computed from the observed electromotive forces by employing the reference value of 0.831 at 0.05402 molal concentration. Column 6 contains the values of γ computed by Harned's equation. The constants A, B, α, β and α' are given at the bottom of the table.

In Fig. 2 the activity coefficients of the alkali hydroxides have been plotted against $m^{1/2}$. The activity coefficient of cesium hydroxide lies somewhat higher at all concentrations but close to that of potassium hydroxide. The general rule that the hydroxides show the reverse distribution to the chlorides is verified.

Summary

1. The activity coefficients of cesium chloride and hydroxide in aqueous solution at 25° have been obtained by measurements of the cells,

$$Ag/AgCl/CsCl(m)/Cs_xHg/CsCl(m_0)/AgCl/Ag, \text{ and}$$
$$H_2/CsOH(m)/Cs_xHg/CsOH(m_0)/H_2$$

respectively.

2. The constants of Hückel's equation have been obtained from these results.

3. The constants of Harned's equation have been computed. From these, the vapor pressures of the chloride solutions may be calculated. The vapor pressures of the hydroxide solutions have been computed.

4. Both the chloride and hydroxide activity coefficients are of the expected order of magnitude, and conform with the distribution of the same quantities in the cases of the other alkali chloride and hydroxide solutions

New Haven, Connecticut

[Contribution from the Sterling Chemistry Laboratory of Yale University]

THE ACTIVITY COEFFICIENT AND DISSOCIATION OF WATER IN CESIUM CHLORIDE SOLUTIONS[1]

By Herbert S. Harned and Orion E. Schupp, Jr.

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In a series of studies, values for the variation of the dissociation and the ionic activity coefficient of water in some uniunivalent halide solutions were computed from measurements of three types of cells without liquid junction.[2]

In the present communication these same quantities have been determined in cesium chloride solutions. Further, a somewhat different method

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[1] Constructed from part of the thesis presented by O. E. Schupp, Jr., to the Faculty of the Graduate School of Yale University in candidacy for the degree of Doctor of Philosophy, 1930.

[2] (a) Harned, This Journal, **47**, 930 (1925); (b) Harned and Swindells, *ibid.*, **48**, 126 (1926); (c) Harned and James, *J. Phys. Chem.*, **30**, 1060 (1926).

of calculation has been employed which shows that the determined values depend only on strict thermodynamic principles and one experimentally demonstrated proposition. Secondly, as a check, an alternate method has been employed. We shall proceed directly to a consideration of the experimental results, and let the procedure of calculation develop during this discussion.

The Activity Coefficient of Hydrochloric Acid in Cesium Chloride Solutions.—The electromotive forces of the cells

$$\mathrm{Ag} \mid \mathrm{AgCl} \mid \mathrm{HCl}(0.01),\ \mathrm{CsCl}(m) \mid \mathrm{H_2} \mid \mathrm{HCl}(0.01) \mid \mathrm{AgCl} \mid \mathrm{Ag} \qquad \text{(Type I)}$$

are related to the activity coefficients and concentrations involved by the equation

$$E = 0.1183 \log \frac{\gamma_{\mathrm{HCl}}}{0.904} \frac{(m + 0.01)}{0.01} \qquad (1)$$

This double cell was not measured directly but was obtained by subtracting the electromotive force of the cell

$$\mathrm{H_2} \mid \mathrm{HCl}(0.01),\ \mathrm{CsCl}(m) \mid \mathrm{AgCl} \mid \mathrm{Ag} \qquad (E_1)$$

from that, E_0, of the same cell containing 0.01 M hydrochloric acid only. The results are given in Table I. The headings of the columns are self-explanatory. The final column contains the activity coefficients calculated by Equation 1 from the value of 0.904 at 0.01 M given by Randall and Young.[3] The measurements were carried out with the usual type of cell, and the electrodes made in the usual manner. Up to a concentration of 0.7 M cesium chloride the measurements proved to be very satisfactory. At this concentration and above, reproducibility decreases with increasing salt concentration.

TABLE I

THE ACTIVITY COEFFICIENT OF 0.01 MOLAL HYDROCHLORIC ACID IN CESIUM CHLORIDE SOLUTIONS

Molality of CsCl	E. m. f., E_1	Maximum diff., mv.[a]	Number of cells	$E_0 - E_1$	γ, HCl
0.0000	0.46456	±0.09 mv	25	0	0.904
.01	.44846	.07	4	0.00610	.874
.03011	.43296	.07	6	.03160	.835
.07	.41781	.07	3	.04675	.794
.1	.41110	.02	4	.05346	.772
.2	.39739	.04	4	.06717	.729
.4	.38350	.07	4	.08106	.684
.7	.37162	.05	2	.09294	.655
1.0	.36353	.31	5	.10103	.643
1.3434	.35643	.02	2	.10813	.6375
1.5	.35363	.03	2	.11093	.638
2.0	.34610	.08	2	.11846	.640
3.0	.33325	.07	2	.13131	.671

[a] Represents the maximum difference of any measurement from the mean value recorded in Column 2.

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[3] Randall and Young, THIS JOURNAL, 50, 989 (1928).

That the results obtained are in accord with expectations is shown by Fig. 1, in which γ of hydrochloric acid in alkali halide solutions is plotted against the square root of the ionic strength. The cesium chloride curve falls in the expected position.

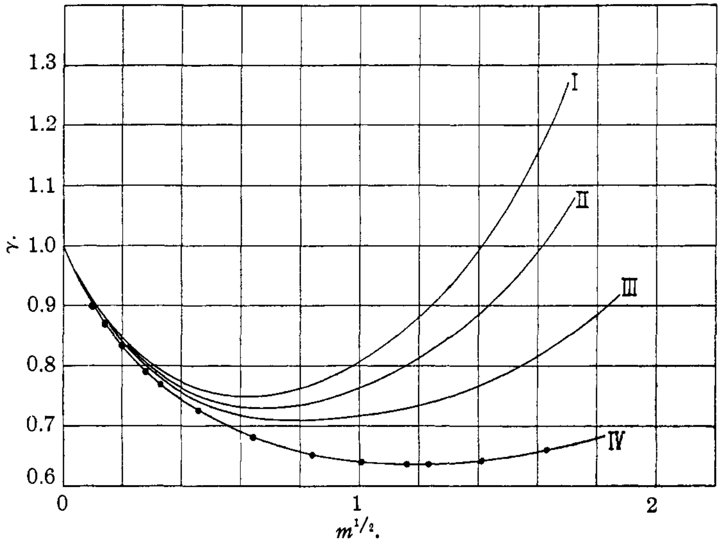

Fig. 1.—The activity coefficient of hydrochloric acid in alkali chloride solutions: I, LiCl; II, NaCl; III, KCl; IV, CsCl.

The Activity Coefficient of Cesium Hydroxide in Cesium Chloride Solutions.—The electromotive forces of the cells

$$H_2 \mid CsOH(m_0),\ CsCl(m) \mid Cs_xHg \mid CsOH(m_0) \mid H_2$$

may be employed to determine the activity coefficient of cesium hydroxide in cesium chloride solutions by means of the equation

$$E = 0.1183 \log \frac{\gamma'}{\gamma'_0} \frac{(m_0 + m)}{m_0} \qquad (2)$$

$$= 0.1183 \log \frac{\gamma}{\gamma_0} \frac{(m_0 + m)}{m_0} + 0.05915 \log \frac{a_{H_2O(0)}}{a_{H_2O}} \qquad (3)$$

γ is equal to $\sqrt{\gamma_{Cs}\gamma_{OH}}$, γ' equals $\sqrt{\gamma_{Cs}\gamma_{OH}/a_{H_2O}}$ in the salt solutions, and γ'_0 and γ_0 are like quantities in the pure hydroxide solution of concentration m_0. To evaluate the second member on the right of Equation 3, we have made use of the method of Harned[4] for evaluating the vapor pressure ratio of cesium chloride solutions. The constants of Harned's equation were obtained from Table I, and the calculations made by Equation 6 of a previous communication.[5] This necessitated the assumption that the vapor pressures of 0.05 and 0.1 *M* cesium hydroxide solutions

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[4] Harned, THIS JOURNAL, **44**, 252 (1922).

[5] Harned and Schupp, *ibid.*, **52**, 3886 (1930).

were the same as those of the corresponding strengths of the chloride solutions. Since the term under consideration is small, this assumption introduces no appreciable error. Two series of results were obtained with cesium hydroxide solutions of 0.05 and 0.1 M, respectively, of which the 0.05 series occurs in Table II. Since it was necessary for further calculation to know γ' at concentrations corresponding to the hydrochloric acid–cesium chloride system, the observed electromotive forces were used to construct a curve from which the results in Col. 3 were obtained. Column 5 contains the vapor pressure ratio from which the second member in the right of Equation 3 was computed.

Table II

The Values of $\gamma'_{CsOH} = \gamma_{CsOH}/a_{H_2O}$ and the True Activity Coefficient of 0.05 Molal Cesium Hydroxide in Cesium Chloride Solution ($m_0 = 0.05$)

m, CsCl	E, measured	E, curve	γ' curve	$p_s/p_{0.05}$	γ curve
0.0000	....	....	0.831	1.000	0.831
.09563	0.02241	0.02240	.753	0.997	.752
.1	....	.02300	.751	.997	.750
.1028	.02344	.02340	.750	.997	.749
.1522	.02933	.02925	.730	.995	.728
.2	....	.03370	.716	.994	.714
.3511	.04353	.04350	.684	.989	.681
.3534	.04358	.04355	.683	.989	.679
.5	....	.05020	.666	.985	.661
.5479	.05197	.05200	.661	.983	.656
.7058	.05690	.05718	.650	.978	.643
.7269	.05863	.05780	.649	.978	.642
.9411	.06337	.06350	.642	.972	.633
1.00	....	.06493	.642	.970	.632
1.1752	.06983	.06883	.641	.965	.630
1.2835	....	.07108	.642	.961	.629
1.5	....	.07516	.645	.955	.630
1.7077	.07797	.07860	.647	.949	.631
2.1253	.08660	.08460	.654	.937	.633
3.6896	.10248	.10248	.706	.887	.665

The Ionic Activity Coefficient and Dissociation of Water in Cesium Chloride Solutions.—It has been shown by Harned[6] that even at high concentrations log γ of hydrochloric acid in a uni-univalent chloride solution at constant total molality varies linearly with the acid concentration. This statement is given by the equation

$$\log \gamma = \alpha m_1 + \log \gamma^0 \tag{4}$$

in which α is a constant, m_1 is the acid concentration and log γ^0 is the logarithm of the activity coefficient of hydrochloric acid at zero concentration in the halide solution of concentration m. Harned and Harris[7]

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[6] Harned, This Journal, **48**, 326 (1926).

[7] Harned and Harris, *ibid.*, **50**, 2633 (1928).

found that in the case of very concentrated sodium and potassium hydroxide solutions there is a small deviation from this law. This makes no theoretical difference since the only information we require is the value of log γ^0, and, consequently, if the results can be extrapolated to zero concentration of hydroxide by a function which fits the experimental material, the data necessary for our calculation are available. In the present instance we make no error greater than the experimental by assuming that Equation 4 represents the correct relationship both in the case of the acid and hydroxide.

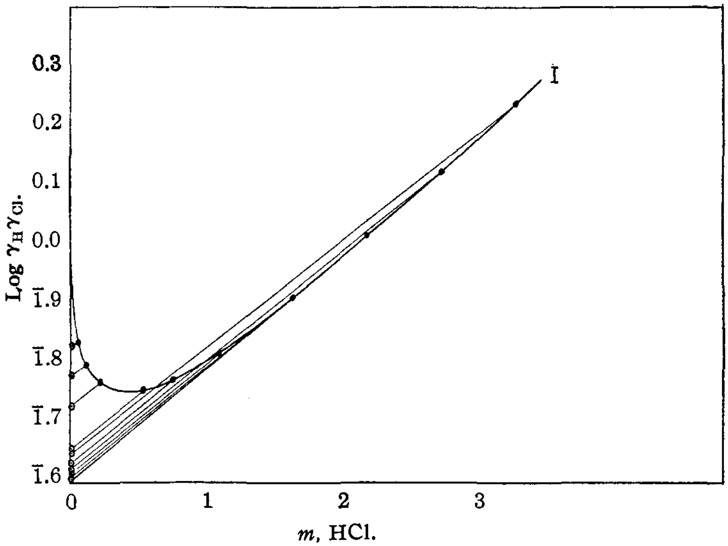

Fig. 2.—m_{HCl}– log $\gamma_H\gamma_{Cl}$ plots at constant total molalities.

In Fig. 2 the logarithm of the square of the activity coefficient of hydrochloric acid in pure aqueous solution (shaded circles) and of 0.01 M hydrochloric acid in cesium chloride solutions of the same total concentration (circles) are plotted against the acid concentration. The straight lines are drawn through the corresponding points at the same constant total molality. The parallel character of these plots leaves nothing to be desired. A short extrapolation to zero acid concentration gives 2 log γ^0 or log $\gamma^0_{H^+}\gamma^0_{Cl^-}$.

In Fig. 3 similar plots have been drawn in the case of cesium hydroxide and the hydroxide–chloride results. The extrapolation gives us the value of 2 log $\gamma^{0\prime}$ or log $\gamma^0_{Cs^+}\gamma^0_{OH^-}/a_{H_2O}$.

It is very important to observe that both $\gamma^0_{H^+}\gamma^0_{Cl^-}$ and $\gamma^0_{Cs^+}\gamma^0_{OH^-}/a_{H_2O}$ are now known in the pure aqueous cesium chloride solutions. Consequently, they may be multiplied to obtain $\gamma^0_{H^+}\gamma^0_{OH^-}\gamma^0_{Cs^+}\gamma^0_{Cl^-}/a_{H_2O}$. If this quantity be divided by $\gamma^0_{Cs^+}\gamma^0_{Cl^-}$ which we have already evaluated in a previous communication,[5] we obtain $\gamma^0_{H^+}\gamma^0_{OH^-}/a_{H_2O}$, the ionic activity coefficient product of water in cesium chloride solutions, which we shall denote by $K_{\gamma(s)}$. This method is free of all assumptions extraneous to exact thermodynamics other than the use of Equation 4 to extrapolate to zero concentration of acid or hydroxide. The necessary condition for this calculation is that at constant molality the log γ may be extrapolated to zero acid or hydroxide concentration.

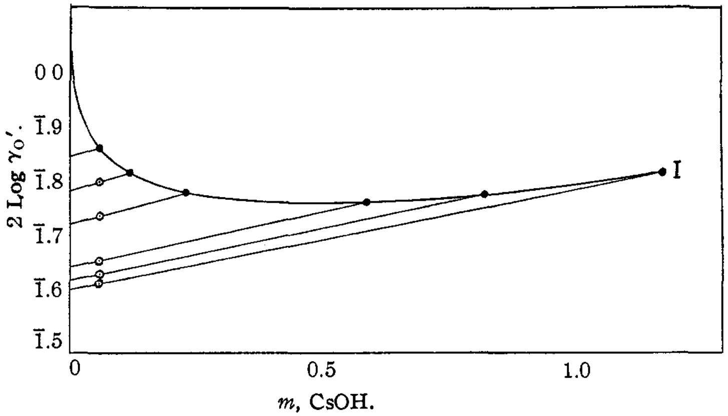

Fig. 3.—m_{CsOH}– log $\gamma_{Cs}\gamma_{OH}/a_{H_2O}$ plots at constant total molalities.

The thermodynamic equilibrium for the dissociation of water into ions is given by the equation

$$K = K_{\gamma(s)}\, m_{H^+} m_{OH^-} \tag{5}$$

Therefore, since $K_{\gamma(s)}$ has been computed, the variation of the dissociation of water with change in salt concentration may be evaluated. The results are given in Table III. Column 1 contains the total concentration of acid and salt, or hydroxide and salt; Col. 2 the value of γ^0_{HCl},

TABLE III

THE ACTIVITY COEFFICIENT AND DISSOCIATION OF WATER IN CESIUM CHLORIDE SOLUTIONS

1 m, CsCl	2 γ^0_{HCl}	3 $\gamma^{0'}_{CsOH}$	4 γ_{CsCl}	5 $K_{\gamma(s)} = \frac{\gamma_{H^+}\gamma_{OH^-}}{a_{H_2O}}$	6 $\frac{1}{a_{H_2O}} = \frac{p_0}{p_s}$	7 $\sqrt{\gamma_{H^+}\gamma_{OH^-}}$	8 $m_{H^+} = m_{OH^-}$
0.05	0.822	0	0.803	0	1.0017		
.1	.777	0.765	.747	0.634	1.0033	0.795	1.259 × 10^{-7}
.2	.731	.720+	.685	.591	1.0065	.766	1.305
.5	.671	.663	.598	.552+	1.0158	.738	1.350
.7	.655	.646	.568	.555	1.0220	.744	1.346
1.0	.642	.636	.537	.577+	1.0312	.748	1.320
1.5	.636	..	.507	..	1.0471	..	...
2.0	.638	..	.488	..	1.0636	..	...
2.5	.648	..	.476	..	1.0810	..	...
3.0	.669	..	.467	..	1.0995	..	...

Col. 3 that of $\gamma^{0'}_{CsOH}$, Col. 4 γ_{CsCl} and Col. 5 the computed value of $K_{\gamma(s)}$. Column 6 contains the values of the activity of water calculated from the vapor pressures by the method of Harned. Column 7 contains the values of $\sqrt{\gamma_{H^+}\gamma_{OH^-}}$, and Col. 8 the values of the hydrogen- or hydroxyl-ion concentrations computed by Equation 5, and the value of 1.005×10^{-14} for the dissociation constant of water.

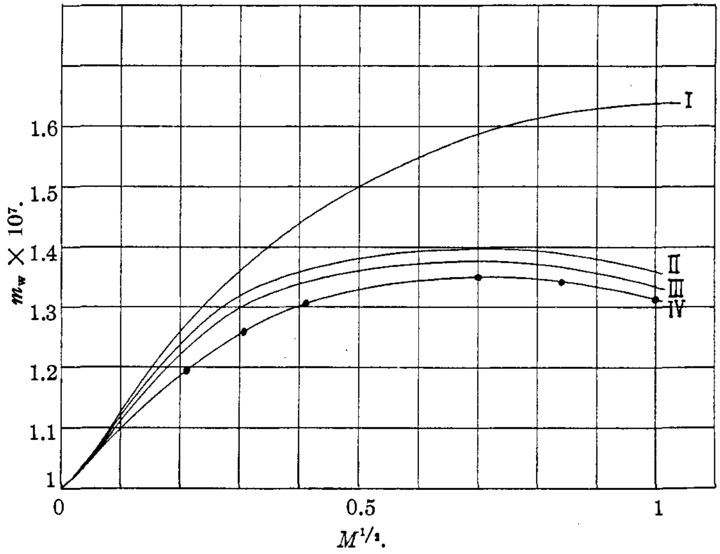

Fig. 4.—The hydrogen- or hydroxyl-ion concentrations in aqueous alkali chloride solutions: I, LiCl; II, NaCl; III, KCl; IV, CsCl.

In Fig. 4 are plotted the values of m_w for the cases of the alkaline chlorides up to 1.0 molal. The results for cesium chloride solutions conform to the expected distribution and show the characteristic maximum.

An Alternate Method of Evaluating the Ionic Activity Coefficient Product in a Salt Solution.—The electromotive force of the cell

$$H_2 \mid CsOH(m_0),\ CsCl(m) \mid AgCl \mid Ag$$

is given by the equation[8]

$$E = E_0 - 0.05915 \log \gamma_{H^+}\gamma_{Cl^-}m_{H^+}m_{Cl^-} \qquad (6)$$

If we substitute for m_{H^+}, its values derived from the thermodynamic equation for the dissociation of water into ions, namely, $Ka_{H_2O}/\gamma_{H^+}\gamma_{OH^-}m_{OH^-}$, we obtain

$$\left[E + 0.05915 \log \frac{m}{m_0} - E_0\right] = -0.05915 \log Ka_{H_2O} - 0.05915 \log \frac{\gamma_{H^+}\gamma_{Cl^-}}{\gamma_{H^+}\gamma_{OH^-}} \qquad (7)$$

E_0 is the standard electromotive force of the cell, which we take to be 0.2225, and K is the dissociation constant of water. If we plot the left-

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[8] The first measurements of this type of cell were made in this Laboratory by Dr. Elliott J. Roberts, This Journal, **52**, 3877 (1930).

hand member of this equation against μ, its value at zero μ is equal to 0.05915 log K, since at zero ionic strength a_{H_2O} is unity and by reason of the definition of activity coefficients the second member on the right of the equation vanishes. If we rearrange this equation as follows

$$0.05915 \log \frac{\gamma_{H^+}\gamma_{OH^-}}{a_{H_2O}} = E - E_0 + 0.05915 \left[\log \frac{m}{m_0} + \log K + \log \gamma_{H^+}\gamma_{Cl^-}\right] \quad (8)$$

it is clear that the ionic activity coefficient product of water, $\gamma_{H^+}\gamma_{OH^-}/a_{H_2O}$, in the cesium chloride solution may be evaluated, since $\gamma_{H^+}\gamma_{Cl^-}$ in this salt solution may be obtained from Table III.

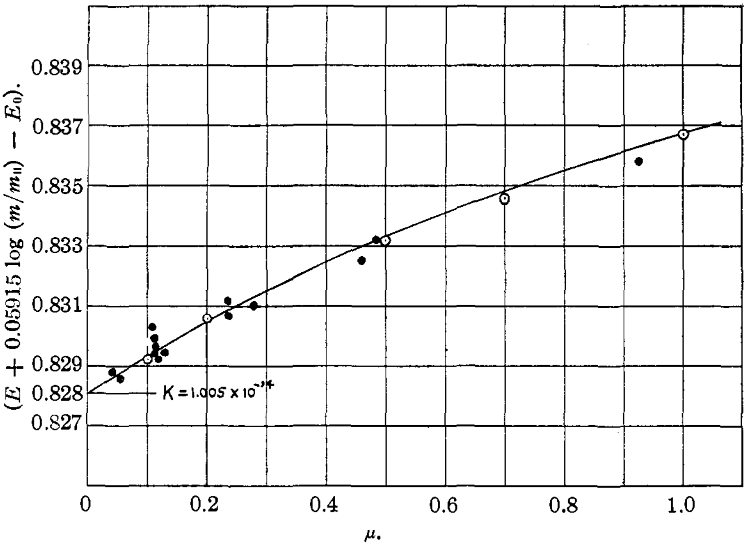

Fig. 5.—Plot of the left side of Equation 7 against the ionic strength.

The cell measurements are given in Table IV, Col. 3. Column 4 contains the values of (E + 0.05915 log (m_{Cl^-}/m_{OH^-}) − E_0) obtained from them. Even though careful vacuum technique was employed, the measurements were not entirely satisfactory. The electromotive force rose quickly to a maximum and then slowly fell off. The maximum values were recorded. We have, therefore, not employed the results to compute $\gamma_{H^+}\gamma_{OH^-}/a_{H_2O}$. On the other hand, we have computed the value of (E + 0.05915 log (m_{Cl^-}/m_{OH^-}) − E_0) from the values of $\gamma_{H^+}\gamma_{Cl^-}$ contained in Table I, $\gamma_{H^+}\gamma_{OH^-}/a_{H_2O}$ given in Table III and the value of 10^{-14} for K. In Fig. 5 we have plotted these values which are given in Table IV against the ionic strength, μ (circles). The inked in circles are the results obtained by the second method and given in Col. 4, Table IV. Up to 1.0 M the agreement with our previously determined values is good although there is a scattering of ±0.5 mv. in the results.

TABLE IV

CALCULATIONS ACCORDING TO EQUATION 7

m, CsOH	m, CsCl	E. m. f.	$(E + 0.05915 \log (m/m_0) - E_0)$
0.02214	0.02113	1.05255	0.8288
.02204	.03184	1.04162	.8286
.02228	.07492	1.02101	.8297
.02237	.08724	1.01756	.8301
.02202	.09391	1.01470	.8295
.02238	.2330	0.99331	.8310
.02203	.2558	.99047	.8310
.02216	.4377	.97835	.8325
.02232	.4596	.97724	.8325
.02225	.9351	.96193	.8354
.02211	1.3467	.95404	.8371

μ	0.1	0.2	0.5	0.7	1.0
From results of Table III $(E + 0.05915 \log (m/m_0) - E_0)$	0.8292	0.8306	0.8332	0.8346	0.8367

Summary

1. The activity coefficient of hydrochloric acid in cesium chloride solutions at 25° has been determined from measurements of the cells

$$H_2/HCl(m_0),\ CsCl(m)/AgCl/Ag$$

2. The activity coefficient of cesium hydroxide in cesium chloride solutions at 25° has been obtained from the cells

$$H_2/CsOH(m_0),\ CsCl(m)/Cs_xHg/CsOH(m_0)/H_2$$

3. An exact method, similar to that previously employed by Harned, has been used for computing the dissociation of water in cesium chloride solutions.

4. Another method for determining the ionic activity coefficient product and dissociation of water in salt solutions has been described which employs cells of the type

$$H_2/MOH(m_0),\ MCl(m)/AgCl/Ag$$

Measurements of such cells containing cesium hydroxide and chloride have been made, and it is shown that the results conform with those of the method previously used.

5. The values for the dissociation of water in cesium chloride solutions conform with those previously obtained in the cases of the other alkali halides.

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