the **water** determination. While these reactions prevent application of the method to the determination of water in acetone, acetone concentrations of the order of 0.1% or less cause only minor errors when the reaction medium is chiefly acetonitrile. In the water determination of acetonitrile (5 cc. of $RSO_3H - (CH_3CO)_2O$ mixture and 10 cc. of acetonitrile, titrated after three hours) to which 0.1 and 0.01% of acetone had been added, less than 1 mole per cent. of the added acetone reacted as water. In the case of the more protracted reaction in ether the error is more serious so that the presence of acetone should be excluded by specific tests. The fractions of the added acetone reacting as water were, with ether as the medium

Vol. % acetone added		1	0.1	0.01
Mol. % acetone reacted after	1 day	4.7	31	—
	2 days	5.2	37	85

In the case of the 1 and 0.1% acetone concentrations a yellow deposit was formed in the solutions and a very rapid fading of the blue titration end-point took place. It seems probable that the precipitation phenomenon contains the explanation for the inverse variation of the extent of the pseudo water reaction with the acetone concentration.

The question as to how far the respective reaction kinetics make the alcohol method practicable for higher alcohols, phenols, thiol compounds, etc., has not been covered in the present work, as the method is primarily intended for determining the purity of inert solvents with respect to their more common contaminants water and lower alcohols. For the same reason application to the water determination in alcohols has been left in abeyance for the present.

Thanks and appreciation are expressed to Merck and Company, Rahway, N. J., who generously supplied the acetonitrile used in this investigation.

Summary

The vigorous catalytic acceleration by strong acids in non-aqueous media, of the hydrolysis and alcoholysis of acetic anhydride is shown to be useful as a basis for the separate determination of water and alcohols in inert solvents. The error in concentrations of the order of one per cent. is less than ±1%. The lower limit of response is less than 0.001%.

PHILADELPHIA, PA. RECEIVED JULY 17, 1935

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Application of the Glass Electrode to Unbuffered Systems

BY SAMUEL B. ELLIS AND SAMUEL J. KIEHL

Introduction

In the realm of unbuffered or very weakly buffered systems the measurement of hydrogen-ion concentration or *p*H value becomes exceedingly difficult and involves considerable uncertainty. Most of the familiar methods of determining the *p*H value have been modified for use in such systems, but complete success can hardly be claimed for practical accurate measurement. For application of the hydrogen electrode to unbuffered systems reference may be made, among others, to the work of Beans and Hammett,[1] Kolthoff and Kameda,[2] and Hammett and Lorch.[3] Similar use of the quinhydrone electrode is described by Best.[4] Colorimetric methods have been discussed by numerous workers, among whom are Stern,[5] Acree and Fawcett,[6] and Kolthoff and Kameda.[2b]

The glass electrode with its obvious adaptability for use in unbuffered systems appears to have received definite attention only recently. Burton, Matheson and Acree,[7] who used a Thompson glass electrode, have given a brief account of some measurements on dilute buffers and distilled water. The development of glass electrode technique to its ultimate refinement has, however, been merely started and the field offers many possibilities for further research.

Accordingly, an extension of the use of the glass electrode and the development of methods whereby the accurate determination of the *p*H

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(1) Beans and Hammett, THIS JOURNAL, **47**, 1215 (1925).

(2) (a) Kolthoff and Kameda, *ibid.*, **51**, 2888 (1929); (b) **53**, 821 (1931).

(3) Hammett and Lorch, *ibid.*, **55**, 70 (1933).

(4) Best, *J. Phys. Chem.*, **34**, 1815 (1930).

(5) Stern, *J. Biol. Chem.*, **65**, 677 (1925).

(6) Acree and Fawcett, *Ind. Eng. Chem., Anal. Ed.*, **2**, 78 (1930).

(7) Burton, Matheson and Acree, *ibid.*, **6**, 79 (1934).

value may be made conveniently in the most difficult of unbuffered systems—highly purified water itself—were undertaken.

The Glass

The very soft glasses of low electrical resistance which have met with considerable favor for making glass electrodes have the serious disadvantage of being relatively soluble and of causing weakly buffered solutions with which they are in contact to become more alkaline, as the following experiment will illustrate. Three glass electrodes made of Corning 015[8] glass and of the type, to be described, were soaked in water for five weeks; then, under protection from atmospheric contamination, they were filled with distilled water and the *p*H value determined at intervals; at first the *p*H rose rapidly—approximately one *p*H unit per hour; even after twelve hours with a *p*H of 9, there was still a slow drift. In general the behavior of Corning 015 glass with unbuffered solutions was found to be quite erratic and unsatisfactory.

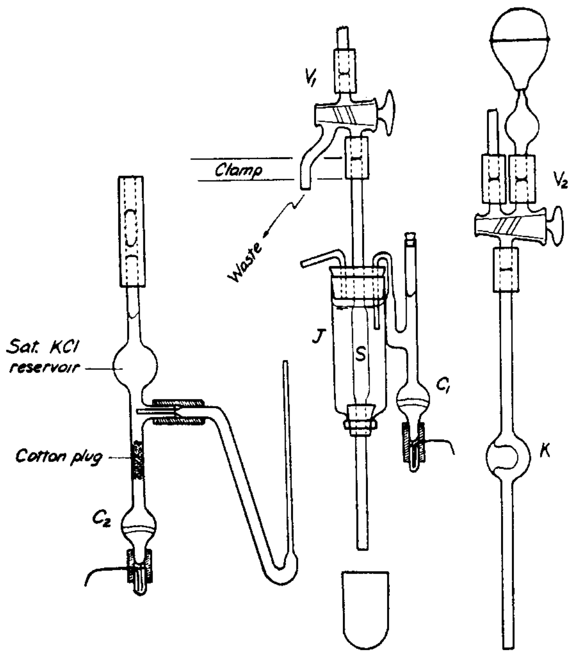

Fig. 1.—Glass electrode assembly.

From the standpoint of solubility, the ordinary soft (soda-lime) glass is much to be preferred to any of the special glasses. Electrodes made from it have much higher resistances, but a suitably designed electrical circuit will meet this difficulty.[9] Asymmetry potentials are also higher than those of Corning 015 glass, but in our experience they were just as constant—the important consideration. Again, ordinary soft glass does not agree with the hydrogen electrode over as wide a range as does Corning 015 glass. The work of Hughes,[10] of MacInnes and Dole,[8] of Sokolov and Passinski,[11] and of Lengyel and Blum,[12] in alkaline solutions indicate this. The matter of agreement with hydrogen electrode and the consistency of glass electrode measurements at extreme *p*H values and under varying conditions have not, however, been studied sufficiently to warrant the adoption of any particular glass to the exclusion of all others.

The measurements recorded in the work which follows were obtained by use of ordinary soft glass electrodes which had been carefully checked against the hydrogen electrode by use of phosphate and borate buffers over the *p*H range of 4 to 9.

Glass Electrode Assembly

The device used for measuring electromotive force was a sensitive vacuum tube potentiometer described by the authors elsewhere.[9]

The glass electrode, Fig. 1, was designed especially for convenient application to unbuffered solutions. The solution being measured is either sucked or siphoned into the tube, S, which drawn out thin in its central portion constitutes the glass membrane. This membrane of cylindrical shape is made by simultaneously blowing and drawing the central portion of an ordinary soft glass tube (6–7 mm. diameter). It is important and a little difficult to blow a sufficiently thin membrane. The required thinness however may be judged roughly by its flexibility when the membrane is depressed by a pointed instrument. Thicker membranes, even when their resistance is not exorbitant, are more likely to be erratic and unsatisfactory. The fixed portion of the system in the jacket surrounding the membrane is 0.1 *N* hydrochloric acid connected directly to a 0.1 *N* hydrochloric acid calomel cell C_1 of Hughes.[10] The liquid junction of the solution with a second calomel cell C_2 (saturated potassium chloride type) is effected either at the bottom of the tube S or at a point inside it, depending upon circumstances.

An easier method of forming the thin glass membrane is indicated by K of Fig. 1, which will be recognized as the familiar sucked-in-bulb type of Kerridge.[13] Although easier to make, the Kerridge bulb electrodes compared with the cylindrical type have several disadvantages: (1) their asymmetry potentials are less stable; (2) they are less easily washed, rinsed, and flushed free of air bubbles; (3) the Kerridge electrodes are more fragile and are easily broken by a sudden movement of the liquid inside; (4) the junction with a reference electrode must be formed somewhere below or above the active membrane, which, as will be shown later, is sometimes undesirable. With one exception, included for illustrative purposes, all the measurements reported in the following pages were obtained by use of the cylindrical type of electrode.

A rigid mounting of the membrane within a jacket by use of rubber or cement is more desirable and trustworthy than a glass seal because even slight heating produces noticeable deterioration of the glass electrode. The permanent combination on the outside of the membrane, including hydrochloric acid and hydrochloric acid–calomel cell C_1 is used merely to complete the electrical circuit and ensure constancy of e. m. f.—the prime consideration.

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[8] This is the special electrode glass developed by MacInnes and Dole [THIS JOURNAL, **52**, 29 (1930)] and made commercially by Corning Glass Co.

[9] Ellis and Kiehl, *Rev. Sci. Inst.*, **4**, 131 (1933). A description is given of the electrical measuring circuit which was used during the present work.

[10] Hughes, *J. Chem. Soc.*, 491 (1928).

[11] Sokolov and Passinski, *Z. physik. Chem.*, **A160**, 366 (1932).

[12] Lengyel and Blum, *Trans. Faraday Soc.*, **30**, 461 (1934).

[13] Kerridge, *J. Sci. Instruments*, **3**, 404 (1926).

The second calomel cell C_2 of the saturated potassium chloride type requires no other comment than to call attention to its removable (interchangeable) tip (Fig. 1) of which several may be available for special requirements. The tip is used to form the liquid junction inside the glass electrode tube during flow of the liquid being measured.

Of the various devices available for filling the glass electrode the two which have been found most satisfactory are illustrated by the sketch of Fig. 1. A three-way stopcock located at the top of the glass electrode may be employed in either of two ways, V_1 or V_2. By use of V_1 the electrode filled through the top may be kept full of liquid at all times. To eliminate all air bubbles from the electrode tube itself, from which expulsion is sometimes difficult, and rigorously to avoid atmospheric contamination, a preliminary flushing through the waste tube is necessary. By V_2 the glass electrode may be rinsed and filled either from the top by means of a siphon tube or from the bottom by means of suction. Either entrance may be reserved for the standard reference buffer, while the other is used for the solution of which the *p*H value is desired. Thus for a continuous record a solution may be passed through the siphon tube with an interruption of flow only for purposes of comparison with a standard buffer during which the rubber bulb or a second siphon tube may be utilized. As another alternative, the top entrance may be used for rinse water through the siphon tube, while all solutions to be measured are admitted at the bottom. By this scheme the electrode may be washed with distilled water by a turn of the stopcock and may be filled ready for a measurement by squeezing the bulb a few times. The rubber bulb may, however, be displaced by another siphon tube. For rigorous exclusion of atmospheric contamination the electrode must always be filled through a closed tube.

In supporting any glass electrode assembly it is important to insulate very carefully one side of the membrane. The outside of the membrane therefore was insulated by means of a Bakelite support which clamped the electrode at the top only (Fig. 1). The HCl–calomel cell C_1 was connected by a short lead directly to the highly insulated terminal of the vacuum tube potentiometer.

Measuring Technique

In making a measurement the procedure is essentially that of comparing the solution of unknown *p*H with a standard reference buffer by means of their respective potentials in the glass electrode. The simple mathematics described by Clark[14] and Britton[15] needs no discussion. The reference buffer was without exception 0.05 molar potassium acid phthalate, *p*H 3.97.

Solutions having a small buffering capacity (*e. g.*, 0.01 *M* disodium hydrogen phosphate) are very easily measured by almost any technique which might be suggested in connection with the glass electrode assembly described above. However, if the liquid or solution being measured (*e. g.*, potassium chloride solution) has little or no buffering capacity, the contamination occurring at the glass surface may change the e. m. f. and produce erroneous results. Even though the ordinary soft glass used for all electrodes in the present work is very much better than Corning 015 or other similar electrode glass as regards solubility, it is still not ideal.

The most obvious procedure for sensitive unbuffered solutions is to complete the measurement as quickly as the system could be expected to reach equilibrium under ordinary circumstances and disregard subsequent drifting. Since glass electrodes do not always reach their stable equilibrium potentials in the same length of time, the question of how soon to accept such a reading is difficult to answer. Readings should be repeated, however, until successive trials check each other. When this procedure is used with solutions of appreciable conductivity, fair results may be obtained—results which check within possibly a millivolt of those obtained by the improved technique to be described below.

Even if one is satisfied, however, to accept an e. m. f. reading which is in the initial stages of a steady drift, the method has further faults when applied to a liquid of relatively low conductivity like purified water.[16] After the glass electrode is flushed and filled with highly purified water,[16] the electromotive force shows various anomalous effects which indicate the generation and subsequent slow dissipation of electrical charges. The time required for apparent dissipation of the charges is variable, but in general the effects last for a sufficient time (a few minutes to half an hour) to vitiate the measurement. The trouble is very much less pronounced with water of less purity.

To satisfactorily overcome the alkaline effects due to the glass, the contents of the electrode should be continuously renewed by flow while the measurement is being made When very dilute solutions or purified water are measured, such flow may cause trouble with streaming potentials,[17] unless the liquid junction is established at the center of the glass electrode. By moving the liquid junction (tip of calomel cell C_2) to different positions within the glass electrode and the tube below it, the presence or absence of streaming potentials may be readily determined.

When the liquid junction is located at the center of the cylindrical membrane S (Fig. 1), it seems highly unlikely that any streaming potential of appreciable magnitude may be superimposed upon the measured electromotive force. This theoretical conclusion is supported by subsequent experimental evidence that the electromotive force is independent of the rate of flow when other factors are eliminated. As the liquid junction is moved downward below the membrane, streaming potentials increase rapidly (water charged positively with respect to the glass). Near the center of the cylindrical membrane, however, a small displacement of the potassium chloride junction causes little change in the measured electromotive force. Therefore the liquid junction need not be located with extreme accuracy; the central position as judged by the eye is entirely satisfactory.

With the Kerridge sucked-in-bulb type of electrode, unless it is of distorted and impractical proportions, the liquid junction cannot be located at a central position with regard to the active membrane. The best that may be

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[14] Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, Md., 1928.

[15] Britton, "Hydrogen Ions," D. Van Nostrand Co., Inc., New York, 1932.

[16] The term "purified water" is used to indicate the best product obtainable by the methods described by Ellis and Kiehl [This Journal, **57**, 2145 (1935)].

[17] Michaelis, Chapter 26 of Alexander's "Colloid Chemistry," 1926.

done is to bring the junction to a point immediately under the thinnest portion of the membrane. It is therefore difficult if not impossible to eliminate small streaming potentials when the Kerridge electrode is used for measuring a liquid whose conductivity is unusually low (*e. g.*, highly purified water).

Typical Measurements

When electromotive force (or *p*H) is determined at different rates of flow, the results depend in general upon the type of solution. A number of typical examples of this are illustrated by Figs. 2 and 3. The data for the most part are given in graphical form only because the exact numbers are of little consequence to the present discussion. In Fig. 2, curve A illustrates the general behavior of highly purified water when it is measured in an electrode (C5) of the cylindrical type. The horizontal portion of the curve indicates the *p*H of the water. The fairly sudden break in the curve at a flow of about 25 cc./min. is typical of such systems, and the behavior is suggestive of a transition from streamline to turbulent flow. However, that such a transition did not occur was proved by several experiments in which a fine colored band of methylene blue was used. Turbulence did not commence until a flow of about 150 cc./min. was reached.

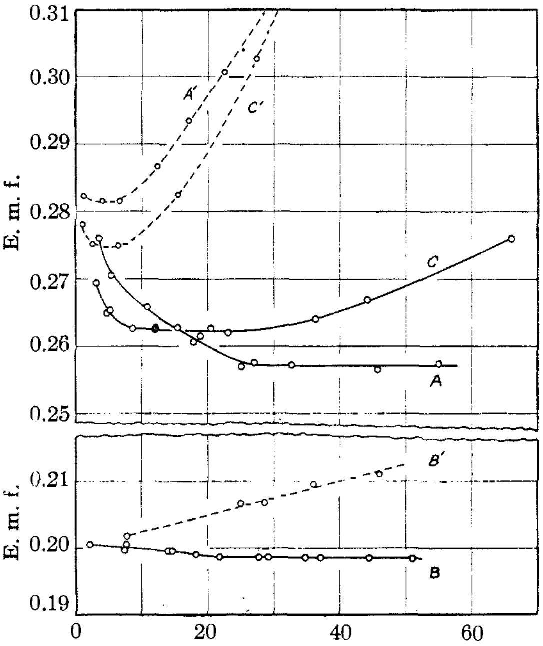

Fig. 2.—A and A', purified water measured in cylindrical electrode, C5; B and B', Columbia distilled water measured in C5; C and C', purified water measured in Kerridge electrode K10. Dashed curves indicate streaming potentials; data obtained by same method as for solid curves except that the potassium chloride junction was located 9 cm. below the bottom of the membrane.

Curve B of Fig. 2 represents the behavior of the stock distilled water[18] in the same cylindrical electrode, C5. The pronounced difference between curves B and A illustrates a perfectly general behavior which is of considerable interest and importance. The stock distilled water, a high grade commercial distilled water, is practically unaffected at low rates of flow by alkali from the glass, whereas the highly purified water shows a large increase in *p*H value. The stock distilled water in comparison with the purified water is evidently buffered by minute traces of carbon dioxide and ammonia, evidence and confirmation for which appear in another paper.[16]

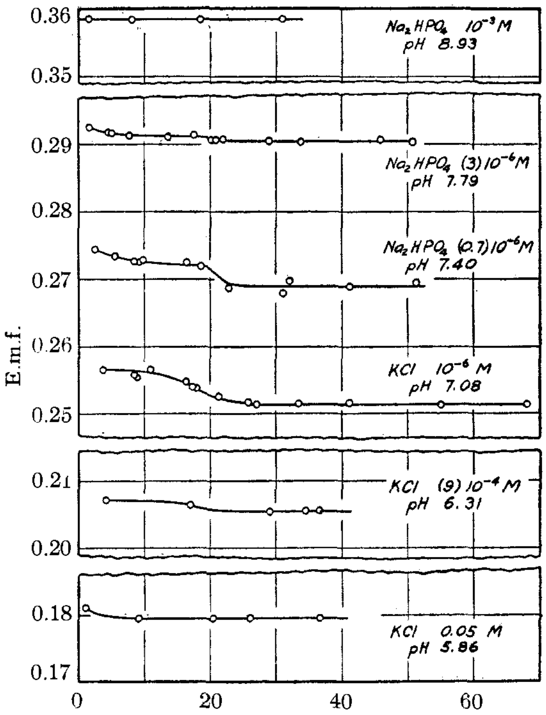

Fig. 3.

When an electrode made of Corning 015 glass was used for measuring the stock distilled water, the curve (not shown) was similar to A of Fig. 2 except for the horizontal portion which it lacked. If the flow was increased to 60 cc./min. the *p*H value was still decreasing but was nevertheless

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[18] "Stock distilled water" refers to the distilled product furnished in the Havemeyer Chemical Laboratories of Columbia University; specific conductivity in the neighborhood of 10^{-6} reciprocal ohms and *p*H from 6.1 to 6.5.

0.16 *p*H unit higher than that obtained by use of the ordinary soft glass electrode. By this experiment the stock distilled water was shown to be very sensitive to changes of *p*H value which were caused by the solubility of Corning 015 glass.

The dashed curves A′ and B′ of Fig. 2 were obtained in exactly the same way as A and B, except that the potassium chloride junction was moved down to a position about 9 cm. below the bottom part of the active membrane. The measured e. m. f. in this case included a streaming potential superimposed upon the same e. m. f. previously shown in A and B. The difference between the ordinates of A and A′ gives the streaming potentials for purified water; the difference between B and B′ gives the streaming potentials for the stock distilled water.

Curves C and C′ of Fig. 2 illustrate the use of a Kerridge type of electrode for the measurement of purified water. Its general characteristics are similar to those of the cylindrical electrode but its shape prevents centering of the potassium chloride junction and, consequently, there is definite evidence of streaming potentials at the higher rates of flow.

In Fig. 3 some typical curves are shown illustrating the measurement of dilute salt solutions. The solutions were very carefully prepared by distilling highly purified water[16] directly into "No-solvit" and Pyrex glass receivers, containing a weighed quantity of purified salt.

A very pure potassium chloride was further purified by three crystallizations from distilled water and dried at 100°. The disodium hydrogen phosphate, of very good quality, was crystallized four times and dried under vacuum at 30°. For the more dilute solutions a 2-liter quantity of water was used and the salts were weighed out by means of a micro-balance. Rigorous protection from acid or basic constituents of the atmosphere was maintained in all cases, just as was done with purified water itself.

The curves in the center of Fig. 3 for the most dilute solutions show the alkaline effect of the glass at the lower rates of flow, but their shape is different from that obtained when purified water was measured. The characteristic inflected form of the curves indicates that the buffering capacity of these extremely dilute solutions is less if they are relatively pure (flowing rapidly) than they are if contaminated by alkali from the glass. This is to be expected since it is a familiar fact that weak acids or bases show less resistance to *p*H change (smaller buffering capacity) if pure than if partially neutralized. The exact nature of the material dissolved from the glass and the detailed mechanism of the buffering reactions, are investigations beyond the scope of the present problem.

As the solutions of Fig. 3 are made more concentrated the alkaline effect from the glass rapidly becomes less pronounced, and the inflection of the curves disappears. It is quite evident from the experiments that even such a solution as potassium chloride has a definite, though very small, buffering capacity which increases with the concentration.

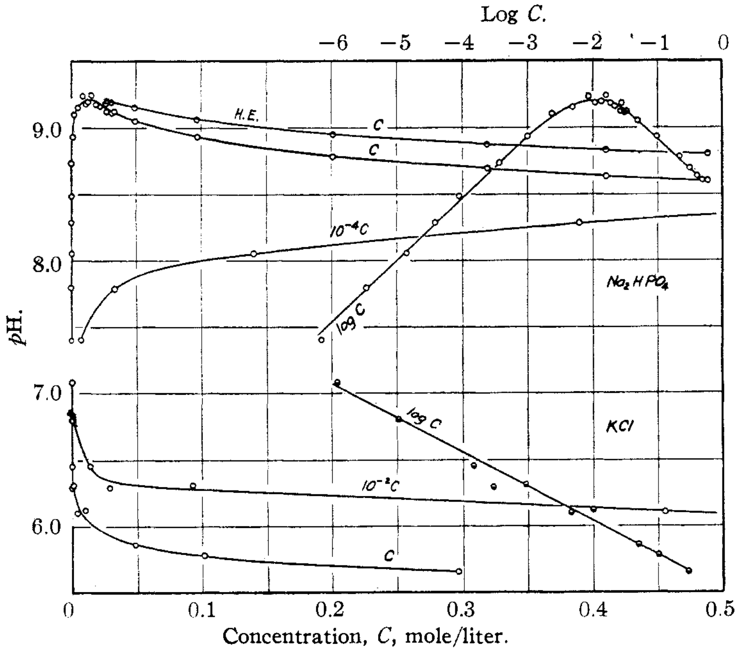

Fig. 4.

The *p*H values of the salt solutions, potassium chloride and disodium hydrogen phosphate, were measured over a wide range of concentrations, extending from millionth molar to half molar. The results listed by Tables I and II are shown graphically by Fig. 4, where *p*H is plotted against concentration (*C*) and also against log *C*. In the curves marked 10^{-4} *C* and 10^{-2} *C* the abscissas should be multiplied by 10^{-4} or 10^{-2}, respectively, in order to obtain the correct scale. These two curves afford a magnified view of the extremely dilute region and include only the first few points which on the normal scale of abscissas (C curves) appear as vertical lines.

TABLE I

THE *p*H OF DISODIUM HYDROGEN PHOSPHATE SOLUTIONS[a]

Solution	C 10^3	Room temp., °C.	ΔE	*p*H	*p*H by hydrogen electrode
1	0.00070	29	0.2056	7.40	
2	.0033	28	.2282	7.79	
3	.014	28	.2440	8.05	
4	.039	30	.2587	8.28	
5	.0895	28.5	.2696	8.48	
6	.366	30	.2863	8.73	
7	1.016	28.5	.2966	8.93	
8	2.40	28	.3062	9.10	
9	4.93	30	.3111	9.15	
10	8.85	27.5	.3138	9.23	
11	11.02	30	.3130	9.18	
12	13.08	29.5	.3135	9.19	
13	15.76	27.5	.3144	9.24	
14	18.80	29.5	.3125	9.18	
15	22.07	29	.3113	9.16	
16	26.96	28.5	.3082	9.12	9.20
17	27.32	27.5	.3104	9.18	
18	31.55	28.5	.3074	9.11	9.19
19	33.53	29	.3088	9.12	
20	49.07	28.5	.3041	9.05	9.15
21	97.33	28.5	.2969	8.93	9.06
22	201	28.5	.2881	8.78	8.95
23	319	28.5	.2826	8.69	8.87
24	410	28.5	.2793	8.63	8.83
25	489	28.5	.2769	8.60	8.80

[a] ΔE represents the potential difference as determined by the glass electrode, between the solution being measured and the standard phthalate buffer, *p*H 3.97. C represents the molar concentration of the salt solutions.

TABLE II

THE *p*H OF POTASSIUM CHLORIDE SOLUTIONS[a]

Solution	C 10^3	Room temp., °C.	ΔE	*p*H
1	0.00122	25.5	0.1847	7.08
2	.0105	25	.1672	6.80
3	.144	30.5	.1490	6.45
4	.288	25.5	.1376	6.29
5	.932	25.5	.1387	6.31
6	4.55	27.5	.1269	6.10
7	9.98	27.5	.1285	6.12
8	48.6	27.5	.1128	5.86
9	102	27.5	.1078	5.78
10	296	27	.0998	5.65

The upper curve for disodium hydrogen phosphate marked H. E. (Fig. 4) shows some measurements made in the more concentrated region by means of the hydrogen electrode. The discrepancy between the hydrogen and the glass electrode measurements is about what should be expected on the basis of the investigations of MacInnes and Belcher.[19] As the phosphate solutions are made more dilute, however, the discrepancy rapidly decreases. The agreement would probably be very close in the dilute region, which is most difficult for application of the hydrogen electrode. Calibration of the glass electrode against the hydrogen electrode in various buffers indicated that there was no significant difference at *p*H values less than 8 (extreme acid range not included).

The definitely acidic character of the purified potassium chloride merits notice. If this behavior could be substantiated with samples of the salt purified with extreme precaution, it would be of considerable interest. Perhaps of even greater interest is the shape of the disodium hydrogen phosphate curve, reported by Kiehl and Loucks,[20] with a maximum *p*H at a concentration of approximately 0.015 molar. The straight line character of the respective logarithmic curves, with two branches for the disodium hydrogen phosphate is of singular interest.

The curves of Fig. 4 are presented for the purpose of illustrating the practical possibility of making consistent *p*H measurements in extremely dilute weakly buffered systems. The consistency of the measurements over the entire range of concentration is best demonstrated by the logarithmic curves.

The data of Fig. 4 support the other data of this investigation in proving beyond question that the glass electrode offers important opportunities for research in unbuffered systems.

The authors take this opportunity of expressing their appreciation to Professor John R. Dunning of the Physics Department, for his many helpful suggestions and advice during the development of the electrical measuring circuit.

Summary

The practical measurement of *p*H in the most difficult of unbuffered aqueous systems has been accomplished by means of the glass electrode. General technique has been developed, and some examples are given.

NEW YORK, N. Y. RECEIVED MAY 29, 1935

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(19) MacInnes and Belcher, THIS JOURNAL, **53**, 3315 (1931); *Ind. Eng. Chem., Anal. Ed.*, **5**, 199 (1933).

(20) Kiehl and Loucks, *Trans. Am. Electrochem. Soc.*, **67**, 81 (1934).