THE VALIDITY OF THE GLASS ELECTRODE IN AMMONIUM CHLORIDE BUFFERS.

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In the course of experiments on the cytolysis of luminous bacteria it became necessary to know accurately the pH values of 0.5 M solutions of ammonium salts from about pH 5.0 to pH 9.6. Partly because of the high salt concentration colorimetric methods were insufficiently accurate, especially on the alkaline side. On account of the oxidation of quinhydrone in alkaline solutions the quinhydrone electrode could not be applied to more than one-half of the range of values desired. The statements in the literature as to the action of ammonia as a hydrogen electrode poison are conflicting,[1] and also the hydrogen electrode is too slow to be used conveniently when the number of determinations may exceed 100 in a single experiment. The glass electrode seemed to offer the best solution to the problem, being free of salt errors and of all other errors due to changes in the solution as a result of the examination itself. It is said to be accurate to 0.01 pH.[2] The statements as to the accuracy of the glass electrode in alkaline solutions vary. Brown[3] reports good agreement with the formula $E = 0.058 \log (C_1/C_2)$ from pH 4.0 to pH 10.0. Hughes[4] reports approximate agreement with the hydrogen electrode below pH 11.0 and in another paper[5] states that the electrode values were unaffected by large changes in sodium ion concentration below pH 9.0. Since the writer has occasion to use ammonium solutions above pH 9.0 both in presence and absence of sodium chloride, the

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[1] *Cf.* Clark, The determination of hydrogen ions, 3rd ed., 1928, p. 439.

[2] Kerridge, P. M. T., *J. Sci. Ins.*, 1926, iii, 404.

[3] Brown, W. E. L., *J. Sci. Ins.*, 1924, ii, 12.

[4] Hughes, W. S., *J. Am. Chem. Soc.*, 1922, xliv, 2860.

[5] Hughes, W. S., *J. Am. Chem. Soc.*, Feb., 1928, p. 491.

813

experiments described herein were made to determine the validity of the glass electrode in the class of solutions employed. Since others also may be interested in the use of fairly accurately determined ammonium buffers of relatively high concentration, these experiments are recorded here.

In the dry air of the winter laboratory sulfur was found an excellent insulating material and no trouble was experienced from leakage. The
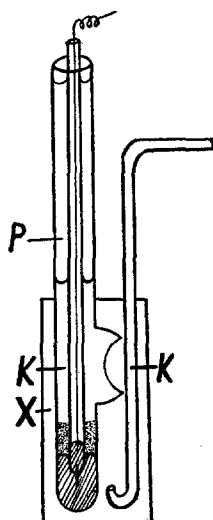

FIG. 1. Glass electrode vessel. K = Saturated KCl. P = Paraffine oil. X = Unknown solution.

form of electrode used is a combination of those of Hughes[4] and Kerridge,[6] a modification suggested by Anson and Mirsky,[7] and further slightly modified by the writer. In the form finally adopted, illustrated in Fig. 1, the delicate glass membrane is protected from the breakage which is inevitable when solutions are pipetted in and out of the cup as suggested by Kerridge,[6] and is to be preferred when 15 or 20 cc. of solution is available for the test. A saturated calomel

[6] Kerridge, P. M. T., Biochem. J., 1925, xix, 611.

[7] Anson, M. L., and Mirsky, A. E., Proc. Soc. Exp. Biol. and Med., 1928, xxv, 346.

electrode is made in the lower part of the glass electrode vessel and the saturated KCl in contact with the glass membrane is standardized daily against M/20 KH phthalate. All calculations are made from its pH of 3.97 by the formula

$$pH_x = 3.97 \pm \frac{E_s - E_x}{0.0581}, \text{ at } 20°,$$

where E_s = p.d. of KH phthalate,

E_x = p.d. of unknown.

A Lindeman electrometer is used as the null instrument.

In the first experiment, 0.5 M ammonium chloride plus 0.5 M ammonia was diluted with successive equal portions of 0.5 M am-

TABLE I.

Activity Coefficients of Several Concentrations of Ammonium Chloride.

f_{a1} is the empirical value, f_{a2} that calculated from Bjerrum's formula.

[NH₄Cl]	[NH₃]	pH	f_{a1}	f_{a2}
0.01	0.00207	8.65	0.8335	0.8532
0.1	0.0207	8.70	0.7437	0.7104
0.25	0.05075	8.73	0.6804	0.6286
0.5	0.1015	8.75	0.6502	0.5564

monium chloride until the concentration of ammonia approached 0.001 M. A similar series was prepared in which 0.5 M ammonium chloride plus 0.5 M sodium chloride plus 0.5 M ammonia was diluted with 0.5 M ammonium chloride plus 0.5 M sodium chloride. The pH values of these solutions were taken and plotted against the logarithm of the concentration of ammonia (Fig. 2). For the ammonia plus ammonium chloride series these values fall on a straight line within the experimental error of the electrode, showing that there is no error due to any change in the electrode at the higher concentrations of hydroxyl ions. For the ammonia plus ammonium chloride plus sodium chloride series the values fall on the same straight line until about pH 8.6, the deviation from this point increasing until there is an error of −0.07 pH at pH 9.4. Considering the experimental error of the method (0.01 pH), corrections are unnecessary below pH 8.6 in the
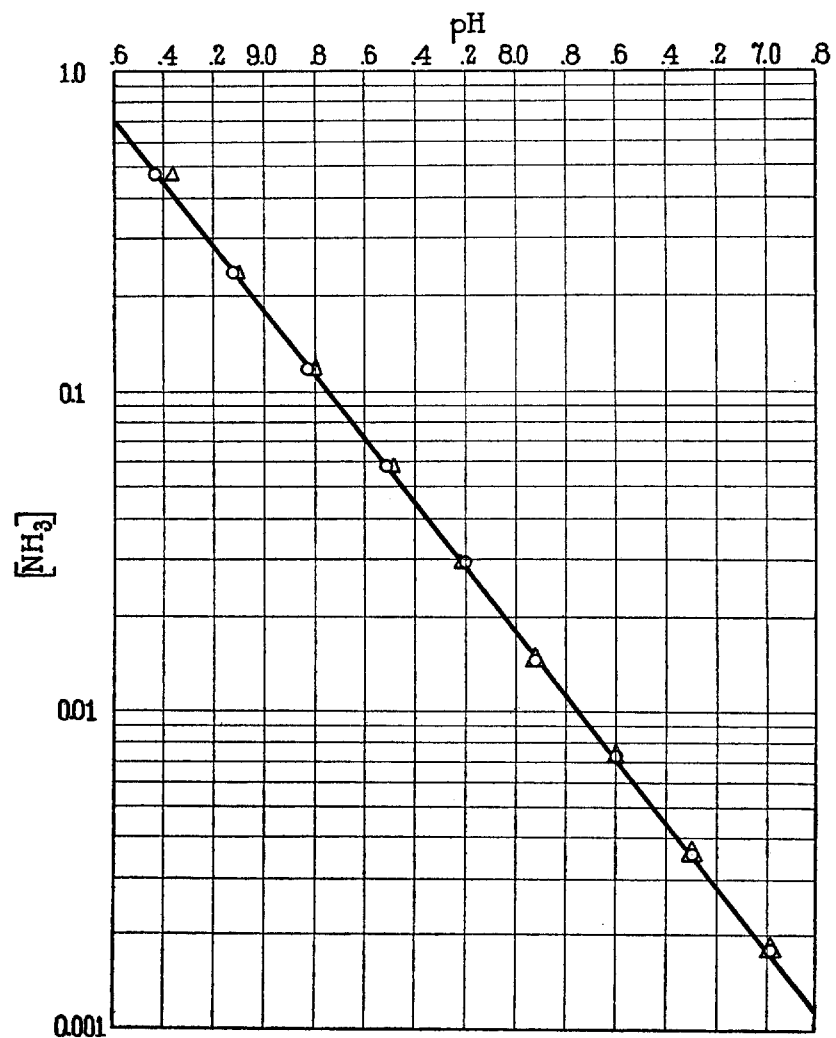
FIG. 2. O = pH of indicated concentration of ammonia in presence of 0.5 M ammonium chloride.   Δ = pH of indicated concentration of ammonia in presence of 0.5 M ammonium chloride plus 0.5 M sodium chloride.

series containing sodium chloride and unnecessary at any value as far as determined in the absence of sodium ions (and perhaps the ions of the other alkali metals). For ammonium chloride solutions in presence of 0.5 M sodium chloride the corrections given in Table II are suggested.

In the physiological study in question, the relation of concentration of ammonia to concentration of hydrogen ions is of considerable importance and can be calculated readily if the activity coefficients of the ammonium salts are known. The formulae for calculating these values accurately are of such an involved nature as to be useless for

TABLE II.

Apparent pH of Ammonium Chloride Buffers 0.5 M With Respect to Ammonium Chloride in Presence of 0.5 M Sodium Chloride, With Corrections.

pH	Correction
8.6	$+.01$
8.8	$+.02$
9.0	$+.03$
9.2	$+.04$
9.4	$+.07$

the average worker in the biological laboratory.[8] The activity coefficient may be determined empirically from the pH values and the concentrations of ammonia and ammonium chloride. Choosing for an example the sample containing 5.8×10^{-2} mols ammonia per liter, pH 8.51, which happens to give the average value for the series, and applying the buffer equation:

$$[OH^-] = \frac{K_b\ [NH_3]}{f_a\ [NH_4]}$$

$$f_a = \frac{1.8 \times 10^{-5} \times 5.8 \times 10^{-2}}{3.24 \times 10^{-6} \times 0.5} = 0.6444$$

The empirical values were determined for several concentrations of ammonium chloride and these are compared in Table I with the

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[8] *Cf.* Lewis, G. N., and Randall, M., *J. Am. Chem. Soc.*, 1921, xliii, 1112.
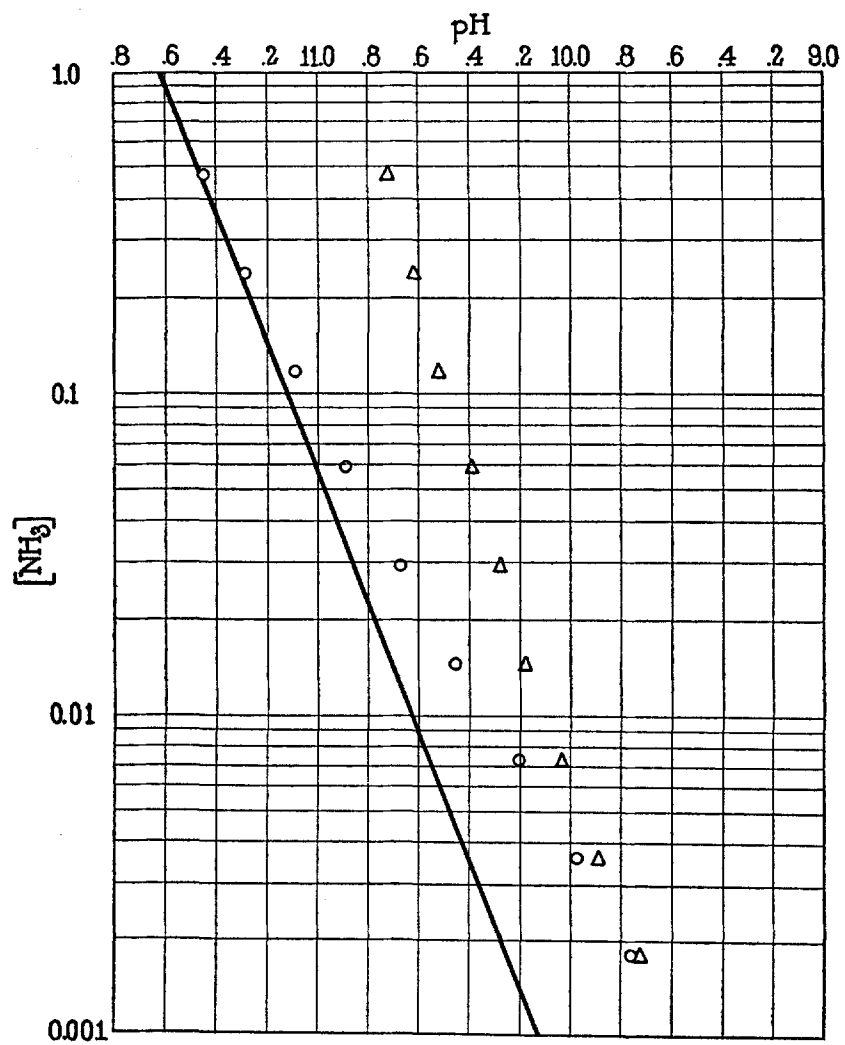
FIG. 3. Comparison of theoretical pH of ammonia in water with that observed with the glass electrode. O = Ammonia in water. Δ = Ammonia in 0.5 M sodium chloride solution.

calculated values from the simplified approximation formula of Bjerrum,[9] said not to be valid above about 0.1 M.

$$- \log f_a = \frac{26}{D} n^2 \sqrt[3]{c};$$

D is the dielectric constant of the solvent, and n the valence of the ions. As may be seen by reference to the table the agreement is not remarkable at any concentration, but is much better for 0.01 M and 0.1 M than for 0.25 M and 0.5 M solutions. The writer is inclined to think the empirical value for 0.5 M ammonium chloride the more accurate, and will use it in his calculations.

The measurement of pH of ammonia in water and in 0.5 M sodium chloride was less satisfactory. In the biological work involved, exclusion of carbon dioxide is not possible, so it was not attempted in this case. At the lower concentrations of ammonia the carbon dioxide introduced a serious error by the formation of an ammonium bicarbonate buffer system. At high concentrations of ammonia where the error due to carbon dioxide is negligible, there was no significant deviation from the calculated values in pure water, while in 0.5 M sodium chloride there was a large negative variation, 0.74 pH at pH 11.46. This variation decreased progressively as the ammonia was diluted and the manner of approach of the curves suggests its disappearance at about pH 9.0. For ammonia solutions from which sodium chloride is absent, the glass electrode may be used without appreciable error to pH 11.4 and perhaps higher. If sodium chloride is present a correction must be applied above pH 8.6, and will probably have to be determined anew for each electrode by the use of appropriate buffer solutions in which sodium ions are present in approximately the same concentration as in the unknown solution.

SUMMARY.

It is shown that the glass electrode may be used without appreciable error to measure pH of ammonia or ammonium chloride buffers, but that corrections must be applied above pH 8.6 if sodium ions are present in the unknown solution. Corrections are given for values from pH 8.6 to 9.4. A slight further modification of form of glass electrode used by previous workers is described.

[9] Cf. Michaelis, Hydrogen ion concentration, p. 121.