It will be seen from these results, as was found by Ellis in the case of hydrochloric acid, that:

(1) The activity coefficient at first decreases with increasing concentration, but passes through a minimum at a concentration of about 0.5 molal, and then increases rapidly.

(2) Up to concentrations of 0.5 molal the activity coefficient has a much smaller value than the conductance-viscosity ratio (thus 7% smaller at 0.1 molal, and 11% smaller at 0.2 molal), thus again showing that this ratio, even at these moderate concentrations, is not even an approximate measure of the effective ionization of largely ionized substances.

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[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 123.]

THE ACTIVITIES OF THE IONS IN SOLUTIONS OF MIXED ELECTROLYTES.

BY MING CHOW.

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1. Introduction.

This investigation consisted in measurements of the electromotive force of voltaic cells of the type

$$H_2 \text{ (1 atm.)}, HCl\ (c_1) + KCl\ (c_2), Hg_2Cl_2 + Hg,$$

in which the separate concentrations c_1 and c_2 were varied, but their sum $c_1 + c_2$ was kept constant, namely, in these experiments, at 0.1 *N*. The purpose of the research was to determine directly the value of the product of the activities of the hydrogen ion and chloride ion, and to draw conclusions as to the separate activities of these two ions in the mixture.[1]

A similar research with the same object in view has already been published by Loomis, Essex, and Meacham;[2] but as it was found possible in the present investigation to secure more constant and reproducible electromotive forces, and as the data lead to conclusions somewhat different from those drawn by these authors, it seems desirable to present here the results of my measurements. Reference should also be made to the work of Harned,[3] who measured the same type of cell, but kept the concentration of the hydrochloric acid, not that of the mixed electrolytes, constant.

This research was carried out at the suggestion of Prof. A. A. Noyes,

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[1] In regard to the concept of activity and activity coefficients here employed, see the first section of the preceding article.

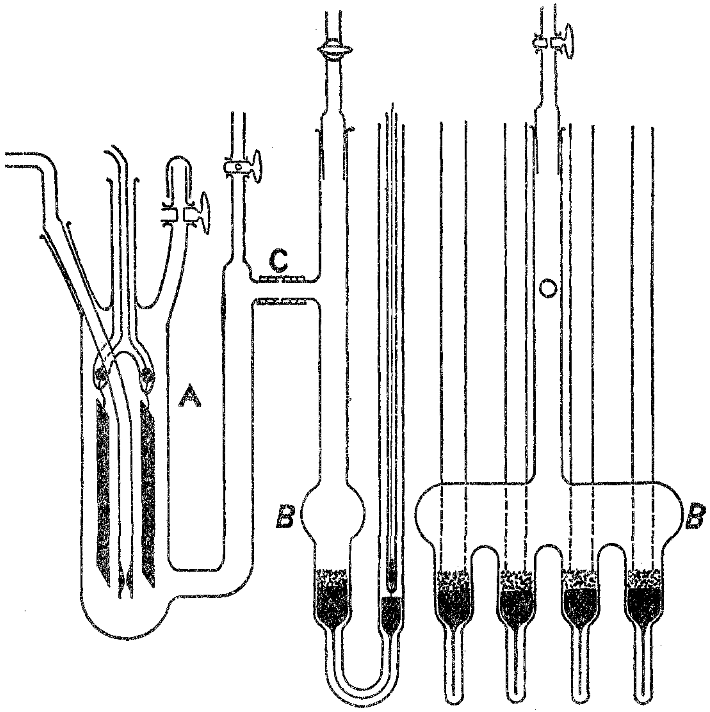
[2] THIS JOURNAL, 39, 1133 (1917).

[3] *Ibid.*, 38, 1988 (1916).

with the aid of a grant made to him by the Carnegie Institution of Washington. I wish to express my indebtedness to him also for his assistance in the preparation of this article for publication. I wish also to thank Dr. Duncan A. MacInnes for his interest and suggestions throughout the progress of the work.

2. Apparatus and Experimental Procedure.

The form of calomel half-cell used is shown in the figure, in which 2 cross-sections of the half-cell at right angles to each other are represented. It will be seen that these half-cells had 4 compartments containing 4 separate calomel electrodes. The hydrogen half-cell used differs from that described by Noyes and Ellis[1] only in the respect that the inlet tube for the hydrogen was set in a separate tubulus with a ground joint, so that it could be removed for cleaning.



Before introducing the solutions into the calomel half-cell, they were saturated with calomel by agitating the mixture of mercury, calomel, and the solution in a sealed pipet at room temperature in a shaking machine for 5 to 10 hours. In most cases the air was boiled out under reduced pressure, and the solutions were transferred to the half-cell without coming into contact with the air. This precaution of removing the

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[1] This Journal, 39, 2534 (1917).

air seemed, however, to make little, if any, difference; but the agitation of the calomel with the solution is essential.

The method of making the observations and the corrections applied were the same as those described by Ellis.[1] Two standard cells were employed which had been recently certified by the National Bureau of Standards.

3. Preparation of the Substances and Solutions.

The mercury was purified by blowing air through a mass of the liquid covered with dil. nitric acid, and subsequently distilling it in a current of air at reduced pressure.

The calomel was made electrolytically as described by Ellis.

The hydrogen was made by the electrolysis of sodium hydroxide solution. It was purified by passing it through a wash bottle containing water kept slightly acid with hydrochloric acid with the aid of an indicator. For use in the cells a 0.1 N hydrochloric acid solution was made by diluting by weight with freshly distilled conductivity water the constant boiling acid, prepared as decribed by Hulett and Bonner.[2] The accuracy of its acid content as given by Hulett has been repeatedly checked in this laboratory by gravimetric determinations of the chlorine as silver chloride.

The potassium chloride used was an imported preparation, which had been dried for several days at 100°. A solution of this containing 0.1 mol. of potassium chloride per 1000 g. of water was made up. To determine how nearly neutral this solution was, its hydrogen concentration was determined by placing in it a hydrogen electrode and combining it with a calomel half-cell containing potassium chloride at the same concentration. The various solutions prepared were thus found to have hydrogen ion concentrations lying between 1 and 5×10^{-7}. The larger of these quantities would produce an error of only 0.5% in the acid concentration in the most dilute solution investigated (0.0001 molal). Fused potassium chloride, on the other hand, gave a solution distinctly alkaline, with an hydroxide ion concentration of about 10^{-6}.

The mixtures of hydrochloric acid and potassium chloride were prepared by weighing out definite quantities of the two 0.1 molal solutions. This yielded mixtures always containing just 0.1 mol of chloride per 1000 g. of water. The contents in hydrochloric acid and potassium chloride were calculated from the weights taken.

4. The Experimental Results.

Table I contains the results of the experiments. The first and second columns give the concentrations, in millimols per 1000 g. of water, of the hydrochloric acid and potassium chloride, respectively. The third col-

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[1] This Journal, 38, 748–749 (1916).

[2] *Ibid.*, 31, 390 (1909).

umn contains the corresponding values of the electromotive forces of the cells at 25°. These values are the means of the observations for the 4 calomel electrodes with the 2 hydrogen electrodes (which always checked each other within about 0.01 millivolt). The fourth column contains the average deviations of these values from the mean. The fifth column gives the reduced barometric pressure. The sixth column gives the observed values reduced to a hydrogen pressure of one atmosphere. These values were corrected in the usual way, taking into account the vapor pressure of the solutions and variation of the barometric pressure from one atmosphere, as described in detail by Ellis.

TABLE I.

Electromotive Force of the Cells at 25° in Millivolts.

Millimols per 1000 g. water.		Electromotive force observed.	Average deviation.	Barometric pressure.	Electromotive force corrected.
HCl.	KCl.				
100.0	0.00	..	..	...	399.04[a]
31.71	68.29	428.35	0.04	76.04	428.70
10.00	90.00	458.07	0.06	76.04	458.52
3.065	96.93	488.55	0.05	76.04	488.90
1.055	98.94	515.52	0.01	76.01	515.89
1.000	99.00	516.98	0.03	76.82	517.21
0.339	99.66	544.68	0.08	76.02	545.06
0.316	99.68	546.50	0.03	75.65	546.96
0.304	99.70	547.72	0.08	76.22	548.06
0.223	99.78	555.45	0.11	76.02	555.83
0.100	99.90	574.48	0.08	76.02	576.43

[a] This value is that found by Ellis (*loc. cit.*, p. 754). It agrees substantially with the values (0.3990, 0.3991, 0.3988) found by others as summarized by Lewis, Brighton and Sebastian (THIS JOURNAL, **39**, 2257 (1917)). In their summary, these authors made a slight mistake in quoting Ellis' value as 0.3988, instead of 0.3990.

5. Discussion of the Activity Coefficients.

By subtracting the first of the electromotive-force values given in the last column of Table I from the succeeding values there is obtained the electromotive force of cells of the following type:

H_2 (1 atm.), HCl (c) + KCl (0.1-c), Hg + Hg_2Cl_2, HCl (0.1) H_2 (1 atm.)

The free-energy decreases obtained by multiplying these differences by 96500 are those attending the transfer of 1 HCl from the 0.1 molal hydrogen chloride solution to the mixture in which the hydrogen chloride concentration is c. From these free energies we may calculate the ratio of the product of the activity coefficients (α_H and α_{Cl}) of the hydrogen ion and chloride ion constituents in the mixture to the same product in the 0.1 molal solution. Namely, when one faraday (F coulombs) of electricity passes through the cell from left to right, there is a transfer of one mol of hydrogen ion from a solution in which its activity (or effective concentration) is 0.1 $(\alpha_H)_{0.1}$ to one in which its activity is $c\alpha_H$, and a transfer of one mol of chloride ion from a solution in which its activity is 0.1 $(\alpha_{Cl})_{0.1}$ to one in which its activity is 0.1 (α_{Cl}); whence follows the following expression for the free-energy decrease $(-\Delta F)$:

$$-\Delta F = (\mathrm{E} - \mathrm{E}_{0.1})\mathrm{F} = RT \log \frac{0.1\ (\alpha_H)_{0.1}\ (\alpha_{Cl})_{0.1}}{c\alpha_H \alpha_{Cl}}.$$

The following table gives the so-calculated ratios of the products of the activity coefficients:

TABLE II.

Activity Coefficients of Hydrochloric Acid in the Mixture.

Millimols HCl per 1000 g. of water.	$\frac{\alpha_H \alpha_{Cl}}{(\alpha_H)_{0.1}(\alpha_{Cl})_{0.1}}$.
100.00	1.000
31.71	0.994
10.00	0.987
3.065	0.988
1.055	1.003
1.000	1.005
0.339	1.003
0.316	1.005
0.304	0.995
0.223	1.003
0.100	1.003

These data show that the activity coefficient of the hydrochloric acid has substantially (within 1%) the same value in all the mixtures. Thus the deviations from unity show no steady progression, and the maximum deviation of 1.3% corresponds to a variation in the electromotive force of 0.65 millivolt. In other words, the product of the activities of the ions is proportional to the product of the concentrations of hydrogen ion and chloride ion constituents, even when the concentration of the acid is varied from 0.0001 to 0.1 *N* provided, as in this case the total concentration of electrolyte in the solution remains constant.

If we make the assumption rendered probable by the considerations recently presented by MacInnes,[1] that the chloride ion has the same activity in solutions in which the chloride concentration is the same, whatever may be the cation associated with it, we reach the conclusion that the hydrogen ion has an activity proportional to its concentration. In other words, that it behaves as a perfect solute, so long as the total ion concentration in the solution remains unchanged. Since the hydrogen ion might be expected to be especially sensitive to disturbing influences, this result substantiates the principle that the activity coefficient a/c of the univalent ions of largely ionized substances is in general a function of the total salt or total ion concentration, and not of its own concentration.

If, on the other hand, we do not make the assumption that the chloride ion has the same activity in the different mixtures, we must accept the

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[1] THIS JOURNAL, 41, 1086 (1919).

alternative that it has a variable activity which is just compensated by an opposite variation in the activity coefficient of the hydrogen ion. As this alternative is improbable, the result lends support to the assumption itself, namely, to the principle that the activity of the chloride ion in solutions of different largely ionized univalent chlorides or of mixtures of them is determined by its own concentrations and is independent of the cations associated with it.

Finally, reference must be made to the results of Loomis, Essex and Meacham,[1] who measured the electromotive force of the same type of cells also with potassium chloride and hydrochloride acid at a total concentration of 0.1 *N*. Their data, unlike those above presented, show with increase in the proportion of potassium chloride, a progressively increasing deviation of the observed electromotive forces from those calculated under the assumption that the activity coefficient of the hydrochloric acid remains constant. Moreover, the variation is in the direction that corresponds to greater activity of the chloride ion in the acid than in the salt solution, which accords with the results of Noyes[2] on the relative effects of hydrochloric acid and the alkali-element chlorides on the solubility of thallous and plumbous chlorides. The deviation amounts, however, to only 1.28 millivolts even in the mixture most dilute in hydrochloric acid (that 0.01 *N* in hydrochloric acid and 0.09 *N* in potassium chloride); while the check measurements with the same mixtures often differed by 0.5 millivolt.[3] This deviation of 1.28 millivolt, if not due to experimental error, corresponds to a variation of 5% in the product of the activity coefficients. Inasmuch as the calomel electrode used by these investigators showed accidental variations 10 times as great as those used in the research here presented, it seems justifiable to give greater weight to the data of this article and to regard as most probable the conclusion drawn from them as to the constancy of the activity coefficients in the mixture.

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[1] THIS JOURNAL, 39, 1133 (1917).

[2] *Z. phys. Chem.*, 9, 609, 623 (1892).

[3] It may be mentioned that the authors referred their concentrations to one liter of solution, while in the present research they are referred to 1000 g. of water; but calculation shows that this affects the ratio of the concentrations in the two limiting cases by only 0.1%.