The writer wishes to thank Dr. H. S. Taylor for initiating and sustaining this work with his helpful suggestions.

Summary

It has been shown that in a mixture of zinc and copper oxides the zinc oxide is completely reduced with hydrogen at 300°.

An explanation of the reduction at this relatively low temperature has been offered.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE ACTIVITY COEFFICIENT OF HYDROGEN CHLORIDE IN AQUEOUS SOLUTIONS WITH BARIUM AND LANTHANUM CHLORIDES AT 25°[1]

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In this paper are given the results of three series of measurements of the electromotive force of the hydrogen-calomel cell, with hydrochloric acid and with mixtures of hydrogen and barium chlorides and hydrogen and lanthanum chlorides, respectively. The concentration of both chlorides in each series was varied over wide limits.

Other investigators have measured similar cells, using hydrochloric acid at fixed concentrations, 0.001, 0.01, or 0.1 *M*, but the results of the measurements do not permit an adequate test of the principle of the ionic strength, in solutions of constant ionic strength, when the proportion of the acid is varied.[2] Loomis, Essex and Meacham[3] used mixtures of hydrogen chloride and potassium chloride at a total constant molality of chloride ion of 0.1 *M*, but their results are inconclusive. Since the presentation of this work Güntelberg[4] has published measurements with the hydrogen-silver chloride cell and mixtures of hydrogen chloride with potassium, sodium, cesium and lithium chlorides at 0.1 *M* total chloride ion concentration.

Harned and Åkerlöf[5] have also published measurements of the hydrogen-calomel cell with mixtures of lithium, sodium and potassium chlorides at constant molalities of 0.1, 1 and 3 *M*.

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[1] Presented at the Symposium on Strong Electrolytes, Los Angeles Meeting of the American Chemical Society, August 4, 1925.

[2] For a discussion of the methods of calculating activity coefficients in mixtures, and discussion of the older work, see (a) Lewis and Randall, THIS JOURNAL, **43**, 1112 (1921); (b) "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923**, Chap. XXVIII. Also (c) Harned and Brumbaugh, THIS JOURNAL, **44**, 2729 (1922). (d) Harned, *ibid.*, **48**, 326 (1926).

[3] Loomis, Essex and Meacham, *ibid.*, **39**, 1133 (1917).

[4] Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926).

[5] Harned and Åkerlöf, *Physik. Z.*, **27**, 411 (1927).

Solutions.—Barium chloride, c. p., was twice recrystallized from conductivity water. Lanthanum nitrate was converted into the chloride by digestion with concd. hydrochloric acid, and the chloride then twice recrystallized by passing hydrogen chloride gas into the solution. The crystals were dried over sulfuric acid, in a vacuum desiccator, for several days, and finally dehydrated in an atmosphere of hydrogen chloride gas. Constant-boiling hydrochloric acid was prepared from c. p. acid.

Stock solutions, in conductivity water, of hydrochloric acid, barium chloride and lanthanum chloride were made up by weight and the chloride contents checked by precipitation as silver chloride. The individual solutions for the cell measurements were made up by weight from these stock solutions. Vacuum corrections were made in each case. Concentrations are expressed in moles per 1000 g. of water.

In the case of the hydrogen chloride-barium chloride mixtures, six series of cells were measured; in each series the hydrogen chloride and barium choride were varied in such manner as to keep the total stoichiometrical molality of the chloride ion constant. The chloride-ion concentrations in these six series were 0.05, 0.1, 0.2, 0.5, 1.0 and 2.0 *M*, respectively. Each of the series includes four determinations in which the molal ratio of hydrogen chloride to barium chloride was 3 moles of HCl to 0.5 mole of $BaCl_2$, 1 mole of HCl to 1 mole of $BaCl_2$, 1 mole of HCl to 1.5 moles of $BaCl_2$, and 1 mole of HCl to 4.5 moles of $BaCl_2$.

In the case of the lanthanum chloride-hydrogen chloride mixtures the same procedure was followed, except that only four series of measurements were obtained. The chloride-ion concentration in these four series was 0.05, 0.1, 0.2 and 0.5 *M*, respectively. Each of the series includes three determinations in which the molal ratio of hydrogen chloride to lanthanum chloride was 3 moles of HCl to $^1/_3$ mole of $LaCl_3$, 2 moles of HCl to $^2/_3$ mole of $LaCl_3$, and 1 mole of HCl to 1 mole of $LaCl_3$.

Cells.—The hydrogen and calomel electrodes, and the electrical-measuring system with its accessories, were the same as those described by Lewis, Brighton and Sebastian,[6] except the platinum plates in the hydrogen electrodes, which were covered with platinum black. These electrodes were entirely satisfactory. Two cells at each concentration were prepared, and the difference in the electromotive force of the duplicate cells was always less than 0.2 millivolt. The electromotive force was read to 0.01 mv., corrected to 1 atm. of hydrogen pressure, and the mean of the results of the two cells to the nearest 0.1 mv. is given in the tables

The Hydrochloric Acid Series.—The results of a few measurements of the cell Pt, H_2(g), HCl(aq.), HgCl(s), Hg are given in Table I. Col. 1 gives the molality, *m*, Col. 2 the square root of the molality, $m^{1/2}$, and Col. 3 the measured electromotive force, **E**.

TABLE I

ELECTROMOTIVE FORCE OF THE CELL PT, H_2(G), HCL (AQ.), HGCL (S), HG AT 25°

m	$m^{1/2}$	**E**	$\log \gamma$	$(\log \gamma)/m^{1/2}$	γ
0.05	0.2236	0.4323	−0.0811	−0.363	0.830
.10	.3162	.3989	− .0997	− .314	.795
.20	.4471	.3651	− .1150	− .257	.767
.50	.7071	.3186	− .1200	− .170	.759
1.00	1.0000	.2793	− .0888	− .089	.815

These results will be reviewed in another place, where it will be shown that we may take the standard electromotive force, **E**°, of this cell to be

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[6] Lewis, Brighton and Sebastian, THIS JOURNAL, 39, 2245 (1917).

0.2688 v. Col. 4 gives the value of the logarithm of activity coefficient calculated by the equation[7]

$$\log \gamma = [E^\circ - (E + 0.1183 \log m)]/0.1183 \qquad (1)$$

The last column gives the value of the activity coefficient. These values are also plotted as Curve A in Figs. 1 and 2. They agree with values obtained by other authors.

For interpolation purposes the plot of the activity coefficient of hydrochloric acid, or its logarithm, against a simple function of the molality, as in Curve A of Fig. 1, is not convenient because of the decided minimum in the curve at about 0.5 *M*. Therefore, we sought a function of the activity coefficient which would enable us to obtain a plot showing a nearly linear variation with some simple function of the molality. Such a function is suggested by an equation of the form[8]

$$(\log \gamma)/m^{1/2} = A + Bm^{1/2} + \ldots \qquad (2)$$

Col. 5 of Table I gives the values of $(\log \gamma)/m^{1/2}$, which are plotted as Curve A on Fig. 2. The intercept of the curve on the ordinate gives the value of *A* and the slope the value of *B*.

The Barium Chloride Series.—The results for the hydrogen chloride-barium chloride series are given in Table II. Col. 1 gives the molality of the hydrogen chloride; Col. 2 the molality of the barium chloride; Col. 3 the square root of the ionic strength, $\mu^{1/2}$; Col. 4 the observed value of the electromotive force of the cell Pt, H_2(g), HCl(aq.) + $BaCl_2$(aq.), HgCl(s), Hg; Col. 5 the value of the logarithm of the activity coefficient,

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[7] Ref. 2b, p. 334.

[8] Lewis and Linhart [THIS JOURNAL, **41**, 1954 (1919)] wrote

$$\log \gamma = -(\alpha + 1)\beta m^{\alpha}/2.303\alpha \qquad (3)$$

where α and β are constants. Since α for uni-univalent electrolytes is nearly 0.5, Lewis and Randall (see Ref. 2a, and 2b, p. 343; Equation 3 is in the simplified form used by them) wrote as an approximate formula

$$\log \gamma = -3\beta m^{1/2}/2.303 = Am^{1/2} \qquad (4)$$

Harned [*ibid.*, **42**, 1808 (1920); **44**, 252 (1922); Ref. 2c] used an equation $\log F_a = \alpha c - \beta c^m$, which in our notation is

$$\log \gamma = Am^n + Bm \qquad (5)$$

where *A*, *B* and *n* are empirically determined constants. Brönsted [*ibid.*, **44**, 938 (1922); **45**, 2898 (1923)], taking $n = 1/2$, simplified this equation and wrote

$$\log \gamma = Am^{1/2} + Bm \qquad (6)$$

where *A* is now the same constant for salts of the same valence type. Brönsted and LaMer [*ibid.*, **46**, 555 (1924)] pointed out that the equation of Brönsted corresponds more closely to the Debye and Hückel derivation [*Physik. Z.*, **24**, 185 (1923)] than does that of Harned. His equation is identical with the approximate equation of Lewis and Randall (Equation 4), with the exception of the added term *Bm*. By dividing by $m^{1/2}$, Equation 6 becomes Equation 2, which we shall use as an empirical equation.

An equation similar to Equation 2 has been recently used by Randall [THIS JOURNAL, **48**, 2512 (1927). Randall and White, *ibid.*, **48**, 2514 (1927)] for representing the divergence functions *h* and *j* derived from measurements of the colligative properties of the solvent.

log γ of the hydrogen chloride; Col. 6 the quotient (log γ)/$\mu^{1/2}$; and Col. 7 the value of the activity coefficient, γ.

Table II

The Activity Coefficient of Hydrogen Chloride in Solutions of Barium Chloride at 25°

m HCl	m $BaCl_2$	$\mu^{1/2}$	E	log γ	(log γ)/$\mu^{1/2}$	γ
Ratio: 3 moles of HCl to 0.5 mole of $BaCl_2$						
0.0375	0.00625	0.237	0.4404	−0.0847	−0.3574	0.823
.0750	.0125	.336	.4069	− .1047	− .3116	.786
.1500	.0250	.474	.3731	− .1202	− .2536	.758
.3750	.0625	.750	.3272	− .1282	− .1709	.744
.7500	.1250	1.061	.2886	− .1047	− .0987	.786
1.5000	.2500	1.500	.2420	− .0119	− .0079	.973
Ratio: 2 moles of HCl to 1 mole of $BaCl_2$						
0.0250	0.0125	0.250	0.4514	−0.0918	−0.3672	0.810
.0500	.0250	.354	.4180	− .1107	− .3127	.775
.1000	.0500	.500	.3842	− .1265	− .2530	.747
.2500	.1250	.790	.3384	− .1369	− .1733	.730
.5000	.2500	1.120	.3009	− .1208	− .1079	.757
1.000	.5000	1.580	.2549	− .0331	− .0209	.927
Ratio: 1 mole of HCl to 1.5 moles of $BaCl_2$						
0.0125	0.01875	0.262	0.4701	−0.0993	−0.3790	0.796
.0250	.0375	.371	.4366	− .1174	− .3164	.763
.0500	.0750	.524	.4030	− .1345	− .2567	.734
.1250	.1875	.829	.3573	− .1464	− .1766	.714
.2500	.3750	1.171	.3198	− .1305	− .1115	.741
.5000	.7500	1.658	.2749	− .0515	− .0311	.888
Ratio: 1 mole of HCl to 4.5 moles of $BaCl_2$						
0.0050	0.0225	0.269	0.4936	−0.0993	−0.3691	0.796
.0100	.0450	.381	.4605	− .1208	− .3171	.757
.0200	.0900	.538	.4272	− .1398	− .2599	.725
.0500	.2250	.852	.3819	− .1548	− .1817	.700
.1000	.4500	1.204	.2314	− .1422	− .1181	.721
.2000	.9000	1.704	.2995	− .0603	− .0354	.870

In Fig. 1 the values of the activity coefficient given in Table I are plotted against the square root of the ionic strength. Curves B to D represent the experimental data for the four different molal ratios. Curve A represents the data for pure hydrochloric acid solutions as given in Table I. Each of the curves for the mixtures shows a minimum similar to the behavior of the acid itself. However, the minimum is shifted in the direction of higher concentration as the ratio of barium chloride to hydrogen chloride increases.

Just as in the case of pure aqueous hydrochloric acid, the plot of log γ against $\mu^{1/2}$ is not suitable for interpolation purposes, because of the pronounced minimum in the curves. We accordingly set up an equation

$$(\log \gamma)/\mu^{1/2} = A + B\mu^{1/2} + \ldots, \qquad (7)$$

which is identical with Equation 2, except that we have used the ionic strength in place of the molality. We have plotted $(\log \gamma)/\mu^{1/2}$ against $\mu^{1/2}$ in Fig. 2. It is seen that the curves which represent solutions containing a constant proportion of hydrochloric acid and barium chloride appear to approach the same value of the intercept on the $(\log \gamma)/\mu^{1/2}$ axis, as does the curve for pure hydrogen chloride, but the value of B appears to be somewhat smaller as the percentage of barium chloride increases.

For each of the curves A to E we have calculated points represented by triangles in Fig. 1, corresponding to that ionic strength at which the molality of the hydrogen chloride would be equal to 0.1. The broken curve F, therefore, represents the activity coefficient of a series of mixtures in which the concentration of the hydrogen chloride is constant and equal to 0.1 M. Harned and Brumbaugh[2c] calculated the activity coefficients of hydrogen chloride in several such mixtures containing 0.1 M hydrochloric acid. Their results recalculated to $\mathbf{E}^\circ = 0.2688$ are represented by squares in Fig. 1. The values are seen to agree with ours.

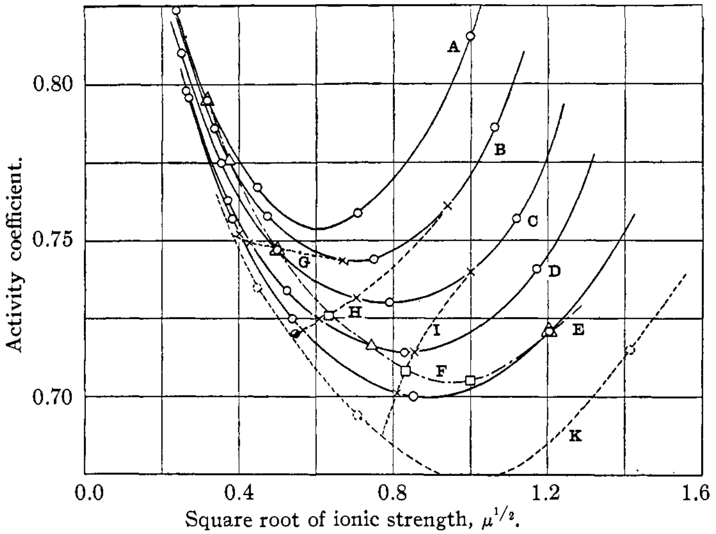

Fig. 1.—The activity coefficient of hydrochloric acid in mixtures with barium chloride. A, pure HCl; B, 6 HCl : 1 $BaCl_2$; C, 2 HCl : 1 $BaCl_2$; D, 2 HCl : 3 $BaCl_2$; E, 2 HCl : 9 $BaCl_2$; F, HCl, m = 0.1; G, $BaCl_2$, m = 0.05; H, $BaCl_2$, m = 0.1; I, $BaCl_2$, m = 0.2; K, 1 HCl:∞$BaCl_2$; □, H and B, HCl, m = 0.1; ◑, 1 HCl : 50 $BaCl_2$.

Curves G, H and I are for solutions of constant barium chloride content, the concentration of the barium chloride being 0.05, 0.1 and 0.2 M, respectively. Each of these curves will end abruptly, as shown, at a point corresponding to the ionic strength of the pure barium chloride solution.

This point should, therefore, represent the value of the activity coefficient of hydrogen chloride in barium chloride solutions containing an infinitely small amount of hydrogen chloride. This extrapolation is perhaps not as certain as one which we shall consider later, and from which the dotted curve K, shown in Figs. 1 and 2, is obtained.

Lanthanum Chloride Series.—The results for the hydrogen chloride-lanthanum chloride series are given in Table III. The column headings are the same as those for Table II.

TABLE III

THE ACTIVITY COEFFICIENT OF HYDROGEN CHLORIDE IN SOLUTIONS OF LANTHANUM CHLORIDE AT 25°

m HCl	*m* $LaCl_3$	$\mu^{1/2}$	**E**	log γ	(log γ)/$\mu^{1/2}$	γ
Ratio: 3 moles of HCl to $^1/_3$ mole of $LaCl_3$						
0.0375	0.00417	0.250	0.4406	−0.0882	−0.3528	0.816
.0750	.00834	.354	.4073	− .1080	− .3051	.780
.1500	.01680	.500	.3736	− .1242	− .2484	.751
.3750	.04167	.791	.3272	− .1305	− .1650	.741
Ratio: 2 moles of HCl to $^2/_3$ mole of $LaCl_3$						
0.0750	0.00833	0.274	0.4514	−0.0918	−0.3350	0.810
.0500	.01667	.387	.4184	− .1141	− .2948	.769
.1000	.03334	.548	.3852	− .1345	− .2454	.734
.2500	.0833	.866	.3397	− .1476	− .1704	.712
Ratio: 1 mole of HCl to 1 mole of $LaCl_3$						
0.0125	0.0125	0.296	0.4703	−0.1009	−0.3409	0.793
.0250	.0250	.418	.4374	− .1236	− .2957	.752
.0500	.0500	.592	.4040	− .1428	− .2412	.720
.1250	.1250	.936	.3584	− .1554	− .1660	.699

In Fig. 3 the values of γ given in Table III are plotted against $\mu^{1/2}$. Curves L, M and N represent the experimental data for the three molal ratios, while Curve A again represents the data for pure hydrochloric acid. These data are also represented in Fig. 2 by the lower group of Curves L, M, N, where (log γ)/$\mu^{1/2}$ is plotted against $\mu^{1/2}$. Here again the intercept *A* for solutions containing a constant proportional amount of lanthanum chloride and hydrogen chloride is seen to be the same as that for pure hydrochloric acid, while the value of *B* is somewhat smaller. The curves P are for solutions containing an infinitely small amount of hydrochloric acid.

Variation of the Activity Coefficient at Constant Ionic Strength.—Lewis and Randall,[2b] in proposing the principle of the ionic strength, namely, that the activity coefficient of hydrogen chloride would depend only on the ionic strength, stated that this was a limiting rule, and one which, in the absence of any experimental knowledge, must of necessity be considered as a first approximation to the truth. They also limited their rule to dilute solutions, where the activity coefficient of pure substances is nearly unity. Their discussions point out deviations from the rule in moderately dilute solutions, but their summary of the data affords a remarkable confirmation of the principle, especially that part which states that the activity coefficient depends more particularly upon that function of the concentration which they called the ionic strength, rather than upon the equivalent concentration, or some other function of the concentration.

Brönsted[9] considered the variation of the activity coefficient at constant total molality, and made three conclusions for the case of a binary mixture of uni-univalent electrolytes containing a common ion at a fixed concentration, for example, sodium and potassium chlorides containing 0.1 *M* chloride ion: (1) that the activity coefficient of the sodium chloride in the solution containing an infinitely small amount of this salt was equal to the activity coefficient of the potassium chloride in the solution containing an infinitely small amount of potassium chloride; (2) that the logarithm of the activity coefficient in this limiting case (identified by the first conclusion) is the mean of the logarithm of the activity coefficient of the two salts at 0.1 *M*; (3) that the variation of the logarithm of the activity coefficient of sodium chloride between these two limits is a linear function of the ratio of the sodium chloride to the total sodium and potassium chlorides, and conversely.

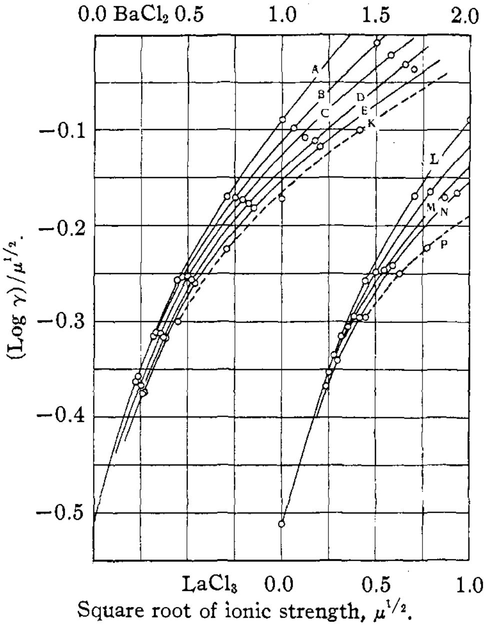

Fig. 2.—Variation of the function $(\log \gamma)/\mu^{1/2}$ with the square root of the ionic strength at 25°. A, pure HCl; B, 6 HCl : 1 $BaCl_2$; C, 2 HCl : 1 $BaCl_2$; D, 2 HCl : 3 $BaCl_2$; E, 2 HCl : 9 $BaCl_2$; K, 1 HCl : ∞ $BaCl_2$; L, 9 HCl : 1 $LaCl_3$; M, 3 HCl : $LaCl_3$; N, 1 HCl : 1 $LaCl_3$; P, 1 HCl : ∞ $LaCl_3$.

Harned[2d] found that the change in the logarithm of the activity coefficient of hydrochloric acid in mixtures with sodium, potassium and lithium chlorides at 0.1 *M* total chloride content was proportional to the fraction of metal ion to total positive ion present. The results were in agreement with the third conclusion of Brönsted,[9] but not with the second. The result was again verified by Güntelberg[4] with very accurate measure-

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[9] Brönsted, THIS JOURNAL, **45**, 2898 (1923).

ments of mixtures with these salts and with cesium chloride, and again by Harned and Åkerlöf[5] in mixtures with lithium, potassium and sodium chlorides at 0.1, 1 and 3 *M*. These authors, from the empirical constants calculated from the equation of Hückel,[10] were able to obtain approximate values of the activity coefficients in the mixtures.

In considering the composition of a solution of a mixture of chlorides, such as a mixture of hydrogen and lanthanum chlorides, the usual custom when a common ion is present is to take the concentration of the hydrogen chloride as that of the hydrogen-ion constituent, and that of the lanthanum chloride as that of the lanthanum ion constituent. The activity of these substances is dependent, however, not upon the molality of the positive-ion constituent alone, but upon the geometrical mean of the molality of both ion constituents, and we should perhaps think of the mean molality, rather than the molality of the hydrogen ion, as representing the real concentration of the hydrogen chloride present in the mixture with a common ion.

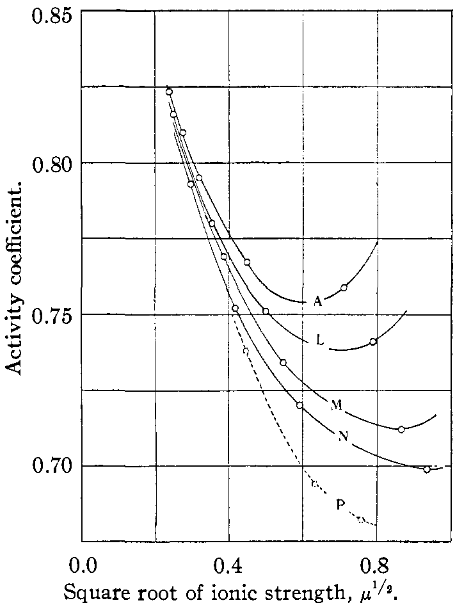

Fig. 3.—Activity coefficient of hydrochloric acid in mixtures with lanthanum chloride. A, pure HCl; L, 9 HCl : 1 $LaCl_3$; M, 3 HCl: 1 $LaCl_3$; N, 1 HCl : 1 $LaCl_3$; P, 1 HCl:$\infty$$LaCl_3$.

Our measurements offer an opportunity of testing the ionic-strength rule over a wide range of concentrations. In studying the activity coefficient of solutions of constant ionic strength, it seemed evident, since we were dealing with the mean activity coefficient, that the most useful function of the concentration would be the ratio of the mean molality of the salt whose activity coefficient was being considered to the mean molality of the same salt when pure. In Table IV are given the values of log γ of hydrochloric acid in solutions of barium chloride at various constant ionic strengths. Col. 1 gives the composition of the solution, Col. 2 the ratio of the mean molality of the acid in the mixture to the molality of pure acid of the same ionic strength, Col. 3 the ratio of the ionic strength of the hydrogen chloride (molality of hydrogen ion) to the total ionic strength; Cols. 4 and 6 give the values of the function $(\log \gamma)/\mu^{1/2}$ as read from Fig. 2, and Cols. 5 and 7 the values of log γ.

[10] Hückel, *Physik. Z.*, **26**, 93 (1925).

TABLE IV

VARIATION OF THE ACTIVITY COEFFICIENT WITH THE MEAN MOLALITY AT CONSTANT IONIC STRENGTH

$\frac{m(\text{HCl})}{m(\text{BaCl}_2)}$	$\frac{m_{\pm}(\text{HCl})}{m(\text{pure HCl})}$	$\frac{\mu\ \text{HCl}}{\mu\ (\text{total})}$	$\frac{\log \gamma}{\mu^{1/2}}$	$\log \gamma$	$\frac{\log \gamma}{\mu^{1/2}}$	$\log \gamma$
			μ = 0.2 *M*		μ = 0.5 *M*	
1:0	1.000	1.000	−0.257	−0.115	−0.170	−0.120
6:1	0.772	0.667	− .265	− .118	− .182	− .129
2:1	.566	.400	− .275	− .123	− .193	− .136
2:3	.365	.182	− .281	− .126	− .204	− .144
2:9	.218	.069	− .290	− .130	− .215	− .152
0:1	.000	.000	− .300	− .134	− .225	− .159
			μ = 1.0 *M*		μ = 2.0 *M*	
1:0	1.000	1.000	−0.089	−0.089	0.006	0.008
6:1	0.772	0.667	− .111	− .111	− .027	− .038
2:1	.566	.400	− .125	− .125	− .048	− .068
2:3	.365	.182	− .141	− .141	− .071	− .100
2:9	.218	.069	− .153	− .153	− .085	− .120
0:1	.000	.000	− .172	− .172	− .103	− .146

Similar calculations for the lanthanum chloride series are given in Table V. The column headings are the same as those for Table IV.

TABLE V

VARIATION OF THE ACTIVITY COEFFICIENT WITH THE MEAN MOLALITY AT CONSTANT IONIC STRENGTH

$\frac{m(\text{HCl})}{m(\text{LaCl}_3)}$	$\frac{m_{\pm}(\text{HCl})}{m(\text{pure HCl})}$	$\frac{\mu\ \text{HCl}}{\mu\ (\text{total})}$	$\frac{\log \gamma}{\mu^{1/2}}$	$\log \gamma$	$\frac{\log \gamma}{\mu^{1/2}}$	$\log \gamma$	$\frac{\log \gamma}{\mu^{1/2}}$	$\log \gamma$
			μ = 0.2 *M*		μ = 0.4 *M*		μ = 0.6 *M*	
1:0	1.000	1.000	−0.257	−0.115	−0.193	−0.122	−0.148	−0.115
9:1	0.693	0.667	− .268	− .120	− .207	− .131	− .170	− .132
3:1	.471	.333	− .276	− .123	− .223	− .141	− .187	− .145
1:1	.286	.143	− .283	− .127	− .234	− .148	− .201	− .156
0:1	.000	.000	− .295	− .132	− .251	− .159	− .223	− .173

We have plotted in Fig. 4 the values of log γ from Tables IV and V against the ratio of the mean molality of the hydrochloric acid to the molality of the acid when pure. The plots on the left are for the mixtures with barium chloride, and on the right those with lanthanum chloride. The various curves represent mixtures at constant ionic strengths as indicated. These curves show a nearly linear variation of log γ with the fraction of hydrochloric acid. It is the intercept of these lines on the axis of zero mean molality of hydrogen chloride which we have used in constructing the dotted curves K and P in Figs. 1, 2 and 3.

It was found difficult to obtain a reproducible potential when the ratio of the hydrogen chloride to the barium chloride was small. Since it is the mean molality of the hydrogen and chloride ions rather than the molality of the hydrogen ion which determines the potential, and which is the variable in the curves of Fig. 4, the concentration of the hydrogen must be relatively very small if we are to test the principle of the ionic strength near the right in those figures. We obtained only one measurement which was reproducible, and this measurement indicates that the curves in the figures continue as straight lines. The composition of this solution was 0.2 *M* with respect to chloride ion, and the ratio of hydrogen chloride to barium chloride was 1 mole of hydrogen chloride to 50 moles of barium chloride. The potential of this cell was 0.4871 v., which gives a value of 0.718 for the activity coefficient of the hydrogen chloride. The ionic strength of this solution was 0.289, or $\mu^{1/2} = 0.547$. By referring to Fig. 1 it will be seen that this point (shaded circle) falls very close to the terminus of Curve H, which constitutes the series of solutions of constant 0.2 *M* barium chloride content.

The same rule has been applied[11] to the data of Güntelberg[4] and of Harned and Åkerlöf.[5] The variation of the logarithm of the activity coefficient with the ratio of the mean molality of the acid to the mean molality of pure acid at the same ionic strength is in no case linear for added univalent chloride. The curves in plots corresponding to Fig. 4 are all concave upwards, but the limiting value at zero acid concentration is the same within the error of extrapolation.

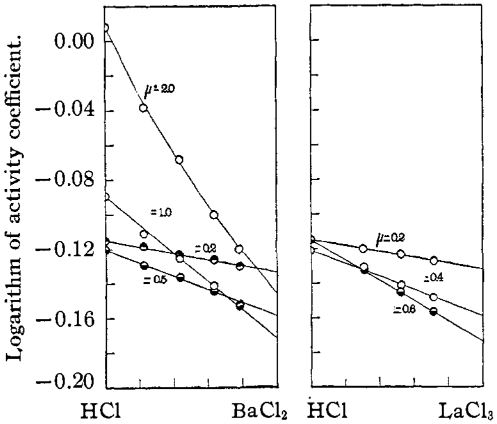

Fig. 4.—Variation of the logarithm of the activity coefficient at constant ionic strength.

Harned's[2d] equation assumes that the "ionic diameter" of all the ions is the same. He finds that the logarithm of the activity coefficient should vary as the ratio of the ionic strength of the acid by the total ionic strength. Plots of our data similar to those of Fig. 4, with abscissas corresponding to those of Col. 3 in Tables IV and V, are all convex upwards with about the same limit at zero acid concentration.

The measurements of Harned and Brumbaugh[2c] for mixtures with barium chloride are in agreement with our results. It is possible that the linear variation with the ratio of the mean molality in the case of added polyvalent salts is accidental, for we present no theoretical basis for this rule. It seems reasonable that the activity of hydrochloric acid should be approximately the same in solutions of the same ionic strength whether

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[11] The senior author is alone responsible for portions of this paper dealing with work appearing after May, 1925.

the added salt contains common or non-common ions, providing these have the same characteristics. According to our rule this would not be true. There are no measurements for such a case.

Summary

1. New measurements of the electromotive force of the hydrogen-calomel cell with hydrochloric acid at 0.05 to 1 M are presented.

2. A new plot for the interpolation of activity coefficient values is shown.

3. Measurements of the electromotive force of the hydrogen-calomel cell with mixtures of hydrogen chloride with barium and lanthanum chlorides are presented.

4. The logarithm of the activity coefficient of the hydrochloric acid in mixtures of constant ionic strength is shown to be a nearly linear function of the ratio of the mean molality of the acid to the molality of pure acid at the same ionic strength.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE ACTIVITY COEFFICIENT OF SULFURIC ACID IN AQUEOUS SOLUTIONS WITH SODIUM SULFATE AT 25°

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Measurements of the electromotive force at 25° of the cell $H_2(g)$, $H_2SO_4 + Na_2SO_4(aq.)$, $Hg_2SO_4(s)$, $Hg(l)$, have been recently published by Harned and Sturgis[1] and by Åkerlöf,[2] from which the activity coefficient in solutions of low hydrogen-ion concentration were calculated. We have employed the same cell, but have used concentrations of acid and salt which enable us to calculate the activity coefficient of sulfuric acid in mixtures of all proportions up to 2 M.

A solution of sodium bisulfate is being used to a large extent as a substitute for sulfuric acid in many industrial processes. From these measurements, the concentration of sodium bisulfate which will give the same effective concentration as a solution of pure sulfuric acid can be calculated.

Four series of cells were measured in which the stoichiometrical molality of the sulfate ion remained constant at 0.2, 0.5, 1.0 and 2.0 M, respectively. In each series the molal ratio of sulfuric acid to sodium sulfate was varied.

The electrical system,[3] hydrogen electrode and mercurous sulfate electrodes were the same as those previously used in this Laboratory,

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[1] Harned and Sturgis, THIS JOURNAL, **47**, 945 (1925).

[2] (a) Åkerlöf, *ibid.*, **48**, 1160 (1926). (b) Harned and Åkerlöf, *Physik. Z.*, **27**, 411 (1926).

[3] (a) Lewis, Brighton and Sebastian, THIS JOURNAL, **39**, 2245 (1917). (b) Randall and Cushman, *ibid.*, **40**, 393 (1918).