equation of state extrapolates to low pressures with a high degree of accuracy.

The values at 0° of the ratio of the pV product at one atmosphere to that at zero pressure, and the weights of a normal liter of CO and N_2O are calculated from their molecular weights and the values of the constants of the equation of state of their isosteres, namely N_2 and CO_2. The agreement with the observed values is very good, and indicates that for many thermodynamic calculations the constants of N_2 and CO_2 can be used for CO and N_2O, respectively.

CAMBRIDGE, MASSACHUSETTS

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

THE IONIC CONCENTRATIONS AND ACTIVITY COEFFICIENTS OF WEAK ELECTROLYTES IN CERTAIN SALT SOLUTIONS

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The electromotive forces of cells of the types

$$Ag \mid AgX \mid HX(m_0),\ MX(m) \mid H_2 \mid HX(m_0) \mid AgX \mid Ag$$

and

$$H_2 \mid MOH(m_0),\ MX(m) \mid M_xHg \mid MOH(m_0) \mid H_2$$

have proved very useful in determining the activity coefficients of some strong acids and hydroxides in certain salt solutions.[2] In the cases so far considered, this method has been applied to the class of strong acids and hydroxides. The question naturally arises as to whether measurements of this kind cannot be extended so as to determine the activity coefficients of weak acids and hydroxides in salt solutions of varying strengths as well as the hydrogen and hydroxyl ion concentrations of weak acids and hydroxides in these solutions.

It is the purpose of this study to show that this information may be acquired by measurements of cells without liquid junction potentials. Furthermore, this result can be accomplished with cells which contain easily reproducible electrodes such as the hydrogen and silver–silver chloride electrodes. The limitations of the method are for the most part experimental and depend on the difficulty of obtaining the reversible electro-

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[1] Commonwealth Fund Fellow, 1927–1929.

[2] (a) Harned, THIS JOURNAL, **38**, 1986 (1916); (b) **42**, 1808 (1920); (c) **47**, 684 (1925); (d) **48**, 326 (1926); (e) Loomis, Essex and Meacham, *ibid.*, **39**, 1133 (1917); (f) Chow, *ibid.*, **42**, 497 (1920); (g) Harned and Brumbaugh, *ibid.*, **44**, 2729 (1922); (h) Åkerlöf, *ibid.*, **48**, 1160 (1926); (i) Harned and Swindells, *ibid.*, **48**, 126 (1926); (j) Harned and James, *J. Phys. Chem.*, **30**, 1060 (1926); (k) Harned and Åkerlöf, *Physik. Z.*, **27**, 411 (1926); (l) Güntelberg, *Z. physik. Chem.*, **123**, 199 (1926); (m) Randall and Breckenridge, THIS JOURNAL, **49**, 1435 (1927).

motive force of the hydrogen electrode in solutions containing hydrogen or hydroxyl ion at very low concentrations and salts at high concentrations.

This opens up a wide field for investigation, since we shall be able to study the effect of the powerful fields of electrolytic solutions upon the characteristic potentials of the organic cations and anions, and make preliminary attempts to parallel this property with the ion constitution. Further, these results may be compared with results obtained from catalytic data by Harned and Hawkins[3] and the values of the ionic activity coefficients of water in salt solutions.[4,2i,j]

Outline of the Method

The activity coefficient of a weak electrolyte may be defined in two ways. Assuming that the activity product, a_Ca_A, of the ions of a uni-univalent weak electrolyte has been determined, we may define an activity coefficient by either

$$\text{(a)} \quad \gamma = \sqrt{\frac{a_Ca_A}{m_Cm_A}} \quad \text{or} \quad \text{(b)} \quad \gamma = \sqrt{\frac{a_Ca_A}{m_+m_-}}$$

In (a) m_C and m_A are the stoichiometrical molalities of the ion groups of the electrolyte which would be computed in just the same way as in the case of a strong electrolyte. Thus, in a solution of HAc(m_1) + NaAc(m_2), m_C equals m_1 and m_A equals ($m_1 + m_2$), and in a solution of HAc(m_1) + NaCl(m_2), m_C equals m_A equals m_1.

In (b), m_+ and m_- are the true molal concentrations of the ionic species. It is the second of these quantities which is the subject of the present study. In fact, the second is the more important since this quantity is directly comparable to the activity coefficients of strong electrolytes and to the potentials of ionic solutions in general.

In the first place, we shall consider the determination of the activity coefficients of a weak acid in a salt solution. Let us consider the simple cells

$$H_2 \mid \text{HAc}(m_1),\ \text{MX}(m_2) \mid \text{AgX} \mid \text{Ag} \qquad (1)$$
$$H_2 \mid \text{HX}(m_0),\ \text{MX}(m_3) \mid \text{AgX} \mid \text{Ag} \qquad (2)$$

where HAc is a weak acid and HX is a strong acid. Subtract (2) from (1) and obtain

$$\text{Ag} \mid \text{AgX} \mid \text{HX}(m_0),\ \text{MX}(m_3) \mid H_2 \mid \text{HAc}(m_1),\ \text{MX}(m_2) \mid \text{AgX} \mid \text{Ag} \qquad (3)$$

The cell reaction of (3) represents the transfer of HX from the solution containing HX to the solution containing HAc. The electromotive force of (3) is therefore given by

$$E = 0.05915 \log \frac{\gamma_{H(2)}\gamma_{X(2)}\ m_0(m_3 + m_0)}{\gamma_{H(1)}\gamma_{X(1)}\ m_Hm_0} \qquad (4)$$

where $\gamma_{H(2)}\gamma_{X(2)}$ is the activity coefficient product of the ions in the solution

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[3] Harned and Hawkins, This Journal, **50**, 85 (1928).

[4] Harned, *ibid.*, **47**, 930 (1925).

containing HX only and $\gamma_{H(1)}\gamma_{X(1)}$ the same in the solution containing HAc; m_H is the stoichiometrical molality of the hydrogen ion.

We shall now consider the conditions under which $\gamma_{H(1)}\gamma_{X(1)}$ may be taken equal to $\gamma_{H(2)}\gamma_{X(2)}$. Throughout this discussion, let it be understood that the total ionic strengths of the two solutions are equal. Thus,

$$m_3 + m_0 = m_H + m_2$$

Assume that the molality of the weak acid is low enough so that the presence of the undissociated molecule of the acid causes no appreciable change in $\gamma_{H(1)}\gamma_{X(1)}$. It has been shown for mixtures of strong electrolytes of these types that a constant total molality of the ions

$$\log \gamma_{HX} = \alpha m_{HX} + \log \gamma_0 \qquad (5)$$

where α is a constant, γ_{HX} equals $\sqrt{\gamma_H\gamma_X}$ and γ_0 equals γ_{HX} when m_{HX} equals zero.[2d,1] The values of the constants α for the different salt solutions are such that γ_{HX} practically becomes independent of the acid concentration in solutions containing less than 0.01 *M* HX. This is illustrated in Fig. 1 in which γ_{HCl} in a potassium chloride solution is plotted against the logarithm of the acid concentration. The total concentration of the acid and the salt is 3 *M*. Thus at concentrations below 0.01 *M* hydrochloric acid, the plot becomes parallel to the abscissa. To be exact, at 0.01 *M*, γ_{HCl} equals 0.860, and at 0.001 *M* it equals 0.859, corresponding to a difference of less than 0.1 mv. Thus, if $m_{H(1)}$ and m_0 are 0.01 *M* or less, $\gamma_{H(1)}\gamma_{Cl(1)}$ may be taken equal to $\gamma_{H(2)}\gamma_{Cl(2)}$ without introducing an error greater than the experimental. Equation 4 becomes

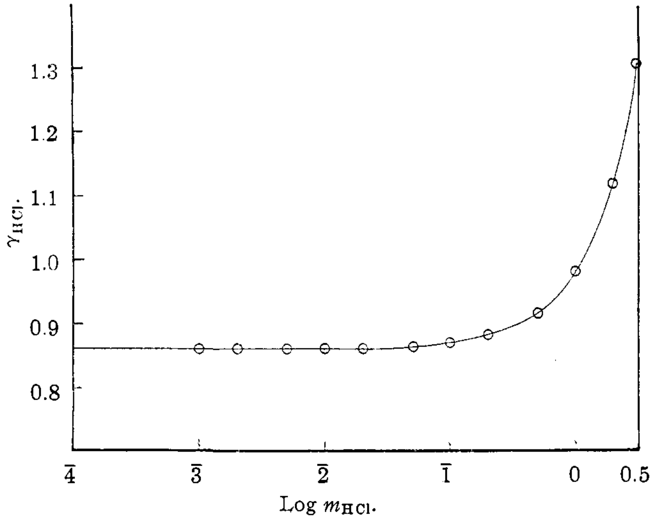

Fig. 1.—γ-log *m* plot of hydrochloric acid in potassium chloride solutions at a constant total molality of 3.

$$E = 0.05915 \log \frac{m_0(m_0 + m_3)}{m_H m_2} \qquad (6)$$

and since m_0, m_2 and m_3 are known, m_H may be computed.

After having computed m_H by Equation 4 or Equation 6, the calculation of $\gamma_H\gamma_{Ac}/\gamma_{HAc}$ becomes a simple matter since the thermodynamic equation for the dissociation of HAc is

$$K = \frac{\gamma_H\gamma_{Ac}}{\gamma_{HAc}} \frac{m_H^2}{m_1 - m_H} \qquad (7)$$

and K, m_1 and m_H are known.

That exactly similar considerations will apply to the determination of the activity coefficient products of weak hydroxides in salt solutions from measurements of cells of the type

$$H_2 \mid MOH(m_0),\ MX(m_3) \mid M_xHg \mid BOH(m_1),\ MX(m_2) \mid H_2 \qquad (3a)$$

where MOH is a strong and BOH a weak hydroxide, may readily be shown.

For this case, the equation corresponding to Equation 4 will be

$$E = 0.05915 \log \frac{\gamma_{M(2)}\gamma_{OH(2)}\ m_0(m_3 + m_0)\ a_{H_2O(1)}}{\gamma_{M(1)}\gamma_{OH(1)}\ m_{OH}\ m_2\ a_{H_2O(2)}} \qquad (4a)$$

where the subscript (2) refers to the solution containing the strong, and (1) to that containing the weak hydroxide. Since the ratio of the activity of water in the two solutions will be unity, and since for low concentrations of the weak base we may take the activity coefficient ratio in the two solutions as unity, we obtain

$$E = 0.05915 \log \frac{m_0(m_3 + m_0)}{m_{OH}\ m_2} \qquad (6a)$$

which corresponds to Equation 6.

In many cases it may be simpler from the point of view of experiment to measure cells with salt bridges such as

$$H_2 \mid HX(m_0),\ MX(m_3) \mid \text{sat. KCl} \mid HAc(m_1),\ MX(m_2) \mid H_2$$
$$H_2 \mid MOH(m_0),\ MX(m_3) \mid \text{sat. KCl} \mid BOH(m_1),\ MX(m_2) \mid H_2$$

In the case of the latter cells, the difference in the two liquid junction potentials will be very small provided that the hydrogen-ion concentrations in the first and the hydroxyl-ion concentrations in the second are the same on both sides of the salt bridge. If we apply the above considerations to these cells, then at small concentrations of HAc and BOH (not above 0.5 *M*), the electromotive force is a measure of the ratio of the hydrogen or hydroxyl-ion concentrations in the two electrode compartments.

So far we have assumed that the concentration of the undissociated molecule, HAc, is so low that it has only a negligible effect on $\gamma_{H(1)}\ \gamma_{X(1)}$. At higher concentrations of HAc, the absolute value of $\gamma_{H(1)}\ \gamma_{X(1)}$ relative to pure aqueous solution will increase with increasing concentration of the undissociated molecule. Thus, Harned and Fleysher[5] have found that

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[5] Harned and Fleysher, THIS JOURNAL, **47**, 82 (1925).

$\gamma_H\gamma_{Cl}$ in a 0.01 *M* acid solution in water increases 3.1 times its initial value on the addition of 25 mole per cent. of ethyl alcohol. From the nature of the plot of their results, the presence of 0.1 *M* ethyl alcohol would cause an increase of somewhat less than 0.5% in $\gamma_{H(1)}\gamma_{X(1)}$. Consequently, Equation 6 is only exactly valid at zero concentration of HAc, but is valid to within less than 1.2% for solutions containing 0.2 *M* HAc or less, if we presume that the effect of undissociated acetic acid upon the activity coefficient is not greater than that of ethyl alcohol. Equation 6 will be strictly valid in the case of the cells

$$Ag \mid AgCl \mid HX(m_0),\ M(m_4),\ MX(m_3) \mid H_2 \mid HAc(m_1),\ MX(m_2) \mid AgCl \mid Ag$$

provided that M is an undissociated molecule at a concentration $m_4 = (m_1 - m_H)$ which produces the same effect on $\gamma_{H(1)}\gamma_{X(1)}$ as does the undissociated acetic acid.

Since the present study contains extensive determinations of $\gamma_H\gamma_{Ac}/\gamma_{HAc}$ and $\gamma_B\gamma_{OH}/\gamma_{BOH}$ in aqueous solutions, we have not thoroughly investigated the above effect at this time. We have, however, obtained a few series of results with acetic acid at high concentrations in sodium chloride solutions which we shall use to illustrate the magnitude of this effect.

Part 1. The Ionic Concentrations and Activity Coefficients of Acetic Acid in Salt Solutions

Experimental Results and Method of Numerical Calculation.—The cells measured were of the type

$$H_2 \mid HAc(m_1),\ MX(m_2) \mid AgCl \mid Ag \qquad (8)$$

Extended series of measurements of cells containing 0.1, 0.2, 0.5, 1.0, 5.0 and 10 *M* acetic acid were made in each of which sodium chloride was varied over a concentration range of 0.02 to 3 *M*. Further, a series of determinations of cells containing acetic acid at a concentration of 0.2 *M* and potassium, lithium and barium chlorides of varying strengths was made, as well as a series of cells with 0.1 *M* acetic acid and potassium chloride. The acetic acid and salts were of a high grade of purity. The potassium and sodium salts were dried at a suitable temperature, barium chloride was used in the form of the dihydrate and the lithium chloride solutions were made by dilution of an analyzed concentrated solution.

The silver–silver chloride electrodes were of the spiral type. The silver oxide paste was heated at 500° on the platinum spiral. No electrolytic silver was deposited on the spiral previous to this operation. Electrodes made in this way have the same potential as those made by the Noyes and Ellis method.

The hydrogen electrodes were of the usual platinum foil type and were found to give reproducible results in all cases except those of the cells containing 0.1 *M* acetic acid. In the latter case, with cells containing either sodium or potassium chlorides, it was found impossible to obtain electromotive forces corresponding to reasonable values of the activity coefficient of acetic acid unless the platinum foils were coated with an extremely thin film of platinum black. With this additional precaution, potential readings were obtained which are thought to be reasonably close to the correct ones, but a high degree of accuracy is not claimed. This source of error is in accord with the experiments of Harned.[2d] He found that in solutions containing hydrochloric acid and sodium or potassium chlorides (of constant total molality) the hydrogen electrode as usually prepared was unreliable at acid concentrations below 0.002 *M* to 0.005 *M*. He showed that very thinly coated electrodes improved the situation but did not completely eliminate the error when the salt to acid ratio was very high. Our observations agreed with his, since the error was found to be the greater. the higher the salt concentrations.

In the cells containing acetic acid at 0.2 *M* or higher, the reproducibility was approximately ±0.2 mv. if the salt concentrations were at 0.05 *M* or higher. Attempts were made to obtain results in solutions of 0.02 *M* salt but they were successful in only a few cases.

Instead of comparing the electromotive force of the cell containing acetic acid with that of the cell containing hydrochloric acid in salt solution of the same total molality according to the Scheme 3 and Equation 4 it was found more convenient to proceed as follows.

If the cell

$$\mathrm{Ag} \mid \mathrm{AgCl} \mid \mathrm{HCl}(m_0),\ \mathrm{MCl}(m_3) \mid \mathrm{H_2} \mid \mathrm{HCl}(0.01) \mid \mathrm{AgCl} \mid \mathrm{Ag} \tag{9}$$

be subtracted from (3) for the case where X equals chlorine, the cell

$$\mathrm{Ag} \mid \mathrm{AgCl} \mid \mathrm{HCl}(0.01) \mid \mathrm{H_2} \mid \mathrm{HAc}(m_1),\ \mathrm{MCl}(m_2) \mid \mathrm{AgCl} \mid \mathrm{Ag} \tag{10}$$

is obtained. But this cell is also obtained by subtracting

$$\mathrm{H_2} \mid \mathrm{HCl}(0.01) \mid \mathrm{AgCl} \mid \mathrm{Ag} \tag{11}$$

from the cells measured, namely

$$\mathrm{H_2} \mid \mathrm{HAc}(m_1),\ \mathrm{MCl}(m_2) \mid \mathrm{AgCl} \mid \mathrm{Ag} \tag{12}$$

Let E' equal the electromotive force of cells (12)[2g,i] and 0.4644 be the electromotive force of (11), then

$$E' - 0.4644 = 0.05915 \log \frac{(0.902)^2(0.01)^2}{\gamma_{\mathrm{H}(1)}\gamma_{\mathrm{X}(1)}\ m_{\mathrm{H}}m_2} \tag{13}$$

if 0.902 be taken as the activity coefficient of hydrochloric acid in water at 0.01 *M*. Equation 13 reduces to

$$E' - 0.2225 = -0.05915 \log \gamma_{\mathrm{H}(1)}\gamma_{\mathrm{Cl}(1)}\ m_{\mathrm{H}}m_2 \tag{14}$$

Neglecting for the present any correction involving the change in solvent caused by the presence of undissociated acetic acid, we let $\gamma_{\mathrm{H}(1)}\gamma_{\mathrm{Cl}(1)}$ equal $\gamma_{\mathrm{H}(2)}\gamma_{\mathrm{Cl}(2)}$, which latter data were obtained from cells of the type (2) containing hydrochloric acid and a chloride.

The experimental data as well as the calculated hydrogen-ion concentrations and activity coefficients are given in Table I; m_1 is the molal concentration of the acetic acid, m_2 the molal concentration of added salt and E' the measured values of the electromotive forces. The values of $\gamma_{H(2)}\gamma_{Cl(2)}$ or $\gamma_{H(1)}\gamma_{Cl(1)}$ were read off plots of the data taken from the tables of Harned and Åkerlöf.[2k] m_H is the hydrogen or acetate-ion concentration calculated by Equation 14. The next column gives the values of $\sqrt{\gamma_A}$ computed by Equation 8 from the values of m_H. The value employed for the dissociation constant of acetic acid[6] was 1.85×10^{-5}. All measurements were made at 25°. Since m_H was unknown in the most dilute solutions,

TABLE I

HYDROGEN OR ACETATE-ION CONCENTRATIONS AND ACTIVITY COEFFICIENTS OF ACETIC ACID IN CHLORIDE SOLUTIONS

A. Potassium Chloride

(1) m_1 = 0.1005 M HAc. Correction for E' = +0.0001 (0.44%)

m_2	E'	$\gamma_{HCl(H_2O)}$	m_H	$\sqrt{\gamma_A}$	$m_{H(corr.)}$	$\sqrt{\gamma_A}$(corr.)
0.05	0.4754	0.810	0.001616	0.837	0.001609	0.841
.1	.4589	.781	.001652	.818	.001645	.822
.2	.4423	.747	.001723	.785	.001716	.788
.5	.4206	.711	.001771	.763	.001763	.766
1.5	.3935	.736	.001582	.855	.001575	.859
2.0	.3857	.777	.001442	.939	.001436	.943
3.0	.3736	.859	.001260	1.075	.001255	1.080

(2) m_1 = 0.2001 M HAc. Correction for E' = +0.0003 (1.16%)

0.05	0.4655	0.810	0.002376	0.805	0.002349	0.814
.1	.4492	.781	.002410	.794	.002382	.803
.194	.4336	.749	.002479	.771	.002451	.780
.5	.4113	.711	.002543	.752	.002514	.761
1.0	.3945	.712	.002438	.785	.002410	.795
1.5	.3840	.736	.002290	.835	.002264	.845
2.0	.3761	.777	.002096	.913	.002072	.924
3.0	.3645	.859	.001795	1.067	.001774	1.079

B. Sodium Chloride

(1) m_1 = 0.1 M HAc. Correction for E' = +0.0001 (0.44%)

m_1	m_2	E'	$\gamma_{HCl(H_2O)}$	m_H	$\sqrt{\gamma_A}$	$m_{H(corr.)}$	$\sqrt{\gamma_A}$(corr.
0.0997	0.02	0.4972	0.864	0.001520	0.887	0.001513	0.891
.0992	.05	.4747	.815	.001640	.819	.001633	.823
.1003	.05	.4744	.815	.001660	.814	.001653	.818
.0991	.1	.4581	.785	.001687	.796	.001680	.799
.1004	.1985	.4415	.752	.001767	.764	.001759	.767
.0991	.2	.4417	.752	.001741	.771	.001733	.774
.1006	.5	.4184	.729	.001835	.753	.001827	.756
.0997	.486	.4197	.729	.001795	.750	.001787	.753
.1050	1.0	.3986	.764	.001806	.765	.001798	.768
.1050	1.489	.3874	.810	.001668	.829	.001661	.833
.1050	2.0	.3773	.891	.001521	.910	.001514	.914
.1003	2.95	.3624	1.085	.001242	1.090	.001237	1.095

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[6] Kendall, *J. Chem. Soc.*, 101, 1275 (1912).

TABLE I (*Continued*)

(2) m_1 = 0.2 M HAc. Correction for E' = +0.0003 (1.16%)

m_1	m_2	E'	$\gamma_{\text{HCl(H}_2\text{O)}}$	m_{H}	$\sqrt{\gamma_{\text{A}}}$	$m_{\text{H(corr.)}}$	$\sqrt{\gamma_{\text{A}}}$(corr.)
0.1965	0.05	0.4653	0.812	0.002382	0.796	0.002350	0.805
.2018	.1	.4484	.782	.002480	.774	.002452	.783
.2018	.2	.4317	.752	.002569	.747	.002540	.756
.2018	.5	.4088	.729	.002666	.720	.002635	.728
.2026	1.066	.3877	.771	.002542	.757	.002513	.766
.2018	1.5	.3777	.817	.002375	.809	.002348	.818
.2018	2.0	.3682	.891	.002176	.883	.002151	.893
.2018	3.0	.3519	1.085	.001838	1.047	.001817	1.059

(3) m_1 = 0.519 M HAc. Correction for E' = +0.0008 (3.16%)

m_2	E'	$\gamma_{\text{HCl(H}_2\text{O)}}$	m_{H}	$\sqrt{\gamma_{\text{A}}}$	$m_{\text{H(corr.)}}$	$\sqrt{\gamma_{\text{A}}}$(corr.)
0.02	0.4746	0.859	0.003706	0.833	0.003593	0.859
.05	.4522	.815	.003939	.784	.003819	.809
.0957	.4362	.784	.004146	.744	.004019	.768
.2285	.4152	.747	.004331	.713	.004198	.736
.614	.3902	.732	.004443	.695	.004307	.717
1.0	.3765	.764	.004268	.723	.004137	.746
1.5	.3646	.811	.004013	.769	.003890	.793
1.54[a]	.3640	.811	.003952	.768	.003831	.792
1.995	.3551	.891	.003619	.853	.003508	.880
2.993	.3387	1.085	.003080	1.003	.002986	1.035

[a] m_1 = 0.502.

(4) m_1 = 1.002 M HAc. Correction for E' = +0.0019 (7.67%)

0.01997	0.4646	0.859	0.005478	0.784	0.005088	0.844
.049	.4429	.815	.005772	.744	.005362	.801
.1	.4255	.780	.006079	.706	.005646	.760
.222	.4061	.748	.006337	.678	.005886	.730
.2	.4085	.752	.006338	.677	.005886	.729
.5	.3865	.729	.006352	.676	.005899	.728
1.0	.3672	.764	.006130	.700	.005677	.754
1.3[a]	.3596	.792	.005898	.726	.005478	.782
2.43	.3377	.960	.005039	.852	.004647	.917
2.96[a]	.3300	1.074	.004455	.963	.004138	1.037

[a] m_1 = 0.998.

(5) m_1 = 5.4 M HAc. Correction for E' = +0.0107 (51.7%)

m_1	m_2	E'	$\gamma_{\text{HCl(H}_2\text{O)}}$	m_{H}	$\sqrt{\gamma_{\text{A}}}$	$m_{\text{H(corr.)}}$	$\sqrt{\gamma_{\text{A}}}$(corr.)
5.41	0.05	0.4092	0.800	0.02180	0.458	0.01438	0.695
5.41	.1	.3923	.774	.02248	.445	.01482	.675
5.39	.2	.3758	.748	.02288	.436	.01509	.661
5.41	.5	.3535	.729	.02295	.436	.01513	.661
5.41	1.0	.3337	.766	.02247	.445	.01481	.675
5.37	1.5	.3237	.812	.01967	.506	.01297	.785
5.39	1.5	.3233	.812	.01998	.499	.01317	.757
5.39	2.0	.3138	.872	.01881	.530	.01240	.804
5.39	3.0	.2990	1.088	.01433	.696	.01189	1.056

TABLE I (*Concluded*)

(6) $m_1 = 10.2\ M$ HAc

m_2	E'	$\gamma_{HCl(H_2O)}$	m_H	$\sqrt{\gamma_A}$
0.05	0.3888	0.782	0.05048	0.272
.0992	.3726	.765	.04995	.274
.257	.3509	.738	.04821	.284
.5	.3351	.730	.04685	.293
1.0	.3181	.766	.04124	.332
1.49	.3057	.814	.03972	.345
2.0	.2975	.885	.03444	.398
2.96	.2814	1.085	.02897	.474

C. Lithium Chloride

(1) $m_1 = 0.2\ M$ HAc. Correction for $E' = +0.0003$ (1.16%)

m_1	m_2	E'	$\gamma_{HCl(H_2O)}$	m_H	$\sqrt{\gamma_A}$	$m_{H(corr.)}$	$\sqrt{\gamma_A}_{(corr.)}$
0.2122	0.04467	0.4669	0.817	0.002475	0.796	0.002477	0.805
.2090	.08933	.4501	.788	.002559	.764	.002530	.773
.2107	.2	.4301	.760	.002677	.733	.002646	.741
.2037	.5	.4059	.751	.002813	.685	.002781	.693
.2145	1.0	.3842	.804	.002856	.689	.002823	.697
.2110	1.568	.3674	.902	.002783	.705	.002751	.713
.2100	2.069	.3541	1.027	.002730	.717	.002699	.725
.2081	3.112	.3313	1.340	.002590	.753	.002560	.762
.2037	4.533	.2993	2.115	.002481	.778	.002453	.787

D. Barium Chloride

(1) Cells of the type (2). $m_0 = 0.01\ M$ HCl.

m_0	m_2	$\sqrt{\mu}$	E	γ_{HCl}	m_0	m_2	$\sqrt{\mu}$	E	γ_{HCl}
0.01	0.02	0.27	0.4295	0.796	0.00936	0.466	1.19	0.3615	0.712
.00991	.0257	.295	.4249	.790	.01	.463	1.19	.3600	.711
.01	.05143	.405	.4109	.760	.00944	.941	1.67	.3363	.817
.01	.0926	.537	.3991	.728	.01	1.0	1.74	.3330	.821
.00931	.1870	.750	.3856	.700	.00952	1.423	2.07	.3166	.970
.01	.1852	.752	.3838	.702	.01	1.5	2.12	.3128	.994

(2) $m_1 = 0.2035\ M$ HAc. Correction for $E' = +0.0003$ (1.16%)

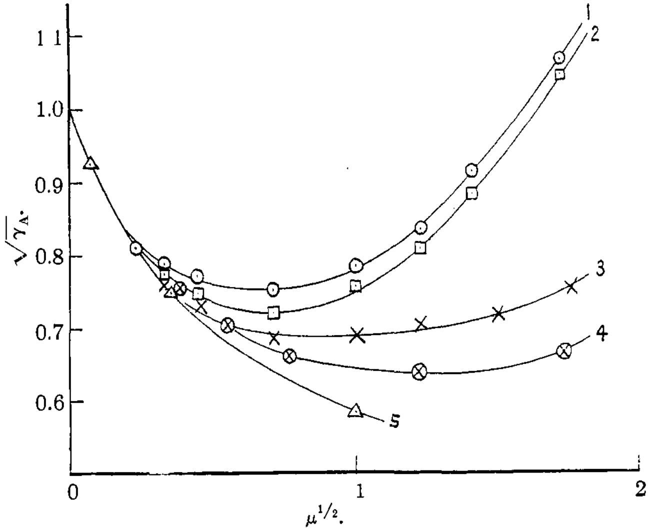
m_2	E'	$\gamma_{HCl(H_2O)}$	m_H	$\sqrt{\gamma_A}$	$m_{H(corr.)}$	$\sqrt{\gamma_A}_{(corr.)}$
0.01984	0.4712	0.803	0.002440	0.791	0.002412	0.800
.0496	.4493	.761	.002549	.757	.002520	.766
.0992	.4323	.725	.002721	.708	.002690	.716
.1984	.4147	.699	.002905	.663	.002872	.671
.496	.3891	.714	.003017	.638	.002983	.645
.992	.3651	.822	.002897	.665	.002864	.673
1.484	.3478	.990	.002618	.736	.002588	.744
1.5	.3471	.994	.002640	.730	.002610	.738

and therefore the total molality was unknown, γ_{HCl} or $\gamma_{H(1)}\gamma_{Cl(1)}$ was obtained approximately by trial and a first rough value of m_H determined. From this a more accurate value of the total ionic molality was computed and a more accurate value of γ_{HCl} was obtained; m_H could then be calculated with certainty.

It was found necessary to determine γ_{HCl} in 0.01 M hydrochloric acid–barium chloride mixtures by means of cells of type (2). These are included in the table and will be found to agree excellently with some recent values of Randall and Breckenridge.[2m]

Discussion of the Properties of the Acetic Acid–Salt Systems

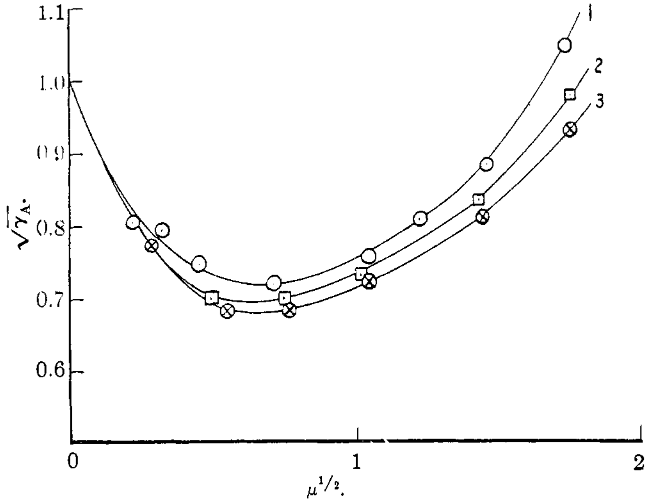
(a) **General Considerations.**—From the data in Table I, it is obvious from the behavior of m_H that in all cases the first addition of salt increases the dissociation of the acid. As the concentration of the added salt increases this dissociation reaches a maximum, and in the more concentrated solutions decreases with increasing salt concentration. On the other hand, γ_A decreases, passes through a minimum and then increases upon the addition of the salt. This latter behavior is in accord with that of all strong acids in salt solutions, of the ionic activity coefficient product of water in salt solutions, and of the ionic activity coefficient of the mono- and dichloro-acetic acids as computed from catalytic data.



1, KCl; 2, NaCl; 3, LiCl; 4, $BaCl_2$; 5, Debye and Hückel theory.
Fig. 2.—The ionic activity coefficients of 0.2 M acetic acid in salt solutions.

Figure 2 contains plots of $\sqrt{\gamma_A}$ in the four salt solutions against the square root of the ionic strength, $\mu^{1/2}$. These were obtained from the cells containing 0.2 M acetic acid. Since for the present we have neglected the effect of the change in solvent due to the presence of the undissociated molecule, these results for $\sqrt{\gamma_A}$ may all be low to the extent of approximately 0.5%. Exactly the same order and approximately the same arrangement of results is obtained as was found by Harned[4,7] in the case of the ion activity coefficient of water, of strong hydroxides in the corresponding chloride solutions, of formic acid in salt solutions, and by Harned and Hawkins[3] in the case of the mono- and dichloro-acetic acids in halide solutions.

In Fig. 3, the values of $\sqrt{\gamma_A}$ for acetic acid and dichloro-acetic acid in potassium and sodium chloride solutions are plotted. Since in the case of the dichloro-acetic acid a greater curvature appears at the lower concentration, it would seem that its activity coefficient should always lie below that of the acetic acid. The values of γ_A have therefore been taken as calculated by Harned and Hawkins. The value of γ_A of monochloro-acetic acid in sodium chloride solutions is also given. Thus, in aqueous



1, CH_3COOH; 2, $CH_2ClCOOH$; 3, $CHCl_2COOH$.

Fig. 3.—The ionic activity coefficients of acetic, mono- and dichloro-acetic acids in sodium chloride solutions.

salt solutions, it would appear that γ_A decreases as the chlorine substitution increases up to the formation of dichloro-acetic acid. The plots in the upper part of Fig. 4 show the effect of change of concentration of the acetic acid on the activity coefficients relative to unity at infinite dilution of the pure aqueous solutions and calculated according to Equation 14. It is interesting to note that the upper four plots are parallel.

As previously pointed out, Equation 6 is not valid in the case where considerable concentrations of undissociated acetic acid are present and, therefore, to compute the activity coefficients relative to unity at infinite dilution for each separate solvent, cells equivalent to those represented by (8) are necessary. Equation 14 would be valid in the form

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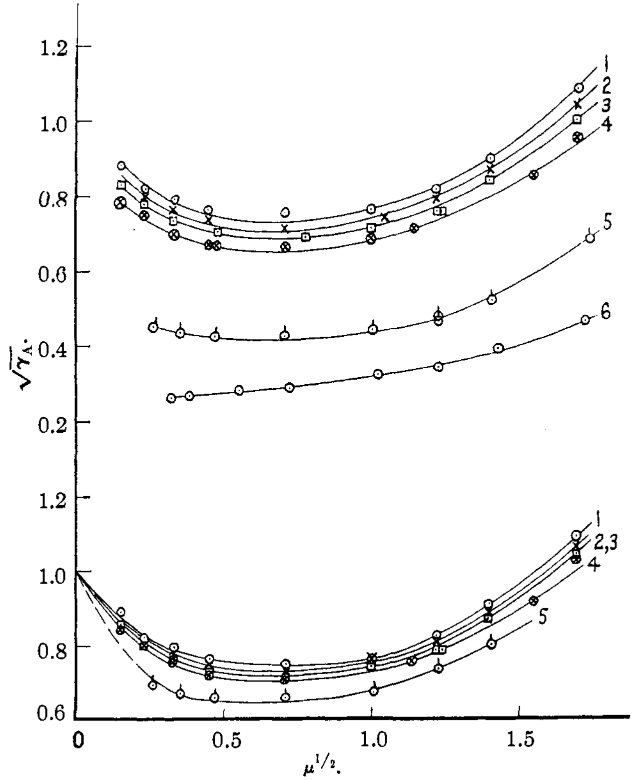
[7] Harned, This Journal, 49, 1 (1927).

$$
\begin{aligned}
E' - 0.2225 &= -0.05915 \log \gamma'_{\mathrm{H}(1)}\gamma'_{\mathrm{Cl}(1)}\, m_{\mathrm{H}} m_2 \\
&= -0.05915 \log \gamma_{\mathrm{H}(1)}\gamma_{\mathrm{Cl}(1)}\, m_{\mathrm{H}} m_2 - 0.05915 \log \frac{\gamma'_{\mathrm{H}(1)}\gamma'_{\mathrm{Cl}(1)}}{\gamma_{\mathrm{H}(1)}\gamma_{\mathrm{Cl}(1)}} \qquad (14a)
\end{aligned}
$$

where $\gamma'_{(\mathrm{H}1)}\gamma'_{\mathrm{Cl}(1)}$ is the activity coefficient of hydrochloric acid in a solution containing the acetic acid and salt relative to $\gamma_{\mathrm{H}(1)}\gamma_{\mathrm{Cl}(1)}$ in the salt solution in pure water. The second member on the right is, therefore, the correction term for the electromotive force E which will take into account the change in solvent.



1, 0.1 M; 2, 0.2 M; 3, 0.5 M; 4, 1.0 M; 5, 5.4 M; 6, 10.2 M.

Fig. 4.—The ionic activity coefficients of acetic acid at different molalities, M, in sodium chloride solutions.

To correct for this change in solvent, we have used a method which, although approximate, yields results of the right magnitude and illustrates the effect of the correction. We make the assumption that up to 5.4 M concentration the effect of the undissociated acetic acid on the activity coefficient of the hydrochloric acid is the same as that of ethyl alcohol. Further, owing to the parallel nature of the plots in Fig. 4, we assume that at a given acetic-acid concentration the correction is independent of the salt concentration. To this end we have plotted the electromotive forces of the cells

$$H_2 \mid HCl(0.01) \mid AgCl \mid Ag$$

in water and water–alcohol mixtures against the mole per cent. of alcohol, and have read off this plot the changes in electromotive forces produced by the addition of 0.1, 0.2, 0.5, 1 and 5.4 M alcohol. These were found to be 0.1, 0.3, 0.8, 1.9 and 10.7 millivolts, respectively. These corrections, which correspond to the second member on the right of Equation 14a, we have added to E'. Subsequently, m_H was recalculated and $\sqrt{\gamma_A}$ computed by Equation 7. The corrected results are given in the last columns of Table I, and the corrected values of $\sqrt{\gamma_A}$ are plotted in the lower part of Fig. 4. It is obvious upon inspection of these curves that this correction brings the curves much closer together. The distribution is also what is to be expected from the change in the dielectric constant produced by the addition of the undissociated acid.

Since acetic acid has a dielectric constant lower than that of water, the value of the ionic activity coefficient product of the acid relative to unity in infinite dilution in a given solvent will decrease with increasing acetic-acid concentration. The extent of the variation may be calculated approximately in the case of dilute solutions by the equation

$$\frac{\log \sqrt{\gamma_{A(1)}}}{\log \sqrt{\gamma_{A(2)}}} = \left(\frac{D_2}{D_1}\right)^{3/2} \tag{14b}$$

derivable from the Debye and Hückel theory. This calculation requires a knowledge of the dielectric constants of acetic acid–water mixtures. These data are not available, although we find that the dielectric constant of pure acetic acid is 9.7.[8] Assuming that the dielectric constant of acetic-acid–water mixtures varies in the same way as that of alcohol–water mixtures, and taking the dielectric constant of pure water as 81, we obtain 80, 78, 75 and 58 for the dielectric constants of 0.2, 0.5, 1 and 5.4 M acetic-acid solutions, respectively. We now select a concentration (0.3μ) at which $\sqrt{\gamma_A}$ equals 0.800 in pure water. Substituting the values of the above dielectric constants in Equation 14b, we obtain the values of $\sqrt{\gamma_A}$ in the different solvents which are given in the third line of Table II. These may be compared with the values read off the curves in the lower part of Fig. 4, which are given in the second line.

TABLE II

COMPARISON OF THE OBSERVED ACTIVITY COEFFICIENTS WITH THOSE COMPUTED BY EQUATION 14b

HAc concn.	0.0	0.2	0.5	1.0	5.4
$\sqrt{\gamma_A}$ (obs.)	0.800	0.796	0.79	0.77	0.69
$\sqrt{\gamma_A}$ (calcd.)	0.800	0.796	0.79	0.78	0.70

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[8] Francke, *Wied. Ann.*, **50**, 163 (1893).

These results show that the procedure which we have adopted and which is necessarily an approximation, gives results of the correct order of magnitude and illustrate very well the influence of the various factors which come into force when the nature of the solvent medium is altered.

Part 2. The Ionic Concentrations and Activity Coefficients of Ammonia and its Methyl Derivatives in Salt Solutions

Experimental

As this investigation is intended as a preliminary survey of the possibilities of determining the activity coefficients of weak electrolytes in salt solutions rather than a very accurate determination of such activity coefficients, it was considered advisable to employ cells with liquid junctions, rather than cells of the type (3a), in the determination of the activity coefficients of the weak hydroxides. Cells of the type (3a) can undoubtedly be used for the accurate determination of these activity coefficients (provided that there is no reaction between the amalgam and the cation of the base), but cells of the type

$$H_2 \mid MOH(m_0),\ MX(m_2) \underset{A}{\mid} MX(m_2) \mid AgCl \mid Ag \mid AgCl \mid MX(m_2) \underset{B}{\mid} BOH(m_1),\ MX(m_2) \mid H_2 \tag{15}$$

obtained by difference of the half-cells

$$H_2 \mid MOH(m_0),\ MX(m_2) \mid MX(m_2) \mid AgCl \mid Ag \tag{16}$$

$$H_2 \mid BOH(m_1),\ MX(m_2) \mid MX(m_2) \mid AgCl \mid Ag \tag{17}$$

which can be constructed with greater ease and rapidity, probably give quite accurate results.[9]

Cells of this type were therefore constructed, in which MOH was sodium hydroxide at a concentration of 0.01 *M* and MX was sodium chloride at concentrations varying between 0.02 and 3.0 *M*. Five bases were used, as follows: ammonia, mono-, di- and trimethylamines, and tetramethyl ammonium hydroxide. BOH therefore represents one of these hydroxides in a sodium chloride solution of the same concentration as that in the left half of the cell (15). Junction between these two solutions was made by means of silver–silver chloride electrodes in solutions of sodium chloride at the same concentration as in the hydroxide solutions. In practice the two halves of the cell were measured separately.

In this case two liquid junctions are encountered, at A and B. Virtually, however, this reduces to one liquid junction, namely, that at the boundary

$$NaOH(m_0),\ NaCl(m_2) \mid BOH(m_1),\ NaCl(m_2) \tag{18}$$

When the concentration of the sodium chloride is great compared with that of the hydroxide, the liquid junction potential must be very small

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[9] Note that we have made $(m_0 + m_2)$ equal to $(m_{OH} + m_2)$ so that the ionic strengths in each are equal.

and, indeed, negligible. Even in the lowest sodium-chloride concentrations which were used (0.02 *M*), the liquid junction potential must be very small, since we endeavored to work with concentrations of the weak hydroxide such that its hydroxyl-ion concentration was around 0.01 *M*, that is, nearly that of the sodium hydroxide in the left half of cell (15).

The mono- and dimethylamines were used at a concentration of approximately 0.2 *M*. The ammonia was 0.5 *M*, giving a hydroxyl-ion concentration of about 0.005 *M*. Trimethylamine was used at 0.2 *M*, giving a hydroxyl-ion concentration of between 0.005 *M* and 0.01 *M*. Tetramethylammonium hydroxide was used at 0.01 *M*, since we were able to show that in all probability it belongs to the class of "completely dissociated" electrolytes.

Two difficulties were encountered. In the first place, preliminary measurements of sodium-chloride solutions of sodium hydroxide at low concentrations of the latter (0.0025 *M*) showed that the hydrogen electrode would not give accurate potentials at this concentration of hydroxyl ion. This is in accordance with our experience with the hydrogen electrode in acetic-acid solution, as previously described.

Secondly, in the 0.02 *M* and 0.05 *M* sodium-chloride solutions of ammonia and trimethylamine, difficulty was experienced in determining the potentials accurately. This is probably due to one of two causes. (1) Diminution of the salt concentration lowers the hydroxyl-ion concentration. It may be, therefore, that in the above two salt concentrations we are approaching the limit of the hydroxyl-ion concentration at which the hydrogen electrode will work efficiently. (2) The liquid junction according to the scheme (18) will probably no longer be of negligible magnitude if the sodium-hydroxide concentration is 0.01 *M* and the hydroxyl-ion concentration of the weak hydroxide is approximately 0.005 *M*. As the salt concentration increases, most of the ionic transference is due to the sodium and chloride ions; and therefore it is likely that for solutions of concentrations 0.1 *M* sodium chloride and greater, the liquid junction potential may be neglected with safety. We have therefore omitted measurements in 0.02 *M* and 0.05 *M* sodium-chloride solutions of ammonia and trimethylamine.

Cells were also measured containing potassium chloride and either ammonia or methylamine against cells containing 0.01 *M* potassium hydroxide in potassium chloride solutions, and also similar series with lithium chloride as salt.

The electrodes were of the type already described. Measurements were made at 25°. The liquid junctions were of the static type, a capillary tube containing the hydroxide–salt solution being dipped into a cup containing the pure salt solution.

Calculation of Results

Table III gives the electromotive forces of the half-cells (16) and (17) measured, that is, cells containing 0.01 *M* sodium, potassium or lithium hydroxides in the respective salt solutions,-the five hydroxides in sodium-chloride solution, and ammonia and methylamine in potassium- and lithium-chloride solutions.

TABLE III

ELECTROMOTIVE FORCES OF CELLS (16) AND (17) CONTAINING HYDROXIDES AND ALKALI CHLORIDES

A. Sodium Chloride

Salt concn.	0.01 *M* NaOH	0.5030 *M* NH_3	0.1989 *M* CH_3NH_2	0.1987 *M* $(CH_3)_2NH$	0.1891 *M* $(CH_3)_3N$	0.01 *M* $(CH_3)_4NOH$
0.02	1.0197	....	1.0221	1.0239	....	....
.05	1.0015	....	1.0060	1.0077	....	....
.1	.9858	0.9646	.9924	.9945	0.9653	0.9855
.2	.9689	.9494	.9781	.9813	.9515	.9692
.5	.9452	.9282	.9583	.9614	.9332	.9467
1.0	.9273	.9125	.9432	.9476	.9192	.9285
1.5	.9166	.9025	.9342	.9390	.9113	.9181
2.0	.9086	.8946	.9277	.9330	.9048	.9099
3.0	.8973	.8835	.9177	.9240	.8973	.8985

B. Potassium Chloride

Salt concn.	0.01 *M* KOH	0.1910 *M* CH_3NH_2	0.5030 *M* NH_3	Salt concn.	0.01 *M* KOH	0.1910 *M* CH_3NH_2	0.5030 *M* NH_3
0.02	1.0207	1.0235	....	1.0	0.9380	0.9511	0.9199
.05	1.0044	1.0090	....	1.5	.9294	.9437	.9119
.1	.9900	.9967	0.9688	2.0	.9226	.9378	.9055
.2	.9749	.9832	.9546	3.0	.9140	.9304	.8969
.5	.9537	.9647	.9347				

C. Lithium Chloride

Salt concn.	0.01 *M* LiOH	0.5030 *M* NH_3	0.1910 *M* CH_3NH_2	Salt concn.	0.01 *M* LiOH	0.5030 *M* NH_3	0.1910 *M* CH_3NH_2
0.02	1.0167	....	1.0207	1.0	0.9145	0.9016	0.9343
.05	.9974	....	1.0040	1.5	.8981	.8888	.9219
.1	.9801	0.9590	.9896	2.0	.8866	.8781	.9125
.2	.9624	.9433	.9739	3.0	.8667	.8613	.8974
.5	.9371	.9208	.9528				

Considerations similar to those which led to Equation 4 will show that the electromotive forces of the cells (15) are given by

$$E = 0.05915 \log \frac{\gamma_{H(2)}\gamma_{X(2)}\, C_{H(2)}\, m_2}{\gamma_{H(1)}\gamma_{X(1)}\, C_{H(w)}\, m_2} = 0.05915 \log \frac{\gamma_{OH(1)}\gamma_{X(2)}\, a_{H_2O(2)}\, m_2 m_{OH}}{\gamma_{OH(2)}\gamma_{X(1)}\, a_{H_2O(1)}\, m_2 m_0} \qquad (19)$$

Since the concentrations of BOH have been taken low enough to render the dielectric constant correction negligible, the activity and activity coefficient ratios may again be taken as unity. Equation 19 becomes

$$E = 0.05915 \log \frac{m_{OH}}{m_0} \qquad (20)$$

which is comparable to Equation 6. We can therefore calculate m_{OH}

from a knowledge of the difference of the two half-cells (16) and (17), one containing the strong base and the other the weak base. Table IV contains the hydroxyl-ion concentrations of the weak hydroxides in sodium, potassium and lithium-chloride solutions, calculated by Equation 20.

TABLE IV

HYDROXYL-ION CONCENTRATIONS OF WEAK HYDROXIDES IN SALT SOLUTION

A. Sodium Chloride

Salt concn.	0.5030 *M* NH_3	0.1989 *M* CH_3NH_2	0.1987 *M* $(CH_3)_2NH$	0.1891 *M* $(CH_3)_3N$
0.02	......	0.01098	0.01178	......
.05	......	.01191	.01273	......
.1	0.004382	.01293	.01403	0.004502
.2	.004683	.01431	.01620	.005080
.5	.005159	.01665	.01879	.006268
1.0	.005621	.01857	.02204	.007296
1.5	.005776	.01984	.02410	.008136
2.0	.005821	.02103	.02585	.008625
3.0	.005844	.02212	.02827	.010000

B. Potassium Chloride

Salt concn.	0.5030 *M* NH_3	0.1910 *M* CH_3NH_2
0.02	......	0.01085
.05	......	.01196
.1	0.004382	.01298
.2	.004537	.01381
.5	.004773	.01534
1.0	.004943	.01665
1.5	.005060	.01745
2.0	.005139	.01807
3.0	.005139	.01893

C. Lithium Chloride

Salt concn.	0.5030 *M* NH_3	0.1910 *M* CH_3NH_2
0.02	......	0.01124
.05	......	.01293
.1	0.004398	.01448
.2	.004754	.01564
.5	.005300	.01843
1.0	.006052	.02161
1.5	.006964	.02526
2.0	.007183	.02741
3.0	.008104	.03304

$\gamma_B\gamma_{OH}/\gamma_{BOH}$ or γ_R may be computed from m_{OH} by

$$K = \frac{\gamma_B\gamma_{OH}}{\gamma_{BOH}} \frac{m^2_{OH}}{m_1 - m_{OH}} \tag{21}$$

employing the law of mass action in a manner identical with that previously used in the case of acetic acid (compare Equation 8).

In the case of ammonia,[10] the dissociation constant was taken to be 1.85×10^{-5}. In the case of mono- and dimethylamines, it was assumed that in 0.02 *M* sodium-chloride solution, the value of $\sqrt{\gamma_B\gamma_{OH}/\gamma_{BOH}}$ or $\sqrt{\gamma_R}$ was equal to the activity coefficient of sodium hydroxide in this concentration of sodium chloride, that is, 0.830. On this assumption a value of K was calculated. In the case of trimethylamine, as the variation of $\sqrt{\gamma_R}$ with the sodium-chloride concentration was very similar to the corresponding variation of $\sqrt{\gamma_R}$ in the case of dimethylamine, we assumed that the values of $\sqrt{\gamma_R}$ for these two bases are identical at a sodium chlor-

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[10] Lundén, *J. chim. phys.*, **5**, 574 (1907); Noyes, Kato and Sosman, *Z. physik. Chem.*, **73**, 1 (1910).

ide concentration of 0.1 M, that is, 0.709. It is to be realized that the choice of a reference point for the calculation of K is a somewhat arbitrary matter, and therefore the values of K used in the calculation of $\sqrt{\gamma_R}$ are to be considered tentative and subject to revision should more accurate values be forthcoming.

Table V contains the values of K calculated in the above manner, compared with the values obtained by Bredig from conductivity measurements.[11]

TABLE V

DISSOCIATION CONSTANTS OF AMINES AT 25°

Base	Present authors	Bredig
Monomethylamine	4.42×10^{-4}	5.0×10^{-4}
Dimethylamine	5.12×10^{-4}	7.4×10^{-4}
Trimethylamine	5.27×10^{-5}	7.4×10^{-5}

Using these values of K, $\sqrt{\gamma_R}$ was calculated and these values are given in Table VI.

TABLE VI

ACTIVITY COEFFICIENTS OF WEAK HYDROXIDES IN SALT SOLUTION

A. Sodium Chloride

Salt concn.	0.5030 M NH_3	0.1989 M CH_3NH_2	0.1987 M $(CH_3)_2NH$	0.1891 M $(CH_3)_3N$
0.02	...	0.830	0.830	...
.05	...	.763	.767	...
.1	0.693	.701	.693	0.693
.2	.648	.631	.597	.613
.5	.588	.539	.511	.495
1.0	.540	.481	.432	.424
1.5	.525	.448	.394	.380
2.0	.521	.422	.364	.358
3.0	.519	.400	.330	.307

B. Potassium Chloride

Salt concn.	0.5030 M NH_3	0.1910 M CH_3NH_2
0.02	...	0.822
.05	...	.744
.1	0.693	.683
.2	.669	.641
.5	.636	.574
1.0	.614	.527
1.5	.600	.502
2.0	.591	.484
3.0	.591	.461

C. Lithium Chloride

Salt concn.	0.5030 M NH_3	0.1910 M CH_3NH_2
0.02	...	0.793
.05	...	.686
.1	0.691	.610
.2	.639	.563
.5	.573	.474
1.0	.501	.417
1.5	.435	.339
2.0	.422	.310
3.0	.373	.253

Discussion of the Properties of the Hydroxide–Salt Systems

In Fig. 5 the activity coefficients of four bases in sodium chloride solutions are plotted against $\mu^{1/2}$. It appears that as substitution of the am-

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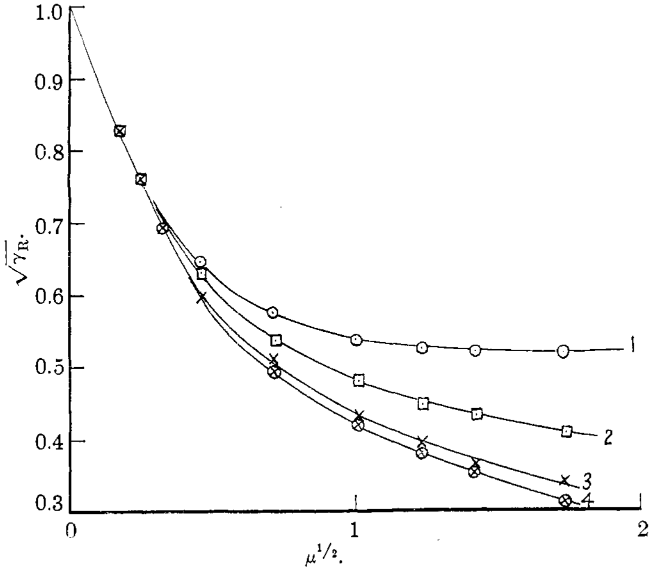
[11] Bredig, *Z. physik. Chem.*, 13, 191 (1894).

monium ion by the methyl groups occurs, lower values for the activity coefficients are obtained. This is in accord with our results on acetic acid and the chloro-substituted acetic acids. The results are of the expected order of magnitude but no great accuracy can be claimed, particularly in the dilute solutions where errors due to small liquid junction potentials are possible.

That the order of the salt effects corresponds to that of acetic acid in the simple halide solutions is shown by the plots in Fig. 6.



1, NH_4OH; 2, CH_3NH_3OH; 3, $(CH_3)_2NH_2OH$; 4, $(CH_3)_3NHOH$.

Fig. 5.—The ionic activity coefficients of ammonia and amines in sodium chloride solutions.

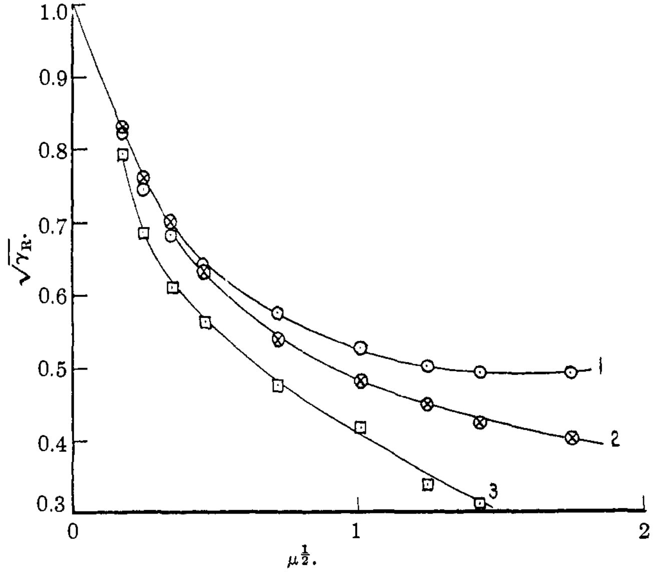
The activity coefficients of tetramethylammonium hydroxide cannot be determined by this method but it is of very great interest to note that our measurements show that, in the presence of sodium chloride, this hydroxide is more highly dissociated than sodium hydroxide. The ratios of hydroxyl-ion molalities, $m_{OH(T)}/m_{OH(NaOH)}$, at the various salt concentrations computed by Equation 20, are given in Table VII.

TABLE VII

HYDROXYL-ION CONCENTRATION RATIOS OF TETRAMETHYLAMMONIUM HYDROXIDE TO SODIUM HYDROXIDE IN SODIUM-CHLORIDE SOLUTIONS

Salt concn.	0.1	0.2	0.5	1.0	1.5	2.0	3.0
$m_{OH(T)}/m_{OH(NaOH)}$	0.988	1.012	1.052	1.048	1.060	1.052	1.048

Since the stoichiometrical concentrations of the hydroxides were both 0.01 *M*, the liquid junction potential must indeed be small at 0.1 *M* salt concentration, and certainly negligible at high salt concentrations. Thus, at 0.5 *M* sodium chloride and higher the amine is between 4.8 and 6% more strongly dissociated than the sodium hydroxide. At 0.1 *M* salt, it appears to be somewhat less dissociated. Since the amine possesses a high dissociation constant, the addition of salt would increase its dissociation somewhat due to the decrease in γ_R. If γ_R decreases more rapidly than $\gamma_{Na}\gamma_{OH}$ upon salt addition, and if sodium hydroxide is not completely dissociated, we may account for this observation. That sodium and lithium hydroxides are probably not dissociated to the extent of the halides of the alkali metals has already been pointed out by Harned.[12]



1, KCl; 2, NaCl; 3, LiCl.

Fig. 6.—The ionic activity coefficient of methylamine in potassium, sodium and lithium chloride solutions.

We desire to take this opportunity of expressing our thanks to the Commonwealth Fund for the grant of a Fellowship, which has made this joint contribution possible.

General Considerations and Summary

1. A method has been discussed whereby the activity coefficients and dissociation of weak acids and bases in salt solutions may be computed from the electromotive forces of cells without liquid junctions containing easily reproducible electrodes.
2. This method has been employed to obtain the activity coefficient of

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[12] Harned, *Z. physik. Chem.*, 117, 1 (1925).

acetic acid in potassium, sodium, lithium- and barium-chloride solutions. In this case, the cells employed were

$$H_2 \mid HX(m_0),\ MX(m_3) \mid AgX \mid Ag$$
$$H_2 \mid HAc(m_1),\ MX(m_2) \mid AgX \mid Ag$$

Measurements of the second type have been made.

3. A modified method employing cells with negligible liquid junction potentials was employed for the determination of the activity coefficients of the bases. In this case, the cells measured were

$$H_2 \mid MOH(m_0),\ MX(m_2) \mid MX(m_2) \mid AgX \mid Ag$$
$$H_2 \mid BOH(m_1),\ MX(m_2) \mid MX(m_2) \mid AgX \mid Ag$$

where MOH is a strong and BOH a weak hydroxide.

4. The dissociation constant of a weak electrolyte in a given solvent or in salt solutions in this solvent, is given by $K = (C_C C_A/C_{CA})(\gamma_C \gamma_A/\gamma_{CA}) = K_c\gamma^2$. When the electrolyte is at infinite dilution so that γ^2 equals unity, K equals K_c. Thus, K is a constant which measures the dissociation of the weak electrolyte in the pure solvent. γ^2 is a measure of the effect of the presence of the attractive and repulsive forces of the electrical field produced by the addition of the salts on the electrical potentials of the ions of the weak electrolyte. K_c is an absolute measure of the dissociation of the weak electrolyte under varying conditions of salt concentration. Although the change of K_c upon salt addition depends upon the variation of γ^2, its absolute value does not. This is shown clearly by the behavior of the methyl derivatives of ammonia. Thus, K_c increases in the order ammonia, tri-, mono-, dimethylamine, whereas, at a given salt concentration, γ^2 increases in the order tri-, di-, monomethylamine, ammonia.

5. We may generalize our results of the specific relative salt actions by the following brief rules. *A*. The ionic activity coefficients of acetic, mono- and dichloro-acetic acids are less in the solution of a given strength of that salt which possesses the higher activity coefficient in pure water. *B*. The same is true for ammonia and monomethylamine. It seems highly probable that it would also be the case for di- and trimethylamine. This order agrees with that found for the ionic activity coefficients of water, and is the reverse of the order found for the activity coefficients of halide acids in salt solutions.

6. Our results show that a 0.01 *M* solution of tetramethylammonium hydroxide containing 0.1 *M* sodium chloride has a slightly lower hydroxyl-ion concentration than that of an identical salt solution containing sodium hydroxide. At higher salt concentrations, however, sodium hydroxide is about 6% less dissociated.

7. The effect of the change in the solvent caused by large quantities of the undissociated molecules has been discussed, and approximately computed.

8. The method here employed, as well as the results, should prove very useful for studying salt effects in organic and biological media. It is far more sound from a kinetic or a thermodynamic point of view than the usual method which employs single electrodes and ordinary salt bridges.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

THE FORMATION OF OZONE BY CATHODE RAYS

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The purpose of this investigation was to secure quantitative data on a supposedly simple reaction, the production of ozone from oxygen under the influence of high velocity electrons, which could be used in the interpretation of more complicated reactions. It has been found, however, due to the secondary decomposition of the ozone formed, that an analysis of the results is far from simple. The cathode ray tube recently described by Coolidge[1] was used, which allows one to obtain an intense source of very high velocity electrons. The various controllable variables, such as duration of exposure, average velocity and number of electrons, size and shape of the reaction chamber, were studied separately.

Not much work has been reported in the literature on the chemical effects of high velocity electrons in gaseous systems. Krüger and Moeller[2] have studied the formation of ozone with very low intensity, low velocity electrons and their work has been subsequently very materially amplified by Krüger and Utesch.[3] The latter worked with a hot cathode tube as a source of electrons and used an aluminum foil, 0.011 to 0.005 mm. thick, supported on a brass plate containing 65 holes 0.8 mm. in diameter as a window through which they obtained electrons from their tube. The source of voltage was a 500-cycle, high voltage transformer with a single kenotron rectifier giving peak voltages up to 60 kv. The largest current used in the tube was 0.4 milliampere. With a tube current of 3×10^{-4} ampere, 4.5×10^{-5} ampere was incident on the aluminum foil and of this 2.0×10^{-6} ampere passed through into the reaction chamber. The maximum amount of energy entering the reaction vessel in any experiment was estimated to be 0.12 watt. In one set of experiments a vessel containing two condenser plates placed 26 mm. apart was fastened to the window end of the tube. The plates were 4×2.5 cm. The diameter of the cathode ray beam at the window was 19 mm. and the authors be-

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[1] (a) Coolidge, *J. Franklin Inst.*, December, 1926, p. 693; (b) *Am. J. Röntgenol. Radium Therapy*, **19**, 313 (1928).

[2] Krüger and Moeller, *Physik. Z.*, **13**, 1040 (1912).

[3] Krüger and Utesch, *Ann. Physik*, **78**, 113 (1925).