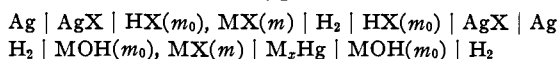


[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

The Ionization Constant of Water and the Dissociation of Water in Potassium Chloride Solutions from Electromotive Forces of Cells without Liquid Junction¹

BY HERBERT S. HARNED AND WALTER J. HAMER

In a series of earlier contributions² the ionic activity coefficient of water was determined at 25° in a number of salt solutions by the combined measurements of three cells of the types



and



More recently, Harned and Schupp,⁴ and Harned and Mason⁵ have shown that the same quantities can be determined with greater certainty by the more easily measurable cells



and



Since this was found to be the case, and since the latter cells are readily adapted for investigating the effect of temperature, we have greatly extended this work both in scope and accuracy by their use. In the present study, aqueous solutions of potassium chloride are considered. Values of the dissociation constant of water from 0 to 60° have been evaluated as well as the heat of ionization of water. The ionic activity coefficient of water, $\sqrt{\gamma_{\text{H}}\gamma_{\text{OH}}/a_{\text{H}_2\text{O}}}$, and the dissociation, $m_{\text{H}}m_{\text{OH}}$, have been determined from 0 to 60° throughout the concentration range from 0 to 3.5 *M*. Other important data involving activity coefficients and relative partial molal heat contents of hydrochloric acid in potassium chloride solutions have also been evaluated.

Apparatus and Materials

Cells.—A vacuum technique with air freed solutions was employed. The cells were of the usual H-type, were fixed in the thermostat and had their drainage tubes through the bottom of the thermostat. At temperatures above 45°, the solubility of silver chloride was sufficient to cause plating out of the silver on the hydrogen electrode. This produced a gradual lowering of the electromotive force due both to the slight

(1) The present communication contains material presented to the Graduate School in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1932.

(2) Harned, *THIS JOURNAL*, **47**, 930 (1925); Harned and Swindells, *ibid.*, **48**, 126 (1926); Harned and James, *J. Phys. Chem.*, **30**, 1060 (1926); Harned, *Z. physik. Chem.*, **27**, 411 (1926); Harned and Åkerlöf, *Physik. Z.*, **117**, 1 (1926).

(3) A general survey of the use of this method is given by Harned in Chap. XII, pp. 806 to 808, of Taylor, "Treatise on Physical Chemistry," 2d edition. D. Van Nostrand Co., New York, 1931.

(4) Harned and Schupp, *THIS JOURNAL*, **52**, 3892 (1930).

(5) Harned and Mason, *ibid.*, **54**, 3112 (1932).

increase in hydrogen-ion concentration and the covering of silver on the hydrogen electrode which prevented the absorption of the hydrogen gas. This difficulty was easily eliminated by inserting 20 cm. of a capillary tube (3-mm. bore) between the two electrode compartments of the cell.

Hydrogen.—The first measurements were made with hydrogen generated by electrolysis of a concentrated sodium hydroxide solution. Later, tank hydrogen purified by passing over copper heated to 700° was employed. Identical results were obtained with the gas from these two sources.

Hydrogen Electrodes.—Platinum foil electrodes were used. These were plated in a chloroplatinic acid solution for three to four minutes at a current density of 400 milliamperes. At the temperatures above 45°, they were coated two minutes longer. This prevented a slight fluctuation in electromotive force which occurred at the higher temperatures when too thinly plated electrodes were employed.

Silver–Silver Chloride Electrodes.—The electrodes were of type (2) described by Harned.⁶ Freshly prepared hydrogen and silver–silver chloride electrodes were employed in each cell.

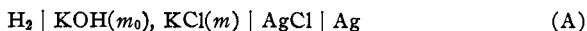
Hydrochloric Acid.—Twice distilled hydrochloric acid was analyzed gravimetrically, and diluted to desired strength. The concentration of the solutions was known with an accuracy of $\pm 0.01\%$.

Potassium Chloride.—An analyzed chemical of high grade was twice recrystallized, and kept dry in an oven at 110°.

Potassium Hydroxide.—The potassium hydroxide solution was made carbonate free by adding to the saturated solution a barium hydroxide solution until no further precipitation of carbonate occurred. The solution gave no sulfuric acid test for the barium ion. This solution was diluted to desired strength and analyzed by titration against the standard acid. The estimated accuracy of this titration was $\pm 0.02\%$.

Experimental Results

Constant measurements of the cell



were obtained, although it is somewhat more difficult to measure than the similar cell containing hydrochloric acid in place of the hydroxide. A very extensive series of measurements of the cells containing approximately 0.01 *M* potassium hydroxide was made at forty concentrations of salt which was varied from 0.005 to 3.5 *M* and at temperatures from 0 to 60° at 5° intervals. Each measurement was the mean of four cells which in all cases agreed within ± 0.03 mv.

These results were first corrected to round concentrations of hydroxide by use of the equation

$$\Delta E = \frac{RT}{NF} \ln \frac{m_{\text{Cl}} m'_{\text{OH}}}{m_{\text{OH}} m'_{\text{Cl}}} \quad (1)$$

where *m* represents the experimental molalities and *m'* the desired molality, which in the present instance is 0.01 *M* potassium hydroxide. This involves the assumption that the activity coefficients are constant over the very small concentration range under consideration. No appreciable error is involved by this procedure.

If the first order differences in the electromotive forces at the different

(6) Harned, *THIS JOURNAL*, **51**, 416 (1929).

temperatures are plotted against T ,⁷ straight lines are obtained as shown by Fig. 1. This is very sensitive as witnessed by the ordinate, which is given in tenths of millivolts. The maximum deviation of the experimental results from the curves is ≈ 0.05 mv., but the great majority of the points lie considerably closer than this. Taking the 25° electromotive forces to be correct, the values at the other temperatures were smoothed from these graphs. The electromotive forces at round concentrations obtained by this procedure are given in Table I.

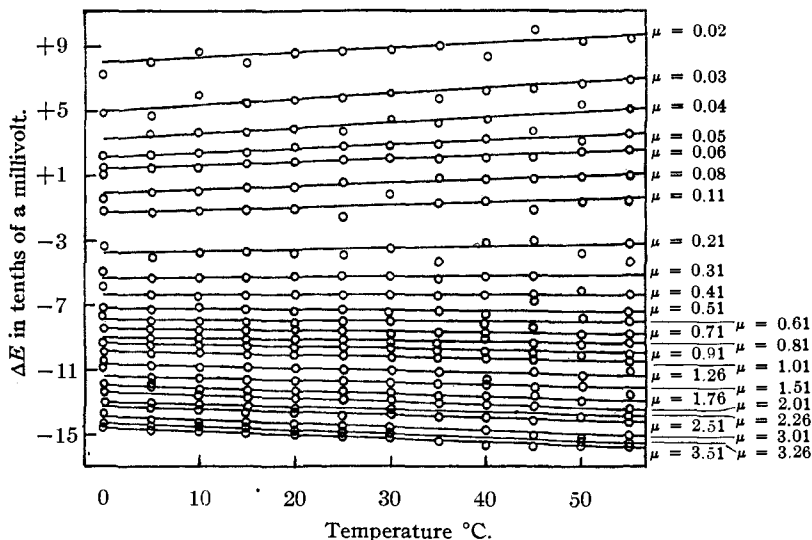


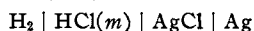
Fig. 1.—Plots of the first order differences of electromotive force of the Cell A, $E_{t-5} - E_t$, against the temperature.

The observed measurements of the electromotive forces of the cells

$$\text{H}_2 \mid \text{HCl}(m_0), \text{KCl}(m) \mid \text{AgCl} \mid \text{Ag} \quad (\text{B})$$

were treated in a manner exactly similar to the hydroxide cells and the smoothed results at round concentrations are given in Table II. The results of the cell without salt containing 0.01 M hydrochloric acid agree within a few hundredths of a millivolt with those obtained by Harned and Ehlers.⁸

The Ionization Constant of Water from 0 to 60° at 5° Intervals.—The dissociation constant of water may be determined by two methods. The first involves the cells of the type A containing the hydroxide-salt mixtures and the normal potential, E_0 , of the cell



The second method involves the measurements of both the cells A and B containing the hydroxide-chloride mixtures, and the acid-chloride mix-

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

(8) Harned and Ehlers *ibid.*, **54**, 1350 (1932).

TABLE I

ELECTROMOTIVE FORCES OF THE CELL: $H_2 \mid KOH (0.01), KCl(m) \mid AgCl \mid Ag$, CORRECTED BY ΔE AGAINST TEMPERATURE PLOTS													
μ	0°	5°	10°	15°	20°	25°	30°	35°	40°	45°	50°	55°	60°
0.01	1.04615	1.04695	1.04777	1.04860	1.04944	1.05030	1.05117	1.05210	1.05295	1.05386	1.05479	1.05573	1.05669
.02	1.04618	1.04698	1.04780	1.04863	1.04947	1.05033	1.05120	1.05208	1.05298	1.05389	1.05482	1.05576	1.05673
.03	1.02990	1.03040	1.03092	1.03147	1.03203	1.03260	1.03318	1.03376	1.03438	1.03501	1.03566	1.03634	1.03703
.04	1.02040	1.02073	1.02109	1.02146	1.02183	1.02223	1.02264	1.02305	1.02348	1.02393	1.02439	1.02485	1.02535
.05	1.01364	1.01385	1.01408	1.01433	1.01458	1.01486	1.01515	1.01545	1.01576	1.01609	1.01643	1.01678	1.01713
.06	1.00841	1.00855	1.00869	1.00883	1.00903	1.00922	1.00942	1.00961	1.00982	1.01002	1.01023	1.01048	1.01073
.08	1.00054	1.00053	1.00053	1.00054	1.00057	1.00061	1.00067	1.00074	1.00082	1.00090	1.00098	1.00107	1.00117
.11	0.99217	0.99204	0.99192	0.99181	0.99170	0.99160	0.99151	0.99143	0.99136	0.99129	0.99123	0.99118	0.99114
.21	.97605	.97567	.97529	.97492	.97455	.97418	.97380	.97344	.97309	.97274	.97239	.97204	.97170
.31	.96680	.96626	.96571	.96518	.96464	.96410	.96357	.96304	.96251	.96198	.96145	.96093	.96041
.41	.96029	.95965	.95901	.95837	.95773	.95708	.95643	.95578	.95513	.95448	.95383	.95318	.95283
.51	.95537	.95464	.95391	.95318	.95244	.95170	.95096	.95022	.94948	.94873	.94798	.94723	.94648
.61	.95138	.95058	.94978	.94898	.94817	.94736	.94655	.94574	.94492	.94410	.94328	.94246	.94164
.71	.94805	.94720	.94634	.94548	.94462	.94375	.94288	.94201	.94113	.94025	.93936	.93847	.93758
.81	.94517	.94427	.94337	.94246	.94154	.94062	.93970	.93877	.93784	.93690	.93596	.93501	.93406
.91	.94271	.94177	.94082	.93987	.93891	.93795	.93698	.93600	.93502	.93403	.93304	.93204	.93104
1.01	.94065	.93966	.93866	.93766	.93665	.93564	.93462	.93360	.93257	.93153	.93049	.92944	.92839
1.26	.93604	.93497	.93389	.93280	.93171	.93061	.92950	.92838	.92726	.92613	.92500	.92386	.92271
1.51	.93234	.93120	.93005	.92890	.92774	.92657	.92539	.92420	.92301	.92181	.92060	.91939	.91817
1.76	.92955	.92835	.92714	.92592	.92469	.92346	.92224	.92097	.91971	.91844	.91717	.91587	.91460
2.01	.92703	.92579	.92454	.92328	.92201	.92073	.91934	.91804	.91673	.91541	.91408	.91274	.91139
2.26	.92501	.92371	.92240	.92108	.91975	.91841	.91706	.91571	.91435	.91297	.91159	.91020	.90880
2.51	.92309	.92176	.92042	.91908	.91772	.91635	.91497	.91358	.91218	.91077	.90935	.90792	.90648
2.81				.91806	.91566	.91424	.91282	.91139					
3.01	.92004	.91864	.91723	.91580	.91437	.91292	.91146	.90999	.90851	.90702	.90652	.90401	.90249
3.26	.91875	.91732	.91587	.91441	.91294	.91146	.90997	.90847	.90675	.90542	.90388	.90233	.90077
3.51	.91751	.91605	.91458	.91310	.91160	.91009	.90857	.90705	.90550	.90394	.90237	.90079	.89920

TABLE II

ELECTROMOTIVE FORCES OF THE CELL: $\text{H}_2 \mid \text{HCl} (0.01), \text{KCl}(m) \mid \text{AgCl} \mid \text{Ag}$, CORRECTED BY THE ΔE AGAINST TEMPERATURE PLOTS

μ	0°	5°	10°	15°	20°	25°	30°	35°	40°	45°	50°	55°	60°
0.01	0.45789	0.45945	0.46086	0.46212	0.46323	0.46420	0.46501	0.46567	0.46618	0.46653	0.46673	0.46678	0.46668
.02	.44318	.44448	.44563	.44663	.44749	.44821	.44878	.44920	.44948	.44961	.44960	.44944	.44914
.03	.43473	.43589	.43690	.43777	.43849	.43906	.43948	.43975	.43988	.43986	.43969	.43938	.43892
.04	.42876	.42981	.43072	.43148	.43210	.43258	.43291	.43310	.43314	.43304	.43280	.43241	.43188
.06	.42044	.42135	.42212	.42274	.42321	.42354	.42372	.42376	.42365	.42339	.42299	.42245	.42176
.11	.40814	.40881	.40934	.40973	.40999	.41012	.41011	.40996	.40970	.40928	.40872	.40803	.40723
.21	.39491	.39536	.39567	.39585	.39589	.39580	.39557	.39520	.39470	.39406	.39329	.39238	.39134
.51	.37664	.37677	.37675	.37661	.37634	.37595	.37543	.37478	.37401	.37312	.37210	.37096	.36970
1.01	.35935	.35920	.35893	.35854	.35803	.35741	.35667	.35580	.35481	.35370	.35247	.35112	.34965
1.51	.34816	.34784	.34741	.34687	.34622	.34546	.34459	.34361	.34252	.34132	.34001	.33859	.33706
2.01	.33887	.33842	.33786	.33720	.33644	.33559	.33464	.33358	.33242	.33115	.32978	.32831	.32674
3.01	.32430	.32368	.32296	.32215	.32125	.32026	.31917	.31799	.31681	.31534	.31387	.31231	.31066
3.51	.31830	.31762	.31685	.31599	.31504	.31400	.31287	.31165	.31034	.30894	.30745	.30587	.30421

TABLE III

THE IONIZATION CONSTANT AND HEAT OF IONIZATION OF WATER

Temp., °C.	K_w (exp.) $\times 10^{14}$	K_w (eq.) $\times 10^{14}$	ΔH_i	ΔC_p
0	0.115 \pm 0.0003	0.115	14,513	-40.1
5	.186 \pm .0004	.186	14,312	-40.6
10	.293 \pm .0005	.293	14,109	-41.0
15	.452 \pm .001	.452	13,901	-41.5
20	.681 \pm .001	.681	13,692	-42.0
25	1.008 \pm .001	1.008	13,481	-42.5
30	1.471 \pm .002	1.460	13,267	-43.0
35	2.088 \pm .004	2.081	13,051	-43.4
40	2.916 \pm .005	2.915	12,833	-43.9
45	4.016 \pm .006	4.019	12,612	-44.4
50	5.476 \pm .008	5.469	12,390	-44.9
55	7.297 \pm .013	7.297	12,164	-45.3
60	9.614 \pm .020	9.637	11,936	-45.8

tures, respectively. We shall employ both methods. For the first, the electromotive forces in Table I and the E_0 values of Harned and Ehlers⁸ will be employed, and in the second method, the electromotive forces in Tables I and II will be used. This affords an excellent check both upon the values of E_0 , and upon the general accuracy of all these results.

The electromotive forces of the cells of the type A are given by

$$E_A = E_0 - \frac{RT}{NF} \ln \gamma_H \gamma_{Cl} m_{HCl} \quad (2)$$

The equilibrium constant for the ionization of water is

$$K = \frac{\gamma_H \gamma_{OH}}{a_{H_2O}} m_{H} m_{OH} \quad (3)$$

Elimination of m_H from (2) and (3), and rearrangement of resulting terms gives

$$E_A - E_0 + \frac{RT}{NF} \ln \frac{m_{Cl}}{m_{OH}} = \frac{RT}{NF} \ln \frac{\gamma_H \gamma_{OH}}{a_{H_2O}} - \frac{RT}{NF} \ln K - \frac{RT}{NF} \ln \gamma_H \gamma_{Cl} \quad (4)$$

If the left side of equation (4) be plotted against μ , its value at zero μ is equal to $(-RT/NF \ln K)$, since at zero μ , a_{H_2O} is unity, and by reason of the definition of activity coefficients, the two other members on the right of the equation vanish.⁹ The values of E_0 necessary for this calculation were those determined by Harned and Ehlers, namely, 0.23634, 0.23392, 0.23126, 0.22847, 0.22551, 0.22239, 0.21912, 0.21563, 0.21195, 0.20821, 0.20437, 0.20035 and 0.19620, at 0, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55 and 60°, respectively.⁸ A large plot was made of the function

$$E_A - E_0 + \frac{RT}{NF} \ln \frac{m}{m_0}$$

against $(m + m_0)$, and since so many experimental points were available at the lower concentrations, the extrapolation could be made with a very high degree of accuracy. The character of the plots is apparent from Fig. 2, although for the purpose of clearness many of the points have been omitted. The fact that the curves are nearly straight and possess a reasonably small slope increases the value of this extrapolation. The values of the ionization constant, K , computed from the extrapolated values of the above function are given in the second column of Table III. The values check those given by Lewis and Randall¹⁰ to within 1% except at temperatures above 25°, at which temperatures the check is within 3%. At 25° our value of 1.008 is in close agreement with 1.005 which was computed by Lewis, Brighton and Sebastian.¹¹

The Heat of Ionization of Water from 0 to 60°.— K varies with the temperature according to the equation of van't Hoff

$$\frac{d \log K}{dT} = \frac{\Delta H_i}{RT^2} \quad (5)$$

(9) Roberts, *THIS JOURNAL*, **52**, 3877 (1930); Harned and Schupp, Jr., *ibid.*, **52**, 3892 (1930), have employed this equation for similar purposes.

(10) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923, p. 486.

(11) Lewis, Brighton and Sebastian, *THIS JOURNAL*, **39**, 2245 (1917).

in which ΔH_i is the heat of ionization. We assume that ΔH_i varies with T according to

$$\Delta H_i = A + BT + CT^2 \quad (6)$$

Upon substitution of (6) in (5) and integration we obtain

$$\log K = -\frac{A}{2.303 RT} + \frac{B}{R} \log T + \frac{C}{2.303 R} T + D \quad (7)$$

Since K has been evaluated at thirteen temperatures, we obtained thirteen equations, the constants of which were evaluated by the method of least squares. The equation with the numerical values is

$$\log K = -\frac{4787.3}{T} - 7.1321 \log T - 0.010365 T + 22.801 \quad (8)$$

The values of K computed by this equation are given in the third column of Table III.

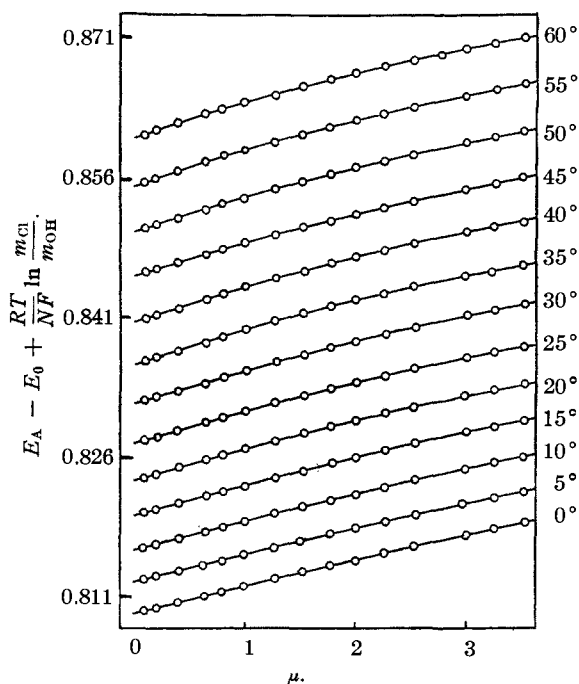


Fig. 2.—Plots employed for the determination of the dissociation constant of water by means of equation (4).

The heat of ionization is given in calories by

$$\Delta H_i = 21,926 - 14.18212 T - 0.04746 T^2 \quad (9)$$

and, ΔC_p , or $C_p(\text{H}_2\text{O}) - (C_p(\text{H}^+) + C_p(\text{OH}^-))$, by

$$\Delta C_p = -14.18212 - 0.09492 T \quad (10)$$

Values of ΔH_i and ΔC_p computed by these equations are given in the fourth and fifth columns of Table III. The ΔH_i value at 20° checks the

value, 13,693, obtained by Richards and Rowe.¹² At 18° we obtain 13,776 which agrees with 13,780 computed by Lewis and Randall¹⁰ from Wörmann's¹³ data, but is considerably higher than that recently computed by Rossini.¹⁴

The Method of Evaluation of K from Cells of Types A and B which is Independent of E_0 .—If we represent the electromotive forces of the cells A by

$$E_A = E_0 - \frac{RT}{NF} \ln m'_H m'_{Cl} \gamma'_H \gamma'_{Cl} \quad (11)$$

and the cells B by

$$E_B = E_0 - \frac{RT}{NF} \ln m''_H m''_{Cl} \gamma''_H \gamma''_{Cl} \quad (12)$$

and subtract, we obtain

$$E_A - E_B = + \frac{RT}{NF} \ln \frac{\gamma''_H \gamma''_{Cl} m''_H m''_{Cl}}{\gamma'_H \gamma'_{Cl} m'_H m'_{Cl}} = + \frac{RT}{NF} \ln \frac{m''_H m''_{Cl}}{m'_H m'_{Cl}} \quad (13)$$

if we assume that the activity coefficient of hydrochloric acid is the same in the acid-chloride mixtures as in the hydroxide-chloride mixtures at the same ionic strength. The acid and hydroxide are at a sufficiently low concentration to render this assumption justifiable. If we substitute for m'_H its value derivable from equation (3), we obtain

$$E_A - E_B = + \frac{RT}{NF} \ln \frac{m''_H m''_{Cl} m'_{OH}}{m'_{Cl}} + \frac{RT}{NF} \ln \frac{\gamma_H \gamma_{OH}}{\alpha_{H_2O}} - \frac{RT}{NF} \ln K \quad (14)$$

In dilute solution

$$\ln \frac{\gamma_H \gamma_{OH}}{\alpha_{H_2O}} = -2 \times \frac{2.954 \times 10^6}{D^{3/2} T^{3/2}} \sqrt{2\mu} + \beta\mu \quad (15)$$

which is simply the limiting law of the theory of Debye and Hückel with an additional linear term. Substitution in equation (14) gives, upon rearrangement of terms

$$E_A - E_B - \frac{RT}{NF} \ln \frac{m''_H m''_{Cl} m'_{OH}}{m'_{Cl}} + \frac{RT}{NF} \frac{5.908 \times 10^6}{D^{3/2} T^{3/2}} \sqrt{2\mu} = - \frac{RT}{NF} \ln K + \beta\mu \quad (16)$$

Since E_A and E_B are the measured electromotive forces, and m''_H , m''_{Cl} , m'_{OH} and m'_{Cl} are known concentrations, the left side of this equation is known, and if it be plotted against μ its value at zero μ is $-(RT/NF) \ln K$. Wyman's¹⁵ values of the dielectric constant were used. The character of the extrapolation is shown in Fig. 3. For the sake of brevity further numerical data have been omitted. We can sum the matter up with the statement that the values of K obtained by this method are the same as those obtained by the method involving E_0 within the estimated limit of accuracy which is ± 0.04 mv. This constitutes an excellent confirmation of both the accuracy of these results and the values of E_0 determined by Harned and Ehlers.

(12) Richards and Rowe, *THIS JOURNAL*, **44**, 684 (1922).

(13) Wörmann, *Ann. Physik*, [4] **18**, 775 (1905).

(14) Rossini, *Bur. Standards J. Research*, **6**, No. 309 (1931).

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

TABLE IV
ACTIVITY COEFFICIENTS OF 0.01 MOLAL HYDROCHLORIC ACID IN POTASSIUM CHLORIDE SOLUTIONS

μ	0°	5°	10°	15°	20°	25°	30°	35°	40°	45°	50°	55°	60°
0.01	0.903	0.905	0.905	0.905	0.904	0.904	0.904	0.902	0.900	0.899	0.900	0.900	0.900
.02	.873	.874	.875	.874	.873	.873	.873	.870	.869	.867	.866	.865	.864
.03	.853	.854	.852	.853	.852	.851	.851	.849	.848	.845	.844	.844	.843
.04	.838	.840	.839	.839	.837	.836	.836	.833	.832	.829	.828	.826	.825
.06	.817	.818	.816	.817	.815	.815	.814	.811	.810	.807	.806	.805	.804
.11	.784	.785	.785	.784	.782	.781	.780	.777	.775	.771	.769	.767	.765
.21	.751	.752	.751	.750	.748	.747	.746	.742	.740	.737	.734	.733	.730
.51	.710	.711	.710	.709	.707	.705	.704	.700	.697	.693	.690	.686	.684
1.01	.729	.726	.727	.725	.722	.719	.716	.711	.707	.700	.697	.693	.688
1.51	.756	.756	.753	.750	.746	.742	.738	.731	.726	.720	.713	.707	.700
2.01	.799	.798	.795	.791	.785	.780	.773	.766	.759	.751	.743	.735	.727
3.01	.890	.889	.881	.875	.867	.859	.851	.840	.829	.818	.808	.797	.786
3.51	.936	.932	.925	.917	.907	.898	.888	.876	.865	.851	.839	.827	.814

The Activity Coefficient of Hydrochloric Acid in Potassium Chloride Solutions.—The activity coefficient of the acid in the chloride solutions

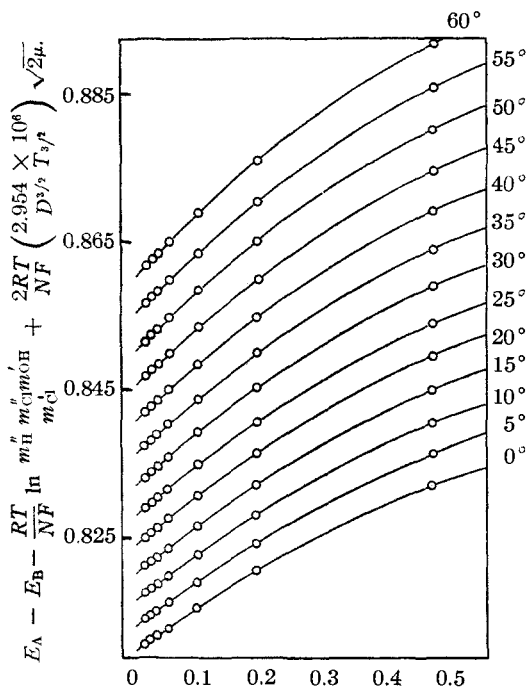


Fig. 3.—Plots of the left side of equation (16) used for the determination of the dissociation constant of water by the method which is independent of E_0 .

was computed by equation (2) from the electromotive forces in Table II. The results are given in Table IV. This very comprehensive series of values is more reliable than those previously given by Harned, and Harned and Åkerlöf,¹⁶ since a vacuum technique was employed. At 25°, the previously determined values of 0.779, 0.717, 0.777, 0.859 at 0.11, 1.01, 2.01 and 3.01 agree quite well with those recently obtained.

Sometimes the activity coefficient of the acid at zero concentration in a salt solution of concentration M is desired. These values can be obtained by subtracting 0.001 from the results in Table IV.

The Relative Partial Molal Heat Content of Hydrochloric Acid in Potassium Chloride Solutions.—The electromotive forces of the cells of the type B when no salt is present may be expressed by

(16) Harned, *THIS JOURNAL*, **48**, 326 (1926); Harned and Åkerlöf, *Physik. Z.*, **27**, 411 (1926).

$$E_B^{\circ} = E_{25}^{\circ} + a(t - 25) + b(t - 25)^2 \quad (17)$$

and by

$$E_B = E_{25} + a'(t - 25) + b'(t - 25)^2 \quad (18)$$

when salt is present. Upon subtracting and differentiating with respect to T , we obtain

$$\frac{d(E_B^{\circ} - E_B)}{dT} = \frac{dE'}{dT} = (a - a') + 2(b - b')(t - 25) \quad (19)$$

where dE'/dT is the temperature coefficient of the cells representing the transfer of the acid from the salt solution to the pure acid solution at 0.01 M . Thus, if we substitute this value of the temperature coefficient in the Gibbs-Helmholtz equation, as well as the corresponding partial free energy, we obtain the partial molal heat content of the acid in the salt solution relative to its value in 0.01 M hydrochloric acid.

In order to evaluate the heat data, we have resorted to the graphical method suggested by Harned and Nims.¹⁷ The constants a , b , a' and b' were obtained from the plots of the first order differences against temperature which we have already described in connection with the smoothing of the original electromotive forces and which are shown in Fig. 1, b is one-tenth the slope of these curves, and a is equal to one-fifth of the 20-25° intercept plus $5b$. Values of these quantities are given in the second and third columns of Table V. The other columns of this table contain the values of the partial molal heat content of the acid in the salt solution relative to its value in 0.01 M hydrochloric acid.

TABLE V
THE RELATIVE PARTIAL MOLAL HEAT CONTENT OF 0.01 M HYDROCHLORIC
ACID IN POTASSIUM CHLORIDE SOLUTIONS

μ	$a \times 10^6$	$b \times 10^6$	0°	5°	10°	15°	20°	25°	30°	35°	40°	45°	50°	55°	60°
0.01	179.0	-3.0	0	0	0	0	0	0	0	0	0	0	0	0	0
.02	129.0	-3.0	24	24	24	25	25	25	24	25	24	23	22	21	21
.03	101.0	-2.95	27	31	33	37	40	43	47	51	54	57	61	64	68
.04	81.5	-2.9	26	33	39	46	52	59	66	73	79	87	93	100	107
.06	51.5	-2.9	29	35	40	49	54	61	68	75	82	89	96	103	110
.11	11.0	-2.8	28	39	55	66	78	92	106	119	133	147	161	175	188
.21	-31.7	-2.75	43	60	77	94	111	129	147	165	183	202	221	240	250
.51	-90.5	-2.5	19	51	83	115	149	182	217	252	288	324	360	398	436
1.01	-137.0	-2.4	94	127	170	210	249	290	332	374	417	460	504	549	594
1.51	-163.0	-2.2	125	175	227	279	333	388	443	498	556	614	673	732	793
2.01	-181.0	-2.0	162	226	290	356	424	492	560	631	702	775	849	924	988
3.01	-208.0	-1.9	297	369	438	511	584	659	735	813	890	971	1052	1134	1217
3.51	-217.0	-1.8	348	424	501	580	660	742	824	909	995	1082	1170	1260	1351

The Ionic Activity Coefficient Product and Dissociation of Water in Potassium Chloride Solutions.—The values of the ionic activity coefficient product of water, $\gamma_H \gamma_{OH}/a_{H_2O}$, may be computed by means of equation (4). The left side of this equation has been computed previously and used for obtaining the values of K given in Table III. From these values, and by introducing the values of $\gamma_H \gamma_{Cl}$ at zero acid concentra-

(17) Harned and Nims, THIS JOURNAL, 54, 423 (1932).

tion in the presence of the salt at the concentration in question which are obtainable from the data in Table IV, the values of $\gamma_H\gamma_{OH}/a_{H_2O}$ given in Table VI have been computed.

TABLE VI
VALUES OF THE IONIC ACTIVITY COEFFICIENT PRODUCT OF WATER IN POTASSIUM CHLORIDE SOLUTIONS

μ	0°	5°	10°	15°	20°	25°	30°	35°	40°	45°	50°	55°	60°
0.01	0.819	0.818	0.818	0.818	0.816	0.816	0.816	0.812	0.809	0.809	0.811	0.309	0.810
.02	.765	.762	.764	.762	.759	.760	.760	.754	.753	.751	.750	.747	.745
.03	.732	.729	.726	.727	.726	.726	.725	.720	.718	.715	.713	.714	.711
.04	.707	.709	.706	.706	.701	.702	.702	.696	.694	.691	.687	.686	.684
.06	.672	.672	.669	.671	.667	.668	.667	.662	.661	.655	.655	.652	.650
.11	.621	.621	.622	.623	.619	.618	.617	.612	.611	.605	.602	.598	.595
.21	.574	.576	.576	.576	.572	.574	.573	.567	.565	.562	.558	.555	.550
.51	.534	.536	.537	.538	.535	.534	.534	.527	.524	.519	.514	.506	.503
1.01	.600	.596	.601	.599	.595	.592	.588	.580	.574	.563	.558	.549	.540
1.51	.688	.689	.686	.683	.677	.672	.665	.652	.643	.633	.620	.607	.595
2.01	.816	.815	.813	.807	.795	.787	.774	.761	.744	.728	.710	.692	.675
3.01	1.128	1.126	1.109	1.095	1.075	1.056	1.037	1.006	.979	.948	.925	.894	.864
3.51	1.313	1.301	1.285	1.264	1.234	1.205	1.183	1.147	1.109	1.075	1.043	1.005	.967

At all temperatures these results show the characteristic minima which are typical of the behavior of hydrochloric acid in halide solutions. It is

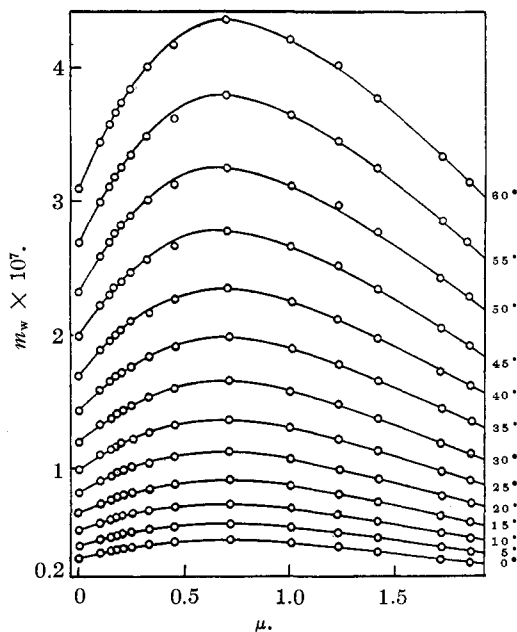


Fig. 4.—The dissociation of water in potassium chloride solutions

to be noted that like hydrochloric acid, the activity coefficient product is greater at the lower temperatures. We have not computed $\gamma_H\gamma_{OH}$ since the activity of the water in potassium chloride solutions over this temperature range is not available.

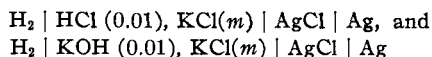
Values of the dissociation of water, m_w , or $\sqrt{m_H m_{OH}}$, computed by equation (3) are plotted in Fig. 4.

At this juncture it is a matter of importance to consider more carefully what meaning is to be attached to $\gamma_H\gamma_{OH}/a_{H_2O}$, and $m_H m_{OH}$. Equation (14) is the most convenient for illustration since it contains all the quantities involved. For the molalities in the first term on the right we have substituted the stoichiometrical molalities of the solutes. Therefore, $\gamma_H\gamma_{OH}/a_{H_2O}$ is the stoichiometrical activity coefficient. When

we come to consider $m_{\text{H}}m_{\text{OH}}$ as computed by equation (3), it is important to note that this will equal the true concentration product if, and only if, the stoichiometrical molalities equal the true molal concentrations of the ions. This condition will be true if the acid, hydroxide and salt are completely dissociated. Also it follows that the more highly dissociated the solutes involved are, the more nearly $m_{\text{H}}m_{\text{OH}}$ represents the true dissociation. In any case, the effect of the ratio of the chloride-ion concentrations will be negligible, so that the factor which determines the deviation of $m_{\text{H}}m_{\text{OH}}$ from the true dissociation is the product of the hydrogen-ion concentration in hydrochloric acid and the hydroxyl-ion concentration of the hydroxide. In the present case, the evidence indicates that this effect will be very small since both hydrochloric acid and potassium hydroxide are very strong electrolytes and any mass action effect due to potassium chloride will be small. On the other hand, it is quite possible that the deviation involved will be greater for cells containing sodium and still greater for those containing lithium hydroxide. As pointed out by Harned,¹⁸ the activity coefficients of these three hydroxides are peculiar in their behavior, and this peculiarity may be due in part to incomplete dissociation. Since the problem of the dissociation of such electrolytes is by no means solved, we can go no further with our computations.

Summary

1. Extensive and accurate measurements of the cells



have been made. The salt concentration has been varied from 0.01 to 3.5 M and the temperature from 0 to 60°.

2. The dissociation constant of water, K , from 0 to 60° has been computed and is given by

$$\log K = -\frac{4787.3}{T} - 7.1321 \log T - 0.010365 T + 22.801$$

3. The heat of ionization of water in calories throughout this temperature range can be computed from

$$\Delta H_i = 21,926 - 14.812 T - 0.04746 T^2$$

4. The activity coefficient of hydrochloric acid in potassium chloride solutions from 0 to 60° has been computed.

5. The partial heat content of the acid in the salt solutions has also been computed.

6. The ionic activity coefficient product and dissociation of water in potassium chloride solutions have been calculated. A brief discussion re-

(18) Harned—see Taylor, "Treatise on Physical Chemistry," D. Van Nostrand Co., N. Y., Vol. I, 2d ed., p. 823.

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

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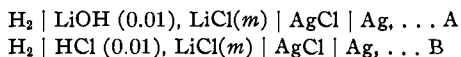
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

The Dissociation of Water in Lithium Chloride Solutions'

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 Swindells² 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



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 | AgCl(s) | 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 hydroxide⁴ 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 fulfillment 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).