Precise Measurements with the Glass Electrode. Part II.*
The Cell: Glass Electrode|HCl(m_1)|HCl(m_2)|Glass Electrode.
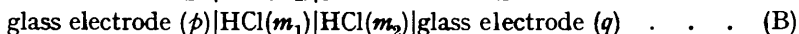
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It is shown that glass electrodes can be used for precise electrochemical measurements on cells with transport. Values obtained for the activity coefficient of hydrochloric acid are compared with those from other sources.

CONCENTRATION cells with two similar electrodes have been widely used in physicochemical studies. For instance, precise activity-coefficient values can be obtained by the combination of e.m.f. measurements on cells with transport-number data obtained by the moving-boundary technique (Brown and MacInnes, *J. Amer. Chem. Soc.*, 1935, **57**, 1356). Unfortunately, in many cases suitable electrodes are not available. Previously it has been impossible to make satisfactory measurements on cells of the type: glass electrode|Solution 1|Solution 2|glass electrode. By a development of the procedure described in Part I * we show that it is now possible to make precise measurements on concentration cells with two glass electrodes, which will greatly extend the range of solutions amenable to exact study by e.m.f. techniques. We report a determination of activity coefficient values for hydrochloric acid which we compare with other exact data. We are now using a similar procedure in studies of solutions of nitric, perchloric, and other oxidizing acids for which no suitable electrode has been available before. We have also repeated Shedlovsky and MacInnes's measurements (*J. Amer. Chem. Soc.*, 1936, **58**, 1970) on hydrochloric acid concentration cells with silver–silver chloride electrodes, since we suspect that their results were vitiated by a failure to deoxygenate the solutions.

In our experiments with the glass electrode we have measured the e.m.f.'s of pairs of cells :

$$\text{glass electrode } (p)|\text{HCl}(m_1)|\text{glass electrode } (q) \quad . \quad . \quad . \quad . \quad . \quad \text{(A)}$$

$$\text{glass electrode } (p)|\text{HCl}(m_1)|\text{HCl}(m_2)|\text{glass electrode } (q) \quad . \quad . \quad . \quad \text{(B)}$$

where " glass electrode " denotes a glass electrode filled with hydrochloric acid and containing an internal silver–silver chloride reference electrode. By a time-extrapolation procedure we obtain values of the e.m.f.'s E_A and E_B that the cells A and B would have at the moment of transfer of the glass electrodes from one cell to the other. The sum of the asymmetry potentials, equal to E_A, is therefore the same in the two cells, and the e.m.f. $E = E_B - E_A$ is the e.m.f. of the thermodynamically equivalent cell

$$\text{H}_2,\text{Pt}|\text{HCl}(m_1)|\text{HCl}(m_2)|\text{Pt},\text{H}_2$$
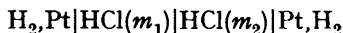
This e.m.f. is given by

$$E = \frac{2RT}{F} \int_{m_1}^{m_2} t^- \, d \ln (m\gamma) \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where γ is the mean ionic activity coefficient at molality m and t^- is the value of the transport number of the chloride ion. Expressing t^- in the form $t^- = t_1 + \Delta t$, where t_1 is the transport number of the chloride ion at molality m_1, we obtain

$$\log \frac{\gamma_2}{\gamma_1} = \frac{E}{t_1 RT \ln 10/F} - \log \frac{m_2}{m_1} - \frac{1}{t_1} \int_{m_1}^{m_2} \Delta t \, d \log m - \frac{1}{t_1} \int_{\gamma_1}^{\gamma_2} \Delta t \, d \log \gamma \quad . \quad . \quad (2)$$

The value of the third term on the right-hand side of equation (2) is obtained by graphical integration from a plot of Δt against $\log m$. The fourth term is small and is given with sufficient accuracy by graphical integration using values of $\log \gamma$ obtained from equation (2) with this fourth term omitted.

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* Part I, preceding paper

We represent the activity coefficient values as in Part I by the expression

$$\log \gamma = - A m^{\frac{1}{2}}/(1 + m^{\frac{1}{2}}) + Bm \quad \ldots \ldots \quad (3)$$

where A is the Debye–Hückel constant, and B an empirical parameter. Defining a standard value γ^{st} of the activity coefficient by setting $B = 0$ in (3), we obtain $\log \gamma - \log \gamma^{st} = Bm$, and denoting by Δ the difference between values at m_1 and m_2, we have
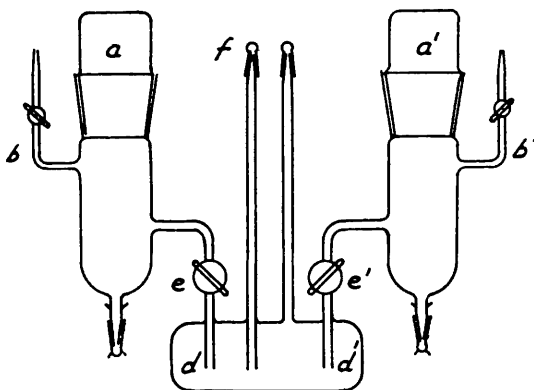
$$\Delta \log \gamma - \Delta \log \gamma^{st} = B \Delta m \quad \ldots \ldots \quad (4)$$

We therefore plot values of $\Delta \log \gamma - \Delta \log \gamma^{st}$ against Δm to obtain a value for B.

EXPERIMENTAL

Solutions of hydrochloric acid were prepared as in Part I. They were deoxygenated immediately before use by passage of a stream of purified and pre-saturated nitrogen. The electrodes and the electrical circuit were the same as those described in the previous paper.

FIG. 1.

Procedure.—The electrode vessel used is shown in Fig. 1. The taps e,e' were fitted to prevent disturbance of the junction either by removal or insertion of electrodes, or by convection currents due to thermal gradients when the vessel was first placed in the thermostat. The taps were lightly greased with a Silicone grease.

In the filling procedure the stoppers a,a' were held in place by rubber bands and the vessel was inverted. One of the solutions was forced into the left-hand compartment through b until the liquid level had reached the end of tube d. The right-hand compartment was filled similarly with the other solution, after which taps e and e' were closed and the vessel was returned to its original position. The more concentrated of the two solutions was now carefully admitted through f until the central compartment was full. The vessel, supported in a brass frame, was now transferred to the thermostat, taps e,e' being kept closed until temperature equilibrium had been reached. The glass electrodes (stored in distilled water at 25°) were washed with solution of molality m_1 at 25° and placed in the electrode vessel of cell A (see p. 3701) also in the thermostat. Readings of the e.m.f. of cell A were taken every minute for 5 min., the electrodes were transferred (with appropriate washing) to the concentration cell B, and the taps e,e' opened. Readings were again taken at 1-min. intervals for 10 min., the electrodes were transferred back to cell A, and e.m.f. readings taken for a further 5 min. The whole procedure was repeated, the position of the electrodes in cell B being reversed.

Measurements were also made by using silver–silver chloride electrodes. A steady potential with fluctuations of only a few microvolts was reached in 90 min. Electrodes with bias potentials less than 20 µv were chosen. No correction was applied for any residual bias potential but in a series of measurements with increasing m_2 an electrode was used alternately in the dilute or concentrated solution.

RESULTS AND DISCUSSION

A typical set of e.m.f. readings with the glass electrode cells with $m_1 = 0.1093$ mole kg.$^{-1}$ and $m_2 = 0.02118$ mole kg.$^{-1}$ is shown in Fig. 2, and the results of the extrapolations in Table 1. The e.m.f. of the cell with the electrode positions in cell B reversed we denote by

E_C, and therefore $E = E_C + E_A$. Occasionally the two pairs of values of E disagreed and the results were rejected. The mean value of E in this experiment was therefore 13·51 mv. The results obtained are summarized in Table 2. The corresponding results for the silver–silver chloride cell are given in Table 3, and Shedlovsky and MacInnes's results (*loc. cit.*)

TABLE 1.

Time (min.)	E_A (mv)	E_B (mv)	E (mv)	Time (min.)	E_A (mv)	E_C (mv)	E (mv)
5	−5·05	8·46	13·51	20	−5·05	18·57$_5$	13·52$_5$
15	−5·05	8·44$_5$	13·49$_5$	30	−5·00	18·50$_5$	13·50$_5$

recalculated on the molality scale are given in Table 4. In this we have used density values interpolated from Redlich and Bigeleisen's data (*J. Amer. Chem. Soc.*, 1942, **64**, 758) and converted international volts to absolute volts by using the relation 1 int. v = 1·00034 v. In all calculations we have used the value of the fundamental constants given in Part I, and transport-number data interpolated from Longsworth's results (*ibid.*, 1932, **54**, 2741).

The results of the three sets of experimental work are plotted together in Fig. 3, on which is also shown the change in $\Delta \log \gamma - \Delta \log \gamma^{st}$ caused by a change of 0·1 mv in E for
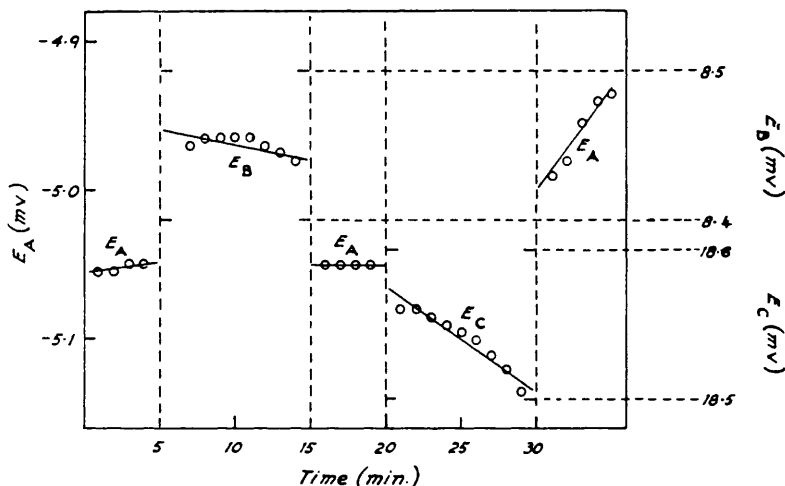
FIG. 2.

TABLE 2. *Glass electrode results.*

$m_1 = 0\cdot1093$ mole kg.$^{-1}$, $t_1 = 0\cdot1682$.

$10^3 m_2$ (mole kg.$^{-1}$)	E (mv)	t^-	$-\Delta \log \gamma$	$\Delta \log \gamma$ $-\Delta \log \gamma^{st}$	Δm
5·930	24·42	0·1761	0·06831	0·02166	0·1034
13·04	17·61	0·1744	0·05499	0·01923	0·0962
21·18	13·51	0·1732	0·04439	0·01734	0·0881
30·03	10·60	0·1722	0·03514	0·01609	0·0792
45·02	7·25	0·1711	0·02441	0·01294	0·0643
49·73	6·42	0·1708	0·02199	0·01163	0·0595
62·40	4·58	0·1702	0·01463	0·01008	0·0469
72·06	3·38	0·1697	0·01188	0·00685	0·0372

TABLE 3. *Silver–silver chloride electrode results.*

$m_1 = 0\cdot1093$ mole kg.$^{-1}$, $t_1 = 0\cdot8318$.

$10^3 m_2$ (mole kg.$^{-1}$)	E (mv)	t^+	$-\Delta \log \gamma$	$\Delta \log \gamma$ $-\Delta \log \gamma^{st}$	Δm
5·434	120·85	0·8237	0·06904	0·02238	0·1038
5·930	117·22	0·8239	0·06848	0·02149	0·1034
13·04	85·27	0·8256	0·05360	0·02062	0·0962
21·18	65·73	0·8268	0·04268	0·01905	0·0881
30·03	51·68	0·8978	0·03460	0·01663	0·0792
45·02	35·48	0·8289	0·02424	0·01311	0·0643
49·73	31·53	0·8292	0·02110	0·01252	0·0595
62·40	22·46	0·8298	0·01496	0·00975	0·0469
72·06	16·68	0·8303	0·01129	0·00744	0·0372

the glass or silver–silver chloride electrode cells.   The best straight line through our results with the silver–silver chloride electrode has a slope of $B = 0\cdot217$ mole^{-1} kg.; the line does not pass through the origin, but the negative intercept on the ordinate corresponds to an error of only $0\cdot1\%$ in m_1, which is within the accuracy with which we knew the value of m_1. The deviation of the points from the line never exceeds a value corresponding to $0\cdot02$ mv,

TABLE 4.   *Recalculated results of Shedlovsky and MacInnes.*

$m_1 = 0\cdot1048$ mole kg.$^{-1}$, $t_1 = 0\cdot8314$.

$10^3 m_2$ (mole kg.$^{-1}$)	E (mv)	t^+	$-\Delta \log \gamma$	$\Delta \log \gamma$ $-\Delta \log \gamma^{st}$	Δm
3·457	136·310	0·8234	0·06981	0·02438	0·09702
5·275	118·855	0·8239	0·06541	0·02254	0·09520
10·049	92·560	0·8251	0·05505	0·02100	0·09043
10·061	92·511	0·8251	0·05503	0·02100	0·09042
19·980	64·752	0·8266	0·04124	0·01817	0·08050
20·103	64·486	0·8266	0·04137	0·01787	0·08038
20·200	64·304	0·8266	0·04103	0·01807	0·08028
40·640	36·226	0·8286	0·02420	0·01288	0·05984
60·068	20·607	0·8297	0·01373	0·00856	0·04041
78·417	9·951	0·8306	0·00646	0·00469	0·02206

FIG. 3.

$\triangle$ Ag–AgCl. $\bigcirc$ Glass. $+$ Ag–AgCl (*Shedlovsky and MacInnes*).
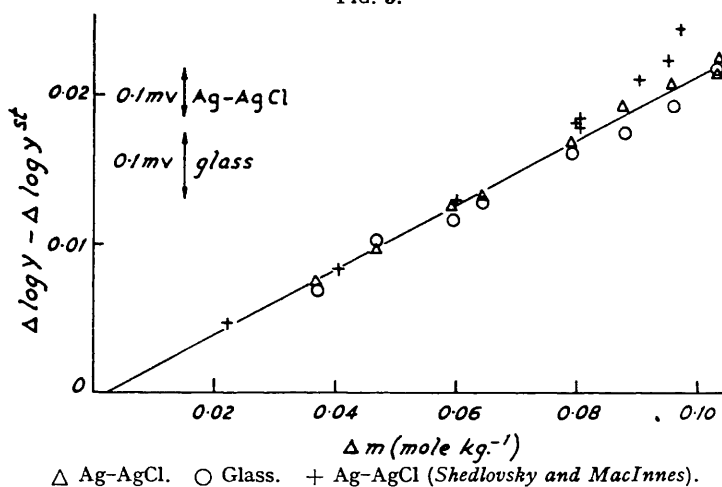
and the points obtained with the glass electrode do not deviate from this line by more than $0\cdot03$ mv.   The results of Shedlovsky and MacInnes (*loc. cit.*) at the higher dilutions (the right-hand side of the figure) agree less well.   This, we suspect, was due to a failure to deoxygenate their solutions since they make no mention of this precaution.

Our results show that two glass electrodes can be used for concentration-cell measurements of high precision.   We conclude from this and the preceding paper that in dilute aqueous solutions of a strong acid the glass electrode is capable of yielding results as precise as those which can be obtained with the hydrogen, calomel, or silver–silver chloride electrodes.

The value for B agrees with the value $0\cdot214$ mole^{-1} kg. obtained in Part I.   That it is slightly lower (corresponding to $\frac{1}{2}\%$ in γ at $0\cdot1m$) than the value $0\cdot234$ mole^{-1} kg. calculated from the results of Hills and Ives by Guggenheim and Prue (*Trans. Faraday Soc.*, 1954, **50**, 231) may be significant, since an analysis of the freezing-point data for hydrochloric acid (Guggenheim and Prue, " Physicochemical Calculations," North-Holland Publishing Co., Amsterdam, 1955, p. 223) gives a value for B of $0\cdot216$ mole^{-1} kg., again lower than that obtained from cell measurements with the hydrogen electrode at $0°$.