THE ACTIVITY COEFFICIENT OF HYDROCHLORIC ACID IN AQUEOUS SALT SOLUTIONS

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The present investigation is concerned principally with the calculation of the activity coefficients of hydrochloric acid in mixtures of solutions of hydrochloric acid and chlorides of both the alkali and alkaline-earth metals. In addition, data have been accumulated from which some approximate conclusions may be drawn regarding the individual hydrogen- and chloride-ion activities of the solutions containing hydrochloric acid and barium, strontium and calcium chlorides. The partial molal heat content changes of hydrochloric acid in the mixtures have also been measured.

Harned[1] has measured cells of the type

$$H_2 \mid MeCl_x \ (c) \ \text{in HCl} \ (c_1) \mid HgCl \mid Hg \qquad \text{Type I}[2]$$
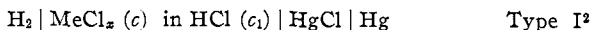
when $x = 1$, Me was potassium, sodium or lithium, and $c_1 = 0.1$. To supplement these data, measurements of cells of Type I where Me represents calcium, strontium and barium chlorides, $x = 2$, and $c_1 = 0.1$ are presented in this communication. Further, measurements of $H_2 \mid KCl \ (c)$ in HCl $(c_1) \mid AgCl \mid Ag$, and $H_2 \mid KCl \ (c)$ in HCl $(c_1) \mid HgCl \mid Hg$, containing hydrochloric acid at concentrations of 0.01 M and 0.001 M, respectively, have been included. Measurements of all of these cells have been carried out at 18°, 25° and 30°. From these results, the free-energy and heat-content changes of the cell reaction in the presence of the salts have been computed, the activity coefficients of hydrochloric acid in the mixtures, and also the partial molal heat-content changes of hydrochloric acid. The determination of the heat-content changes are of little value for the purpose of the present investigation, but since considerable care was exercised in making up the cells, and the determination of the temperature coefficients is not a matter of great difficulty, the results have been included. Such results, however, will be of considerable value in a complete thermodynamic treatment of these solutions.

In addition, measurements of the electromotive forces of the cells

$$H_2 \mid MeCl_x \ (c) \ \text{in HCl} \ (c_1) \mid \text{sat. KCl} \mid HgCl \mid Hg \qquad \text{Type II}[3]$$
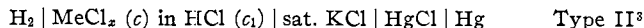
have been made where Me represents calcium, strontium and barium, $x = 2$ and $c_1 = 0.1$. Harned[4] has made measurements of the same cells, but did not extend his measurements to as high concentrations as were

[1] Harned, (a) THIS JOURNAL, 38, 1986 (1916); (b) ibid., 42, 1808 (1920).

[2] This kind of cell will be referred to as Type I.

[3] This kind of cell will be referred to as Type II.

[4] Harned, THIS JOURNAL, 37, 2460 (1915).

desired for the present purpose.   For this reason they have been repeated. From the latter data, in combination with the data on cells of Type I, approximate conclusions may be drawn concerning the activities and activity coefficients of the hydrogen and chloride ions in the mixtures.

General Equations and Nomenclature

Only cells of Types I and II will be considered.   The electromotive forces of cells of Type I will be denoted by $E(1)$, of Type II, $E(2)$; also, let $E_0(1)$ equal $E(1)$ when c, the molal salt concentration, equals zero; and let $E_0(2)$ equal $E(2)$ when c equals zero.

$2E(1) \times 96,500$ will be the free energy decrease of the cell reaction $H_2 + 2HgCl = 2Hg + 2HCl(c_1)$ in the presence of the acid and the acid-salt mixtures.   Further,

$$(E_0 (1) - E (1)) \times 96,500 = (-\Delta \bar{F})_1 = RT \, ln \frac{a_{H(s)} \, a_{Cl(c+c_1)}}{a_{H(c_1)} \, a_{Cl(c_1)}} \tag{1}$$

where $(-\Delta \bar{F})_1$ is the free energy of transfer of 1 mole of hydrochloric acid from $MeCl_x + HCl(c_1)$ to $HCl(c_1)$, or the partial molal free-energy change, $a_{H(S)}$ is the activity of the hydrogen ion in the salt-acid mixture, $a_{Cl(c+c_1)}$ the activity of the chloride ion in the salt-acid mixture, $a_{H(c_1)}$ and $a_{Cl(c_1)}$ are, respectively, the activities of the hydrogen and chloride ions in $c_1 M$ hydrochloric acid.

From the activity product $a_{H(S)}a_{Cl(c+c)}$, the mean activity coefficients of hydrochloric acid in the mixtures may be readily computed.   Thus, F'_a, the mean activity coefficient,[5] is given by

$$F'_a = \sqrt{\frac{a_{H(s)} \, a_{Cl(c+c_1)}}{c_1(c + c_1)}} \tag{2}$$

From cells of Type II, if the saturated potassium chloride eliminates the liquid junction potentials, we obtain

$$(E_0 (2) - E (2)) \, 96,500 = (-\Delta \bar{F})_2 = RT \, ln \, \frac{a_{H(s)}}{a_{H(c_1)}} \tag{3}$$

For the calculation of $(-\Delta H)$, the heat-content decrease, use will be made of the fundamental equation

$$\Delta H = \Delta F - T \, \frac{d \Delta F}{dT} \tag{4}$$

Measurements of the Cells

The cells employed were similar to those described by other investigators[6] and since no striking new features were employed, they need not be discussed here.   All materials were carefully purified.   The solutions were

[5] Lewis and Randall, This Journal, **43**, 1112 (1921).

[6] (a) Acree, *Am. Chem. J.*, **46**, 632 (1911).   Harned, Ref. 4; (b) Ellis, This Journal, **38**, 737 (1916).   (c) Noyes and Ellis, *ibid.*, **39**, 2532 (1917).   (d) Lewis, Brighton and Sebastian, *ibid.*, **39**, 2245 (1917); etc.

made up by weighing carefully analyzed solutions of hydrochloric acid, and of the salts, and then adding the correct weight of water to give the desired molality.

The Cells: $H_2 \mid MeCl_2(c)$ in $HCl(0.1) \mid HgCl \mid Hg$.—All the necessary precautions were taken in constructing the cells. The values of the complete cells were nearly always reproduced to within ± 0.2 of a millivolt. Repeated readings of the electromotive forces were taken at 18°, 25° and 30° over a period varying from 3 to 5 days. These values were cor-

TABLE I

E.M.F. OF CELLS OF TYPE I IN VOLTS

c	$BaCl_2$	$SrCl_2$	$CaCl_2$
0.000	0.39898	0.39898	0.39898
0.100	0.37530	0.37500	0.37462
0.200	0.36337	0.36318	0.36305
0.300	0.35503	0.35449	0.35326
0.500	0.34155	0.34031	0.33986
0.750	0.32786	0.32630	0.32529
1.000	0.31678	0.31471	0.31276
1.300	0.30358	. . . . .	. . . . .

rected so as to equal the electromotive forces of the cells at a hydrogen pressure of 1 atmosphere at the indicated temperature. The mean values at $25.00 \pm 0.02°$ are given in Table I. The value of the cell containing 0.1 M hydrochloric acid and no salt is taken from Harned's data.[7]

TABLE II

MEAN TEMPERATURE COEFFICIENTS IN MILLIVOLTS

c	$BaCl_2$		$SrCl_2$		$CaCl_2$	
	18–25°	25–30°	18–25°	25–30°	18–25°	25–30°
0.000	0.161	0.130	0.161	0.130	0.161	0.130
0.100	0.125	0.098	0.108	0.083	0.098	0.070
0.200	0.092	0.069	0.062	0.044	0.049	0.019
0.300	0.064	0.044	0.027	0.012	0.010	−0.020
0.500	0.018	0.000	−0.025	−0.040	−0.053	−0.082
0.750	−0.028	−0.046	−0.076	−0.095	−0.117	−0.145
1.000	−0.070	−0.089	−0.120	−0.146	−0.172	−0.200
1.300	−0.120	−0.140	. . . .	. . . . .	. . . . .	. . . . .

Table II contains the mean temperature coefficients between 18° and 25°, and 25° and 30°, respectively. These values were read from a plot of the observed mean temperature coefficients against the molal salt

[7] Ref. 1b, Table I.

concentrations. The observed values were consistent enough to determine the plot to within ± 0.003 of a millivolt throughout the concentration range.

The Cells: (1) $H_2|$ KCl (c) in HCl (c_1) | AgCl | Ag; (2) H_2 | KCl (c) in HCl (c_1) | HgCl | Hg.—Since the calomel electrode is unsatisfactory in very dilute solutions, the silver chloride electrode was employed in those cells which contained potassium chloride up to 0.1 M. These cells were prepared as described by Noyes and Ellis.[6c] Above 0.1 M salt concentration, calomel electrodes were employed. Table III contains the measured values of these electromotive forces corrected to a hydrogen pressure of 1 atmosphere.

TABLE III

CELLS CONTAINING KCl (c) IN HCl (0.01)

E.m.f. in volts

Cell	c	$E(1)$ 18°	$E(1)$ 25°	$E(1)$ 30°
1	0.000	0.46309	0.46437	0.46513
	0.050	0.42284	0.42312	0.42318
	0.100	0.40959	0.40972	0.40968
2	0.100	0.45388	0.45618	0.45783
	0.300	0.43153	0.43360	0.43485
	0.500	0.41993	0.42153	0.42267
	1.000	0.40231	0.40360	0.40440
	2.00	0.38142	0.38168	0.38181
	3.00	0.36472	0.36475	0.36473

CELLS CONTAINING KCl (c) IN HCl (0.001)[a]

Cell	c	$E(1)$ 18°	$E(1)$ 25°	$E(1)$ 30°
1	0.000	0.57482	0.57877[b]	0.58136
	0.050	0.48216	0.48392	0.48499
	0.100	0.46733	0.46884	0.46983
2	0.100	0.51353	0.51713[c]	0.51958
	0.300	0.48860	0.49164	0.49372
	0.500	0.47564	0.47837	0.48026
	1.000	0.45720	0.45940	0.46093
	2.000	0.43086	0.43265	0.43371
	3.000	0.41030	0.41194	0.41270

[a] These results are simply measurements of one series and were not repeated. Consequently, their accuracy may be less than the results of the other series.

[b] Noyes and Ellis (Ref. 6c) obtained 0.57893.

[c] Ming Chow (Ref. 15) obtained 0.51721 for the cell containing KCl (0.099) in HCl (0.01).

The Cells: H_2 | MeCl$_2$ (c) in HCl (0.1) | sat. KCl | HgCl | Hg.—Harned[4] measured cells of this type with varying strengths of calcium, strontium and barium chlorides. Since his measurements were made with volume

normal solutions, they have been repeated, using weight molal solutions and extending the measurements to somewhat higher concentrations. The mean of several observations of this cell containing acid alone, $E_0(2)$, was 0.3101.[8] In Table IV, the values of $E_0(2) - E(2)$ are given. These values represent the electromotive forces of the cells without transference, $H_2 \mid HCl(0.1) \parallel MeCl_2(c)$ in HCl (0.1) $\mid H_2$, if the differences in liquid-junction potentials between $HCl(0.1) \mid$ sat. KCl and $MeCl_2(c)$ in $HCl(0.1)$ $\mid$ sat. KCl are equal to zero.[9]

TABLE IV

$[E_0 \, (2) - E \, (2)]$ IN VOLTS

c	$BaCl_2$	$SrCl_2$	$CaCl_2$
0.100	0.00140	0.00160	0.00194
0.200	0.00301	0.00337	0.00390
0.300	0.00480	0.00530	0.00599
0.500	0.00882	0.00959	0.01041
0.750	0.01432	0.01531	0.01641
1.000	0.01989	0.02141	0.02310
1.300	0.02658	.....	.....

The measurements in Table IV were all made with the same calomel electrode.

The Decrease in Free Energy and Heat Content of the Cell Reaction, $H_2 + 2HgCl = 2Hg + 2HCl$ (c_1), and the Partial Molal Free-energy and Heat-content Changes of Hydrochloric Acid at 25°

From the data in Tables I, II and III, the free-energy decreases in joules of the cell reaction at 25° in the presence of the salts at different concentrations were obtained by multiplying the corresponding electromotive forces by $2 \times 96{,}500$. The heat-content change of the cell reaction at 25°, $(-\Delta H)_{25}$, was computed in the following manner. The free-energy values at 18°, 25° and 30°, were plotted against the temperatures and the temperature coefficients, $\dfrac{d(-\Delta F)}{dT}\bigg]_{25}$, in the neighborhood of 25°, were read from these plots; $(-\Delta H)_{25}$ was then computed by Equation 4. Further, by subtraction of $(-\Delta F)_{25}$ and $(-\Delta H)_{25}$ at a salt concentration c from the corresponding value at zero salt concentration, the decrease in partial molal free energy, $(-\Delta \bar{F})_{25}$, and partial molal heat content, $(-\Delta \bar{H})_{25}$, of transfer of 2 gram-ions of the hydrogen ion and 2 gram-ions of the chloride ion from $MeCl_x(c)$ in HCl (c_1) to $HCl(c_1)$ were obtained. All these data are compiled in Table V.

[8] Fales and Mudge, [THIS JOURNAL, **42**, 2434 (1920)] obtained 0.3103.
[9] Indicated by a double bar $\parallel$.

TABLE V

FREE ENERGIES AND HEAT CONTENTS OF CELL REACTION, AND PARTIAL MOLAL FREE ENERGIES AND HEAT CONTENTS OF TRANSFER OF HYDROCHLORIC ACID

1 BaCl$_2$

	c	$(-\Delta F)_{25}$	$\dfrac{d(-\Delta F)}{dT}\Big]_{25}$	$(-\Delta H)_{25}$	$(-\Delta \bar{F})_{25}$	$(-\Delta \bar{H})_{25}$
	0.000	77003	29.0	68361	. . .	. . . . .
	0.100	72433	21.0	66175	4570	2186
	0.200	70130	14.5	65809	6873	2552
	0.300	68521	9.5	65690	8482	2671
	0.500	65919	1.3	65474	11084	2887
	0.750	63277	− 7.0	65363	13726	2998
	1.000	61139	−15.5	65758	15864	2603
	1.300	58591	−25.0	66041	18402	2320

2 SrCl$_2$

	0.100	72375	19.0	66731	4628	1648
	0.200	70094	10.8	66935	6909	1426
	0.300	68417	4.05	67225	8586	1136
	0.500	65680	− 6.4	67557	11323	804
	0.750	62976	−17.5	68191	14027	170
	1.000	60739	−27.5	68934	16264	− 573

3 CaCl$_2$

	0.100	72302	15.0	67832	4701	529
	0.200	70069	5.0	68579	6934	− 218
	0.300	68179	− 2.3	68864	8824	− 503
	0.500	65593	−14.0	69646	11410	−1285
	0.750	62781	−25.5	70380	14212	−2025
	1.000	60170	−35.5	70749	16833	−2388

4 KCl (c) in HCl (0.01)[a]

1	0.000	89580	32.9	79776	. . .	. . . .
	0.050	81662	5.7	79965	7918	− 189
	0.100	78797	0.0	78797	10783	979
2	0.100	88044	63.6	69091	. . .	. . . .
	0.300	83686	53.3	68179	15141	1791
	0.500	81356	44.0	68840	17471	1230
	1.000	77895	33.7	70001	20932	88
	2.000	73665	10.6	70506	25162	− 436
	3.000	70397	0.0	70397	28430	− 327

5 KCl (c) in HCl (0.001)[a]

1	0.000	111710	107.0	79824	. . .	. . . .
	0.050	93398	45.3	80077	18608	− 253
	0.100	90488	40.3	78479	21532	1345
2	0.100	99808	97.0	70902	. . .	. . . .
	0.300	94888	81.8	70512	26524	1735
	0.500	92330	74.0	70278	29120	1969
	1.000	88664	59.2	71022	32850	1225
	2.000	83502	44.5	70241	38105	2006
	3.000	79504	27.0	71347	42162	900

[a] The first 3 results of both of these series measure the free-energy, etc., changes of the cell reaction $H_2 + 2AgCl = 2Ag + 2HCl$ (c_1).

There are two points of interest in connection with these results and those previously determined by Harned:[1a] (1) The character of the plot of $(-\Delta\bar{H})_{25}$ against c is entirely different in the presence of the bivalent chlorides than in the presence of the uni-univalent chlorides. (2) The fact that $(-\Delta\bar{H})_{25}$ of transfer from KCl(c) in HCl(0.01) to HCl(0.01) or from KCl(c) in HCl(0.001) to HCl(0.001) decreases first, then increases, and finally decreases as the salt concentration is increased, is evidence that the hydrogen ion and chloride ion in the mixtures have to some extent individual partial molal heat contents.

The Activity Coefficients of Hydrochloric Acid in the Mixtures

The activity products of the hydrogen and chloride ions in the mixtures may be calculated from the partial free-energy differences, $(-\Delta\bar{F})$, by Equation 1 when the activity product in pure hydrochloric acid at a con-
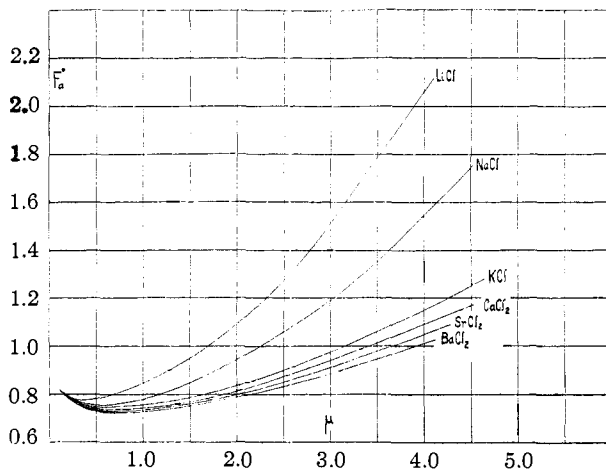

Fig. 1.—Activity coefficients of hydrochloric acid $(0.1\ M)$ in solutions of salts of ionic strength.

centration c_1 is known. The mean activity coefficients of hydrochloric acid in the mixtures may be obtained by Equation 2. The activity coefficients of hydrochloric acid at 0.1 M, 0.01 M, and 0.001 M have been taken to be 0.820, 0.910, and 0.967, respectively.[10] The mean activity coefficients of hydrochloric acid obtained from the data of Harned[11] as well as from the data in this communication are given in Tables VII and X in the following sections.

Throughout the following discussion, use will be made of the concept of ionic strength, μ, as defined by Lewis and Randall.[5] Thus, multiply "the molality of each ion by the square of its valence. Then, the sum of

[10] Calculated by the formula log $F'_a = 0.2c - 0.288c^{0.434}$. See Harned, This Journal, **44**, 252 (1922).

[11] See Ref. 1b and 5, Table XVII.

these quantities divided by two will be the ionic strength." For example, take a mixture of 0.1 M hydrochloric acid and 1 M barium chloride. Then μ will be $\dfrac{[0.1 + 2.1 + 4]}{2}$ or 3.1. In cases where the added salt is uni-univalent, μ is equal to the total concentration.

The plots of the values thus obtained in the 0.1 M hydrochloric acid mixtures against μ are given in Fig. 1. It is important to note that each of these curves possesses a minimum similar to a similar plot of the activity coefficients of pure hydrochloric acid.

There is another complexity of considerable importance. Thus, the activity coefficients of hydrochloric acid in 0.001 M hydrochloric acid solutions containing potassium chloride are (in solutions of ionic strength greater than 0.10 M) in all cases higher at the same ionic strength than
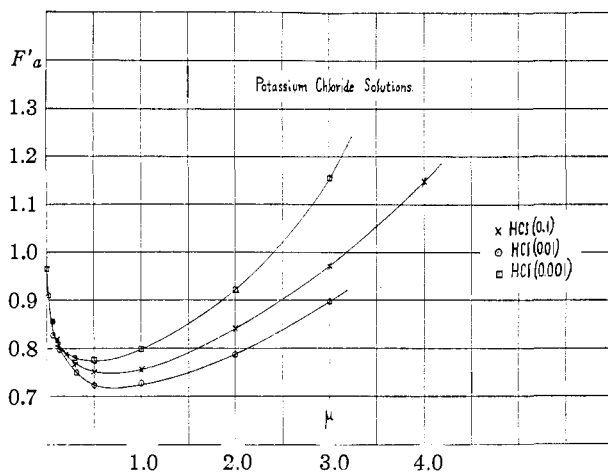

Fig. 2.—Activity coefficients of hydrochloric acid (0.1 M, 0.01 M and 0.001 M) in solutions of potassium chloride of ionic strength.

those in the 0.1 M and 0.01 M acid solutions, and the values in the 0.1 M are higher than in the 0.01 M at the same ionic strength. The plots of F'_a against μ are given in Fig. 2 clearly showing this important behavior.

The Calculation of the Activity Coefficients of Hydrochloric Acid in the Mixtures of Higher Acid Concentration

Harned[1b,10] has shown that the individual activity coefficients, F_a, and the mean activity coefficients, F'_a, of single electrolyte solutions may be calculated with considerable accuracy by means of the formulas

$$\log F_a = \alpha c - \beta c^m; \quad \log F'_a = \alpha' c - \beta' c^{m'} \tag{5}$$

respectively; c is the concentration in gram-ions in 1000 g. of water,

or in moles in 1000 g. of water. α, β, m, and α', β', m', are constants, Equation 5 may be split up into two equations. Thus

$$\log f'_a = -\beta c' m' \tag{6}$$

which was found to be valid at high dilutions by Lewis and Linhart.[11a] f'_a was denoted by Harned as "the ideal activity coefficient." f'_a is related to F'_a, the observed activity coefficient, by the equation

$$\log \frac{F'_a}{f'_a} = \alpha' c \tag{7}$$

This equation expresses variations caused by abnormal behaviors in concentrated solutions. It was further pointed out by Harned that the constants α_{Li}, α_{Na}, and α_K for the univalent ions denoted by subscripts were roughly proportional to their relative ionic hydration values as computed by Washburn.[12]

For the present, Equation 5, modified to meet the conditions imposed by the presence of salts, will be used in calculating the activity coefficients of hydrochloric acid in the mixtures. For the acid alone, we have, $\log F'_a = \alpha'c_1 - \beta'c_1{}^{m'}$, where c_1 is the acid concentration. The constant, α', expresses, as above stated, the effect of change of environment on F'_a, but since this constant is different for hydrochloric acid than for some of the other salts, the addition of different salts affects F'_a differently. It becomes necessary to add another term to (5), similar to $\alpha'c_1$, to make it applicable to the mixtures. Thus,

$$\log F'_a = \alpha'c_1 - \beta'\mu^{m'} + \alpha'' (\mu - c_1) \tag{8}$$

μ being the ionic strength, which for uni-univalent electrolytes equals the sum of the concentrations of the salt and acid, or $(c + c_1)$; α'' is another constant. The term $\alpha''(\mu - c_1)$ represents the effect of change in environment on the activity coefficient produced by the added salt, and functions in the calculation of the mixtures, in a manner similar to $\alpha'c_1$.

If the behavior of the mixtures was simple, α'' would equal α'_s, where α'_s is the value of the constant for the single salt. This, however is not the case, because in all the examples $\alpha'' > \alpha'_s$.[13] By the use of this equation and a table of constants, it will be shown that the activity coefficients of the acid in the presence of the salts can be calculated with a considerable degree of accuracy. In Table VI are compiled the values of the constants. α', β' and m' were taken from Table VI in Harned's

[11a] Lewis and Linhart, THIS JOURNAL, 41, 1951 (1919).

[12] Washburn, *ibid.*, 31, 322 (1909); 35, 751 (1913); 37, 694 (1915).

[13] Lewis and Randall (Ref. 5) have observed that the activity coefficient of hydrochloric acid in lithium chloride solutions at the higher concentrations is greater than in pure hydrochloric acid solutions of the same ionic strength, but that the activity coefficient of hydrochloric acid alone is greater than that of lithium chloride at the same ionic strength. This is expressed by $\alpha'' > \alpha'_s$.

paper (Ref. 1b) and are the values used in calculating the activity coefficients of pure hydrochloric acid solutions.

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TABLE VI

CONSTANTS OF EQUATION 8

</div>

$\alpha'=0.200;\ \beta'=0.288;\ m'=0.434$ Mixture		$\alpha'=0.200;\ \beta'=0.288;\ m'=0.434$ Mixture	
	α''		α''
KCl + 0.01	0.150	BaCl$_2$ + 0.10	0.135
KCl + 0.10	0.150	SrCl$_2$ + 0.10	0.140
NaCl + 0.10	0.178	CaCl$_2$ + 0.10	0.148
LiCl + 0.10	0.215		

Table VII contains the observed activity coefficients and those calculated by means of Equation 8.

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TABLE VII

OBSERVED AND CALCULATED ACTIVITY COEFFICIENTS

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	0.1 M HCl							0.01 M HCl	
	KCl		NaCl		LiCl			KCl	
μ	F'_a (obs.)	F'_a (calc.)	F'_a (obs.)	F'_a (calc.)	F'_a (obs.)	F'_a (calc.)	μ	F'_a (obs.)	F'_a (calc.)
0.100	0.820	0.820	0.820	0.820	0.820	0.820	0.010	0.910	0.910
0.200	0.791	0.780	0.793	0.785	0.794	0.791	0.060	0.826	0.841
0.300	0.768	0.758	0.770	0.764	0.778	0.778	0.110	0.796	0.808
0.500	0.750	0.746	0.759	0.752	0.790	0.791	0.310	0.749	0.748
1.000	0.756	0.740	0.784	0.780	0.860	0.845	0.510	0.722	0.728
2.000	0.843	0.824	0.945	0.931	1.088	1.095	1.010	0.728	0.730
3.000	0.973	0.980	1.189	1.180	1.481	1.512	2.010	0.788	0.813
4.000	1.148	1.199	1.488	1.544	2.059	2.063	3.010	0.901	0.966

<div align="center">0.1 M HCl</div>

	BaCl$_2$		SrCl$_2$		CaCl$_2$	
0.100	0.820	0.820	0.820	0.820	0.820	0.820
0.400	0.744	0.736	0.756	0.739	0.762	0.743
0.700	0.734	0.715	0.739	0.720	0.744	0.728
1.000	0.731	0.713	0.739	0.721	0.753	0.734
1.600	0.755	0.741	0.768	0.753	0.774	0.771
2.350	0.816	0.806	0.842	0.827	0.862	0.862
3.100	0.894	0.900	0.926	0.930	0.962	0.985
4.000	1.011	1.048				

The calculated results agree particularly well with the observed in cases where α'' has a value nearly equal to α'. Thus, the agreement is excellent with the lithium chloride solutions. All the other mixtures show fair agreement. In all cases, with the exception of lithium chloride, the calculated value is somewhat less than the observed at concentrations up to 1 M, and above 1 M it rises somewhat more rapidly than the observed. This uniformity indicates that the deviation is not due to experimental error.

The calculations by means of Equation 8 may be relied on to within $\pm 3\%$ to concentrations as high as an ionic strength of 3 in the most unfavorable cases. In the more favorable cases, a much greater accuracy is obtained.

A fact of importance is the agreement between the calculated and observed values for the mixtures of potassium chloride in both 0.1 M and 0.01 M hydrochloric acid solutions, using, in all cases, the same values for the parameters. This shows that Equation 8 can be used to calculate within a few per cent. the activity coefficient of hydrochloric acid in solutions containing any composition of acid and salt, providing the acid concentration is not less than 0.01 M. On the other hand, Equation 8 can not be used for calculating mixtures containing 0.001 M acid. There is, in the cases where the salt-acid ratio is high, an effect which depends on this ratio. This will be the subject of the next section.

Calculation of the Activity Coefficients of Hydrochloric Acid in Acid-Salt Mixtures of Low Acid Concentrations

The questions of interest in this section can best be considered by first studying the case where the total acid and salt concentration is kept constant. The activity coefficients of hydrochloric acid in solutions of potassium chloride at constant molality have to a limited extent been measured. Loomis, Essex and Meacham[14] found that in solutions of 0.1 total molality

TABLE VIII

ACTIVITY COEFFICIENT OF HYDROCHLORIC ACID IN SOLUTIONS OF POTASSIUM CHLORIDE AT CONSTANT TOTAL MOLALITY

c_1	F'_a Total 3 M	F'_a Total 1 M	F'_a Total 0.1 M	
			Ming Chow	H. and B.
3.000	1.366	. . .	. . .	. . .
1.000	1.175	0.912	. . .	. . .
0.100	0.973	0.755	0.820	0.820
0.010	0.901	0.730	0.814	0.804
0.001	1.156	0.798	0.821	0.810

the activity coefficient of hydrochloric acid was somewhat greater in solutions which contained the larger quantity of hydrochloric acid. Ming Chow[15] from measurements of the same cell found no deviation greater than 1.3%. Table VIII contains values of F'_a computed from the results of the present investigation at total molalities 3 M, 1 M and 0.1 M, respectively. The values computed from Ming Chow's data are also included.

In all cases, there is a minimum at about 0.01 M acid concentration.

[14] Loomis, Essex and Meacham, THIS JOURNAL, 39, 1133 (1917).
[15] Ming Chow, ibid., 42, 488 (1920).

When the total concentration is 0.1 M, the minimum is not pronounced. The drop from 0.820 to 0.814 (Ming Chow's results) corresponds to a variation in electromotive force of 0.65 millivolts. This is hardly due to experimental error. In Fig. 3, the values of F'_a at different total molalities are plotted against the log c_1. Pronounced minima are obtained at the higher total molal concentrations. These are not predicted by the use of Equation 8, nor can the activity coefficients of hydrochloric acid at concentrations below 0.01 M be computed by Equation 8. To account partially for this phenomenon, it becomes necessary to add another term to the
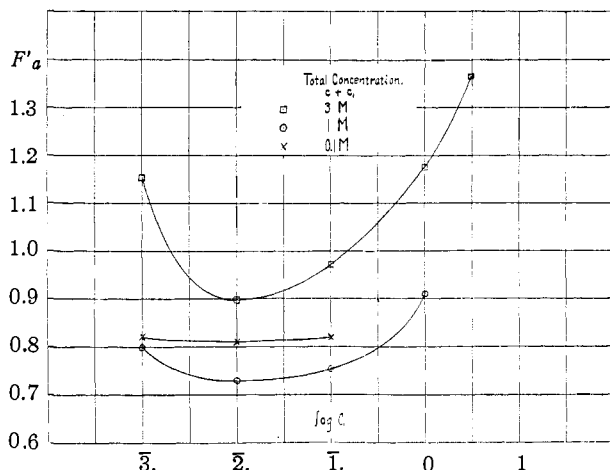

Fig. 3.—Activity coefficients of hydrochloric acid in solutions of hydrochloric acid and potassium chloride of constant total concentration.

equation which makes the rapid upward trend of the activity coefficient in dil. acid solutions containing salts at high concentrations some function of the ratio of total concentration to acid. Thus

$$\log F'_a = \alpha' c_1 - \beta' \mu^{m'} + \alpha'' (\mu - c_1) + f\left(\frac{\mu - c_1}{c_1}\right) \tag{9}$$

There are not enough data at our disposal to determine the exact nature of this function, such that F'_a could be calculated at all dilutions of the acid. It will, therefore, be assumed that $f\left(\dfrac{\mu - c_1}{c_1}\right)$ takes the simple but approximate form $\gamma'\left(\dfrac{\mu - c_1}{c_1}\right)$, where γ' is a constant.[15a] If α'' takes the value 0.145, γ' the value of 0.0000306, and α', β', and m' the values

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[15a] Equation 9 has the disadvantage that $\dfrac{\mu - c_1}{c_1}$ becomes infinity in infinitely dilute acid solution, if we neglect the hydrogen-ion activity of the water molecule. It might have been better to make $f\left(\dfrac{\mu - c_1}{c_1}\right)$ equal to $\gamma' \log\left(\dfrac{\mu - c_1}{c_1}\right)$.

in Table VII, approximate agreement between the observed and calculated values can be obtained for all solutions containing acid of not greater dilution than $0.001\ M$ acid concentration. This is shown by Table IX.

TABLE IX

F'_a IN SOLUTIONS OF CONSTANT MOLALITY, CALCULATED BY EQUATION 9

	0.1 Total M			1 Total M		3 Total M	
c_1	Ming Chow	H. and B.	Calc.	Obs.	Calc.	Obs.	Calc.
3.000	...	...	...	...	...	1.366	1.366
1.000	...	...	...	0.912	0.912	1.175	1.173
0.100	0.820	0.820	0.820	0.755	0.741	0.960	0.939
0.010	0.814	0.804	0.812	0.728	0.726	0.901	0.957
0.001	0.821	0.810	0.816	0.798	0.772	1.156	1.156

In Table X are given the observed and calculated values of F_a', at constant acid and varying salt concentrations at 0.001, 0.010, and 0.100 acid concentrations, respectively. The calculated values have been obtained by Equation 9.

TABLE X

F'_a IN SOLUTIONS OF HYDROCHLORIC ACID AND POTASSIUM CHLORIDE OF DIFFERENT CONCENTRATIONS

	0.1 M HCl			0.01 M HCl			0.001 M HCl	
μ	F'_a Obs.	F_a' Calc.	μ	F'_a Obs.	F'_a Calc.	μ	F'_a Obs.	F'_a Calc.
0.100	0.820	0.820	0.010	0.910	0.910	0.001	0.967	0.967
0.200	0.791	0.779	0.060	0.826	0.836	0.051	0.857	0.851
0.300	.0.768	0.756	0.110	0.796	0.806	0.101	0.810	0.815
0.500	0.750	0.733	0.310	0.749	0.747	0.301	0.781	0.762
1.000	0.756	0.730	0.510	0.722	0.726	0.501	0.779	0.750
2.000	0.843	0.808	1.010	0.728	0.726	1.001	0.798	0.772
3.000	0.973	0.949	2.010	0.788	0.809	2.001	0.920	0.917
4.000	1.148	1.150	3.010	0.901	0.957	3.001	1.156	1.156

Although the equation employed in these calculations is admittedly but a first approximation, and can probably not be used for extrapolation in mixtures containing hydrochloric acid below $0.001\ \dot{M}$, the results of the calculation show that the activity coefficient of the acid in the mixtures is not only a function of the total concentration but also of the ratio of salt concentration to acid concentration. This is a point of considerable importance, particularly in reference to the neutral salt effect in very dilute solutions of one electrolyte in the presence of another electrolyte of high concentration.

Summary and General Considerations on the Calculation of Activity Coefficients

The equations

$$\log F_a = \alpha c - \beta c^m; \quad \log F'_a = \alpha' c - \beta' c^{m'} \tag{5}$$

have been shown by Harned[1b,10] to be valid for calculating the variation of

F_a, and F'_a with the concentration, for many single electrolytes throughout the range of concentration from 0.001 M or 0.01 M to 3 M. As mentioned in a previous section, this equation may be divided into two parts, one of which expresses the behavior of very dilute solutions, where abnormalities such as those due to ionic hydration influence the activity coefficient very little, and another which expresses the change in environment in concentrated solutions.

Brönsted[16] employs Equation 5 for a similar purpose, but adds some interesting considerations. Thus, for all electrolytes, he makes

$$\log F'_a = \alpha'c - f'(c) \tag{10}$$

where $f'(c)$ is a universal function associated with the Milner effect, and $\alpha'c$ is associated with the "salting-out" effect. For uni-univalent electrolytes, Brönsted makes $f'(c) = 0.96 \sqrt{c}$, or β' equal to 0.96 and m' equal to 0.500. Substitution of the above value for $f'(c)$ in Equation 10 and 0.62 for α' gives an equation by means of which F'_a for hydrochloric acid computed from Ellis' data[6b] may be calculated at high dilutions. Brönsted has calculated by the same method the osmotic coefficients of potassium chloride and nitrate, and sodium chloride up to 0.1 M concentration. On the other hand, the activity coefficients and osmotic coefficients of these uni-univalent salts possess minima at certain salt concentrations. The correct position of these minima cannot be computed by using Brönsted's constants. Harned has employed a graphical method using the best available data between 0.01 M and 3 M concentration. He found that the constants β' and m' have the same values for potassium and sodium chlorides, but different values for lithium chloride and hydrochloric acid. Thus, using Equation 5, we are inclined to believe that if $f'(c)$ is of the form $\beta'c^{m'}$, β' and m' will not have the same values for all uni-univalent electrolytes. However, Equation 5 would probably not have to be much modified to meet Brönsted's contentions.

The influence of one electrolyte on the activity coefficient of another electrolyte is a subject of great complexity. By modifying Equation 5 in such a way as to make it applicable to the mixtures, the activity coefficients of hydrochloric acid (0.1 M) in the 6 salt solutions may be calculated with a considerable degree of accuracy. Thus Equation 5 may be employed in the form

$$\log F'_a = \alpha'c_1 - \beta'\mu^{m'} + \alpha''(\mu - c_1) \tag{8}$$

This is the same as (5), where $\alpha''(\mu - c_1)$ simply plays the same role as $\alpha'c$ in the formula for a single electrolyte. Equation 8 is applicable in the cases of the more concentrated solutions of both electrolytes in the mixtures. Further, according to this equation, the activity coefficient of the acid in the mixture is a function of the total molality or the ionic strength. That the problem is complex is shown by the fact that α'' has

[16] Brönsted, THIS JOURNAL, **44**, 938 (1922).

not the same value as α'_s, the parameter in Equation 5 for the single added salt, but, in all cases, $\alpha'' > \alpha'_s$. This indicates, for example, that in concentrated solutions, potassium chloride has an effect on the activity coefficient of hydrochloric acid different from that which it has on its own activity coefficient.

In the salt solutions containing very dilute hydrochloric acid, Equation 8 is no longer valid, but it was found that there was an influence on F'_a which was not only a function of the total concentration, but also most probably of the ratio of the concentrations of the salt to the acid. Thus, with solutions of constant and high molality, the activity coefficient of hydrochloric acid possesses a pronounced minimum in the neighborhood of $0.01\ M$ acid concentration. By introducing another term into Equation 8, an approximation equation which will partially account for this phenomenon may be obtained. Thus

$$\log F'_a = \alpha'c_1 - \beta'\mu^{m'} + \alpha''\,(\mu - c_1) + \gamma'\left(\frac{\mu - c_1}{c_1}\right)$$

By this equation it is possible to calculate approximately F'_a in mixtures containing hydrochloric acid down to $0.001\ M$ concentration.

Since no great error is made in assuming that the chloride ion has the same activity in solutions containing high dilutions of the acid, this effect must be due to an increase in activity coefficient of the hydrogen ion caused by the presence of the potassium ion. It is not likely that this phenomena is peculiar to the hydrogen ion alone. If this behavior occurs with all ions, it will be of great importance in the calculation of the solubility of sparingly soluble salts in solutions of other salts. Thus, take, for example, the solubility of thallous chloride in sodium and potassium chloride solutions of the same strength. According to exact thermodynamic principles in the saturated solution of thallous chloride, $a_{Tl}a_{Cl}$ will equal a constant. It would be possible for a_{Cl} to be the same in both the sodium chloride and potassium chloride solutions and, at the same time, the solubility of the thallous chloride to be different, if the sodium and potassium ions influence a_{Tl} differently. This point is of interest, particularly, in connection with the important recent advances made by Brönsted[17] on the problem of the solubility of sparingly soluble salts in salt solutions.

In general, it may be said tentatively that the activity coefficient of a strong uni-univalent electrolyte may be expressed by an equation of the form

$$\log F'_a = \alpha'c - \beta'c^{m'}$$

and that the activity coefficient of an electrolyte in a solution of another electrolyte may be expressed by an equation of the form

$$\log F'_a = \alpha'c_1 - \beta'\mu^{m'} + \alpha''\,(\mu - c_1) + f'\left(\frac{\mu - c_1}{c_1}\right)$$

[17] Brönsted, (a) THIS JOURNAL, **42**, 761 (1920); (b) **44**, 877 (1922); etc.

where μ is the ionic strength and c_1 the concentration of one of the electrolytes in the mixture.

The only other attempts to calculate activity coefficients of single electrolytes and mixtures in concentrated solutions have been made by Bjerrum[18] and Schreiner.[19]   They have based their calculations on two very interesting theoretical assumptions, made by Bjerrum, which are, first, the chemical theory of ionic hydration, and, second, the assumption that the electromotive-force method measures the activity of the non-hydrated ions. On this basis, they have succeeded in deducing equations which predict the general nature of the some of the observed results but, as is to be expected, they have not been able to attain the numerical accuracy obtainable by the present empirical method.

Individual Activity Coefficients of the Hydrogen and Chloride Ions in Solutions of $MeCl_2$ + HCl(0.1 M)

The exact calculation of the individual ion-activity coefficients in concentrated solutions from electromotive-force measurements is a problem accompanied by considerable difficulty owing to the unavoidable presence of liquid-junction potentials which cannot be accurately calculated when the solutions involved are concentrated.   At present, the best method at our disposal is to eliminate as far as possible these liquid-junction potentials by the use of a saturated potassium chloride solution.   From previous results obtained by Harned[1b] it was shown that the assumption that the difference in liquid-junction potential between HCl (0.1 M)| sat. KCl and $MeCl$ (c) + HCl (0.1 M)| sat. KCl is very small, not amounting to more than a millivolt, is in accord with the following hypothesis suggested by MacInnes.[20]

1. "That the activities of the cation and anion of a solution of an electrolyte may differ from one another at a given concentration and temperature.

2. "That, at any concentration of potassium chloride, the activities of the potassium and chloride ions are the same.

3. "That in solutions of strong uni-univalent chlorides at the same concentration at constant pressure and temperature, the chloride ion will have the same activity."[21]

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[18] Bjerrum, Z. anorg. Chem., 109, 280 (1920).

[19] Schreiner, ibid., 121, 321 (1922).

[20] MacInnes, THIS JOURNAL, 41, 1086 (1919).

[21] In a very interesting paper by Brönsted (Ref. 17b), objection is made on thermodynamic grounds to the third of these postulates, especially, the more generalized statement of it by Harned (Ref. 1b) which was, "In solutions of the same strength and at the same temperature of different electrolytes (of the same type) possessing a *common ion*, the *common ion* will have the same activity independent of the ion or ions associated with it."   Brönsted interprets this as involving "the necessity that all activity coefficients of the ions remain constant," when a dilute salt solution is gradually changed into another salt solution of the same concentration.   From this, he shows by a form of Duhem's equation that this ends in the assumption of equal activity coefficients of all ions or, what amounts to the same thing, equal freezing-point lowerings, etc.   The above

The data in Tables I and IV afford evidence that in solutions of hydrogen chloride (0.1 M) containing barium, strontium, or calcium chlorides, at a given concentration, the chloride-ion activities are identical. On the assumption that the difference in potential between HCl (0.1) | sat. KCl and $MeCl_2$ (c) + HCl (0.1) | sat. KCl, is negligible the values of the electromotive forces in Table IV, E_0 (2) $-E$ (2) equal the electromotive forces of the cells without transference, H_2 | HCl (0.1) || $MeCl_2$ (c) + HCl (0.1) | H_2. By Equation 3 $(E_0$ (2) $-E$ (2)) $= 0.05915$ log $\dfrac{a_{H(S)}}{a_{H(0.1)}}$ and by Equation 1 $(E_0$ (1) $-E$ (1)) $= 0.05915$ log $\dfrac{a_{H(S)}\, a_{Cl\,(c+0.1)}}{a_{H(0.1)}\, a_{Cl\,(0.1)}}$ whence

$$E_{Cl} = (E_0 \ (1) - E \ (1)) - (E_0 \ (2) - E \ (2)) = 0.05195 \ \log \ \frac{a_{Cl\,(c+0.1)}}{a_{Cl\,(0.1)}} \qquad (12)$$

The values of E_{Cl} should be the same for all three mixtures, if the chloride-ion activities are identical in each mixture at a given concentration. The values obtained for the three mixtures are given in Table XI.

reasoning is based on a misunderstanding of the principle, which has always been applied as follows. Take 3 solutions of potassium chloride, sodium chloride and lithium chloride, respectively, of mole fraction N_1 in water of mole fraction N_2. Let a_K, a_{Na}, a_{Li}, and a_{Cl} be the ionic activities, and $a_{W_1}, a\,w_2,$ and a_{W_3}, the activities of water in the potassium, sodium and lithium chloride solutions, respectively. According to Duhem's equation at constant pressure and temperature,

$$N_1 \ d \ ln \ a_K \ + \ N_1 \ d \ ln \ a_{Cl} \ + \ N_2 \ d \ ln \ a_{W1} = 0$$
$$N_1 \ d \ ln \ a_{Na} \ + \ N_1 \ d \ ln \ a_{Cl} \ + \ N_2 \ d \ ln \ a_{W2} = 0$$
$$N_1 \ d \ ln \ a_{Li} \ + \ N_1 \ d \ ln \ a_{Cl} \ + \ N_2 \ d \ ln \ a_{W3} = 0$$

In these three solutions, according to the principle, the activity of the common ion, a_{Cl}, is the same. But it has been observed with thermodynamic exactness, that, at the same concentration, $a_{Li}a_{Cl} > a_{Na}a_{Cl} > a_K a_{Cl}$. Therefore, from the above, $a_{Li} > a_{Na} > a_K$; and $a_{W_1} > a_{W_2} > a_{W_3}$. The colligative properties of a solution of sodium chloride will differ from those of potassium chloride, etc.

Second, in a mixture where the total concentration is constant, we have

$$N_1 \ d \ ln \ a_K + N_2 \ d \ ln \ a_{Li} + (N_1 + N_2) \ d \ ln \ a_{Cl} + N_3 \ d \ ln \ a_W = 0$$

Thus, since $a_{Li} > a_K$, in solutions of the chlorides of the same strength and, according to the principle, a_{Cl} is constant, variation of N_1 and N_2, while $(N_1 + N_2)$ is constant, will cause a change in a_W. Thus, the colligative properties will vary, and will depend on the concentrations of each of the species present. Although the original statement of the principle may be a little ambiguous owing to the emphasis on the *common ion*, all applications (Harned, Ref. 10) are consistent with the above reasoning. In reference to hydrochloric acid—uni-univalent chloride mixtures, Harned said, "Although the activity of the common ion has been shown to be identical in solutions of the same normality, this is not true of the hydrogen ion which is not common to both electrolytes." Judging from electromotive-force data, the principle as stated holds to within a few per cent. pu to high concentrations for uni-univalent chloride solutions unless it can be proved that the liquid-junction potentials in Harned's measurements are of a considerable magnitude. There are no available electromotive-force data on other mixtures at high concentrations which can be employed to throw further light on this subject.

The agreement is good and any differences in these values are probably due to experimental error.

From the data in Table XI and by means of Equation 12, the activities of the chloride ion in the mixtures have been computed.   The activity

TABLE XI

VALUES OF E_{Cl} COMPUTED BY EQUATION 12

$$E_{Cl} = 0.05915 \log \frac{a_{Cl\,(c\,+\,0.1)}}{a_{Cl\,(0.1)}}$$

c	BaCl$_2$	SrCl$_2$	CaCl$_2$
0.100	0.0223	0.0224	0.0224
0.200	0.0326	0.0324	0.0320
0.300	0.0392	0.0392	0 0397
0.500	0.0486	0.0491	0.0487
0.750	0.0568	0.0574	0.0573
1.000	0.0623	0.0629	0.0631
·1.300	0.0688	....	....

coefficient of the chloride ion in the 0.1 M acid was taken as 0.779.[10]   By dividing the above activity values by the stoichiometrical concentration of the chloride ion, the activity coefficients given in Table XII were obtained.

TABLE XII

$F_{a(Cl)}$ IN 0.1 M HYDROGEN CHLORIDE SOLUTIONS CONTAINING BaCl$_2$, SrCl$_2$, CaCl$_2$

c	$F_{a(Cl)}$ BaCl$_2$	$F_{a(Cl)}$ SrCl$_2$	$F_{a(Cl)}$ CaCl$_2$	$F_{a(Cl)}$ Mean
0.000	0.779	0.779	0.779	0.779
0.100	0.618	0.620	0.621	0.620
0.200	0.554	0.548	0.540	0.547
0.300	0.510	0.511	0.520	0.514
0.500	0.466	0.475	0.471	0.470
0.750	0.443	0.450	0.449	0.447
1.000	0.417	0.426	0.434	0.426
1.300	0.420	...	...	0.420

Table XIII contains the activity coefficients of the hydrogen ion in the mixtures calculated by means of Equation 3.

TABLE XIII

ACTIVITY COEFFICIENTS OF HYDROGEN ION IN HYDROGEN CHLORIDE SOLUTIONS CONTAINING BARIUM, STRONTIUM AND CALCIUM CHLORIDES

	$F_{a(H)}$		
c	BaCl$_2$	SrCl$_2$	CaCl$_2$
0.000	0.868	0.868	0.868
0.100	0.969	0.974	0.987
0.200	1.029	1.042	1.064
0.300	1.102	1.127	1.151
0.500	1.290	1.332	1.371
0.750	1.599	1.661	1.735
1.000	1.984	2.105	2.248
1.300	2.577	...	...

Finally, in Table XIV are given values of $F_{a(Cl)}$ in mixtures of potassium, sodium and lithium chloride with hydrochloric acid (0.1 M), along with values of $F_{a(Cl)}$ in mixtures of barium, strontium, and calcium chloride with hydrochloric acid (0.1 M) at the same ionic strength. The chloride-ion activity coefficients in the uni-univalent mixtures have been calculated by the formula $\log F_{a(Cl)} = 0.07 \ \mu - 0.292 \ \mu^{0.396}$.

<center>TABLE XIV</center>

<center>ACTIVITY COEFFICIENTS OF CHLORIDE ION IN UNI-UNIVALENT AND BIVALENT CHLORIDE SOLUTIONS</center>

μ	$F_{a(Cl)}$ (MeCl)	$F_{a(Cl)}$ (MeCl$_2$ + HCl (0.1))
0.100	0.779	0.779
0.400	0.668	0.620
0.700	0.625	0.547
1.000	0.600	0.514
1.600	0.576	0.470
2.350	0.569	0.447
3.100	0.576	0.426
4.000	0.594	0.420

The above assumption regarding the liquid junction potentials involved in these measurements leads to the following conclusions: (1) that, in solutions of strong chlorides of the same type, at the same concentration and temperature, the chloride ion will have the same activity; (2) that the activity of the chloride ion in uni-univalent chloride solutions is greater than in bivalent chloride solutions of the same ionic strength.

It is impossible to estimate the accuracy of the above conclusions. It is, however, probable that they are correct to within a few per cent. even in solutions of high ionic strength. Lewis and Randall,[5] in summing up their discussion of the determination of individual ion activities, say, "At the present time we must conclude that the determination of the absolute activities of the ions is an interesting problem, but one which is as yet unsolved." This statement is true inasmuch as we cannot be certain of the present results. No matter what method is employed to solve this problem, at least one assumption is necessary. There is no means known for the direct experimental determination of the liquid-junction potentials, nor are such formulas as those of Planck and Henderson valid even at the lower concentrations. The only other method is the elimination as far as possible of the liquid-junction potentials by a saturated potassium chloride solution. In view of these difficulties, the method adopted in the present study is empirical. From a large number of results, certain assumptions have been made which have appeared most probable and simplest. The results may be an approximation, and the extent of the validity of the conclusions drawn still remains to be determined.

Summary

1. Measurements of cells of the following types have been made.

1. $H_2|MeCl_x(c)$ in HCl (0.1 M)|HgCl|Hg, at 18°, 25° and 30°, where Me denotes barium, strontium or calcium.

2. $H_2|MeCl_x$ in HCl (0.1 M)|sat. KCl|HgCl|Hg at 25°, where Me denotes barium, strontium or calcium.

3. H_2 | KCl (c) in HCl (c_1) | AgCl | Ag; and H_2 | KCl (c) in HCl (c_1) | HgCl | Hg, containing acid at 0.01 M and 0.001 M, at 18°, 25° and 30°.

2. From these data, the free-energy decrease and heat-content decrease of the cell reaction have been computed, as well as the changes in partial molal free energy and heat content of hydrochloric acid in the mixtures.

3. The mean activity coefficients of hydrochloric acid in solutions of potassium, sodium, lithium, calcium, strontium and barium chlorides have been computed.

4. By means of the formula

$$\log F'_a = \alpha'c_1 - \beta'\mu^{m'} + \alpha'' \ (\mu - c_1) \tag{8}$$

F'_a, the mean activity coefficients of hydrochloric acid in the acid-salt mixtures containing acid at concentrations from 0.01 M to 1 M may be computed with considerable accuracy.

5. In solutions of higher dilutions of acid, it is necessary to add a term to Equation 8 which is a function of the salt-to-acid concentration ratio. Thus,

$$\log F'_a = \alpha'c_1 - \beta'\mu^{m'} + \alpha'' \ (\mu - c_1) + \gamma' \left(\frac{\mu - c_1}{c_1}\right) \tag{9}$$

is approximately valid in mixtures containing acid as low as 0.001 M. Thus, when $\left(\dfrac{\mu - c_1}{c_1}\right)$ is very high, a considerable increase in F'_a is observable.

6. It has been pointed out that the effect mentioned in (5) is probably due to an increase in activity of the hydrogen ion. If, as is to be expected, the same phenomenon is observed in mixtures containing other ions, it will be of considerable importance, especially in dealing with the problem of the solubility of sparingly soluble salts in solutions of other salts.

7. Evidence has been obtained which leads to the conclusion that "in solutions of strong bivalent chlorides, at the same concentration and temperature, the chloride ion will have the same activity."

8. Further, evidence has been obtained which indicates that "the activity of the chloride ion in uni-univalent chloride solutions is greater than in bivalent chloride solutions of the same ionic strength."

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