trons largely combined with solvent molecules, the degree of solvation diminishing as the temperature is increased.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

THE ACTIVITY COEFFICIENT OF HYDROCHLORIC ACID IN CONCENTRATED SOLUTIONS OF STRONG ELECTROLYTES

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In previous communications,[1] a few series of electromotive data were obtained from which the activity coefficient of hydrochloric acid could be computed in solutions of the alkaline and alkaline earth chlorides. With the intention of obtaining more complete and more reliable experimental data, this earlier work has been revised and extended.

Recently, a very interesting theory of concentrated solutions of strong electrolytes has been developed by Debye and Hückel,[2] and Hückel[3], by means of which the thermodynamic properties of strong electrolytes and their mixtures are described. Although it is hard to believe that all the factors which influence these properties are included in this theory, it will be shown in the following discussion that there are no outstanding contradictions to be inferred from the numerous series of results on chloride solutions which we shall consider.

Experimental Part

The experimental technique of cells of the types $H_2 | HCl(m_1), MCl_x(m_2) | HgCl | Hg$ and $H_2 | HCl(m_1), MCl_x(m_2) | AgCl | Ag$, has been frequently described elsewhere.[4] No great difficulty has been found in obtaining reliable results in solutions which contained acid of a strength greater than 0.01 *M* and salts at concentrations below approximately 1 *M* as long as the ordinary precautions regarding the electrodes were observed. A critical survey of the earlier results brought to light two sources of experimental error. When, in the earlier work,[1b] the temperature coefficient of the cell with calomel electrodes was measured, the cell was introduced into the thermostat on the day before the measurements were made and then measured at different temperatures during a period of from four to six days. Although the temperature coefficients of the cells containing solutions of concentrations greater than 1 *M* remained the same,

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[1] (a) Harned, THIS JOURNAL, **38**, 1986 (1916); (b) **42**, 1808 (1920). (c) Harned and Brumbaugh, *ibid.*, **44**, 2729 (1922).

[2] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923).

[3] Hückel, *ibid.*, **26**, 93 (1925).

[4] Ref. 1 a. Loomis, Essex and Meacham, THIS JOURNAL, **39**, 1133 (1917). Ming Chow, *ibid.*, **42**, 497 (1920).

their electromotive forces fell slightly during this period and, therefore, some of the electromotive forces in these series have been found to be low in the very concentrated solutions. Upon reconsideration of the kind of apparatus then employed, it is thought that this error was probably caused by the formation by electrolysis of a thin coating of mercury on the hydrogen electrode during the manipulation of the potentiometer circuit. This is more likely to take place in the cells containing concentrated salt solutions, since the solubility of calomel increases with increasing salt concentration. The second source of error in the earlier results proved more difficult to detect and remedy. Our first measurements with solutions containing 0.001 *M* acid in potassium chloride solutions gave results which indicated that the activity coefficient of the acid at constant total concentration decreased, passed through a minimum at 0.01 *M* acid concentration and then increased with decreasing acid strength.[1c] Because of this peculiar behavior, a number of series of similar results were made with acid mixtures containing the alkaline halides. The salts employed were neutral. An apparatus was designed so that the measurements could be carried out in a vacuum. Similar minima were obtained in the first ten series of results, but it was found difficult to reproduce the electromotive forces to within less than ±1 millivolt in the solutions containing acid of concentrations between 0.0005 *M* and 0.003 *M*. This experience led to the suspicion that these apparent minima were the result of a systematic error and a reinvestigation was undertaken, as a result of which it was found that the lack of reproducibility depended entirely upon the way the hydrogen electrodes were prepared. To attain accurate and reproducible results, the following procedure was finally adopted. A freshly coated hydrogen electrode was necessary for each determination. The electrode was introduced into the hydrogen atmosphere of the cell immediately after platinizing and washing with distilled water. A thin coating of platinum black was found to be essential. Good results were obtained by electrolyzing a solution of chloroplatinic acid containing 0.5 g. of platinum in 100 cc. of solution for one minute with a current density of 0.3 ampere per sq. cm. of cathode surface. The sheet platinum electrode was cleaned before each determination by polishing it with a fine emery paper. In Fig. 1, the difference between a series of results determined by means of hydrogen electrodes so prepared and those coated with a thicker covering of platinum black is shown. The activity coefficient of the acid in sodium chloride solutions at 3 *M* total concentration is shown plotted against the logarithm of its concentration. The curve showing the minimum, which was always more pronounced in solutions of greater total concentration, was obtained with thickly, though freshly coated platinum electrodes, while the curve showing no minimum and greater reproducibility was obtained by electrodes prepared according to the procedure described above. Further results were obtained with electrodes with a thinner coating but in no cases were values obtained which gave activity coefficients below the lower curve. Similar results were observed with cells containing solutions of sodium or potassium chlorides at other concentrations. These as well as theoretical considerations leave little doubt that the earlier results were erroneous.

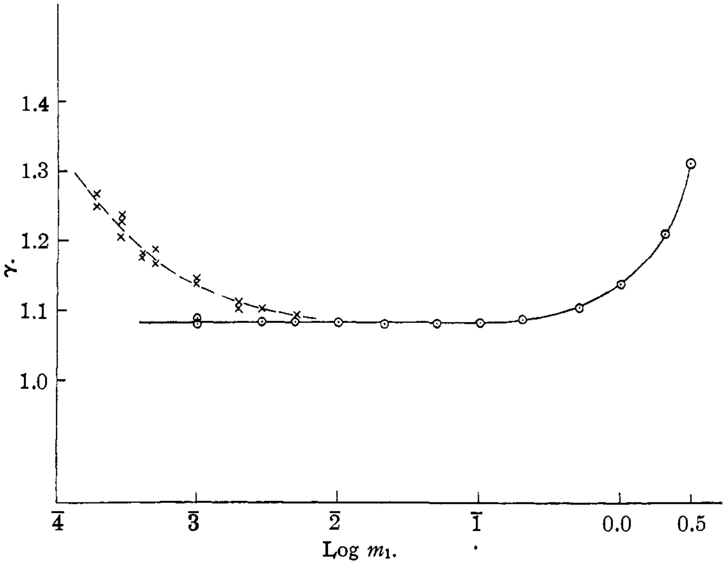

Fig. 1.—Activity coefficients determined by thickly and thinly coated hydrogen electrodes in 3 *M* total NaCl solutions.

The data are given in Table I; m_1 and m_2 are the concentrations of the acid and salt in moles per 1000 g. of water; c_1 and c_2 are their concentrations in moles per liter of solution; E is the electromotive force corrected to one atmosphere of hydrogen of pressure and γ is the activity coefficient. All values of γ are referred to a value of 0.790 at 0.1 *M* pure acid. The reason for using this value will appear later. The value of the cell $H_2 \mid HCl(0.1) \mid HgCl \mid Hg$, was taken to be 0.3989. The activity coefficients were calculated by the equation $0.3989 - E = 0.05915 \log \frac{\gamma_H \gamma_{Cl}\, m_1\, (m_1 + m_2)}{(0.790)^2 \times (0.1)^2}$ or, since $\gamma = \sqrt{\gamma_H \gamma_{Cl}}$.

$$\log \gamma = \frac{0.3989 - E}{0.1183} + (8.8976 - 10) - \frac{1}{2} \log m_1\, (m_1 + m_2) \qquad (1)$$

It is difficult to estimate exactly the experimental error of these results since it differs somewhat from series to series, being greater when the solutions are at high concentrations. The results at constant total molality are consistent with those of constant-acid and varying salt concentrations obtained in earlier investigations. A study of curves of the electro-

Table I

The Activity Coefficient of Hydrochloric Acid in Potassium, Sodium and Lithium Chlorides at Constant Total Molality

	1		2		3		4		6	
	KCl		NaCl		LiCl		LiCl		LiCl	
	$m_1 + m_2 = 0.1$		$m_1 \cdot + m_2 = 0.1$		$m_1 + m = 0.1$		$m_1 + m_2 = 1$		$m_1 + m_2 = 3$	
m_1	E	γ	E	γ	E	γ	E	γ	E	γ
0.001	0.5181	0.776	0.5177	0.782	0.5174	0.787	0.4569	0.807	0.4040	1.309
.003	.4897	.779	.4895	.782	.4892	0.787	...	...	....	...
.005	.4767	.777	.4763	.783	.4760	.788	.4154	.806	.3625	1.310
.01	.4588	.778	.4584	.785	.4583	.786	.3978	.803	.3450	1.302
.03	.4307	.782	.4304	.787	.4302	.789	....	...	....	...
.05	.4172	.782	.4170	.786	.4168	.788	....	...	....	...
.1	.3989	.790	....	...	....	...	.3389	.802	.2860	1.298

	5			7			8			9	
	KCl			KCl			NaCl			NaCl	
	$m_1 + m_2 = 1$			$m_1 + m_2 = 3$			$m_1 + m_2 = 1$			$m_1 + m_2 = 3$	
m_1	E	γ	m_1	E	γ	m_1	E	γ	m_1	E	γ
0.001	0.4638	0.706	0.002	0.4077	0.859	0.00096	0.4609	0.762	0.001	0.4133	1.090
.002	.4456	.712	.005	.3843	.857	.00193	.4430	.763	.001	.4137	1.082
.003	.4356	.706	.01	.3664	.859	.00282	.4331	.765	.00307	.3846	1.087
.005	.4225	.705	.02	.3488	.857	.00481	.4195	.764	.00515	.3710	1.087
.01	.4042	.712	.05	.3252	.856	.01	.4006	.765	.01	.3544	1.085
.02	.3866	.709	.1	.3071	.861	.02	.3828	.765	.0102	.3536	1.088
.03	.3760	.712	.2	.2883	.876	.03	.3724	.765	.0212	.3353	1.080
.05	.3635	.702	.2	.2882	.880	.05	.3593	.764	.05	.3131	1.084
.1	.3450	.713	.5	.2630	.909	.1	.3414	.766	.05	.3132	1.082
.2	.3268	.719	1.0	.2422	.963	.2	.3237	.770	.1	.2953	1.084
.3	.3155	.731	1.0	.2419	.968	.3	.3126	.774	.2	.2773	1.088
.5	.3009	.752	2.0	.2165	1.123	.5	.2990	.782	.5	.2529	1.106
1.0	.2795	.806	3.0	.1981	1.311				1.0	.2338	1.135
									2.0	.2123	1.224

motive forces and the activity coefficient indicated that most of the results are consistent to within ±0.2 millivolt. In some cases, however, the error is of the order of ±0.5 mv. which corresponds to an error of 1% in the activity coefficients.

Calculation of Experimental Results

Empirical Considerations.—Fig. 2 contains plots of γ against log m_1 for the three salts at 1 *M* and 3 *M* total concentrations. The activity coefficient of the acid is found to decrease and finally to approach a constant value as the concentration of the acid approaches zero. Only a very slight decrease of γ was observed in the lithium chloride solutions.

In Fig. 3 the values of log γ have been plotted against m_1 at total concentrations of 1 *M* and 3 *M*. These curves are straight lines within the error of experiment even in solutions as concentrated as 3 *M*. Thus, it appears that in the mixtures at a given total molal concentration, the logarithm of the activity coefficient of a strong uni-univalent electrolyte is a linear function of its concentration. Allowing for experimental error, this law of the linear variation of the logarithm of the activity coefficient, which is certainly a very close approximation in the very concentrated solutions, becomes increasingly exact in the solutions of lower total concentration.

It has been shown elsewhere[5] that if the equation for the variation of the logarithm activity coefficient of an electrolyte is known as a function of its concentration at constant temperature and at low concentrations (0 to 0.01 M), then it may be calculated at the higher concentrations by adding a simple linear term. In the earlier calculations, the linear term was added to the equation which Lewis and Linhart[6] employed in the dilute solutions. Thus, it was found that the equation expressed γ as a

$$\log \gamma = -\beta m^{\alpha'} + \alpha m \qquad (2)$$

function of the concentration in terms of three constants β, α' and α with a considerable degree of accuracy through a long concentration range (0.01 to 3 M). It was also shown[1c] that the activity coefficient of hydrochloric acid in uni-univalent and bi-univalent chloride solutions could be approximately computed in concentrated solutions by the addition of another term to Equation 2 which makes it applicable to the mixtures. This equation was

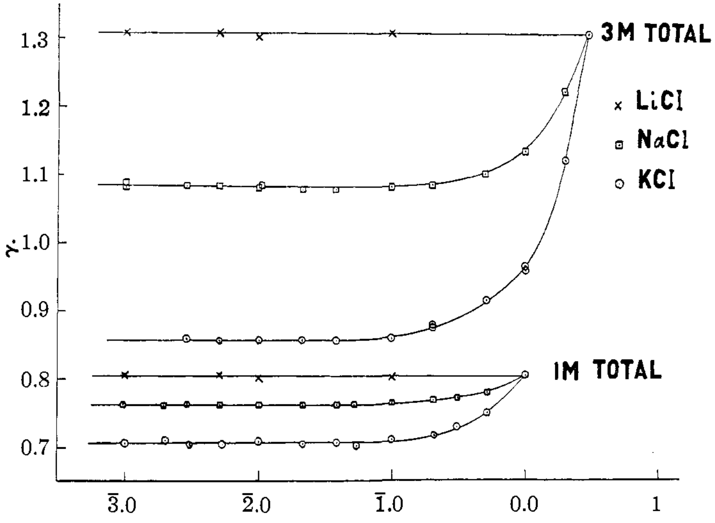

Fig. 2.—Activity coefficients at constant total molality against log m_1.

$$\log \gamma = -\beta\mu^{\alpha'} + \alpha m_1 + \alpha'' (\mu - m_1) \qquad (3)$$

where μ is the ionic strength as defined by Lewis and Randall,[7] β, α' and α the constants of Equation 2 for aqueous solutions of the pure acid and α'' is another constant characteristic of the salt solution employed. From this equation, at constant ionic strength,

$$\log \gamma = \text{constant} + (\alpha - \alpha'')m_1 \qquad (4)$$

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[5] Ref. 1 b. This Journal, **44**, 252 (1922). Taylor, "Treatise on Physical Chemistry," D. Van Nostrand Co., New York, **1924**, Chap. XII, p. 744.

[6] Lewis and Linhart, This Journal, **41**, 1951 (1919).

[7] Lewis and Randall, *ibid.*, **43**, 1112 (1921).

is obtained. Thus, for uni-univalent mixtures at constant total molality, log γ varies linearly with the concentration m_1 and, therefore, the slope of a plot in Fig. 3 equals $(\alpha - \alpha'')$. This result is similar to the conclusion regarding the linear variation of log γ reached by Brönsted[8] except that we have always considered such a variation to be characteristic of the concentrated as well as the dilute solutions.

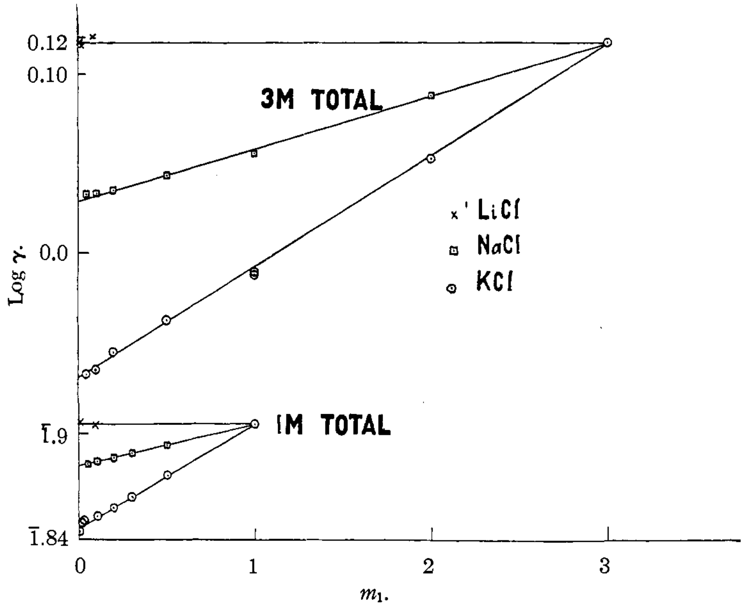

Fig. 3.—Illustrating the linear variation of log γ at constant total molalities and at high total concentrations.

Theoretical Considerations.—More recently, the theory of Debye and Hückel[2] has been extended to very concentrated solutions by Hückel.[3] In the first mentioned work, which was based upon the theory of complete dissociation of strong electrolytes, they deduced an equation which appears to be within the experimental error on solutions of concentrations between 0 and approximately 0.5 *M*. Very convincing experimental evidence for their theory in very dilute solutions has been obtained by Brönsted and La Mer,[9] and in moderately dilute solutions by A. A. Noyes.[10] Hückel has recently extended this theory to very concentrated solutions by assuming a linear variation of the dielectric constant of the medium which is

$$D = D_0 - \Sigma\delta_i c_i \tag{5}$$

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[8] Brönsted, This Journal, **44**, 938 (1922).

[9] Brönsted and La Mer, *ibid.*, **46**, 555 (1924).

[10] Noyes, *ibid.*, **46**, 1080 (1924); **46**, 1098 (1924)

where D is the dielectric constant of the medium, D_0 the dielectric constant of the solvent, c_i the concentration in moles per liter of solution and δ_i a constant characteristic of an ion. The summation is for all ions of which i is of the "i^{th}" kind. In this interesting study, Hückel has deduced a general equation for the activity coefficient of an ion of any kind in a solution containing other ions of any kind. This equation is very complicated but fortunately the term obtained by the introduction of the linear variation of the dielectric constant is itself approximately linear. As a close approximation, Hückel obtains

$$\log f = \frac{-0.354\sqrt{2c}}{1 + A\sqrt{2c}} + B2c \tag{6}$$

for the activity coefficient of a uni-univalent electrolyte; f is equal to the activity "a" of the electrolyte divided by the mole fraction, N; c is the concentration in moles per liter; A depends on the dimensions of the ions (the apparent diameters) and is a constant; B is a constant, and 0.354 is obtained from the dielectric constant of the pure solvent. The first member on the right of this equation was obtained in the earlier theory and the term $B2c$ results from the hypothesis of the linear variation of the dielectric constant. Hückel's equation for γ or a/m becomes

$$\log \gamma = \frac{-0.354\sqrt{2c}}{1 + A\sqrt{2c}} + B2c - \log (1 + 0.002\,wm) \tag{7}$$

where w is the formula weight of the solvent and m the molal concentration (g. per 1000 g. of solvent) of the electrolyte. This follows from Equation 6 since $\gamma m = fN$, and since both f and γ are defined so as to equal unity at infinite dilution. This equation was tested by Hückel and more recently by Scatchard[11] who has found it valid for hydrochloric acid in aqueous and alcoholic solutions of from 0.0 to 1 M concentrations.

Further, as a result of this theory, $\log \gamma$ should be a linear function of the concentration of an electrolyte in a mixture of uni-univalent electrolytes at constant total molality, if the "apparent ionic diameters" of the ions are the same. Therefore, Hückel's equation for $\log \gamma$ in our mixtures may be modified to the following form which is similar to Equation 3.

$$\log \gamma = \frac{-0.354\sqrt{2c_T}}{1 + A\sqrt{2c_T}} + B(2c_1) + B'(2c_T - 2c_1)$$
$$-{}^1/_2 \log (1 + 0.002\,wm_1) - {}^1/_2 \log (1 + 0.002\,wm_T) \tag{8}$$

c_T and m_T are the total normal and molal concentrations, and c_1 and m_1 are the normal and molal concentrations of the acid. Before subjecting the general theory to a more rigorous test, a preliminary calculation by means of this equation will be made.

The values of A and B in Equation 6 or Equation 7 for hydrochloric acid solutions were first evaluated by the method employed by Hückel

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[11] Scatchard, This Journal, **47**, 2098 (1925).

(p. 123). The values 0.3989, 0.2795 and 0.1981 for the electromotive forces of the cells $H_2 | HCl(m) | HgCl | Hg$ at 0.1 M, 1 M and 3 M, or 0.0996 N, 0.980 N and 2.83 N concentrations were employed. As a result A and B were found to be 0.784 and 0.0805, respectively.[12] Throughout this calculation, it was assumed that the "mean apparent diameters" of the ions were the same and, consequently, A was the same for the different salt mixtures. The values of B' in Equation 8 were easily evaluated as follows. At constant total molality, Equation 8 reduces to

$$\log \gamma = \text{constant} + (B - B')\, 2c_1 - {}^1/_2 \log (1 + 0.002\, wm_1) \qquad (9)$$

Thus, it is clear that from the slope of the plot of $[\log \gamma + {}^1/_2 \log (1 + 0.002\, wm_1)]$ and c_1, $(B-B')$ may be evaluated, and subsequently B'. In Table II are given the values of $[\log \gamma_{HCl} + \frac{1}{2} \log (1 + 0.002\, wm_1) - \log \gamma_{HCl(o)MCl}]$ in which $\log \gamma_{HCl}$ and $\log \gamma_{HCl(o)MCl}$ refer to the pure acid solutions and the pure salt solutions respectively and m_1 is the acid strength in a solution containing no salt. These values as well as the slopes of the curves taken from accurate large scale plots similar to those in Fig. 3 are given in Table II.

TABLE II

SLOPES OF PLOTS OF $[\log \gamma + \frac{1}{2} \log (1 + 0.036\, m_1)]$ AGAINST c_1

1. $\left[\log \gamma_{HCl} + \frac{1}{2} \log (1 + 0.036\, m_T) - \log \gamma_{HCl(o)MCl}\right]$

m	KCl	NaCl	LiCl
3	0.2081	0.1067	0.0263
1	.0676	.0326	.0098
0.1	.0071	.0041	.0016

2. $\left[\log \gamma_{HCl} + \frac{1}{2} \log (1 + 0.036\, m_T) - \log \gamma_{HCl(o)MCl}\right]/m_T$

m	KCl	NaCl	LiCl
3	0.0693	0.0356	0.0088
1	.0676	.0326	.0098
0.1	.071	.041	.016

It is interesting to note that the slopes at 1 and 3 total molalities are very nearly the same for each of the salts. The slopes at 0.1 total concentration are all somewhat higher than at the other concentrations but no conclusion should be drawn from this since in these dilute solutions the total change in $\log \gamma$ in going from pure acid to pure salt solution is very small and the percentage error is large.

As a result of this procedure, the values of B' were found to be 0.0453, 0.0634 and 0.0765 for the solutions of potassium, sodium and lithium

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[12] These values are somewhat different from those obtained by Scatchard. This is due to the fact that Scatchard derived the constants from data in more dilute solutions. Equation 7 is an approximation and cannot be expected to be exactly valid from 0.0 to 3 M.

chlorides, respectively. These and the values of 0.784 for A and 0.0805 for B were then substituted in Equation 8 and thus used for the calculation of γ. The agreement between these calculated values and those contained in Table I was very good but will not be included. The same values of the constants were then employed in Equation 8 for the computation of γ in 0.01 M and 0.1 M acid in solutions of varying salt concen-

Table III

Calculated and Observed Values of the Activity Coefficient of Hydrochloric Acid in the Salt Solutions at Constant Acid and Various Salt Concentrations

KCl

$m_1 = 0.1004$ (Ref. 1 a)			$m_1 = 0.01$ (Ref. 1 c)		
m_2	γ (obs.)	γ (calcd.)	m_2	γ (obs.)	γ (calcd.)
0.0601	0.762	0.760	0.02	0.836	0.852
.1004	.750	.747	.04	.812	.822
.1205	.754	.741	.1	.779	.767
.2015	.734	.725	.3	.722	.715
.2420	.735	.720	.5	.712	.698
.4059	.718	.707	1.0	.717	.701
.6120	.716	.703	2.0	.777	.766
.928	.719	.711	..	...	...
1.245	.733	.727	..	...	...
1.913	.778	.777	..	...	...

NaCl

$m_1 = 0.1004$ (Ref. 1 b)			$m_1 = 0.01$		
0.1003	0.760	0.753	0.1	0.784	0.780
.2014	.742	.738	.2	.751	.740
.3636	.746	.732	.5	.729	.727
.5061	.741	.733	.99	.764	.759
.6085	.747	.739	2.0	.891	.902
.918	.771	.766	2.99	1.085	1.101
1.023	.783	.778	..	...	...
1.243	.804	.804	..	...	...
1.871	.907	.903	..	...	...
2.094	.948	.944	..	...	...

LiCl

$m_1 = 0.1$ (Ref. 13)			$m = 0.01$ (Ref. 13)		
0.0705	0.764	0.764	0.00767	0.872	0.880
.1101	.763	.756	.01028	.865	.873
.2004	.751	.746	.01944	.840	.855
.3693	.752	.747	.0422	.822	.825
.704	.772	.778	.0727	.794	.800
1.007	.819	.823	.1209	.774	.776
2.198	1.095	1.121	.1989	.758	.756
3.695	1.675	1.682	.4024	.749	.745
...	...	...	.699	.766	.766
...	...	...	1.004	.805	.807
...	...	...	2.189	1.054	1.066

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[13] Harned and Swindells, This Journal, **48,** 126 (1926).

trations. These latter calculated values are compared with those obtained from results to be found in the references in Table III. This is a good test of the equation since the agreement of the calculated with the observed results is not so close in this case as in the solutions of constant total molality.

From the above values of A and B, γ for the pure solution of the acid is 0.790 at 0.1 M. All values in Table I are, therefore, referred to this one. The agreement between the observed and calculated values is usually very close, amounting in some cases to less than 0.2 mv. through an entire series. The maximum deviation which occurs with only a few results is about 2% in activity coefficient which corresponds to 1 mv. This is excellent considering that the results extend from 0.001 to 3 M acid and from 0.001 to 3.5 M salt solutions, and that the values of the apparent ionic diameters have been assumed to be equal.

More Rigorous Consideration of the Debye and Hückel Theory.—Up to the present we have shown that the law of the linear variation of the logarithm of the activity coefficient is valid in concentrated solutions and that the activity coefficient of the acid in the salt solutions may be calculated approximately by employing an equation which according to the theory should be approximately valid. Hückel attempted to calculate the activity coefficient of hydrochloric acid in the salt mixtures from the knowledge derived from the activity coefficients of the individual electrolytes. In the following, we shall reverse this process and compute the activity coefficients of the salts from our knowledge of the mixtures by means of this theory. We shall also extend the theory to the calculation of the activity coefficients of the alkaline earth chlorides and of hydrochloric acid in solutions of alkaline earth chlorides. To do this, we must consider the theory in somewhat greater detail.

Uni-univalent Electrolytes.—In the case of a uni-univalent electrolyte Equation 5 becomes

$$D = D_0 - (\delta_1 + \delta_2)\, c \qquad (10)$$

where the subscripts 1 and 2 refer to the anion and cation. If we let the apparent diameters, the mean distance to which positive as well as negative ions can approach a given ion, be the same for both ions, then

$$a_1 = a_2 = a;\ x_1^\circ = x_2^\circ = x^\circ \qquad (11)$$

where

$$x^\circ = a \times 2.32 \times 10^8\sqrt{2c} \qquad (12)$$

and a is the mean diameter.[14] Also let

$$\delta = \frac{\delta_1 + \delta_2}{2} \qquad (13)$$

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[14] In the following, Hückel's notation has been largely employed; "a" denotes apparent ionic diameter and not relative activity. However, we have used c for moles per liter, m for moles per 1000 g., and have employed Lewis and Randall's convention regarding the sign of electromotive force.

and separate $\log f$ into two parts as follows.

$$\log f = \log f^{\circ} + \log f^{*} \tag{14}$$

From the general equations 85 to 85c in Hückel's paper, Hückel obtains his Equations 95a and 95b, which are

$$\log f^{\circ} = -0.354\sqrt{2c}\,\frac{1}{1 + x^{\circ}} \tag{15}$$

and

$$\log f^{*} = \frac{0.0194 \times 10^{-8}}{a}\, 2\bar{\delta}\, 2c\,\frac{1}{1 + x^{\circ}} - 0.00225\,\bar{\delta}\,(2c)^{3/2}\,\frac{1}{(1 + x_0)^2} + \frac{0.000246 \times 10^{-8}}{a}\, 3\,(\bar{\delta}\, 2c)^2 \left[\frac{3}{4}\,\frac{1}{1 + x^{\circ}} + \frac{1}{4}\,\frac{1}{(1 + x^{\circ})^2}\right] \tag{16}$$ [15]

respectively. From (12) and (15) it is clear that A in Equation 6 is equal to $a \times 0.232 \times 10^8$ and therefore "a" for hydrochloric acid equals 3.38×10^{-8}, since A was found to be 0.784. Hückel showed that the value of $\log f^{*}$ calculated according to Equation 16 is very nearly a linear function of c or

$$\log f^{*} = B2c \tag{16a}$$

Therefore, from the knowledge of B already obtained δ_{HCl} may be calculated by Equation 16. If we make this calculation at 1 N concentration, $\log f^{*}$ equals 0.161, $\bar{\delta}_{\mathrm{HCl}}$ equals 11.75, and $(\delta_{\mathrm{H}} + \delta_{\mathrm{Cl}})$ equals 23.5.

We shall continue the simplifying assumption that the values of "a" for the lithium, sodium, potassium, hydrogen and chloride ions are the same and consider the mixtures. This assumption is not strictly in accord with the general theory, but will be shown to be sufficient for the present purpose and will be remedied later. At constant total molality, Hückel's Equation 122 is obtained from the general equations. This is

$$\Delta\Gamma = -\frac{0.0194 \times 10^{-8}}{a}\,\frac{\Gamma}{1 + A\sqrt{\Gamma}}\,(\delta_{\mathrm{H}} - \delta_{\mathrm{M}})\,\frac{\bar{c}}{\Gamma} + \frac{0.00225}{(1 + A\sqrt{\Gamma})^2}\,\Gamma^{3/2}\,(\delta_{\mathrm{H}} - \delta_{\mathrm{M}})^2\,\frac{\bar{c}}{\Gamma} - \frac{0.000246 \times 10^{-8}}{a}\left[\frac{3}{4}\,\frac{1}{1 + A\sqrt{\Gamma}} + \frac{1}{4}\,\frac{2}{(1 + A\sqrt{\Gamma})^2}\right]\Gamma^2. \left[(\delta_{\mathrm{H}} - \delta_{\mathrm{M}})\,(\delta_{\mathrm{H}} + \delta_{\mathrm{Cl}})\,2\,\frac{\bar{c}}{\Gamma} - (\delta_{\mathrm{H}} - \delta_{\mathrm{M}})^2\left(\frac{\bar{c}}{\Gamma}\right)\right]^2 \tag{17}$$

where

$$\Delta\Gamma = \log f_{\mathrm{HCl(KCl)}} - \log f_{\mathrm{HCl}} \tag{18}$$

$$\Gamma = \Sigma\, c_i z_i^2 \tag{19}$$

z_i is the valence of the ion, and $\bar{c}$ is the salt concentration. Γ is twice the ionic strength of Lewis and Randall except that the concentration is expressed in moles per liter. For uni-univalent electrolytes Γ equals $2c_T$ where c_T is the total normal concentration. At a given total concentration, everything on the right of this equation is known but $(\delta_{\mathrm{H}} - \delta_{\mathrm{M}})$ since we have found $(\delta_{\mathrm{H}} + \delta_{\mathrm{Cl}})$ to be 23.5. From the data in Table II, we find that $[\log f_{\mathrm{HCl(o)MCl}} - \log f_{\mathrm{HCl}}]$ or $\Delta\Gamma$ equals -0.0676, -0.0326 and -0.0098 for potassium, sodium and lithium chloride solutions, respectively, at 1 M total concentration. Since $f_{\mathrm{HCl(o)MCl}}$ refers to the pure salt solution at 1 N concentration, $\bar{c}/\Gamma$ equals $1/2$. Consequently,

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[15] Owing to a typographical error in Hückel's paper, $(\bar{\delta}\, 2c)^2$ is there written $\bar{\delta}\,(2c)^2$.

by substitution of these values as well as 3.38×10^{-8} for "*a*" and 0.784 for A, we obtain the following three equations for $(\delta_H - \delta_M)$.

$$\left.\begin{aligned} 0.00002998\ (\delta_H - \delta_K)^2 - 0.004823\ (\delta_H - \delta_K) + 0.0676 = 0 \\ 0.00002998\ (\delta_H - \delta_{Na})^2 - 0.004823\ (\delta_H - \delta_{Na}) + 0.0326 = 0 \\ 0.00002998\ (\delta_H - \delta_{Li})^2 - 0.004823\ (\delta_H - \delta_{L.}) + 0.0098 = 0 \end{aligned}\right\} \qquad (20)$$

Solving these, we find that $(\delta_H - \delta_K)$, $(\delta_H - \delta_{Na})$ and $(\delta_H - \delta_{Li})$ equal 15.51, 12.46 and 2.05, respectively. Since, according to the theory, the "δ's" are characteristic of the individual ions and therefore are additive, we may calculate $(\delta_M + \delta_{Cl})$ for each of the salts by subtracting $(\delta_H - \delta_M)$ from $(\delta_H + \delta_{Cl})$; $\bar{\delta}$ may then be obtained by dividing this latter quantity by 2, and B for each of the salts be evaluated by Equation 16. This has been done and the results are given in Table IV. Part I of this table contains the values of $(\delta_M + \delta_{Cl})$ and B calculated by the above method and also values of the activity coefficients computed by Equation 7. These values are compared to activity coefficients recently obtained by Scatchard[16] as a result of a careful study of existing data. Part II of Table IV contains values of "*a*," A, $(\delta_M + \delta_{Cl})$, $\bar{\delta}$ and B which were found

TABLE IV

CALCULATED AND OBSERVED ACTIVITY COEFFICIENTS OF CHLORIDES

PART I

	$a \times 10^8$	A	$(\delta_M + \delta_{Cl})$	$\bar{\delta}$	B
HCl	3.38	0.784	23.5	11.75	0.0805
LiCl	3.38	.784	21.45	10.72	.071
NaCl	3.38	.784	12.46	6.23	.0365
KCl	3.38	.784	8.00	4.00	.0218

	HCl		LiCl		NaCl		KCl	
m	γ (obs.)	γ (calcd.)	γ (obs.)	γ (calcd.)	γ (obs.)	γ (calcd.)	γ (obs.)	γ (calcd.)
0.01	0.899	0.908	0.901	0.904	0.903	0.903	0.899	0.902
.1	(.790)	(.790)	.779	.785	.778	.772	.762	.767
.3	.752	.745	.739	.735	.703	.701	.688	.687
.5	.752	.748	.736	.732	.671	.677	.654	.655
1	(.806)	(.806)	.753	.795	.634	.678	.605	.621
3	(1.31)	(1.31)	1.165	1.22	.686	.759	.569	.624

PART II

	$a \times 10^8$	A	$(\delta_M + \delta_{Cl})$	$\bar{\delta}$	B
LiCl	3.62	0.84	23.0	11.5	0.0698
NaCl	3.62	.84	11.0	5.5	.028
KCl	3.38	.784	6.4	3.2	.017

	LiCl		NaCl		KCl	
m	γ (obs.)	γ (calcd.)	γ (obs.)	γ (calcd.)	γ (obs.)	γ (calcd.)
0.01	0.901	0.905	0.903	0.903	0.899	0.902
.1	.779	.789	.778	.774	.762	.766
.3	.739	.743	.703	.700	.688	.683
.5	.736	.740	.671	.673	.654	.648
1.0	.753	.783	.634	.647	.605	.607
3.0	1.165	1.174	.686	.679	.569	.582

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[16] Scatchard, THIS JOURNAL, **47**, 648 (1925).

to agree more closely with the data of Scatchard. The values of these constants in the case of lithium chloride were obtained by Hückel.

The agreement between the values of γ for the salts calculated by Equation 7 from the constants computed by the mixture Equation 17 from our data with those independently obtained by Scatchard is indeed remarkable up to and including 0.5 M concentration. Above this concentration, the calculated values are somewhat higher. However, as shown in Part II of this Table, the values of "a" and $\bar{\delta}$ or A and B need only be changed very slightly to remedy this slight discrepancy. The magnitude of the mean diameters is of the same order as the values 2.81 $\times 10^{-8}$ and 3.17 $\times 10^{-8}$ obtained by Bragg and Bragg for the distances apart of the atoms in crystals of sodium and potassium chlorides, respectively.

Bi-univalent Electrolytes and Hydrochloric Acid—Bi-univalent Chloride Mixtures.—Hückel's approximate equation for γ of a bi-univalent electrolyte is

$$\log \gamma = -\frac{0.708\sqrt{6c}}{1 + A\sqrt{6c}} + B(6c) - \log (1 + 0.054\, m) \tag{21}$$

which is similar to Equation 7. Electromotive-force data of cells without liquid junction containing calcium, strontium and barium chlorides have been obtained by Lucasse,[17] from which we may compute the activity coefficients, and to which we may apply this equation. Plots of these electromotive forces against the log m were made and the values of E were read off at 0.01 M, 0.1 M and 1 M concentrations. These electromotive forces are given in Table V. The concentrations, c, in moles per liter of solution are also given. These are very nearly the same for all three salts.

Table V

Electromotive Forces of the Cells

$Ag \mid AgCl \mid MCl_2(m) \mid MxHg \mid MCl_2(0.01) \mid AgCl \mid Ag$

m	c	$E(BaCl_2)$	$E(SrCl_2)$	$E(CaCl_2)$
0.01	0.00996	0.0000	0.0000	0.0000
.1	.0993	.0737	.0752	.0769
1	.968	.1542	.1597	.1774

The values of A and B in Equation 21 were evaluated by the method employed by Hückel (p. 123 of his paper) with the following modifications. For bi-univalent electrolytes, we let

$$y = n - \log \frac{1000c}{M_0}(4)^{1/3};\ \log f = -\frac{0.708\sqrt{6c}}{1 + A\sqrt{6c}} + B(6c);\ y = y_0 - \frac{0.708\sqrt{6c}}{1 + A\sqrt{6c}} + B(6c),$$

and $\xi_1 = 6c_1;\ \xi_2 = 6c_2;\ \xi_3 = 6c_3$

The calculation of A, y_0 and B was then made in a manner identical with that described by Hückel. The values of the constants as well as

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[17] Lucasse, This Journal, **47**, 743 (1925).

the calculated and observed activity coefficients are given in Table VI. The observed activity coefficients are taken from Table III of Lucasse's paper. These were changed so that the calculated and observed values were the same at 0.01 *M*.

TABLE VI

CALCULATED AND OBSERVED ACTIVITY COEFFICIENTS OF THE ALKALINE EARTH CHLORIDES

		$BaCl_2$		$SrCl_2$		$CaCl_2$	
m	*c*	γ (obs.)	γ (calcd.)	γ (obs.)	γ (calcd.)	γ (obs.)	γ (calcd.)
0.01	0.00996	0.723	0.723	0.729	0.729	0.732	0.732
.02	.01993	.647	.654	.662	.664	.669	.669
.05	.0496	.554	.559	.571	.575	.582	.585
.07	.0697	.525	.524	.540	.543	.553	.557
.1	.0993	.495	.499	.512	.512	.528	.532
.2	.1983	.439	.433	.465	.463	.492	.499
.5	.492	.395	.390	.427	.431	.510	.525
.7	.684	.392	.388	.427	.436	.572	.575
1	.968	.398	.397	.449	.454	(.725)	(.673)[18]

CONSTANTS

Salt	*A*	$a \times 10^8$	*B*
$BaCl_2$	0.888	3.83	0.0285
$SrCl_2$	1.018	4.39	.0300
$CaCl_2$	1.008	4.35	.060[18]

The agreement between the observed results and those calculated by Equation 21 is excellent up to 1 *M* or an ionic strength of 3 for the barium and strontium chlorides and up to 0.7 *M* or an ionic strength of 2.1 for calcium chloride. Above these concentrations the calculated results are lower than those observed in the cases of the strontium and calcium chloride solutions. Further, 0.723 at 0.01 *M* barium chloride obtained by this method of extrapolation agrees closely with 0.716 which was obtained by Lewis and Linhart,[19] and the values of the mean ionic diameters appear to be of the expected magnitude.

As a further test of this theory, we shall make the calculation of the activity coefficients of hydrochloric acid in barium, strontium and calcium solutions from the constants obtained for hydrochloric acid, and the values of the "δ's" for the bi-univalent salts, and compare them with the values observed by Harned and Brumbaugh.[1c] To do this, it will first be necessary to deduce the equation for a bi-univalent electrolyte from the general equations (85 to 85c in Hückel's paper). As in the cases of the uni-univalent electrolytes, we shall let the apparent diameters be the

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[18] 0.066 was obtained by the above method but this yielded high results at the lower concentrations. Therefore, 0.060 has been employed which throws more weight on the results at concentrations below and including 0.7 *M*.

[19] Ref. 6, p. 1952. Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, **1923**, p. 344.

same for both ions, a simplification which makes a very complicated calculation much less complicated. Then, we obtain

$$a_1 = a_2 = a;\ x_1^\circ = x_2^\circ = x^\circ = A\sqrt{6c} \tag{22}$$

We let

$$\bar{\delta} = (\delta_{\mathrm{M}} + 2\delta_{\mathrm{Cl}})/3 \tag{23}$$

and

$$\log f = \log f^\circ + \log f^* \tag{14}$$

If we now apply the general equations, we obtain

$$\log f^\circ = -0.708\sqrt{\Gamma}/(1 + A\sqrt{\Gamma}) \tag{24}$$

where Γ equals $\Sigma c_i z_i^2$ or $6c$ and

$$\log f^* = \frac{0.0194 \times 10^{-8}}{a} \frac{1}{1 + A\sqrt{6c}}\, 4\,(3c)\,\bar{\delta} - 0.00225\sqrt{6c}\, 3c\,\bar{\delta}\, \frac{1}{(1 + A\sqrt{6c})^2} + \frac{0.000246 \times 10^{-8}}{a} \left[\frac{3}{4}\frac{1}{1 + A\sqrt{6c}} + \frac{1}{4}\frac{1}{(1 + A\sqrt{6c})^2}\right] 6\,(\bar{\delta}\, 3c)^2 \tag{25}$$

where

$$\log f^* = B(6c) \tag{26}$$

From the values of B, A and a, in Table V, $\log f^*$ was calculated for each of the salts for a value of c equal to 1 and then the "$\bar{\delta}$s" were computed by Equation 25. Thus, we obtained 7.14, 8.93 and 14.61 for $\bar{\delta}_{\mathrm{BaCl_2}}$, $\bar{\delta}_{\mathrm{SrCl_2}}$ and $\bar{\delta}_{\mathrm{CaCl_2}}$, respectively. If now we assume that $(\delta_{\mathrm{K}} + \delta_{\mathrm{Cl}})$ equals $2\,\delta_{\mathrm{Cl}}$ or 6.4 (Table III), then according to Equation 23, δ_{Ba}, δ_{Sr} and δ_{Ca} equal 15.0, 20.4 and 37.4, respectively.

It is now necessary to deduce the equation for the activity coefficient of hydrochloric acid in these bi-univalent chloride solutions from the general equations. We let c_1 equal the concentration of the acid and c_2 the concentration of the salt in moles per liter and continue the assumption of the equality of the "apparent diameters." For $\log f^\circ$, we obtain

$$\log f^\circ = \frac{-0.354\sqrt{\Gamma}}{1 + A\sqrt{\Gamma}} \tag{27}$$

where

$$\Gamma = \Sigma c_i z_i^2 = 2(c_1 + 3c_2) \tag{28}$$

and for $\log f^*$

$$\begin{aligned} \log f^*_{\mathrm{HCl(MCl_2)}} = {} & \frac{0.0194 \times 10^{-8}}{a} \frac{\Gamma}{1 + A\sqrt{\Gamma}} \left[\delta_{\mathrm{H}}\left(1 - \frac{3c_2}{\Gamma}\right) + \delta_{\mathrm{M}}\frac{c_2}{\Gamma} + \delta_{\mathrm{Cl}}\left(1 - \frac{c_2}{\Gamma}\right)\right] \\ & - 0.00225\,(\Gamma)^{3/2} \frac{1}{(1 + A\sqrt{\Gamma})^2} \left[\delta_{\mathrm{H}}\frac{c_1}{\Gamma} + \delta_{\mathrm{M}}\frac{c_2}{\Gamma} + \delta_{\mathrm{Cl}}\left(\frac{1}{2} - \frac{c_2}{\Gamma}\right)\right] \\ & + \frac{0.000246 \times 10^{-8}}{a} \left[\frac{3}{4}\frac{1}{1 + A\sqrt{\Gamma}} + \frac{1}{4}\frac{1}{(1 + A\sqrt{\Gamma})^2}\right] \Gamma^2 \left[\delta_{\mathrm{H}}\frac{c_1}{\Gamma} + \delta_{\mathrm{M}}\frac{c_2}{\Gamma} + \delta_{\mathrm{Cl}}\left(\frac{1}{2} - \frac{c_2}{\Gamma}\right)\right] \\ & \left[\delta_{\mathrm{H}}\left(\frac{3}{2} - \frac{3c_2}{\Gamma}\right) + \delta_{\mathrm{M}}\frac{c_2}{\Gamma} + \delta_{\mathrm{Cl}}\left(\frac{3}{2} - \frac{c_2}{\Gamma}\right)\right] \end{aligned} \tag{29}$$

To use this equation, we must know the values of δ for the individual ions. To effect this, we have assumed that δ_{K} equals δ_{Cl} equals 3.2 and hence δ_{H}, δ_{Cl}, δ_{Ba}, δ_{Sr} and δ_{Ca}, equal 20.3, 3.2, 15.0, 20.4 and 37.4, respectively.

For A, we have employed values which lie between that of 0.940 obtained by Scatchard for hydrochloric acid and that of the salt. Thus, we have let A equal 0.905 for the hydrochloric acid-barium chloride mixtures and 0.96 for the acid-strontium and acid-calcium chloride mixtures whence "a" equals 3.9×10^{-8} and 4.15×10^{-8}, respectively. Using these constants in Equations 28 and 29, we have made the calculation at 0.0, 0.2, 0.5 and 1.0 moles per liter salt concentrations. The values of f are thus obtained and then γ is computed by

$$\log \gamma = \log f - \frac{1}{2} \log (1 + 0.036\, m_{\mathrm{H}}) - \frac{1}{2} \log (1 + 0.036\, m_{\mathrm{Cl}}).$$

These values are given in Table VII where they are compared with the experimentally determined values of Harned and Brumbaugh.

TABLE VII

CALCULATED AND OBSERVED ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID IN SOLUTIONS OF THE ALKALINE EARTH CHLORIDES

	$BaCl_2$		$SrCl_2$		$CaCl_2$	
c_2	γ (obs.)	γ (calcd.)	γ (obs.)	γ (calcd.)	γ (obs.)	γ (calcd.)
0.0	0.798	0.798	0.801	0.801	0.801	0.801
.2	.714	.714	.722	.721	.727	.736
.5	.735	.730	.750	.740	.756	.791
1.0	.870	.819	.903	.845	.940	.996

Up to 0.5 M salt concentration or an ionic strength of 1.6, the agreement is remarkable considering the complicated nature of the calculation. Above this concentration, the calculated values of γ in the barium and strontium chloride solutions are somewhat less than the observed, while the reverse is true in the calcium chloride solutions. In the more concentrated solutions a small change in the δ values causes a considerable change in γ and, therefore, any experimental error in either the results with the single electrolytes or the mixtures would cause a considerable disagreement between the observed and the calculated values.

Concluding Remarks and Summary

In this study of the thermodynamics of these chloride electrolytes and their mixtures, we have been unable to find anything which within the limits of concentrations employed contradicts the extended theory of Debye and Hückel. These results along with those of Brönsted and LaMer in very dilute aqueous solutions, the calculations of A. A. Noyes and Baxter of results in dilute solutions of non-aqueous solvents and the calculations of Scatchard of results in concentrated solutions of non-aqueous solvents show that this theory affords a surprisingly accurate description of solutions of these electrolytes. We should remark, however, that the values of $\bar{\delta}$ are so high for lithium chloride and hydrochloric acid that they would lead, according to Equation 5, to an impossible situation, namely, to negative values of the dielectric constant in solutions above about 4 *M* concentration. Therefore, we are led to the conviction that the law of the linear variation of log γ is more general or is applicable to more electrolytes than the unmodified theory. This is also borne out by the fact that Equation 7 may be employed in calculating the activity coefficients of the hydroxides of potassium, sodium and lithium in aqueous solutions, whereas these activity coefficients cannot be calculated by Debye and Hückel's theory without the introduction of another factor.

Summary

1. Measurements of cells of the type, $H_2|HCl(m_1),\ MCl(m_2)|HgCl|Hg$, at constant total molalities have been made.

2. From the results, it appears that the logarithm of the activity coefficient of the acid varies linearly with the acid concentration at constant total molality up to 3 *M* total concentration.

3. Revised measurements of the above cells containing acid at 0.01 *M* and 0.1 *M* and chlorides at various concentrations have been presented.

4. The fifteen series of results with uni-univalent electrolytes have been shown to be calculable to within narrow limits by means of Hückel's approximate equation.

5. From these data on the mixtures, the constants of the individual electrolytes were computed by Debye and Hückel's theory. These were shown to be very nearly the same as the constants derived from data on the individual electrolytes.

6. The activity coefficients of calcium, strontium and barium chlorides were found to be calculable by Hückel's approximate equation and from these data, it was shown that the activity coefficient of hydrochloric acid in these three salt solutions could be calculated.

7. Our calculations show a remarkable agreement between the observed results and the general theory of Debye and Hückel. In fact, nothing seriously contradictory to their general theory has developed from the numerous results on chloride solutions here considered. The theory cannot be applied to solutions of the alkaline hydroxides without the introduction of another factor.

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