281. *The Dissociation Constant of Hypochlorous Acid: Glass-electrode Potential Determinations.*

By John W. Ingham and John Morrison.

The glass electrode has been shown to function normally in solutions containing hypochlorous acid and hypochlorite ions (Davidson, *Shirley Institute Memoirs*, 1933, **XII**, 1) and it has been used to determine the dissociation constant of the acid by Davidson (*loc. cit.*), Britton and Dodd (*Trans. Faraday Soc.*, 1933, **29**, 537), and Yorston (*Pulp and Paper Mag., Canada*, 1931, **31**, 374). The values obtained, with notes on the methods used, are:

(1) Davidson: K' (apparent dissociation constant) $= 3{\cdot}7 \times 10^{-8}$, $p_{K'} = 7{\cdot}43$, at 18—20°, by titrations of 0·02*N*-solutions of sodium or calcium hypochlorite with 0·2*N*-hydrochloric acid, the solutions containing also other salts, chiefly chloride.

(2) Britton and Dodd: $K' = 3{\cdot}2 \times 10^{-8}$, $p_{K'} = 7{\cdot}50$ at 15°, by titrations of (*a*) 0·027*N*-sodium hypochlorite with 0·25*N*-sulphuric acid, the solution containing an unstated amount of sodium chloride, and (*b*) 0·063*N*-hypochlorous acid with 0·2*N*-sodium hydroxide. These authors also carried out titrations of the acid in the presence of known amounts of added sodium chloride and claimed that the neutral salt had negligible effect upon the p_{H} values.

(3) Yorston: $K' = 4 \times 10^{-8}$, by titrations of the acid with sodium hydroxide. This determination is an approximate one. K' and $p_{K'}$ here refer to the constant found by using the Henderson equation, $p_{K'} = p_{\mathrm{H}} - \log\,[\mathrm{Salt}]/[\mathrm{Acid}]$.

These determinations, together with the work now described, dispose of the value found by Noyes and Wilson (*J. Amer. Chem. Soc.*, 1922, **44**, 1630), *viz.*, $K' = 6{\cdot}7 \times 10^{-10}$ at 25°, based upon conductance measurements, and support those of Sand (*Z. physikal. Chem.*, 1904, **48**, 610), who found $K' = 3{\cdot}7 \times 10^{-8}$ at 17° from the solubility of carbon dioxide in hypochlorite solutions, and of Soper (J., 1924, **125**, 2227), $K' = 1 \times 10^{-8}$, from experiments upon the distillation of solutions of the acid and its sodium salt.

This paper presents a more detailed study of the neutralisation curve of hypochlorous acid than is attempted by Britton and Dodd, and also deals with some important points in connexion with the use of glass electrodes. The effect of neutral salts upon the apparent dissociation constant is discussed. Table I gives the results of 10 experiments involving 8 distinct preparations of the acid. Expts. 1—3B are titrations using 0·2*N*-sodium hydroxide, and col. 3 shows the concentration of sodium hypochlorite at the end-point of the electrometric titration. In Expt. 3B a known amount of nitric acid was added before titration. A more exact method of examination by means of separate mixtures of acid and alkali for each $p_{\rm H}$ determination was used in Expts. 4—8, the total hypochlorite concentration being kept constant in a given experiment at the value in col. 3. $p_{K'}$ (Mean) is the mean value for 11 stages of the neutralisation, from 5 to 95% as in Table II; $p_{K'}$ at 50% neutralisation is also given.

TABLE I.

Expt.	Temp.	Concn.	$p_{K'}$ (mean).	$p_{K'}$ (50%).	$K' \times 10^8$.	Expt.	Temp.	Concn.	$p_{K'}$ (mean).	$p_{K'}$ (50%).	$K' \times 10^8$.
1	16·5°	0·061	7·50	7·51	3·16	4	18°	0·063	7·47	7·46	3·47
1A	16·5	0·065	7·53	7·52	2·95	5	20	0·065	7·50	7·51	3·16
2	12	0·06	7·48	7·50	3·24	6	20	0·068	7·46	7·45	3·47
3	17	0·06	7·46	7·46	3·47	7	20	0·067	7·49	7·49	3·24
3B	17	0·05	7·42	7·42	3·80	8	18	0·071	7·47	7·45	3·47

Expt. 8 is, for reasons given later, considered to be the most reliable, and the value $p_{K'} = 7·46$ at 18° is adopted, giving $K' = 3·47 \times 10^{-8}$. Table II contains the full series of values of $p_{K'}$ and $p_{\rm H}$ for Expts. 8 and 3B. The theoretical $p_{\rm H}$ numbers from the Henderson equation and the data of Davidson are included for comparison.

TABLE II.

Neutralisation, %.	$p_{\rm H}$. (Theory.)	$p_{\rm H}$. (Expt. 8.)	$p_{K'}$. (Expt. 8.)	$p_{\rm H}$. (Expt. 3B.)	$p_{K'}$. (Expt. 3B.)	$p_{\rm H}$. (Davidson.)	$p_{K'}$. (Davidson.)
5	6·18	6·20	7·48	5·94	7·22	6·05	7·33
10	6·51	6·53	7·48	6·30	7·25	6·43	7·38
20	6·86	6·86	7·46	6·73	7·33	6·81	7·41
30	7·09	7·11	7·48	6·98	7·35	7·05	7·42
40	7·28	7·28	7·46	7·20	7·38	7·25	7·43
50	7·46	7·45	7·45	7·42	7·42	7·43	7·43
60	7·64	7·63	7·45	7·63	7·45	7·62	7·44
70	7·83	7·84	7·47	7·84	7·47	7·80	7·43
80	8·06	8·07	7·47	8·06	7·46	8·04	7·44
90	8·41	8·42	7·47	8·42	7·47	8·40	7·45
95	8·74	8·76	7·48	8·74	7·46	8·70	7·42

The data in cols. 5—8 show the effects of neutral salts. Expts. 1 and 2 were the only ones with pure hypochlorous acid which gave substantial departure from the form of the curve of the Henderson equation, $p_{\rm H}$ and $p_{K'}$ values in these cases being low in the first half of the neutralisation and high in the second half, the mean $p_{K'}$ for the series agreeing closely with the mid-point value. This departure from the theoretical is also a feature of the results of Britton and Dodd. Britton and Robinson (*Trans. Faraday Soc.*, 1932, **27**, 531) have shown that the glass electrode may give erroneous results near the inflexions of a titration, where the $p_{\rm H}$ is changing rapidly, the errors being in the direction which would explain the results under discussion, although they were actually found in titrations of strong acids and bases and not noted to persist into the regions of less rapid $p_{\rm H}$ change. It seems likely, however, that these errors may under some conditions spread into the better buffered regions, such factors as too rapid titration or sluggishness of an electrode due to films of grease or other adsorbed matter playing a part.

Expts. 1, 1A, and 2 are not sufficiently reliable to give an accurate indication of the temperature coefficient of the constant. The high values of $p_{K'}$ for Expts. 5 and 7 are explained by anomalies in the behaviour of a universal buffer mixture which were discovered after Expt. 7 had been completed.

The calculated $p_{\rm H}$ at the end-point of a titration of hypochlorous acid is given by $p_{\rm H} = 0·5\,(p_{K'} + p_{K_w} + \log C)$, where C is the molar concentration of the partially hydrolysed salt and p_{K_w} is the negative of the exponent of the ionic product of water. With $p_{K_w} = 14·13$ at 18°, the calculation for Expt. 8 ($C = 0·071$) gives $p_{\rm H} = 10·22$, that observed being 10·20.

The value of $p_{K'}$ (7·50) found by Britton and Dodd at 15° may be accurate, but it is difficult to account for the fact that these authors observed no lowering in the presence of 0·1*N*-sodium chloride. Morton (J., 1928, 1401) studied the effects of dilution and of neutral salts upon the p_H values of buffer mixtures, correlating his results by means of the equation $p_K = p_{K'} + A\sqrt{\mu} - B$; p_K refers to the "true" dissociation constant, A is the constant of the Debye–Hückel equations of interionic attraction, μ is the ionic strength (Lewis), and B a specific constant for a salt. Cohn (*J. Amer. Chem. Soc.*, 1927, **49**, 173) and Cohn, Heyroth, and Menkin (*ibid.*, 1928, **50**, 696) have used similar equations in the study of phosphate and acetate buffer systems. Table III gives the available data for hypochlorous acid, p_K values being calculated with $A = 0{\cdot}5$, and $B = 0{\cdot}295$ for sodium chloride and $B = 0{\cdot}358$ for sodium sulphate. It is assumed that the above value of B found by Morton for sodium chloride in acetate mixtures is approximately valid for the uni-univalent sodium salts in the hypochlorite solutions. The value for sodium sulphate is Morton's figure for potassium sulphate in acetate mixtures (0·411) reduced by the difference between the corresponding figures for potassium chloride (0·348) and sodium chloride (0·295).

TABLE III.

Col. 1, total hypochlorite (acid + salt) at 50% neutralisation; col. 2, concentration of other salt or salts as indicated; col. 3, observed $p_{K'}$; col. 4, observed lowering of $p_{K'}$; col. 5, ionic strength, μ; col. 6, calculated value of p_K, the true constant.

Observer.	1.	2.		3.	4.	5.	6.
Authors, Expt. 8	0·071	0		7·46	—	0·0355	7·54
,, Expt. 3B	0·053	0·025	$NaNO_3$	7·42	0·04	0·0515	7·52
Davidson	0·019	0·041	$NaCl + NaClO_3$	7·43	0·03	0·0505	7·53
Britton and Dodd	0·054	0		7·50	—	0·027	7·57
,, ,,	0·054	0·086	NaCl	7·50	0·00	0·113	7·63
,, ,,	0·054	0·216	NaCl	7·45	0·05	0·243	7·63
,, ,,	0·026	0·013	Na_2SO_4	7·50	0·00	0·0325	7·58

It is seen that whereas the present authors' data give results in substantial agreement with that of Davidson for the same temperature, yet there is not the same concordance in the p_K values for the lower temperature calculated on the same basis from the data of Britton and Dodd. If the figure 7·53 be accepted as the true p_K at 18° ($K = 2{\cdot}95 \times 10^{-8}$), then that for 15° might be expected to be about 0·03—0·04 unit higher, *i.e.*, $p_K = 7{\cdot}57$. The still higher value 7·63 cannot then be accepted. It should be noted, too, that the last value in col. 6 is obtained by neglecting the unknown amount of sodium chloride present, allowance for which would raise the calculated p_K.

EXPERIMENTAL.

Approx. 0·2*M*-solutions of hypochlorous acid were obtained by distilling, at 15—20 mm. on a water-bath at 50°, mixtures of 15 g. of bleaching powder, 25 g. of boric acid, and 400 c.c. of water, 250 c.c. of distillate being collected. Previous references to the method (Taylor and Bostock, J., 1912, **101**, 45; Soper, J., 1924, **125**, 1899; Allmand, Cunliffe, and Maddison, J., 1925, **127**, 826) do not give details of the purity of the product. The low pressures here used ensure a high degree of purity. The solutions contained no titratable boric acid, and blank distillations of this acid with water confirmed that it was not appreciably volatile under the conditions of these preparations. A sample of the hypochlorous acid shaken with mercuric oxide for 3 hours and then decanted showed its original iodometric titre unchanged, hence free chlorine was absent. An electrometric titration of a solution to which a known amount of nitric acid had been added gave the first inflexion at the exact point corresponding to the neutralisation of the added acid, showing the absence of any titratable hydrochloric acid in the preparation, although silver nitrate gave an immediate slight opalescence. The hypochlorous acid was estimated by titrations with thiosulphate of the iodine liberated from potassium iodide in the presence of acetic acid. For some unexplained reason, the electrometric titrations always gave slightly higher end-points than those expected from the iodometric values, the maximum discrepancy being 0·5%. Since it would require a shift of 1% in the end-point to alter the mean $p_{K'}$ of an experiment by 0·01 unit the discrepancies were neglected. The titration graphs (E.M.F. against c.c.) showed no indications of the presence of substances other than hypochlorous acid, and the end-points read from them were used in the calculations.

The apparatus used for the electrometric titrations and p_H determinations is a valve potentiometer of the Harrison type (J., 1930, 1528), as modified by Greville and MacLagan (*Trans.*

Faraday Soc., **1931**, **27**, 210), and constructed essentially to their design, except that steel spring strips are used on the special switch and high-grade ebonite replaces Orca at the points requiring special insulation. The valve is a G.E.C. electrometer triode, run at H.T. 4 volts, G.B. −3 volts, the compensating current being taken at 24 volts through 150,000 ohms fixed and 50,000 ohms variable resistances. A Cambridge and Paul potentiometer reading to 0·1 millivolt and an Ayrton–Mather reflexion galvanometer having a sensitivity of 610 mm./microamp. are used. Morton (J., 1931, 2977) has criticised Greville and MacLagan's estimate of the accuracy of their determinations, and has given a method of altering the circuit to a null-ballistic arrangement. It was not found necessary to do this (see also Greville and MacLagan, J., 1932, 720), as the instrument behaved extremely well, the zero drift being so small as to justify the use of an even more sensitive galvanometer.

The cell used is :

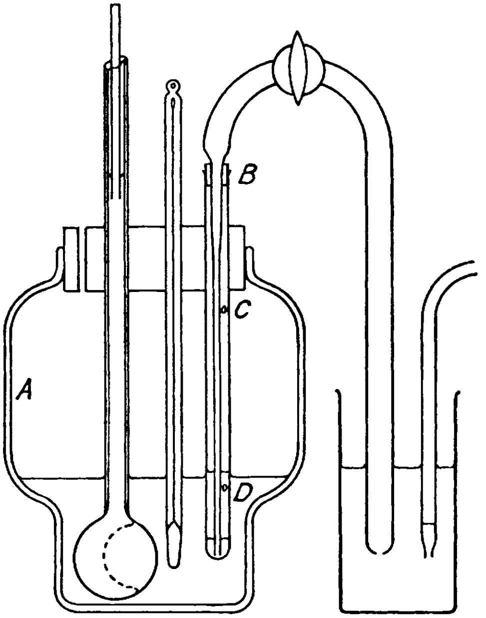
Hg|0·1N-KCl, HgCl (satd.)|Glass|Solution}KCl }0·1N-KCl |Hg
|0·05M-KH phthalate | | X }(satd.)}HgCl (satd.)|

the left hand side being positive when X has a $p_{\rm H}$ below about 4, and negative for higher values. At $p_{\rm H}$ 7 the voltage is about 0·2, assuring a high degree of accuracy in the readings of the potentiometer in the ranges principally concerned in this work. Britton and Robinson (*loc. cit.*) and Britton and Dodd use the cell

Pt|0·1N-HCl |Glass|Solution}KCl }1·0N-KCl |Hg
|Quinhydrone| | X }(satd.)}HgCl (satd.)|

in conjunction with a condenser charge and discharge method of measurement (Morton, *J. Sci. Instr.*, 1930, **7**, 187), readings of galvanometer deflexions being obtained which are not directly convertible into voltages. The first-named workers claim as an advantage of the system that about $p_{\rm H}$ 7 the deflexions pass through zero. This would not appear to be an advantage in work on hypochlorous acid, where the principal $p_{\rm H}$ range concerned is 6·5—8·5.

Fig. 1.



The glass electrodes are of the recessed bulb (Kerridge) type, about 1·5 cm. diameter, the actual membrane having about half this diameter. Glass tubing supplied by Messrs. Dixon and Co., London, is used in making them. Fig. 1 shows a bulb with its associated apparatus. The vessel *A* is designed to hold 100 c.c., if desired, for titrations, though 25 c.c. suffice to cover the bulb of the electrode. A waxed cork carries electrode, thermometer, and bridge. A small vent hole is necessary when the new bridge shown is used, whilst for titrations a small waxed funnel serves for the introduction of reagent. Liquid junction is established to the 0·1N-potassium chloride–calomel half-cell through an intermediate vessel of saturated potassium chloride, either, in titrations, by means of agar-agar (or gelatin)–potassium chloride bridge tubes, or, in the more accurate work with separate mixtures, by means of the new bridge. This bridge was designed to eliminate uncertainties due to the use of bridges containing gels, and at the same time to prevent contamination of the solution. Glass tubing, of about 4 mm. bore, was used in its construction. One limb was drawn out to give a tube of 1 mm. bore. The outer tube, fitted to this by the short rubber sleeve *B*, had two holes, *C*, *D*, of 1 mm. diameter, drilled in the side. For use, the U-tube is filled with saturated potassium chloride solution, the tap closed, and the outer tube fitted. The bridge is placed *in situ* when the liquid in *A* runs into the outer tube through the lower hole. The liquid levels are so adjusted that, when the tap is opened, potassium chloride runs out of the narrow tube and rises a short distance in the outer tube, lifting the liquid before it. Hydrostatic equilibrium is reached in a few seconds. With this arrangement a junction having a horizontal interface with the denser liquid lowermost is obtained, these conditions securing maximum permanency of the junction.

Shaking is permissible, the junction is reproducible, and no contamination of the solution occurs. Used with the hydrogen electrode also, the bridge gave a satisfactory performance.

To ensure against electrical leakage from the side of the bulb connected to the grid of the valve, the stem of the glass electrode is continued for at least 2″ above the cork of vessel *A*. The half-cell with 0·1*N*-potassium chloride and 0·05*M*-potassium hydrogen phthalate, whose side tube dips into the same solution within the glass electrode, is held in an ebonite block supported in a stand resting on a ½″ plate-glass slab 6″ square. The lead from this half-cell to the highly insulated switch contact is air-spaced and shielded by an earthed brass tube. It was not found necessary to use complete screening round the cell, but the whole apparatus stands upon a ground screen of tin-plate and this is sufficient. Tests with standard buffers gave accuracy in p_H determinations to 0·01 unit, and a series of such buffers covering the range p_H 4—10 gave a straight-line calibration graph within the limits of 0·02 unit.

Most of the experiments were based upon calibrations with the Universal Buffer Mixture of Britton and Robinson (J., **1931**, 1456), salts supplied by B.D.H. in tubes ready for making the stock solution being used. This preparation does not easily dissolve in the cold, and the solution requires the addition of a preservative (0·1 g. of thymol was used per litre) if it is to be kept for more than a day or two.

Calibrations by titrations with approx. 0·2*N*-sodium hydroxide were at first employed together with gel bridges, but in later work a separate mixture was made up for each calibration point, and the new bridge was used. Tests with the hydrogen electrode showed that no significant differences were caused by the exchange of bridges. The calibrations gave straight-line graphs (E.M.F.–p_H) over the range of p_H 4—10, with deviations above the latter point of the order found by other workers (*e.g.*, MacInnes and Belcher, *J. Amer. Chem. Soc.*, **1931**, **53**, 3315). The electrodes had high efficiencies, the characteristic slopes for the straight-line portions of their graphs being 95—98% of the theoretical for the hydrogen electrode. In stable buffer solutions equilibrium was rapidly established, agitation of the vessel to mix the liquid and to equalise the temperature sufficing to bring the electrode to its proper potential.

Shifts of the calibration graphs of a glass electrode from day to day are well known, and are allowed for by calibration immediately before use. Lateral shifts due to change of asymmetry potential may have superimposed upon them alterations of slope due either to change of the working temperature or to change in the efficiency of the electrode in terms of the hydrogen electrode. The electrodes used in this work maintained their efficiencies to within 0·5% in successive calibrations over several weeks, except in one case where an electrode, originally showing 99% efficiency, fell after two calibrations to 97%, which was then maintained. The initial fall was not due to newness, since the electrode had been made up some time before the first calibration. Further work on the efficiencies of glass electrodes and on methods of cleaning and storing them is desirable. The calibration graphs of Britton and Robinson (*Trans. Faraday Soc.*, *loc. cit.*) showing rotation around the mid-point near p_H 7, seem, if they are assumed to refer to constant temperature, to indicate considerable changes in the efficiencies of their electrodes. In this connexion it may be noted that a temperature change of 3° is required to alter the slope factor by 1%, and that control to 0·5° ensures accuracy to 0·02 p_H unit over the range p_H 4—10 in the use of a calibration graph for subsequent determinations of unknown p_H values.

Certain unexpected shifts of calibration graphs (Expts. 6 and 7) were traced to changes occurring in the buffer solutions prepared from the stock universal buffer solution when such solutions made up at the commencement of the day's work were used in successive calibrations at intervals during the day. These changes, involving falling p_H values, were most rapid immediately after the solutions had been made; *e.g.*, of three calibrations for Expt. 6, two before and one after the hypochlorous acid titration, the second and third were in fair agreement but showed a big shift from the first. Corrections based upon hydrogen-electrode measurements were therefore applied to the calibrations concerned.

Investigations have shown that stock solutions prepared from tubes of salts supplied ready for use cannot be relied upon to give the p_H values recorded by Britton and Robinson in their original work upon the universal buffer mixture containing veronal.

For the above reasons it was considered necessary to make an independent determination of the $p_{K'}$ of hypochlorous acid with other buffer solutions. Stock solutions of *M*/5-potassium hydrogen phthalate, *M*/5-potassium dihydrogen phosphate, and *M*/5-boric acid + potassium chloride were used to prepare a series of buffer solutions of p_H 3—10, following the tables of Clark and Lubs (Clark, " Determination of Hydrogen Ions," 1928). These buffers checked by the hydrogen electrode were used in Expt. 8.

The potential determinations with hypochlorous acid gave no difficulty, equilibrium being rapidly established. An example of procedure is given :

Expt. 8. Mixtures of 10 c.c. of 0·885*N*/5-hypochlorous acid, *x* c.c. of 0·777*N*/5-sodium hydroxide, with water from a burette to give a total volume of 25 c.c., were made up immediately before use. The calculated end-point (based upon iodometric value) being 11·40 c.c. of alkali, the values of *x* were 0, 0·5, 1·0, thence by 1 c.c. intervals to 10 c.c., then 10·5, 10·75, 11·0 and by 0·1 c.c. intervals past the end-point to 12 c.c., *i.e.*, 23 mixtures in all. The electrode and vessel were washed and drained, the liquid introduced, and the temperature adjusted; the bridge being brought into action, the reading could be taken within a minute or two. The electrometric end-point was 11·45 c.c.

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