10^{-11}

* Directly from K_2 , α (NaH_2PO_4) and $C = 0.1$.

1. *Loc. cit.*