garding the character of these quantities and the present state of our knowledge of this subject has been made.

NEW HAVEN, CONNECTICUT RECEIVED AUGUST 12, 1932
PUBLISHED JUNE 6, 1933

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

The Dissociation of Water in Lithium Chloride Solutions[1]

BY HERBERT S. HARNED AND HARRY R. COPSON

The ionic activity coefficient and dissociation of water in lithium chloride solutions has been determined by Harned and Swindells[2] by the method involving three cells, two of which contained lithium amalgam. In the present communication these quantities and related thermodynamical quantities have been investigated through the temperature range from 15 to 35° by the more accurate method employed recently by Harned and Schupp, Harned and Mason, and particularly by Harned and Hamer.[3]

Measurements of the cells

$$H_2 \mid LiOH\ (0.01),\ LiCl(m) \mid AgCl \mid Ag,\ \ldots\ A$$
$$H_2 \mid HCl\ (0.01),\ LiCl(m) \mid AgCl \mid Ag,\ \ldots\ B$$

have been made at 15, 20, 25, 30 and 35°, containing lithium chloride at concentrations varying from 0.01 to 5 M. From these measurements the following quantities have been computed: (1) the normal electrode potential of the $Ag \mid AgCl(s) \mid Cl^-$ electrode; (2) the dissociation constant of water; (3) the activity coefficient of hydrochloric acid in lithium chloride solutions; (4) the ionic activity coefficient of water in lithium chloride solutions; (5) the dissociation of water in lithium chloride solutions; and (6), the partial molal heat content of hydrochloric acid in lithium chloride solutions.

Apparatus and Materials

The cells as well as electrodes were similar to those recently used in this Laboratory. Vacuum technique and air-free solutions were found to be necessary, particularly with the cells containing lithium hydroxide[4] solutions.

Solutions.—Lithium chloride was purified by recrystallization. A very concentrated solution was prepared and its strength determined by gravimetric analysis of the chlorine content. Its strength was known within ±0.02%.

Redistilled hydrochloric acid was diluted to approximately 0.05 M and this solution was analyzed gravimetrically. Its strength was known to within ±0.01%.

The lithium hydroxide solution was prepared by making a saturated solution, in which lithium carbonate is insoluble. The lithium carbonate was allowed to settle

---

[1] The present communication contains material presented to the Graduate School in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1932.

[2] Harned and Swindells, THIS JOURNAL, **48**, 126 (1926).

[3] Harned and Schupp, *ibid.*, **52**, 3892 (1930); Harned and Mason, *ibid.*, **54**, 3112 (1932); Harned and Hamer, *ibid.*, **55**, 2194 (1933).

[4] Harned and Ehlers, *ibid.*, **54**, 1350 (1932); Harned and Hamer, *ibid.*, **55**, 2194 (1933).

and the clear liquid siphoned off. A very small amount of barium hydroxide was added. This solution was diluted to 0.05 M and standardized by weight titration against the standard hydrochloric acid. The minute trace of barium hydroxide after dilution to 0.01 M had no effect on the accuracy of the results. The strength of the lithium hydroxide was known to within $\pm 0.03\%$.

All solutions were preserved in bottles fitted with siphons and protected from carbon dioxide by soda lime tubes. The mixed solutions of acid and salt or hydroxide and salt were prepared by adding together weighed amounts of the analyzed solutions with a little more than enough water to bring them to the desired strength. They were boiled in a vacuum in weighed flasks and correction made for the water boiled off. They were transferred to the cells without coming in contact with the air.

Experimental Results

The electromotive forces of cells A and B corrected to 1 atm. pressure of hydrogen at many salt concentrations and from 15 to 35° were first obtained. Since in practice the concentrations of the hydroxide in cell A and the acid in cell B were not exactly at 0.01 M, the first step in the calculation was to change them to this molality. In the case of cells A, this was done by the equation

$$\Delta E = \frac{RT}{NF} \ln \frac{\gamma^2_{(m+m_1)}\, 0.01}{\gamma^2_{(m+0.01)}\, m_1} \qquad (1)$$

and in case of the cells B by

$$\Delta E = \frac{RT}{NF} \ln \frac{\gamma^2_{(m+m_1)}\, (m + m_1)\, m_1}{\gamma^2_{(m+0.01)}\, (m + 0.01)\, 0.01} \qquad (2)$$

The values of γ used in these equations were read from suitable concentration plots of the activity coefficient of hydrochloric acid.

In order to make the calculations, it is necessary to know the electromotive forces of the cells A and B at the same lithium chloride concentration. To this end, we employed a method which was different from that used by Harned and Hamer. We plotted functions of the electromotive forces which are nearly linear plots and then interpolated. In the case of the hydroxide cell

$$E + \frac{RT}{NF} \ln \frac{m_{\mathrm{Cl}}}{m_{\mathrm{OH}}} - E_0$$

was plotted against μ (see Fig. 2) and in case of the acid cell

$$E + \frac{RT}{NF} \ln m_{\mathrm{H}} m_{\mathrm{Cl}}$$

was plotted against $\mu^{1/2}$. The electromotive forces of the cells containing 0.01 M hydroxide and acid at round concentrations of lithium chloride were read from these plots and are given in Tables I and II.

The Normal Electrode Potential, E_0, the Silver–Silver Chloride Electrode.—Recently, Harned and Ehlers[4] have determined the standard potential of the silver chloride electrode, E_0, from measurements of the cells B containing hydrochloric acid only. It is known that the activity coefficient of hydrochloric acid in lithium chloride solutions is nearly the

TABLE I

ELECTROMOTIVE FORCES OF THE CELLS

H_2 | LiOH (0.01), LiCl(*m*) | AgCl | Ag

AT ROUND CONCENTRATIONS OF LITHIUM CHLORIDE

μ	15°	20°	25°	30°	35°
0.02	1.04810	1.04897	1.04979	1.05061	1.05149
.03	1.03066	1.03123	1.03175	1.03227	1.03283
.05	1.01298	1.01325	1.01349	1.01369	1.01392
.06	1.00725	1.00743	1.00755	1.00764	1.00774
.10	0.99191	0.99182	0.99167	0.99153	0.99140
.11	.98911	.98898	.98883	.98858	.98844
.15	.98014	.97985	.97954	.97918	.97885
.20	.97190	.97148	.97102	.97052	.97005
.21	.97050	.97005	.96957	.96903	.96856
.25	.96550	.96498	.96441	.96380	.96322
.30	.96026	.95965	.95899	.95829	.95762
.35	.95578	.95509	.95436	.95358	.95284
.40	.95186	.95111	.95031	.94946	.94866
.45	.94835	.94755	.94668	.94578	.94493
.50	.94534	.94448	.94356	.94261	.94171
.51	.94458	.94371	.94277	.94181	.94089
1.01	.92240	.92119	.91992	.91861	.91734
1.51	.90736	.90595	.90447	.90293	.90142
2.01	.89525	.89368	.89203	.89032	.88864
2.51	.88474	.88305	.88127	.87940	.87756
3.01	.87524	.87344	.87154	.86955	.86757
3.51	.86645	.86455	.86254	.86043	.85833
4.01	.85816	.85617	.85407	.85186	.84963
4.51	.85027	.84820	.84600	.84369	.84135
5.01	.84055	.83826	.83585	.83340	.84268

TABLE II

ELECTROMOTIVE FORCES OF THE CELLS

H_2 | HCl (0.01), LiCl(*m*) | AgCl | Ag

AT ROUND CONCENTRATIONS OF LITHIUM CHLORIDE

μ	15°	20°	25°	30°	35°
0.01	0.46208	0.46311	0.46400	0.46483	0.46555
.02	.44641	.44717	.44779	.44835	.44881
.03	.43745	.43807	.43855	.43896	.43927
.05	.42619	.42664	.42696	.42720	.42733
.06	.42217	.42256	.42282	.42300	.42307
.10	.41091	.41118	.41131	.41137	.41131
.11	.40882	.40905	.40917	.40921	.40918
.15	.40202	.40219	.40220	.40215	.40197
.20	.39568	.39574	.39566	.39551	.39523
.21	.39459	.39464	.39453	.39436	.39405
.25	.39065	.39064	.39046	.39022	.38984
.30	.38632	.38625	.38602	.38572	.38526
.35	.38263	.38250	.38221	.38184	.38133
.40	.37931	.37913	.37880	.37838	.37782
.45	.37627	.37609	.37572	.37526	.37466
.50	.37352	.37328	.37289	.37240	.37178

TABLE II (*Concluded*)

μ	15°	20°	25°	30°	35°
0.51	0.37300	0.37274	0.37235	0.37185	0.37124
1.01	.35292	.35249	.35191	.35125	.35047
1.51	.33801	.33747	.33678	.33602	.33514
2.01	.32486	.32426	.32352	.32268	.32173
2.51	.31253	.31187	.31108	.31019	.30918
3.01	.30114	.30044	.29959	.29865	.29760
3.51	.29019	.28943	.28853	.28754	.28643
4.01	.27938	.27853	.27754	.27646	.27526
4.51	.26811	.26711	.26597	.26474	.26339
5.01	.25665	.25554	.25428	.25301	.25256

same as in the pure acid solutions. Therefore, if the electromotive forces of cell B be extrapolated, there should be no change of curvature at 0.01 μ, at which point lithium chloride is no longer present. Since the work of Harned and Ehlers is of a high order of accuracy, a check of their values of E_0 will be excellent confirmation of the accuracy of our measurements of the acid cells in the more dilute regions of concentration. The following extrapolation was carried out independently and simultaneously with that of Harned and Ehlers.

The electromotive forces of cells B are given by

$$E_{\mathrm{B}} = E_0 - \frac{RT}{NF} \ln a_{\mathrm{H}} a_{\mathrm{Cl}} \qquad (3)$$

or

$$E_{\mathrm{B}} + \frac{RT}{NF} \ln m_{\mathrm{H}} m_{\mathrm{Cl}} = E_0 - \frac{RT}{NF} \ln \gamma_{\mathrm{H}} \gamma_{\mathrm{Cl}} \qquad (4)$$

As suggested by Hitchcock,[5] we substitute for $\gamma_{\mathrm{H}}\gamma_{\mathrm{Cl}}$, the value obtainable from the equation

$$\ln \gamma_{\mathrm{H}} \gamma_{\mathrm{Cl}} = -2\alpha \sqrt{\mu} + \beta\mu \qquad (5)$$

and obtain

$$E_{\mathrm{B}} + \frac{RT}{NF} \ln m_{\mathrm{H}} m_{\mathrm{Cl}} - \frac{RT}{NF} 2\alpha \sqrt{\mu} = E_0 - \frac{2RT}{NF} \beta\mu \qquad (6)$$

where α, the universal constant of the Debye and Hückel theory, is given by

$$\alpha = 1.414 \times \frac{2.954 \times 10^6}{D^{3/2}\, T^{3/2}} \qquad (7)$$

and β is an empirical constant. The plot of the left side of equation (6) against μ is nearly linear, and may easily be extrapolated to zero μ where its value equals E_0. The values of the dielectric constant which we used were those obtained from Wyman's[6] data and are 82.22, 80.37, 78.54, 76.75 and 75.00 at 15, 20, 25, 30 and 35°, respectively. The values of $\alpha/2.303$ calculated by equation (7) are 0.498, 0.502, 0.506, 0.511 and 0.516 at these temperatures. The plots are shown in Fig. 1. In Table III are the values obtained for E_0 along with those obtained by Harned and Ehlers. The agreement leaves little to be desired and confirms the accuracy of the acid cells containing the lithium chloride.

---

(5) Hitchcock, THIS JOURNAL, **50,** 2076 (1928).

(6) Wyman, *Phys. Rev.*, **35,** 623 (1930).

TABLE III

THE NORMAL POTENTIAL OF THE SILVER–SILVER CHLORIDE ELECTRODE

T	E_0	E_0 (H. and E.)	ΔE_0 (mv.)
288.1	0.22846	0.22847	−0.01
293.1	.22548	.22551	− .03
298.1	.22237	.22239	− .02
303.1	.21915	.21912	+ .03
308.1	.21567	.21563	+ .04

The Dissociation Constant of Water.—The evaluation of the dissociation constant of water was made simultaneously with that made by Harned and Hamer, and was carried out by the two methods of extrapolation described by them. We employed for the first method their equation (10), namely

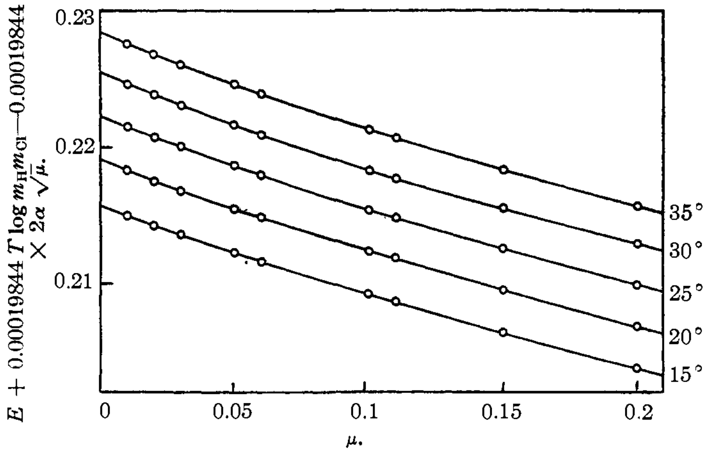

Fig. 1.—Illustrating the extrapolation of the normal electrode potential of the silver–silver chloride electrode according to equation (6).

$$E_{\mathrm{A}} - E_0 + \frac{RT}{NF}\ln\frac{m_{\mathrm{Cl}}}{m_{\mathrm{OH}}} = \frac{RT}{NF}\ln\frac{\gamma_{\mathrm{H}}\gamma_{\mathrm{OH}}}{a_{\mathrm{H_2O}}} - \frac{RT}{NF}\ln K - \frac{RT}{NF}\ln\gamma_{\mathrm{H}}\gamma_{\mathrm{Cl}} \qquad (8)$$

In Fig. 2 (circles), the values of the left side of this equation are plotted against μ and extrapolated to zero μ, at which point the ordinate equals $-0.00019844\, T \log K$.

To apply the second method, which employs cells A and B and the Debye and Hückel theory, we make use of equation (16) of Harned and Hamer, which is

$$E_{\mathrm{A}} - E_{\mathrm{B}} - \frac{RT}{NF}\ln\frac{m''_{\mathrm{H}} m''_{\mathrm{Cl}} m'_{\mathrm{OH}}}{m'_{\mathrm{Cl}}} + \frac{RT}{NF}\frac{5.908 \times 10^6}{D^{3/2}\, T^{3/2}}\sqrt{2\mu} = -\frac{RT}{NF}\ln K + \beta\mu \qquad (9)$$

The second set of curves in Fig. 2 (inked circles) represents a plot of the left side of this equation against μ, and as in the first method the value of the function equals $-0.00019844\, T \log K$ at zero μ.

The present cells containing lithium chloride are particularly valuable for obtaining this extrapolation since the plots by the first and second methods have slopes of opposite signs and approach the same limiting values from quite different directions. We feel certain that we have obtained the correct value of the intercept within ±0.04 mv. Further, the values check those of Harned and Hamer within these limits. 0.452, 0.681, 1.008, 1.472 and 2.088 were obtained for $K \times 10^{14}$ at 15, 20, 25, 30, and 35° with a probable error of less than ±0.2%. This agreement confirms the accuracy of the cells A which contain the hydroxide.

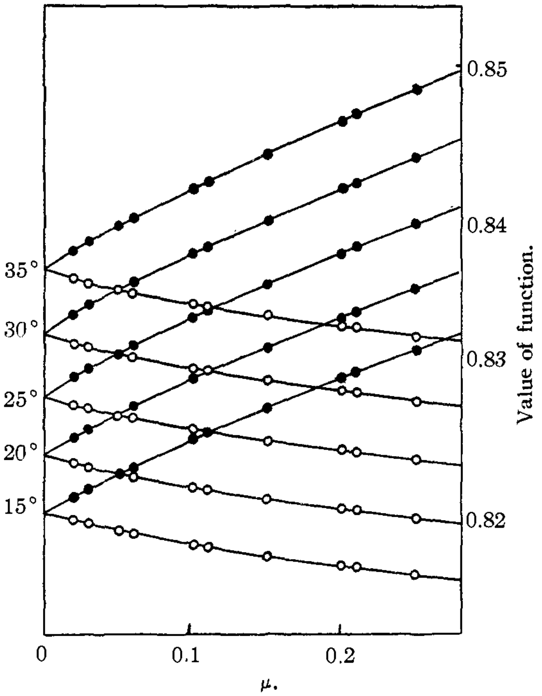

Fig. 2.—Illustrating the extrapolation of the dissociation constant of water by equation (8) and also by equation (9): ○, equation (8); ●, equation (9).

The Activity Coefficient of Hydrochloric Acid in Lithium Chloride Solutions.—If the electromotive force, E_B, of the cell B containing salt be subtracted from that, $E_{0.01}$, which contains only 0.01 M hydrochloric acid, the electromotive force, $E_{0.01} - E_B$, of the cell

$$\mathrm{Ag} \mid \mathrm{AgCl} \mid \mathrm{HCl}\ (0.01),\ \mathrm{LiCl}(m) \mid \mathrm{H_2} \mid \mathrm{HCl}\ (0.01) \mid \mathrm{AgCl} \mid \mathrm{Ag}$$

is obtained. The activity coefficient, γ in the salt solutions can readily be obtained by means of the equation

$$\log \gamma = \log \gamma_{0.01} + \frac{(E_{0.01} - E_B)NF}{4.606\,RT} - \log \sqrt{\frac{(0.01 + m)}{0.01}} \qquad (10)$$

if its value, $\gamma_{0.01}$, at 0.01 M is known. These reference values were taken from the compilation of Harned and Ehlers and are given in the first row of

Table IV. The values of the activity coefficients in the salt solutions are also given in this table. At 25°, these values check those of Harned and Swindells to within 0.2 mv. up to 1 *M*. Above that concentration the agreement is not so good. The present values are more consistent and should be better since a vacuum technique was employed.[2]

TABLE IV

ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID IN LITHIUM CHLORIDE SOLUTIONS

μ	15°	20°	25°	30°	35°
0.01	0.905	0.905	0.904	0.903	0.902
.02	.878	.878	.880	.878	.876
.03	.859	.859	.860	.858	.856
.05	.834	.835	.835	.832	.830
.06	.826	.826	.826	.823	.821
.10	.802	.801	.800	.798	.794
.11	.798	.797	.795	.792	.788
.15	.784	.782	.780	.776	.773
.20	.771	.769	.767	.763	.760
.21	.769	.767	.765	.761	.758
.25	.763	.761	.759	.755	.752
.30	.760	.758	.756	.752	.749
.35	.758	.756	.754	.749	.746
.40	.758	.756	.753	.749	.746
.45	.760	.757	.754	.750	.746
.50	.762	.759	.756	.751	.747
.51	.762	.759	.756	.752	.748
1.01	.812	.806	.800	.792	.786
1.51	.896	.887	.878	.868	.857
2.01	1.012	.999	.985	.971	.957
2.51	1.161	1.142	1.123	1.104	1.084
3.01	1.334	1.308	1.283	1.256	1.231
3.51	1.540	1.506	1.473	1.439	1.407
4.01	1.791	1.748	1.707	1.664	1.624
4.51	2.119	2.066	2.016	1.965	1.929
5.01	2.533	2.465	2.402	2.333	2.229

The Ionic Activity Coefficient and Dissociation of Water in Lithium Chloride Solutions.—Since the left side of equation (8) is known, $\gamma_H\gamma_{OH}/a_{H_2O}$, can readily be obtained after substituting the values of K and of $\gamma_H\gamma_{Cl}$ given in Table IV. Our results at 25° agree within 0.7 mv. with those determined in the 0.1 *M* series by Harned and Swindells. This agreement is good when we consider that their computations involved three cells, two of which contained lithium amalgam. The present values are more consistent and unquestionably better.

The values of the concentration product, m_Hm_{OH}, computed from the data in Table V and the appropriate values of K by the fundamental equation

$$K = \frac{\gamma_H\gamma_{OH}}{a_{H_2O}}\, m_Hm_{OH} \tag{11}$$

are plotted in Fig. 3.

TABLE V

THE IONIC ACTIVITY COEFFICIENT OF WATER IN LITHIUM CHLORIDE SOLUTIONS, $\gamma_H\gamma_{OH}/a_{H_2O}$

μ	15°	20°	25°	30°	35°
0.02	0.756	0.758	0.759	0.759	0.758
.03	.717	.718	.719	.718	.717
.05	.664	.663	.665	.664	.662
.06	.645	.646	.645	.644	.642
.10	.591	.590	.589	.587	.584
.11	.581	.580	.579	.575	.572
.15	.546	.544	.543	.540	.536
.20	.515	.513	.511	.508	.505
.21	.510	.508	.506	.503	.500
.25	.493	.491	.489	.486	.483
.30	.478	.476	.474	.471	.468
.35	.466	.464	.462	.459	.456
.40	.456	.454	.452	.449	.447
.45	.449	.446	.443	.440	.440
.50	.442	.439	.437	.433	.431
.51	.441	.438	.435	.432	.430
1.01	.409	.405	.400	.395	.390
1.51	.408	.402	.397	.390	.383
2.01	.427	.418	.410	.401	.393
2.51	.459	.449	.438	.427	.416
3.01	.496	.483	.470	.456	.442
3.51	.541	.525	.509	.492	.475
4.01	.600	.581	.562	.542	.522
4.51	.687	.666	.644	.621	.598
5.01	.803	.777	.751	.720	.692

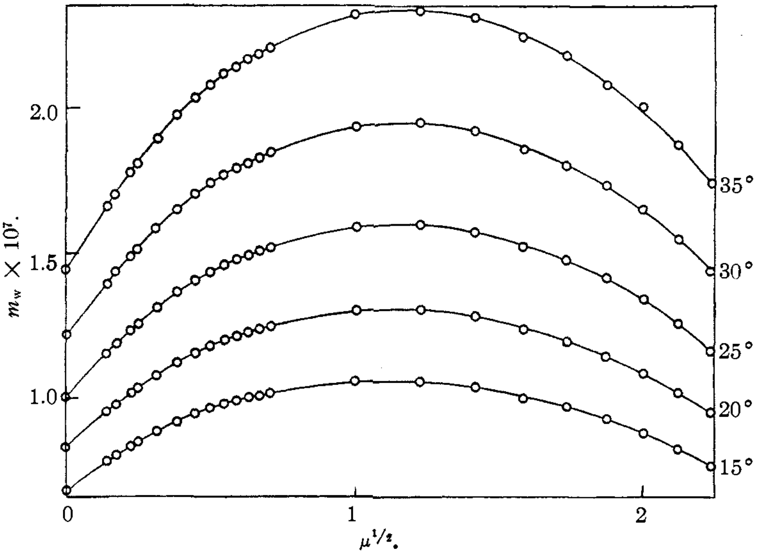

Fig. 3.—Plots of $m_w \times 10^7$ against $\mu^{1/2}$.

The Partial Molal Heat Content of Hydrochloric Acid in Lithium Chloride Solutions.—Since the electromotive forces were obtained at only five temperatures, we have not resorted to the method of least squares but have employed the graphical method of Harned and Nims[7] to determine the constants of the equations which express E as a function of T, namely

$$E^\circ_{\mathrm{B}} = E^\circ_{25} + a(T - 25) + b(T - 25)^2 \qquad (12)$$

when no salt is present, and

$$E_{\mathrm{B}} = E_{25} + a'(T - 25) + b'(T - 25)^2 \qquad (13)$$

when salt is present. By plotting the first order differences against T, the values of a, b, a', and b' given in Table VI were obtained. As far as could be ascertained from these results the values of b and b' were the same at all concentrations. This indicates that $(\overline{C}_p - \overline{C}_{p0.01})$ equals zero, and consequently $(\overline{H} - \overline{H}_{0.01})$ does not vary with the temperature. This is hardly likely, and is probably due to the fact that the electromotive forces have not been measured over a wide enough temperature range to establish this variation. We may take the result to mean that from 15 to 35° $(\overline{H} - \overline{H}_{0.01})$ varies little and that $(\overline{C}_p - \overline{C}_{p0.01})$ is small. The values of $(\overline{H} - \overline{H}_{0.01})$ were calculated by the Gibbs–Helmholtz equation. The results are given in the third and sixth columns of Table VI.

TABLE VI

RELATIVE PARTIAL MOLAL HEAT CONTENT OF HYDROCHLORIC ACID IN LITHIUM CHLORIDE SOLUTIONS AT 25°

$b = b' = -2.2 \times 10^{-6}$

μ	$a \times 10^6$	$(\overline{H} - \overline{H}_{0.01})$	μ	$a \times 10^6$	$(\overline{H} - \overline{H}_{0.01})$
0.01	172	0	0.4	− 75	267
.02	119	9	.45	− 81	298
.03	89	16	.5	− 85	335
.05	55	50	.51	− 88	327
.06	44	90	1.01	−122	565
.1	19	164	1.51	−143	769
.11	17	199	2.01	−157	979
.15	− 3	222	2.51	−169	1183
.2	− 23	236	3.01	−177	1393
.21	− 29	221	3.51	−189	1566
.25	− 41	232	4.01	−206	1703
.3	− 53	252	4.51	−237	1756
.35	− 65	258	5.01	−259	1874

Summary

1. The electromotive forces of the cells

H_2 | LiOH (0.01), LiCl(m) | AgCl | Ag, and
H_2 | HCl (0.01), LiCl(m) | AgCl | Ag

have been determined at 15, 20, 25, 30 and 35°; m has been varied from 0.01 to 5 M.

---

[7] Harned and Nims, THIS JOURNAL, **54**, 423 (1932).

2. The standard potential of the Ag | AgCl | Cl^- electrode has been determined from the cells containing acid and salt, and excellent agreement obtained with the values recently recorded by Harned and Ehlers.

3. The dissociation constant of water has been determined by using both a method depending on E_0, and a method depending on the electromotive forces of the acid and hydroxide–salt cell. The values of K agree within the estimated limit of accuracy (± 0.04 millivolt) with those determined simultaneously by Harned and Hamer.

4. The activity coefficient of hydrochloric acid in the lithium chloride solutions has been computed.

5. The ionic activity coefficient and dissociation of water in lithium chloride solutions have been computed.

6. The partial molal heat content of hydrochloric acid in lithium chloride solutions has been calculated.

NEW HAVEN, CONNECTICUT

RECEIVED AUGUST 12, 1932
PUBLISHED JUNE 6, 1933

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

A Calorimetric Method for Determining the Rates of Interdiffusion of Reacting Liquids

BY FREDERICK BARRY AND ALLAN KAY SMITH

The calorimetric study described in this paper was suggested by Professor H. A. Fales,[1] who called our attention to the fact that physicochemical determinations which necessitate the measurement of electrode potentials are limited at present in both accuracy and scope because we have no means of measuring directly the values of the liquid potentials which are established whenever dissimilar solutions are placed in juxtaposition, as for instance in the salt bridges of primary cells.[2] Such potentials are always associated with the interdiffusion of electrolytes, and are generally assumed to be caused by the oppositely directed movements of ions across a liquid interface. If this assumption is valid, it should be possible to calculate their values from the rates of ionic interdiffusion, if these can be

---

(1) Our indebtedness to Professor Fales for this suggestion which has led to the recognition of several new possibilities in adiabatic calorimetry, is increased by his further criticisms and interpretations of various findings, in the light of their bearing upon general theoretical considerations not here discussed.

(2) In the absence of definite knowledge in this matter, many formulas have been deduced from theoretical premises for calculating liquid junction potentials, among which the best known are those of Nernst, *Z. physik. Chem.*, **2**, 613 (1888); **4**, 129 (1889); Planck, *Wied. Ann.*, **39**, 161 (1889); **40**, 561 (1890); Henderson, *Z. physik. Chem.*, **59**, 118 (1906); Lewis and Sargent, THIS JOURNAL, **31**, 363 (1909); MacInnes, *ibid.*, **37**, 2391 (1915). These are either based on diverse and incompletely verified assumptions, or are applicable only to particular combinations of electrolytes. They are, consequently, of questionable dependability in precise experimental work, excepting in special cases, and the desirability of actual measurements with which to test the assumptions upon which they severally rest is correspondingly clear.