408. *The Application of the Glass Electrode to the Measurement of the* p_H *of Slightly Buffered and Unbuffered Solutions.*

By EDWARD G. EDWARDS and DAVID P. EVANS.

The alkaline drift observed by previous investigators when using the glass electrode in unbuffered solutions has been avoided by agitating the liquid in contact with the membrane, whereby the very small amount of alkali dissolved from the glass is quickly dispersed throughout the test liquid and causes no measurable change in p_H. The soft-glass electrodes usually employed for electrometric purposes yield accurate results for the p_H of acid solutions, conductivity water of p_H about 7·0, very pure water, and solutions of neutral salts. The p_H values thus determined agree very well with those given by the isohydric indicator method. Since, in solutions of p_H less than 7·0, the glass electrode acquires its equilibrium potential within 1 minute, the apparatus is suitable for the measurement of the p_H of slightly buffered acidic solutions in which the hydrogen-ion concentration is slowly changing.

BEFORE the commencement of the present work (early in 1935), the only satisfactory measurements of p_H in unbuffered solutions were those of Kolthoff and Kameda (*J. Amer. Chem. Soc.*, 1931, **53**, 821, 825), who employed the hydrogen electrode and the isohydric indicator method. Burton, Matheson, and Acree (*Ind. Eng. Chem. Anal.*, 1934, **6**, 79) had stated that the glass electrode gave results in good agreement with those obtained by the colorimetric method, but Laug (*J. Amer. Chem. Soc.*, 1934, **56**, 1034) reported drifts in potential indicating a slow development of alkalinity; these drifts were attributed to solution of alkali from the glass membrane (compare Schwabe, *Z. Elektrochem.*, 1935, **41**, 681; also Ellis and Kiehl, *J. Amer. Chem. Soc.*, 1935, **57**, 2139). We have confirmed these observations, and the method described below was based upon the view that such drifts might be avoided by use of a relatively large volume of the test liquid and continuous agitation by a stream of purified air; the dissolved alkali should then be quickly dispersed throughout the liquid with a negligible effect upon the p_H value.* These expectations have been amply confirmed by the consistent and reproducible character of the results and their agreement with those of the isohydric indicator method. In other recent investigations (Ellis and Kiehl, *loc. cit.*; Schwabe, *Z. Elektrochem.*, 1936, **42**, 147) the drift has been eliminated by allowing the test liquid to flow over the glass membrane : our method is simpler and requires less liquid.

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* Recent publications (up to October 1937) make no reference to the use of a non-reactive gas for this purpose, but since the preparation of this paper Cranston and Brown (*Trans. Faraday Soc.*, 1937, **33**, 1455) have described a method in which the alkaline drift is avoided by passage of purified air.

The liquids to which our procedure has been applied include (1) distilled water, (2) conductivity water freed from carbon dioxide, (3) very dilute alkali, (4) very dilute acid, (5) specially pure water, (6) dilute solutions of hydrochloric acid, potassium chloride, ammonium chloride, and lead nitrate. The results are summarised below. In cases 1—5 good agreement with the isohydric indicator method is obtained. The value recorded for 0·01M-potassium chloride confirms that given by Kolthoff and Kameda (*loc. cit.*).

	Liquid.	Temp.	Electrometric p_H.	Colorimetric p_H.
1.	Distilled water	30°	5·12	5·10
2.	Conductivity water	30	7·14	7·25
3.	Very dilute alkali	30	8·18	8·17
4.	,, acid	30	6·50	6·56
5.	Specially pure water	20	7·15	7·15
6.	$0{\cdot}957 \times 10^{-5}$M-HCl	30	5·02	5·02 *
7.	0·01011M-KCl	20—23	6·75	—
8.	0·01M-NH_4Cl	18—19	5·62	—
9.	0·00996M-$Pb(NO_3)_2$	20—20·5	5·34	—

* Theoretical p_H on the assumption of complete ionisation.

EXPERIMENTAL.

Materials.—Specially pure water was obtained by using a block-tin condenser essentially like that of Ellis and Kiehl (*loc. cit.*, p. 2145). In preliminary experiments, distilled water containing from 0·025 to 0·0001M-phosphoric acid was redistilled in the still, but in each case the distillate had a p_H of 6·5—6·7 when freed from carbon dioxide. This acidity, due to the presence of traces of volatile acid in the laboratory distilled water, was removed by distillation from alkaline permanganate before distilling from M/5000-phosphoric acid in the special still. The phosphoric acid was of 'AnalaR' quality, previously heated to fuming point for 30 minutes. The water thus obtained was consistently within the p_H limits 6·9—7·15 when freed from carbon dioxide.

Hydrochloric acid solutions were made in Pyrex flasks from conductivity water and constant-boiling acid. Water of p_H *ca.* 6·5 was obtained by redistilling distilled water from dilute phosphoric acid in the special still; and a rapidly conducted distillation in a Vogel still yielded an alkaline water of p_H *ca.* 8·0. 'AnalaR' Specimens of potassium and ammonium chlorides were thrice recrystallised from pure water, the former salt being fused in a platinum crucible before use. Lead nitrate was purified by the method of Cranston and Brown (*J. Roy. Tech. Coll.*, 1937, **4**, 54). All salt solutions were made in very pure water.

The air used in the preparation of pure water and in the electrometric and the colorimetric determinations of p_H was purified by passing through three 15-inch tubes filled with soda-lime, a wash-bottle containing concentrated sodium hydroxide solution, two wash-bottles filled with dilute phosphoric acid, and lastly through two bubblers containing conductivity or very pure water. In the air-purification train attached to the glass-electrode vessel (*via* the ground glass joint at *J*) the last four bubblers containing the phosphoric acid and water were made of Pyrex-glass-stoppered tubes filled with glass beads and were connected to each other by glass seals. This precaution eliminated the possibility of ammonia exhaling from the rubber connections and entering the test liquid in the cell. Any spray was prevented from passing along with the pure air by plugs of cotton-wool in the top of the last bubbler tube.

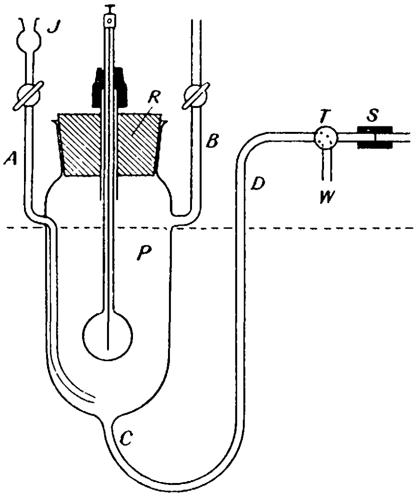
The buffer solutions employed were those of Clark and Lubs (*J. Bact.*, 1917, **2**, 1, 109, 191), and were checked electrometrically at 30° before use with either the quinhydrone electrode or the hydrogen electrode as designed by Lockwood (*J. Soc. Chem. Ind.*, 1935, **54**, 295T). The glass electrodes were of the Haber bulb type with a stem of length 20 cm. These were filled with either an acid buffer saturated with quinhydrone or a 1% solution of chloroplatinic acid 0·01M. with respect to hydrochloric acid (compare Parsy, *J. Soc. Leather Trades Chem.*, 1936, **20**, 188). A long platinum wire, soldered to a gold-plated terminal and covered with Pyrex capillary tubing except for a length of 2 cm. at the lower end, was used for electrical contact with the solution in the electrode bulb. Calibration of the electrode over the p_H range 1—9·5 at 30° was carried out in the apparatus described below. Electrodes made from the special soft glass supplied by Messrs. Dixon and Co., London, attained equilibrium in about 1 minute and exhibited a linear relation between *E.M.F.* and p_H. Electrodes made from ordinary laboratory soda glass, however, showed a linear relation only below p_H 7·0. Above this value the potentials in buffer solutions were lower than theoretical.

In measuring the p_H of a test solution, the electrodes were standardised by determining the *E.M.F.* of the cell filled with a buffer solution of approximately the same p_H as the unknown. The latter was then calculated from the equation $E_X - E_B = 0{\cdot}0601(p_{HX} - p_{HB})$, in which E_x denotes the *E.M.F.* of the cell.

Pt|acid buffer satd. with quinhydrone|glass|soln. p_{HX}|KCl satd., Hg_2Cl_2 satd.|Hg

containing the unknown solution of p_{HX}, and E_B represents that of the cell when filled with the buffer solution of p_{HB}.

The glass-electrode cell is shown in the figure, which is self-explanatory. The vessel *P* was of about 200 ml. capacity, and all parts were made of Pyrex glass. Purified air was passed through the test liquid in *P via* the side tube *A*. The air exit tube *B* was fitted with an all-glass Volhard trap filled with water. Electrical connexion between the test liquid and the saturated potassium chloride of the saturated calomel electrode attached at *S* was made *via* the tube *CD* and the three-way tap *T* as described by Morton (*J. Sci. Instr.*, 1930, **7**, 187). The rubber stopper, *R*, was treated with castor oil at 80° in a vacuum to prevent leakage of ammonia from the rubber. The whole apparatus was immersed to the level of the broken line in a copper bath filled with heavy paraffin oil maintained at 30°. The bath was earthed, and this formed sufficient electrical shielding.



About 100 ml. of test liquid were introduced into the vessel *P*, and the electrode placed in position. The liquid junction was formed by suitably turning tap *T* and drawing a little of the test liquid out through the exit *W*. Next, the tap *T* was turned, and a small volume of saturated potassium chloride solution was withdrawn from the calomel electrode through the same exit. One complete turn of the tap then caused the formation of a thin layer of saturated potassium chloride around the barrel of the tap. This layer provided sufficient electrical connexion, and on closing *T*, the possibility of diffusion of potassium chloride is minimised. When necessary a current of purified air was passed through the test liquid in the manner described. The *E.M.F.* of the cell was read on a valve electrometer p_H meter graduated in mv. or 0·02 p_H, as supplied by the Cambridge Instrument Co.

All colorimetric measurements on unbuffered solutions were carried out by the method of Kolthoff and Kameda (*loc. cit.*).

Results.—Hydrochloric acid. For $0{\cdot}957 \times 10^{-5}$—$0{\cdot}957 \times 10^{-1}$M-solutions, several soft-glass electrodes yielded theoretical results for the p_H, indicating that the junction potential is the same for solutions of moderate and of very small ionic strength. Passage of air through the solutions for several hours did not cause a change in p_H.

Distilled water. The p_H was obtained without aeration. Four soft-glass electrodes gave p_H 5·11±0·01, the colorimetric value being 5·10.

Conductivity water. Water having $\kappa = 1{\cdot}0$ gemmho was boiled for 1 minute and quickly poured into the cell; the electrode was introduced and aeration commenced. After 30 minutes, the liquid junction was formed, and *E.M.F.* readings were taken at intervals. The p_H of the water increased slowly but reached a constant value of about 7·1 after one hour. This value was maintained on continued aeration for long periods (24 hours). A typical set of readings was :

Time (mins.)	3	11	21	27	36	78	18 (hrs.)
p_H	6·94	7·06	7·09	7·10	7·11	7·09	7·12

(Colorimetric p_H 7·20.)

Constancy of the liquid junction was checked by repeated reflushing of both test liquid and saturated potassium chloride through the three-way tap *T* as previously described. If aeration was stopped, a rise in p_H took place, the extent and rate of which varied with each soft-glass electrode. Resumption of the air flow caused the p_H to fall immediately to its former value. For example, after 18 hrs.' aeration the above solution (p_H 7·12) behaved as follows :

Time (mins.)	aeration stopped	2	4	8	15	aeration restarted	16	30
p_H		7·15	7·17	7·20	7·25		7·13	7·12

The rise in p_H is undoubtedly due to dissolution of the soft glass in the water. Although the rate of solution is small, however, the rate of diffusion is smaller, as is indicated by the observation that for all soft-glass electrodes the p_H reached a maximum value of about 0·2—0·5 unit above the previous value on stopping the aeration. This value was then maintained over a considerable period, with a tendency to reach even higher values very slowly. Agitation of the test liquid by the air stream dispersed this alkalinity throughout the bulk of the liquid, causing a fall in p_H to the former value. These results show that agitation of the liquid in contact with the glass electrode precludes the formation of a thin alkaline layer around the membrane and prevents the occurrence of the drift towards the alkaline region as observed by Laug, by Ellis and Kiehl, and by Schwabe (*loc. cit.*). Experiments of the type described above were carried out with glass electrodes made from ordinary laboratory glass, but in general the behaviour of these electrodes in unbuffered solutions was not so consistent and reproducible as that of the special soft type. On the other hand, no alkaline drift was observed on stopping the aeration. The occasional anomalous results given by the laboratory-glass electrodes (due probably to sudden changes in asymmetry potentials) made them less suitable than the special soft electrodes for measurements on unbuffered solutions of p_H about 7.

Slightly acid water. The p_H of such water (p_H *ca.* 6·5) was readily measured, aeration for 2 hours being sufficient to give a constant p_H which agreed with the colorimetric value to within 0·1 unit.

Slightly alkaline water. Aeration for about 200 minutes gave fairly constant p_H values, but the laboratory-glass electrodes (denoted by H) always yielded p_H's higher than those given by the soft-glass electrodes (denoted by S) by about 0·25—0·30 unit. For example :

Electrode	S. 1.			S. 9.		H. 5.		
Experiment :	A.	B.	C.	A.	B.	A.	B.	(Colorimetric).
p_H	8·15	8·18	8·10	8·10	8·04	8·35	8·35	8·17

This discrepancy is probably to be traced to the anomalous behaviour of the H electrodes in buffer solutions. McInnes and Dole (*J. Amer. Chem. Soc.*, 1930, **52**, 29) have shown that the deviations of the potentials of glass electrodes from the theoretical values in alkaline solutions are dependent upon the concentration of alkali-metal ions in solution. This deviation should therefore be greater in the buffer solutions in which $[Na^{\cdot}]$ is approximately 0·05M. than in the slightly alkaline water of the same p_H in which $[Na^{\cdot}]$ is of the order 10^{-6}M. It appears, therefore, that the apparently high values of the p_H of unbuffered solutions of p_H *ca.* 8, as measured by the laboratory-glass electrodes, are due, not so much to the incorrect behaviour of the electrodes in these solutions, as to the departure from theoretical behaviour in the buffer solutions used for calibration.

Very pure water. For the determination of the p_H of such water the cell assembly was modified in order to lower its electrical resistance. The connecting arm *CD* was shortened, and fused in near the bottom of the electrode vessel *P*. The arm was bent vertically downwards before making connexion *via* the three-way tap with the arm of the saturated calomel electrode. This apparatus was suspended in air from a suitably insulated stand. About 100 ml. of pure water were poured quickly into the cell, and the glass electrode inserted. Aeration was commenced, and *E.M.F.* readings taken at intervals, a constant p_H being recorded after 3 hours. Several measurements conducted on different samples of pure water gave results within the p_H range 6·9—7·15 at 20°.

Dilute salt solutions. The modified apparatus was also used in these cases. The p_H–time curves for potassium chloride solutions were similar in shape to, but situated slightly below, those for pure water. After 4—5 hours' aeration the observed p_H was constant at a value reproducible to within 0·02 unit for any given solution of potassium chloride. Results after 5 hours' aeration at 20—23·4° are recorded below :

KCl, M. × 10^6	1011	112	13·2	1·3	(water)
p_H	6·75	6·86	6·90	6·93	6·98

These results are in agreement with those of Kolthoff and Kameda rather than with those of Ellis and Kiehl.

The measurement of the p_H of solutions of ammonium chloride was simply carried out because the effect of carbon dioxide is relatively unimportant. The p_H attained after a few minutes' aeration was constant and remained so for long periods. The mean values obtained at 18—19° by using several S-type electrodes are given below; each electrode agreed to within 0·01 unit of p_H.

NH_4Cl, M.	0·25	0·05	0·01
p_H	5·05	5·41	5·62

The p_H values of solutions of lead nitrate have been measured by Denham and Marris (*Trans. Faraday Soc.*, 1928, **24**, 515), using a quinhydrone electrode, and very recently by Cranston and Brown (*loc. cit.*), using a glass electrode. In the present measurements, constant *E.M.F.*'s were attained in a few minutes and did not alter on long-continued aeration of the solution. All soft-glass electrodes agreed to 0·01 unit of p_H, and the table below gives the mean results.

Lead nitrate solutions. Temperature 20—20·5°.

$Pb(NO_3)_2$, M.	p_H.	$K_H \times 10^8$.	$Pb(NO_3)_2$, M.*	p_H.*
0·1001	4·28	2·76	0·1	4·17
0·0101	4·89	1·66	0·01	4·92
0·00402	5·11	1·77	0·004	5·11
0·00208	5·22	1·77	0·002	5·24
0·00996	5·34	2·10	0·001	5·34

* Results recorded by Cranston and Brown (*loc. cit.*).

The p_H values are in good agreement with those of Cranston and Brown, except for the 0·1M-solution. In this solution, however, a precipitate of lead chloride formed at the liquid junction, no reference to which is made by those authors. In spite of this precipitation, the p_H value of this solution was reproducible in our measurements to 0·02 unit. Further, the hydrolysis constant (K_H) for this solution is in slightly better agreement with that for the lower concentrations than is Cranston and Brown's ($4·60 \times 10^{-8}$).

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TECHNICAL COLLEGE, CARDIFF.

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