71. *The Hydrogen–Calomel Cell. Part III. The Standard E.M.F. at 25° c.*

By G. J. Hills and D. J. G. Ives.

The improvements in the calomel electrode described in the preceding paper have allowed the standard E.M.F. of the hydrogen–calomel cell at 25° to be determined by direct extrapolation of the experimental measurements to zero ionic strength. The standard free energy of formation of mercurous chloride and the activity coefficients of aqueous hydrochloric acid at 25° have been re-evaluated.

Methods by which many of the difficulties associated with the calomel electrode have been circumvented are described in the preceding paper. The resulting improvement in reproducibility of the electrode warranted an attempt to extend measurements of the E.M.F. of the cell $H_2,Pt|HCl(aq.)|Hg_2Cl_2|Hg$ into regions of high dilution, with the object of determining the standard E.M.F. by direct extrapolation to zero ionic strength.

Measurements have been made over the concentration range 0·1—0·002N., the lower limit being set by the effects of ion exchange between the acid solutions and the glass of the containing vessels. In contrast to previous experience, no loss of reproducibility was encountered with decreasing concentration, and an accurate extrapolation gave, for the standard E.M.F., the values $E^0_m = 0{\cdot}26796$ and $E^0_c = 0{\cdot}26781$ absolute volt at 25° c., on the molality and molar concentration scales respectively, with an estimated error not exceeding $\pm 0{\cdot}00001$ v.

The measurements from which these results were derived are given in Table I.

Table I.

Molality of HCl.	E.M.F., abs. v.	Molality of HCl.	E.M.F., abs. v.	Molality of HCl.	E.M.F., abs. v.
0·119304	0·38948	0·037690	0·44516	0·0076938	0·522675
0·094276	0·40088	0·025067	0·46490	0·0050403	0·543665
0·075081	0·41187	0·018871	0·47870	0·0030769	0·56825
0·064718	0·41906	0·013968	0·49339	0·0016077	0·60080
0·051645	0·42994	0·0109474	0·50532		

Some difficulty arises in selecting values for the fundamental constants to be used in these calculations. Birge's values (*Rev. Modern Physics*, 1941, **13**, 233) have been adhered to and, with other relevant quantities, are collected in Table II.

TABLE II.

Absolute temperature corresponding to 0° c.	273·16° K.
J, abs. joules/15°-cal.	4·1855
Electronic charge, $\mathbf{e}$, e.s.u.	4.8025×10^{-10}
Avogadro's number, N	6.0227×10^{23}
Faraday, F, abs. coulombs/equiv.	96,487
Boltzmann constant, k, erg/degree	1.38047×10^{-16}
Molar gas constant, R, abs. joules/mole/degree	8·31436
Absolute volt/international volt	1·00034
Absolute joule/international joule	1·00019
Dielectric constant, D, of water at 25° c.	78·54
Density of water, ρ_0, g./ml. at 25° c.	0·997071
Debye–Hückel constant A for water at 25° c.	0·5091
Debye–Hückel constant β for water at 25° c.	0·3286

The method of extrapolation to zero ionic strength suggested by Hitchcock (*J. Amer. Chem. Soc.*, 1928, **50**, 2076) and used by Harned and Ehlers (*ibid.*, 1932, **54**, 1350; 1933, **55**, 652, 2179) in the determination of the standard E.M.F. of the cell H_2,Pt|HCl(aq.)|AgCl|Ag is based upon the modified Debye–Hückel expression:

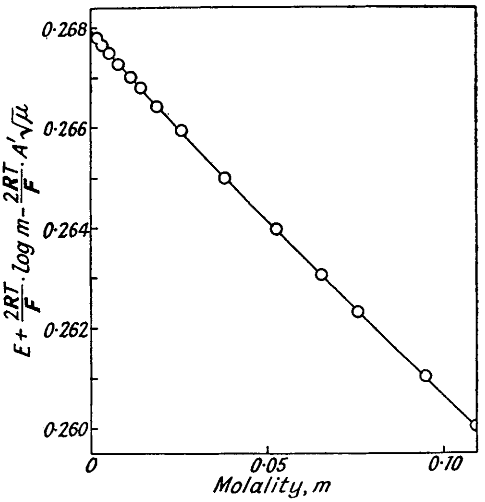
$$\log_{10}\gamma_{\pm} = -A'\sqrt{m} + Bm \quad . \quad . \quad . \quad . (1)$$

where $\gamma_{\pm}$ is the mean molal ionic activity coefficient, m is molality, A' is the Debye–Hückel constant proper to ionic strength calculated in terms of molality ($A' = A\sqrt{\rho_0}$) and B is an arbitrary constant. Substitution in the thermodynamic expression for the E.M.F. of the concentration cell without transport and rearrangement leads to

$$(E + 0.118319 \log_{10}m - 0.118319\,A'\sqrt{m}) = E^0_m - 0.118319\,Bm \quad . \quad . \quad (2)$$

where E is the measured E.M.F. at molality m and E^0_m is the standard E.M.F. on the molality scale. The quantity on the left-hand side of equation (2) is a linear function of m insofar as equation (1) is valid. Treated in this way, the present results for the hydrogen–calomel cell give the curve shown in Fig. 1. The plot is not linear and shows no sign of conforming more closely to equation (2) with decreasing concentration. An extrapolation on this basis is therefore unsatisfactory and cannot fix the value of E^0_m more closely than ± 0.05 mv., which is in fact the uncertainty attributed by Harned and Ehlers to their own extrapolation by this method. There seems little reason to suppose that equation (1) holds accurately over any concentration range and it is unjustifiable to apply the method of least squares to such an extrapolation (cf. Scatchard and Prentiss, *Chem. Reviews*, 1933, **13**, 139).

FIG. 1.



An alternative method first suggested by MacInnes and Brown (*J. Amer. Chem. Soc.*, 1935, **57**, 1356) is better founded in that it uses the full, but unextended, Debye–Hückel expression:

$$\log_{10}\gamma_{\pm} = -\frac{A'\sqrt{m}}{1 + \beta' a_i\sqrt{m}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

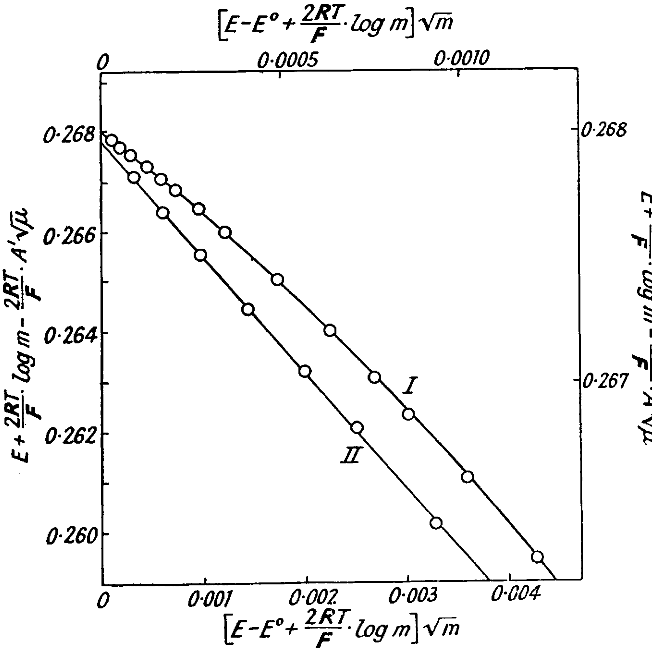
where β' is again the appropriate Debye–Hückel constant adjusted to ionic strength expressed on the molality scale ($\beta' = \beta\sqrt{\rho_0}$) and a_i is the distance of closest ionic approach. Substitution in the thermodynamic expression for the E.M.F. of the concentration cell without transport and rearrangement leads to

$$[E + 0.118319 \log_{10}m - 0.118319\,A'\sqrt{m}] = E^0_m - \beta' a_i\sqrt{m}[E - E^0_m + 0.118319 \log_{10}m] \quad . \quad (4)$$

A plot of the left-hand side of this equation against the quantity $\sqrt{m}[E - E^0_m + 0{\cdot}118319\log_{10}m]$ should give a straight line of slope $\beta'a_i$ and intercept E^0_m. In using this method, it is necessary to conduct a short series of successive approximations until the value of E^0_m used in computing the abscissæ agrees with the value derived from the intercept. The method has been applied to the present measurements on the hydrogen–calomel cell, with the results shown in Fig. 2, Curve I. It is seen that the plot deviates from linearity at abscissæ exceeding 0·001, but below this (corresponding with molalities lower than 0·02) becomes strictly linear. This section is plotted separatedly on a larger scale (Curve II, upper and right-hand axes). The final extrapolation was checked by the " zero sum " method and gave $E^0_m = 0{\cdot}26796$ abs.v. The entire calculation and extrapolation was carried out independently in terms of molar concentrations instead of molalities and gave $E^0_c = 0{\cdot}26781$ abs.v., in complete agreement with the relation $E^0_c = E^0_m\rho_0$.

A similar extrapolation has been carried out using Harned and Ehlers's data (*loc. cit.*) on the hydrogen–silver chloride cell and is shown in Fig. 3. MacInnes (" The Principles of Electrochemistry," Reinhold Publishing Corp., 1947, p. 186), remarking on the rather wide deviations, blames the hydrogen electrode " the variations of which are probably the chief cause of the scattering of the points." It is doubtful if this was the case; in the present work no such loss in reproducibility at lower concentrations was observed and it seems more likely that the silver/silver chloride electrode was the source of error. If this is the case, the silver/silver chloride electrode appears to be considerably inferior to the calomel electrode.

FIG. 2.



The slope of the MacInnes and Brown plot may be used to obtain the distance of closest ionic approach, a_i. The present results lead to 4·96 ± 0·01 A. for aqueous hydrochloric acid, which is not in good agreement with the value of 5·62 A. obtained by MacInnes and Shedlovsky (*J. Amer. Chem. Soc.*, 1936, **58**, 1970) from work on cells with liquid junction, or with the value of 5·50 A. calculated from Harned and Ehlers's results (*loc. cit.*). It may be pointed out, however, that greater uncertainty must attach, on the one hand to data affected by liquid-junction potentials and, on the other, to the slopes of best straight lines drawn through points showing divergences as great as those in Fig. 3.

The new value for the standard E.M.F. of the hydrogen–calomel cell does not represent any important change. Bockris and Herringshaw (*Discussions Faraday Soc.*, 1947, **1**, 328), in a critical summary of recorded electrode potentials, give $E^0 = 0{\cdot}268$ v. for the calomel electrode. There is correspondingly little change in the calculated standard free energy of formation of mercurous chloride. The standard free energy of the cell reaction from the new value of E^0_m is $-12{,}391$ cals. By using $-31{,}350$ cals. for the standard free energy of formation of the chloride ion in aqueous solution (" Values of Chemical Thermodynamic Data," U.S. National Bureau of Standards, Series I, 1947), there is obtained :

$$2Hg + Cl_2 = Hg_2Cl_2;\ \Delta G^\circ = -50{,}309 \text{ cals.}$$

This results is slightly lower than the value, $-50{,}350$ cals., given by the Bureau of Standards (*loc. cit.*), and is advanced as of improved accuracy.

Activity coefficients of hydrochloric acid in aqueous solution at 25° have been calculated from the measured and standard E.M.F.s of the hydrogen–calomel cell and are shown in Table III.

TABLE III.

Molality of HCl.	Mean molal act. coeff.	Molality of HCl.	Mean molal act. coeff.	Molality of HCl.	Mean molal act. coeff.
0·119304	0·7876	0·037690	0·8436	0·0076938	0·9140
0·094276	0·7984	0·025067	0·8639	0·0050403	0·9276
0·075081	0·8095	0·018871	0·8772	0·0030769	0·9416
0·064718	0:8163	0·013968	0·8903	0·0016077	0·9568
0·051645	0·8278	0·0109474	0·9002		

FIG. 3.

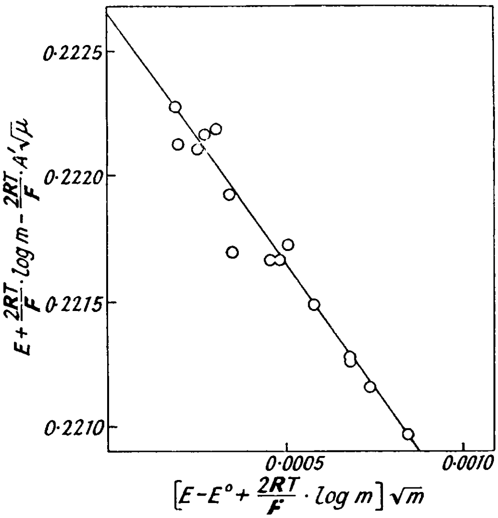
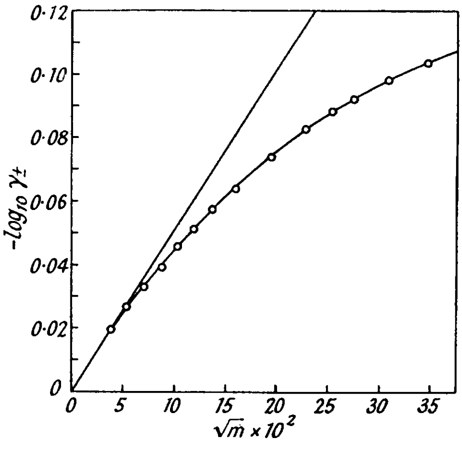


FIG. 4.



Values of $\log_{10}\gamma_\pm$ are plotted against the square root of molality in Fig. 4. The limiting slope of the plot is $0{\cdot}5079 \pm 0{\cdot}0010$, which agrees satisfactorily with the theoretical value of 0·5084. Although this cannot be taken as an independent evaluation of the Debye–Hückel constant, it shows the complete consistency of the data with the limiting theory. No attempt has been made to apply any of the extended equations. Activity coefficients at rounded molalities have been interpolated from a large-scale plot of the type of Fig. 4 and are compared with the figures given recently by Harned and Owen (" The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., 2nd. Edn., 1950, pp. 340, 547) in Table IV.

TABLE IV.

Mean molal activity coefficients of aqueous hydrochloric acid at 25° c.

m.	$\gamma_\pm$, present work.	$\gamma_\pm$, Harned & Owen.	m.	$\gamma_\pm$, present work.	$\gamma_\pm$, Harned & Owen.
0·0001	0·9884	0·9891	0·04	0·8406	—
0·0002	0·9836	0·9842	0·05	0·8296	0·8304
0·0005	0·9745	0·9752	0·06	0·9205	—
0·001	0·9650	0·9656	0·07	0·8129	—
0·002	0·9519	0·9521	0·08	0·8064	—
0·005	0·9280	0·9285	0·09	0·8007	—
0·01	0·9040	0·9048	0·10	0·7958	0·7964
0·02	0·8747	0·8755	0·11	0·7914	—
0·03	0·8551	—	0·12	0·7874	—

Although the discrepancies between the two sets of figures are not large, their effect is shown by the calculation of E^0_m from each experimental E.M.F. of the hydrogen–calomel cell, the Harned and Owen activity coefficients being used. The results show a systematic trend, ranging from 0·26805 v. at m = 0·12 to 0·26795 v. at m = 0·002. This probably arises because the Harned and Owen activity coefficients do not seem to have been recalculated with the new value of $2RT/F$ required by the revision of the fundamental constants by Birge in 1941 (*loc. cit.*).

EXPERIMENTAL.

Fundamental Standards and Instruments.—(*a*) *Mass.* All weights were corrected by reference to standards certified within 1 part in 10^6 by the National Physical Laboratory. Weighings of primary analytical standards were made to 0·01 mg. by a substitution method and were corrected to vacuum. All solutions were prepared by weight, and densities were determined for the calculation of molar concentrations.

(*b*) *Pressure.* Barometric pressures were measured by means of a barometer, at the same level as the apparatus, calibrated by a series of readings from Kew Observatory. Errors in pressure measurements were equivalent to less than 5 μv. variation in hydrogen-electrode potential.

(*c*) *Temperature.* A bomb calorimeter thermometer was provided with a special calibration to within ±0·002° c. at 25° c. by the National Physical Laboratory. This was independently checked against a platinum resistance thermometer calibrated in the laboratory against ice, steam, and sodium sulphate with agreement to within ±0·005° c. A water-filled thermostat was used and maintained at 25° ± 0·005° c.

(*d*) *E.M.F.* The two components of a double Weston cell, calibrated at the National Physical Laboratory, were in very precise agreement with each other and with the standard E.M.F. of 1·01831 abs.v. at 25° c. The cell was mounted in a Dewar vessel and left undisturbed throughout the course of the work. The temperature of the cell was taken when measurements were made, the potentiometer being fitted with a temperature-compensating rheostat. A new Tinsley potentiometer (type 4025) was used and was calibrated internally by a standard method. A check on the overall standardisation was kept by arranging one of the standard cells for use in the measuring circuit; the potentiometer was found to be extremely stable, apart from a small zero error which was measured on every occasion that readings were taken. A Tinsley galvanometer (type S.S. 545) was used, not only as a null-point detector, but to obtain the last significant figure in the E.M.F. measurements. This was done in a manner exactly analogous to the " method of swings " in weighing and is thought to be greatly preferable to final potentiometric subdivision by slide-wire: the ±0·05 microcoulomb involved in each observed galvanometer deflection was a negligible infringement of the requirement of reversibility. All potentiometric equipment was mounted on an " equipotential surface " (White, *J. Amer. Chem. Soc.*, 1914, **36**, 2011), and close attention was paid to insulation, liberal use being made of polythene. Before immersion in the thermostat bath, the experimental cells were externally treated with silicone grease, which effectively eliminated insulation difficulties.

Materials.—*Silver.* A special sample of assay silver of 99·997% purity (Johnson Matthey) was used as a primary analytical standard. It was fused to a mirror-bright button in hydrogen before use.

Potassium chloride. " AnalaR " potassium chloride was freed from other halogens by Pinching and Bates's method (*J. Res. Nat. Bur. Standards*, 1946, **37**, 311) and recrystallised three times from conductivity water, large head and tail fractions being discarded. The dried salt was fused in a platinum vessel in an atmosphere of hydrogen, and was used as a secondary analytical standard. Comparison with the silver by analysis gave an atomic ratio Cl/Ag = 0·99992.

Water. Conductivity water was prepared in a Pyrex still of the Stuart and Wormwell type (*J.*, 1930, 85) and was used in the preparation of all solutions.

Hydrochloric acid, mercury, calomel, hydrogen, and nitrogen. These were prepared for use in the manner described in the previous Parts.

General Arrangements and Ancillary Apparatus.—The hydrogen-electrode assembly and buffer vessel containing the guard hydrogen electrode (Part I) were combined with two calomel electrodes (Part II) to form the complete all-Pyrex cell, the two halves of which were separated by a wide-bore vacuum tap, well lubricated with silicone or " Apiezon L " grease. This tap was opened only momentarily for E.M.F. measurements to be made. It provided perfect insulation, and no evidence was found of ill-effect either from exchange of solution between the two half-cells or from contamination of the electrodes by tap grease. Independent filling tubes were provided for the half-cells, flow of solution through the tap never being allowed. Each of the four electrode vessels was provided with a presaturator and the means of bubbling the appropriate gas through the solution or by-passing it over the surface. The cell was fitted with a *B*29 standard ground cone sealed to the base of the buffer electrode vessel, so that the whole cell, centrally suspended, could be " plugged " into a socket rigidly mounted in the bottom of the thermostat tank. This device greatly facilitated handling of the cell and was effective in minimising vibration. Solutions were prepared and stored in 5-l. or 2-l. Pyrex flasks, fitted with heads so arranged that nitrogen from a scrubber and presaturator could be bubbled through the solution, by-passed over its surface, or used to develop a pressure to blow the solution in a controlled manner through a delivery tube for cell filling. Delivery tubes of polyvinyl chloride were used; they are hydrophobic and unobjectionable for this purpose.

Connections between the electrodes and the potentiometer were made by means of screened, polythene-insulated cable and a selector switch so arranged that readings could be taken in rapid succession of E.M.F.s between (*a*) the four possible combinations of hydrogen and calomel electrodes, (*b*) the hydrogen electrodes proper and the guard electrode in the buffer vessel, and (*c*) any pair of like electrodes, hydrogen or calomel. The criterion was adopted of rejecting all measurements for which the concordance between like electrodes was not within 20 μv..

Procedure.—The hydrochloric acid solutions were kept in the storage flasks with presaturated nitrogen passing for at least 48 hours before use. Analysis was carried out during this period. The preparation of the cell for use has been described in the preceding papers. After introduction of the freshly distilled mercury into the calomel-electrode vessels, a further quantity was pipetted into a clean, glass-stoppered Pyrex bottle and shaken vigorously for two to four minutes with a small quantity of calomel taken directly from the desiccator. Some of the resulting grey " skin " was introduced to each mercury surface by means of a small glass ladle. Instantaneous spreading occurred. The four presaturators filled with the cell solution were attached and the cell transferred to the thermostat with the minimum of shaking. The all-glass connections to the hydrogen and nitrogen supply lines were made and the cell swept out thoroughly with these gases. The electrode vessels were then filled, catalyst added to the appropriate vessel, and the two normal hydrogen electrodes fitted. Hydrogen and nitrogen were bubbled through the solution in the proper half-cells. E.M.F. readings were taken at intervals of 10 minutes, the gases being by-passed over the solution, and became constant in about 2 hours. Readings were continued at intervals for a few hours and the cell left overnight with the gases by-passing the solutions. Slight changes of E.M.F. sometimes occurred overnight, due to imperfection in the gas presaturation arrangements, but these were rectified by cell refilling, and a further set of measurements was carried out. Agreement of results obtained on different days was almost invariably excellent. The only systematic exception arose from the effects of ion exchange between very dilute solutions and the glass of containing vessels. At concentrations exceeding 0·005N., this is inappreciable; between 0·005N. and 0·001N., it is slight and was countered by an extrapolation to zero time. Corrections of this type were applied to the results from the two most dilute solutions and amounted to 20 and 35 μv.

Analysis of Solutions.—Expression of the E.M.F. data to five significant figures required a knowledge of the concentration of hydrochloric acid to an accuracy of 3 parts in 10,000. Use was made of MacInnes and Dole's differential titration method (*J. Amer. Chem. Soc.*, 1929, **51**, 1119), which allows the equivalence point in silver/chloride titrations to be detected unambiguously to 1 part in 10,000.

About 3 g. of silver were dissolved in dilute nitric acid in a tared, closed flask. Nitrous acid was removed from the resulting solution by addition of 0·2 g. of urea and sodium hydroxide solution was added to neutralise the excess of nitric acid. The slightly acid solution (*ca.* 0·01N. with respect to nitric acid) was diluted to 250 ml., and the flask and contents weighed. An accurate blank was carried out on all reagents for traces of chloride and an appropriate small correction applied.

The standard silver nitrate solution was delivered from a weight burette into the titration beaker, diluted to 250 ml., and stirred by a motor-driven glass paddle. The hydrochloric acid solution to be analysed was added dropwise from a second weight burette until a very small excess of silver nitrate remained. The suspension of silver chloride was stirred in the dark for one hour. Two silver/silver chloride electrodes were then introduced, one in the main bulk of the solution and the other enclosed in a " pipette," which could be filled with, and emptied of, solution by means of an attached rubber bulb. The residual E.M.F. between these two electrodes in the same solution was frequently measured throughout the analysis and, although it seldom exceeded a few tenths of 1 mv., was applied as a correction to all the significant differential E.M.F.s. The precise end-point was determined by using tenfold weight dilutions of the reagents, added in small constant volumes (0·10—0·20 ml.) from micro-burettes, the difference in potential between the electrodes after each addition of titrant being recorded and the pipette being flushed after each such reading to bring the difference in potential to zero. Regular curves were obtained, enabling the equivalence point to be interpolated to an accuracy on the whole analysis of 1 part in 25,000. For each analysis the mean of four end-points was taken, obtained in two titrations with each of the reactants as titrant. The agreement between such end-points was well within the required limits of accuracy. A trial estimation, in which the main precipitation was carried out (*a*) by adding silver nitrate solution to the hydrochloric acid, (*b*) by the reverse addition, and (*c*) by adding both reactants slowly and simultaneously to water, showed that adsorption errors were negligible.

BIRKBECK COLLEGE, LONDON, E.C.4.

[*Received, September* 21*st*, 1950.