Covington and Prue :

Precise Measurements with the Glass Electrode. Part I.
The Cell : Glass Electrode|HCl|AgCl|Ag.

By A. K. Covington and J. E. Prue.

It is shown that glass electrodes are capable of giving results of precision comparable to that of the best results obtained with the hydrogen electrode. The electrodes used were of such low resistance that no amplifier was necessary. The effect of asymmetry potentials was eliminated by a simple procedure. Values obtained for the activity coefficient of hydrochloric acid over the molality range 0·005—0·1 are in good agreement with these reported by Hills and Ives (*J.*, 1951, 305) from their accurate work on the hydrogen-calomel cell.
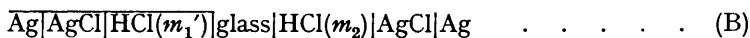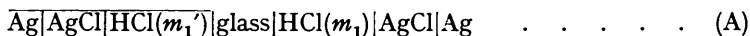
THE introduction of the glass electrode has greatly increased the number of electrolytic solutions which can be studied by e.m.f. cell techniques. Because of the high resistance of the electrodes and the presence of asymmetry potentials, their use for accurate work has been very restricted. Commercial pH meters with electrometer-valve potentiometers are available, but these measure only to ± 1 mv, whereas a precision of about $\pm 0·01$ mv has been attained in the best work with the hydrogen electrode (Hills and Ives, *J.*, 1951, 305). A precision of about $\pm 0·1$ mv has sometimes been reached by using electrostatic electrometers (see, *e.g.*, MacInnes and Belcher, *J. Amer. Chem. Soc.*, 1933, **55**, 2630; Pedersen, *Kgl. Danske Videnskab. Selskabs*, 1937, **14**, No. 9) or specially constructed valve potentiometers (Greville and MacLagan, *Trans. Faraday Soc.*, 1931, **27**, 210). However, glass electrodes with a resistance as low as 0·5 MΩ are now available, as well as robust moving-coil galvanometers of high sensitivity, and we have made accurate measurements with such equipment employing a conventional potentiometer circuit with no special amplifying devices.

We believe, following Beck and Wynne-Jones (*J. Chim. phys.*, 1952, **49**, C 97), that two distinct potentials must be recognized when a glass electrode is placed in a solution, *viz.* : (1) A potential set up instantaneously which varies with the hydrogen-ion concentration of the solution (the hydrogen-electrode function of the glass electrode); and (2) the so-called asymmetry potential, the e.m.f. of the cell

$$Ag|AgCl|HCl(m)|glass|HCl(m)|AgCl|Ag$$
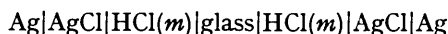
which is due to differences in the two surfaces of the glass membrane. The e.m.f. changes with time and probably depends on the exchange of ions or water between the solution and the glass.

It is usual in work with glass electrodes to make one measurement of asymmetry potential suffice for a series of measurements on test solutions. The precision of our measurements, however, revealed that the e.m.f. of a cell was slowly changing (Fig. 4) and we have therefore used a procedure in which this effect is taken into account. By a simple extrapolation procedure we obtain values of the e.m.f. E_A and E_B that the cells A and B

$$\overline{Ag|AgCl|HCl(m_1')}|glass|HCl(m_1)|AgCl|Ag \quad . \quad . \quad . \quad . \quad . \quad (A)$$

$$\overline{Ag|AgCl|HCl(m_1')}|glass|HCl(m_2)|AgCl|Ag \quad . \quad . \quad . \quad . \quad . \quad (B)$$

would have at the moment of transfer of the glass electrode from one cell to the other; the asymmetry potential is therefore the same for the two cells. The enclosed part on the left of the cells represents the glass electrode filled with hydrochloric acid and containing an internal silver–silver chloride reference electrode.

If the glass membrane is permeable to hydrogen ions only, we can combine cells A and B to obtain a cell which is thermodynamically equivalent to the cell :

$$Ag|AgCl|HCl(m_1)|Pt,H_2 \ldots \ldots \ldots H_2,Pt|HCl(m_2)|AgCl|Ag$$

whose e.m.f. E is given by

$$E = E_B - E_A = -2k \log (m_2\gamma_2) + 2k \log (m_1\gamma_1) \quad . \quad . \quad . \quad . \quad (1)$$

where $k = (RT/F)\ln 10$, and m_1, m_2, and γ_1, γ_2 are the respective molalities and mean ionic activity coefficients of the hydrochloric acid. Since the asymmetry potential makes the same contribution to E_A and E_B, its effect is eliminated. If during a series of measurements cell A is the same, we can regard the electrode assembly as a whole as having a kind of " standard " potential E° and can write

$$E = E^\circ - 2k \log (m_2\gamma_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where

$$E^\circ = 2k \log (m_1\gamma_1) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

A useful way of representing activity coefficients for uni-univalent electrolytes is (Guggenheim and Prue, *Trans. Faraday Soc.*, 1954, **60**, 231) :

$$\log \gamma = -Am^{\frac{1}{2}}/(1 + m^{\frac{1}{2}}) + Bm \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where A is the Debye–Hückel constant and B an empirical parameter. Substituting in (2) we obtain (dropping the subscript 2) :

$$E^{\circ\prime} = E + 2k \log m - 2kAm^{\frac{1}{2}}/(1 + m^{\frac{1}{2}}) = E^\circ - 2kBm \quad . \quad . \quad (5)$$

If we plot $E^{\circ\prime}$ against m, we should obtain a straight line with intercept E° and slope $2kB$.

EXPERIMENTAL

Hydrochloric Acid.—" AnalaR " acid was chlorinated and boiled to free it from other halogens. The purified acid was distilled to give a constant-boiling fraction. The concentration of the acid obtained was determined by interpolation from Foulk and Hollingsworth's concentration-pressure data (*J. Amer. Chem. Soc.*, 1923, **45**, 1220).

Solutions were prepared by weight from conductivity water, made by passing laboratory distilled water through a column of mixed ion-exchange resins, De-Acidite F.F. and Zeo-Karb 315 supplied by the Permutit Co.

Electrodes.—The glass electrodes were Type 9000 (blue trademark) of the Jenaer Glaswerk Schott und Gen., Landshut, Bavaria. Their resistance was 0·3—0·6 MΩ, and their bulb diameter 30 mm. They were mounted as shown in Fig. 1. The split rubber bung held the electrode in a larger Polythene stopper. The central hole was tapered to hold the rubber bung and was large enough to pass the neck of the electrode. The gap below the rubber bung, between the Polythene and the stem, was filled with cotton-wool, and the lower surface of the Polythene stopper and the exposed stem were coated with paraffin wax to suppress electrical leakage. With an electrode whose stem was unwaxed, changing the liquid level by 1 cm. caused the measured e.m.f. to change by 0·3 mv, presumably because of electrical leakage along a film of moisture on the stem and on the Polythene. The electrodes were filled with 0·1M-hydrochloric acid and the internal silver–silver chloride electrode was held in place by a Polythene stopper.

The silver–silver chloride electrodes were of the thermal-electrolytic type. These are type 2 as described by Harned (*J. Amer. Chem. Soc.*, 1929, **51**, 416). The electrodes were stored in 0·1M-hydrochloric acid. Some electrodes showed bias potentials (intercomparison e.m.f. in a common electrolyte) as large as 200 μv but in most cases the bias potentials were less than 60 μv after 24 hr. These differences decreased within a few days. The electrodes chosen for use were from a group which showed the smallest bias potentials. It was found possible to reduce still further the bias potentials of the better electrodes by heating them in water at 50° for 2 hr. as described by Ashby, Crook, and Datta (*Biochem. J.*, 1954, **56**, 190). We chose the silver–silver chloride electrode as the external electrode in these cells, although Hills and Ives (*J.*, 1951, 305) have shown, and we have confirmed, that, provided sufficient care is taken, the calomel electrode is more reproducible. The silver–silver chloride electrode is simpler and

quicker to prepare and may conveniently be rejected if showing a large bias potential. It is well known that oxygen affects the silver–silver chloride electrode in acid solution (Smith and Taylor, *J. Res. Nat. Bur. Stand.*, 1939, **22**, 307), and therefore purified nitrogen was bubbled through the cells before measurements were made. The nitrogen from a commercial cylinder was purified by passage through 5% aqueous potassium hydroxide and an electrically heated silica furnace at 600° packed with alternate sections of reduced copper gauze and filings. Before passing into the electrode vessel (Fig. 2), the gas was presaturated by bubbling through a wash-bottle, immersed in the thermostat, containing hydrochloric acid of the same concentration as that in the vessel. The gas train was of glass, connections being made with ground joints except for two short sections of Polythene tubing to give flexibility. In this Polythene tubing a packing of glass wool allowed the flow of gas to be adjusted by means of screw clips so that the gas could be bubbled through both cells at once.

Circuit.—The potentiometer used was the Tinsley Vernier Potentiometer Type 3126B (1949). The standard cell was checked against a laboratory standard which had been calibrated at the N.P.L. The galvanometer was a Tinsley Type 4500L with a resistance of 400 Ω and a maximum

FIG. 1.

FIG. 2.
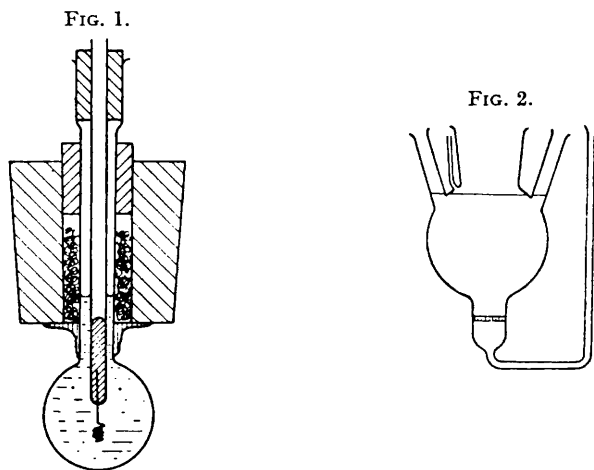
sensitivity of 3040 mm./μA. If the smallest detectable deflection on a scale at one metre is 0·1 mm. and the electrodes have a resistance of 0·3 MΩ, we should be able to detect:

$$\Delta E = (0\cdot1 \times 0\cdot3 \times 10^6 \times 10^{-6}/3040) \text{ v} \simeq 0\cdot01 \text{ mv}$$

We could in fact distinguish a difference in setting of the potentiometer of 0·005 mv.

The galvanometer and potentiometer stood on an " equipotential surface " of copper sheets connected in a series to a common earth (White, " Temperature : Its Measurement and Control in Science and Industry," Reinhold Publ. Corp., New York, 1941, pp. 279—283; see also *J. Amer. Chem. Soc.*, 1914, **36**, 2011). The copper thermostat was also connected to the common earth, as was the shielding of the galvanometer and cell leads. The use of an " equipotential shield " and screened flex for the leads to the galvanometer and cell was found to be essential. Accurate results were not possible without close attention being paid to these details. The electrode vessels were in a thermostat maintained at 25° ± 0·005°. The thermostat thermometer was calibrated against an N.P.L. calibrated thermocouple.

Experimental Procedure.—Two electrode vessels (Fig. 2) were set up in the thermostat containing hydrochloric acid of molalities m_1 and m_2. Two silver–silver chloride electrodes of small bias-potential were inserted, one in each vessel. The cells were left for 1 hr. to come to equilibrium, during the last ½ hr. of which nitrogen was bubbled through the vessels. Meanwhile, the glass electrode was in a jar of distilled water also in the thermostat. The glass electrode was put into the electrode vessel of cell A (see p. 3696) and e.m.f. readings taken every minute for 10 min. The glass electrode was then transferred to the electrode vessel of cell B for 10 min. and then back to A for a further 10 min., e.m.f. readings being taken at 1-min. intervals throughout. Before insertion in an electrode vessel the electrode was washed quickly with some solution of the same molality from a Polythene wash-bottle kept in the thermostat.

While readings were being made on one cell, nitrogen was bubbled through the other. With one filling of the electrode vessels two runs were performed with each of two glass electrodes. The bias potentials of the external silver–silver chloride electrodes were checked before each run and never exceeded 40 μv. No correction was applied for the bias potential.
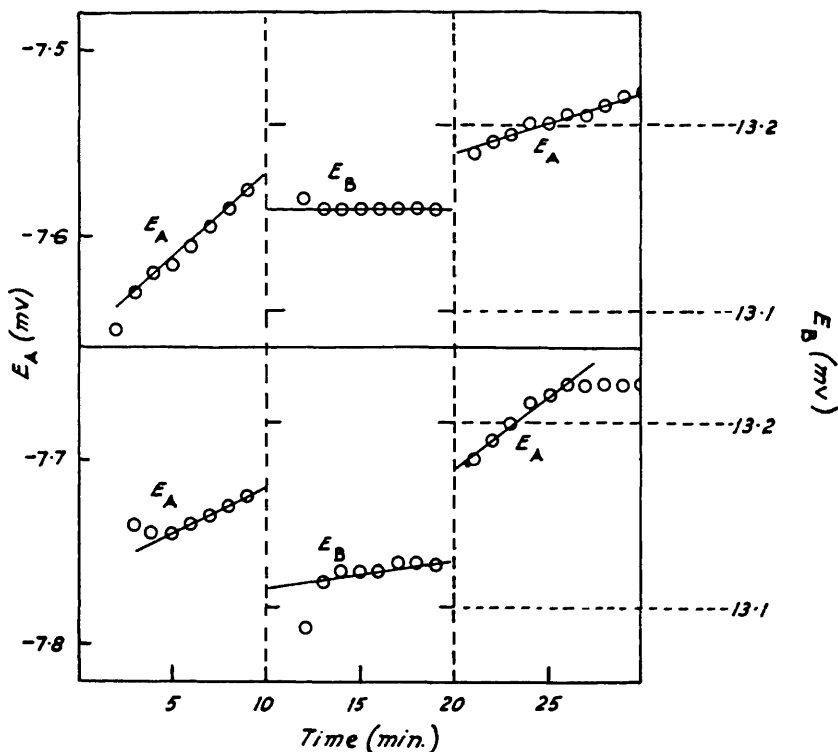
RESULTS AND DISCUSSION

A typical set of e.m.f. readings for $m_1 = 0.1111$ mole kg.$^{-1}$, $m_2 = 0.07222$ mole kg.$^{-1}$ are plotted for one electrode (No. 2) in Fig. 3. In Table 1 singly and doubly primed symbols relate to the extrapolated values at times 10 and 20 min. respectively.

TABLE 1.

Glass electrode no.	E_A' (mv)	E_B' (mv)	E (mv)	E_A'' (mv)	E_B'' (mv)	E (mv)
1	-5.88_5	14·91	20·79_5	-5.87	14·97	20·84
1	-5.87	14·95	20·82	-5.83_5	14·98	20·81_5
2	-7.66_5	13·15_5	20·82	-7.65_5	13·15_5	20·81
2	-7.71_5	13·11	20·82_5	-7.70_5	13·12_5	20·83

FIG. 3.

The mean value of E is 20·82 mv. We have found that the change of e.m.f. with time due to changing asymmetry potential continues indefinitely as shown for a typical cell in Fig. 4. The asymmetry potentials of the electrodes when used were rather high (6—8 mv); even higher values were obtained when the electrodes were first tested, but these were reduced by storage of the electrodes in hydrochloric acid.

The results obtained are summarized in Table 2, where $m_1 = 0.1111$ mole kg.$^{-1}$ throughout. We have used the values $2k = 118.318$ mv and $A = 0.5084$ kg.$^{\frac{1}{2}}$ mole$^{-\frac{1}{2}}$ based on Birge's list of the fundamental constants (*Reports Progr. Phys.*, 1941, **8**, 90) and the value 78·54 for the dielectric constant of water (Wyman and Ingalls, *Phys. Rev.*, 1930, **35**. 623; *J. Amer. Chem. Soc.*, 1938, **60**, 1182).

If $E°'$ is plotted against m_2 a straight line can be drawn from which no point

deviates by more than 0·05 mv. The slope of the best straight line obtained by application of the method of least squares is 25·4 ± 0·5 mv mole^{-1} kg., which gives $B = 0·214 ± 0·004$ mole^{-1} kfl. The value of the intercept is $E° = -125·18$ mv. Values of $E°'$

TABLE 2.

$10^3 m_2$ (mole kg.$^{-1}$)	E (mv)	$-E°'$ (exp.) (mv)	$-E°'$ (calc.) (mv)	$E°'$ (exp.) $- E°'$ (calc.) (mv)
5·36	147·46	125·32	125·32	0·00
11·59	109·40	125·50	125·48	−0·02
22·57	76·96	125·71	125·75	+0·04
30·04	63·02	125·99	125·94	−0·05
42·32	46·52	126·24	126·23	−0·01
47·90	40·60	126·34	126·39	+0·05
60·79	29·05	126·74	126·76	−0·02
72·22	20·82	126·96	127·00	+0·04
81·14	15·13	127·29	127·24	−0·05

calculated from equation (5) by using these values of B and $E°$ are compared with the experimental values in Table 2. The scatter of the experimental points is a little greater than in the work of Hills and Ives (*loc. cit.*) on the hydrogen–calomel cell, but less than in previous work on cells with the hydrogen and silver–silver chloride electrodes (*e.g.*, Harned

FIG. 4.
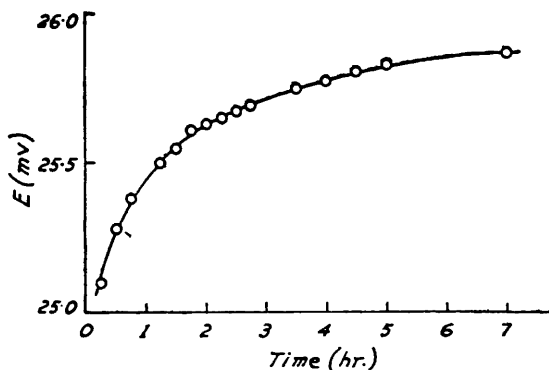
and Ehlers, *J. Amer. Chem. Soc.*, 1932, **54**, 1350; Bates and Bower, *J. Res. Nat. Bur. Stand.*, 1954, **53**, 283) where the scatter is about ±0·1 mv. Our results clearly show that low-resistance glass electrodes can be satisfactorily and conveniently used for electrochemical work of high precision. The deviation from the hydrogen-electrode function is negligible at molalities of hydrochloric acid up to 0·1.

The value $B = 0·214$ mole^{-1} kg. for hydrochloric acid is somewhat lower than a value $B = 0·234$ mole^{-1} kg. calculated by Guggenheim and Prue (*loc. cit.*) from the data of Hills and Ives over the same concentration range. However, if in the analysis of the results of Hill and Ives we neglect the results for the three most dilute solutions ($m \ll 0·005$) and use the results up to a molality of 0·12, we obtain $B = 0·225$ mole^{-1} kg. Smoothed values of γ at rounded concentrations calculated from the various B values are compared in Table 3. We emphasize that a difference in B of 0·01 corresponds to a difference in γ of only $\frac{1}{4}$% at a molality of 0·1.

TABLE 3.

m (mole kg.$^{-1}$)	γ ($B = 0·214$)	γ ($B = 0·225$)	γ ($B = 0·234$)	m (mole kg.$^{-1}$)	γ ($B = 0·214$)	γ ($B = 0·225$)	γ ($B = 0·234$)
0·001	0·9653	0·9653	0·9653	0·02	0·8736	0·8740	0·8744
0·005	0·9279	0·9280	0·9281	0·05	0·8276	0·8285	0·8295
0·01	0·9035	0·9036	0·9039	0·08	0·8036	0·8051	0·8065