[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 164]

# THE ACTIVITIES OF STRONG ELECTROLYTES. I. THE ACTIVITY OF HYDROCHLORIC ACID DERIVED FROM THE ELECTROMOTIVE FORCE OF HYDROGEN–SILVER-CHLORIDE CELLS[1]

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## Introduction

As a preliminary to a study of liquid-junction potentials and of the effect of non-electrolytes on the activities of ions, a series of measurements has been made of the electromotive force of hydrogen–hydrochloric-acid–silver-chloride cells, and the mean activity coefficients of the ions have been calculated from them and earlier measurements on the same type of cells. These values differ markedly from those computed by Lewis and Randall.[2]

The electromotive force of the cell, $Pt,H_2 \mid HCl,HgCl \mid Hg$, has been measured by Ellis[3] and by Linhart.[4] These measurements do not extend to dilute enough solutions to permit the calculation of the activities from them alone, and the discrepancy between different comparisons of the calomel and silver chloride electrodes[5] makes their correlation with the latter uncertain. They have not been used in this paper.

Noyes and Ellis[6] and Linhart[7] have measured the electromotive force of the cell, $Pt,H_2 \mid HCl,AgCl \mid Ag$, in dilute solutions. These measurements have now been extended through the concentration range 0.01–1.5 *M*.

## I. Experimental Procedure

Conductivity water from the still in this Laboratory was used throughout. The solutions of hydrochloric acid were prepared by dilution of a constant-boiling mixture, the late middle fraction of the distillation from C. P. hydrochloric acid diluted with about two parts of water. The acid content of the constant-boiling acid was determined by a chloride analysis, and always checked the value given by Hulett and Bonner[8] within 0.1%. All weights were reduced to vacuum standard.

The hydrogen was prepared from a cell containing 25% sulfuric acid as electrolyte, with zinc amalgam, prepared with C. P. zinc, as one electrode and a large sheet of platinized platinum as the other. This provides a very convenient source of small amounts

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[1] Revised copy received December 11, 1924.

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[2] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., **1923**, p. 336.

[3] Ellis, THIS JOURNAL, **38**, 737 (1916).

[4] Linhart, *ibid.*, **39**, 2601 (1917).

[5] Ref. 2, p. 407, Note 5.

[6] Noyes and Ellis, *ibid.*, **39**, 2532 (1917).

[7] Linhart, *ibid.*, **41**, 1175 (1919).

[8] Hulett and Bonner, *ibid.*, **31**, 390 (1909).

of hydrogen. The gas was passed over copper reduced from the oxide and heated to about 300°, then through water and finally through a wash bottle at 25° which contained the same solution as that in the electrode vessels.

The hydrogen electrodes were made of platinized platinum sheet about 1 × 0.5 cm. The silver chloride electrodes were of platinum gauze of the same size, plated with silver and then chloridized electrolytically in the solution in which they were to be used, according to the directions of MacInnes and Beattie.[9] The electrodes were used within one to three days after preparation. The agreement between two solutions of approximately the same concentration, and between these results and those of Linhart,[7] who used precipitated silver chloride, gives good justification for the use of electrolytic silver chloride prepared in this way.

The work was planned as a preliminary to a study of solutions containing sugar or other non-electrolytes, in which it is necessary to attain equilibrium rather rapidly. The hydrogen cell, therefore, is a modification of the Clark rocking electrode,[10] simplified somewhat by the absence of a liquid junction, and designed for use in a water thermostat. The design of the apparatus, which was made of Pyrex glass, is given in Fig. 1. It has the disadvantage that the solution comes in contact with two rubber stoppers and the rubber tube connecting the electrode vessels. The rubber, however, was boiled with sodium hydroxide solution, then with hydrochloric acid, and finally with water, and there was no indication of any difficulty from this source, unless this is the explanation of the slight divergence of my values from that of Linhart in the 0.01 *M* solution. The rocking device is so designed that the joint between the rubber tubing and the hydrogen electrode vessel is nearly in the axis of rotation, and the rubber stopper in this vessel is directly below that axis. The vessels were immersed in a water thermostat at 25 ± 0.02°.

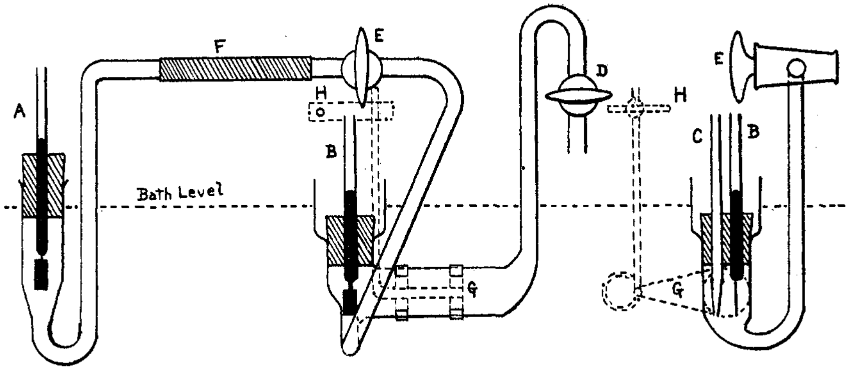

Fig. 1.—A, Silver chloride electrode; B, Hydrogen electrode; C, Hydrogen inlet; D, Stopcock at outlet; E, Stopcock to separate half-cells; F, Flexible rubber connection; G, Clamp; H, Axis of rotation. Scale, 1:3.

The potentiometer was a Leeds and Northrup, Type K instrument. The standard Weston cell was checked during the course of the investigation against two others newly calibrated by the Bureau of Standards.

Six silver chloride electrodes were prepared together, all of which, generally, agreed in electromotive force within 0.02–0.03 mv. The average

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[9] MacInnes and Beattie, This Journal, **42**, 1132 (1920).

[10] Clark, "The Determination of Hydrogen Ions," Williams and Wilkins, **1923**, pp. 181–185.

value was determined, discarding any electrode which differed more than 0.03 millivolt from the average of the others. The electrode nearest this value was used, and correction was made to the average when necessary.

After the electrodes and electrode vessels were rinsed, the vessels, including the glass hydrogen inlet, were completely filled with the solution. When hydrogen had been evolved long enough to displace any air from the pre-saturator and tube, the hydrogen train was connected. With the hydrogen vessel rocked about two-thirds forward, the solution was displaced with hydrogen until gas escaped from Stopcock D. The apparatus was rocked for five minutes. With the vessel rocked completely back, hydrogen was bubbled in long enough to displace all that in the apparatus; the apparatus was rocked for another five minutes. This was done five times before any measurement was made. Before each measurement

TABLE I

ELECTROMOTIVE FORCE IN MILLIVOLTS OF CELLS Pt, $H_2$ | HCl, AgCl | Ag

| Molality $m$ | $E$ measured | Mean dev. from av. | $E_0'$ $E + 118.3 \log m$ | Difference from curve |
|---|---|---|---|---|
| 0.01002 | 463.76 | 0.01 | 227.30 | −0.13 |
| .01010 | 463.31 | .08 | 227.21 | − .27 |
| .01031 | 462.28 | .04 (2) | 227.23 | − .27 |
| .04986 | 385.82 | .03 | 231.77 | − .03 |
| .05005 | 385.68 | .04 | 231.82 | + .02 |
| .09642 | 353.93 | .04 | 233.76 | − .15 |
| .09834 | 353.16 | .01 (2) | 234.00 | + .02 |
| .2030 | 317.74 | .03 | 235.82 | .00 |
| .3063 | 293.32 | .03 | 236.53 | .00 |
| .3981 | 284.07 | .03 | 236.75 | .00 |
| .5009 | 271.97 | .07 | 236.44 | .00 |
| .5013 | 271.95 | .02 | 236.47 | − .02 |
| .6367 | 259.02 | .06 | 235.83 | .00 |
| .9377 | 236.96 | .02 | 233.65 | + .04 |
| 1.0008 | 232.90 | .05 | 232.94 | − .04 |
| 1.5346 | 205.34 | .08 | 227.34 | .00 |
| | | LINHART | | |
| 0.000136 | 680.5 | | 223.1 | − .1 |
| .000242 | 651.4 | | 223.6 | + .1 |
| .000483 | 616.1 | | 223.8 | .0 |
| .001000 | 579.1 | | 224.2 | − .2 |
| .004826 | 500.2 | | 226.2 | .0 |
| .00965 | 465.8 | | 227.4 | .0 |
| .04836 | 387.4 | | 231.7 | .0 |
| | | NOYES AND ELLIS | | |
| .000999 | 578.93 | | 223.98 | − .36 |
| .003378 | 516.96 | | 224.60 | −1.07 |
| .00948 | 466.66 | | 227.32 | +0.08 |
| .03324 | 405.45 | | 230.56 | .00 |
| .09534 | 354.53 | | 233.78 | − .10 |
| .33314 | 293.48 | | 237.02 | + .44 |

Stopcock D was opened momentarily to equalize the pressure. The readings were continued, after each addition of hydrogen and rocking, until three successive ones agreed within 0.02 mv. Generally, the last two were in exact agreement. This required from three to seven readings. The final value never differed from the first reading as much as 0.1 mv.

The measurement was then repeated with the same silver chloride electrode but another hydrogen electrode. The next day similar measurements were made with another silver chloride electrode, with one of the same hydrogen electrodes, and with a third hydrogen electrode, so that four measurements were made on each solution. Table I contains the results of these experiments, together with those of Linhart and of Noyes and Ellis.

The first column gives the concentration; the second, the measured electromotive force in millivolts, corrected in all cases to one atmosphere partial pressure of hydrogen. The third column gives the mean deviation of the four determinations from their average; in the two cases where (2) follows this column, only two determinations were made.

## Calculation of Activity Coefficients from Electromotive-Force Measurements

For the calculation of activity coefficients from electromotive-force measurements, Lewis and Randall define the quantity $E_0'$ by the equations: $E_0' = E + 118.3 \log m = E_0 - 118.3 \log \gamma$, where $E$ is the measured electromotive force, and $E_0$ the value of $E_0'$ at zero concentration, all in millivolts; $\gamma$ is the mean activity coefficient of the ions. The fourth column of Table I contains the values of $E_0'$ calculated from the experiments.

The values of $E_0'$ calculated from the above measurements were plotted against $\sqrt{m}$ on a large scale, and a smooth curve drawn through them. To extrapolate to zero concentration, the curve was made asymptotic to a straight line with slope $59.15\sqrt{m}$.[11] The deviations of the experimental points from the smooth curve are given in the fifth column of Table I. Except for a few points of Noyes and Ellis these deviations are very small. Linhart's values and mine agree exactly at 0.05 $M$. At 0.01 $M$, where there is a discrepancy of 0.2 mv., his value is taken as correct (although he made but one measurement compared to my three at this point) because my apparatus was not designed for work on very dilute solutions.

The agreement of Linhart's results in dilute solutions is remarkable and gives strong confirmation of the equation of Debye and Hückel. It should be noted that Linhart himself, followed by Lewis and Randall, discarded his measurement on the most dilute solution because it did not fit his method of extrapolation.

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[11] This corresponds to the asymptotic limiting law, $\log \gamma = 0.5\sqrt{m}$, of the theory of Debye and Hückel. A discussion and justification of this equation is given in the second paper of this series.

The values of the mean activity coefficients of the ions of hydrochloric acid calculated from the above curve at rounded concentrations ($\gamma_{25}$, e.m.f.) are given in the fifth column of Table II. The values of Lewis and Randall ($\gamma_{25}$, L and R) are given in the second column. The difference between the two series is due to the different values for $E_0'$ through the minimum, where their series is based on a few not very accurate measurements, and at zero concentration, where they use 223.4 and I find 222.6 mv. The two differences tend to compensate in the more concentrated solutions.

TABLE II

MEAN ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID

| Molality | $\gamma_{25}$ L and R | $\gamma_0$ Freezing point R and V | $\gamma_0$ Freezing point S | $\gamma_{25}$ E.m.f. |
|---|---|---|---|---|
| 0.001 | 0.984 | 0.973 | 0.966 | 0.966 |
| .002 | .971 | .962 | .953 | .954 |
| .005 | .947 | .940 | .930 | .932 |
| .01 | .924 | .916 | .907 | .910 |
| .02 | .894 | .884 | .879 | .881 |
| .05 | .860 | .840 | .836 | .836 |
| .1 | .814 | .809 | .804 | .801 |
| .2 | .783 | (.782) | | .774 |
| .3 | .768 | | | .763 |
| .4 | .763 | | | .760 |
| .5 | .762 | | | .763 |
| .6 | .770 | | | .770 |
| .75 | .788 | | | .783 |
| 1.0 | .823 | | | .817 |
| 1.5 | | | | .905 |

## Calculation of Activity Coefficients from Freezing-Point Measurements

Since this paper was originally submitted for publication, Randall and Vanselow[12] have published a series of very accurate freezing-point measurements on dil. hydrochloric acid and have calculated activity coefficients from them. From these coefficients and the electromotive force measurements in the more concentrated solutions, they find a value of 223.0 mv. for $E_0$ of the hydrogen–silver-chloride cell. From their data it is possible to compute $E_0'$ at any concentration.

The deviations in millivolts of Linhart's measurements from the curve of Randall and Vanselow are, in order of increasing concentrations, —0.4, —0.1, —0.2, —0.25, +0.1, 0.0, —0.15. In Fig. 2 are given the experimentally determined values of $E_0'$ up to 0.05 $M$ plotted against $\sqrt{m}$. The upper full line is the rectilinear asymptote with slope 59.15 $\sqrt{m}$, the lower full line is the curve determined from the electromotive-force measurements, and the dotted line is the curve calculated from Randall and Vanselow's

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[12] Randall and Vanselow, THIS JOURNAL, **46,** 2418 (1924).

data. It is obvious that the full line fits Linhart's experimental data much better than the dotted curve. It is not impossible, however, that the deviations are within the experimental error of his observations.

It is certain that the deviations are within the experimental error of the freezing-point determinations. Randall and Vanselow represent the values of $j$ (one minus the ratio of the molal freezing-point depression to the molal depression at zero concentration) up to 0.01 $M$ by the equation,

$$j = 0.316\, m^{0.513} \tag{1}$$

They also show that the $j$ values can be satisfactorily represented through the same range by the equation, $j = 0.302\, m^{0.5}$, in which $m$ has the exponent 0.5 required by the simple Debye-Hückel equation, but in which the coefficient is smaller than the value required by their theory. It seems also of interest to show that they can be represented by an equation of the form required by the Debye-Hückel theory when the size of the ions is considered (see the following article). Fig. 3 shows with what degree of accuracy the $j$ values are represented by the equation,

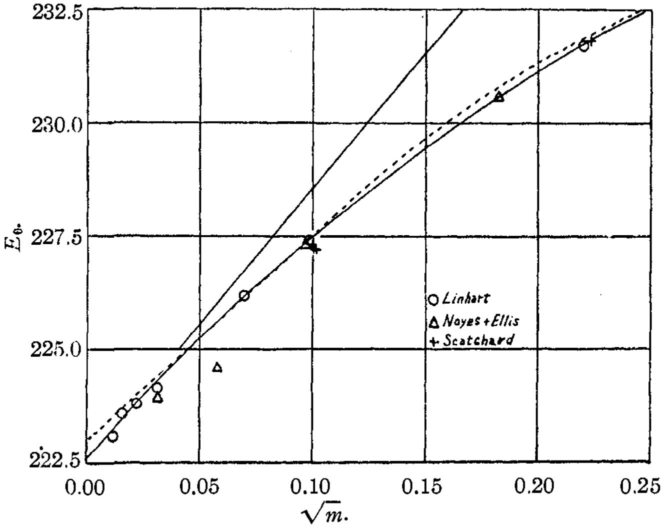

Fig. 2.—Electromotive-force measurements.

$$j = 0.38\, m^{0.5} - 0.85\, m \tag{2}$$

which gives $-\log \gamma = 0.495 \sqrt{m} - 0.738\, m$. In this figure the values of $j$ from Randall and Vanselow's paper are plotted against $\sqrt{m}$. The upper full line is the straight-line asymptote $j = 0.38 \sqrt{m}$. Up to 0.01 $M$ the dotted line is the curve of Equation 1, the lower full line that of Equation 2; at higher concentrations both curves are smooth graphic extensions of the curves at lower concentrations.

It is seen that the curve of Equation 2 does not fit the $j$ values as well as that of Equation 1; and the average deviation of the points is found to correspond to 0.00017° for Equation 2 and to 0.00010° for Equation 1. However, between 0.003 and 0.01 *M* the difference between duplicate conductivity measurements is 0.10–0.15%, which corresponds to one-half to three-quarters of the maximum difference between the two curves. (The diameters of the circles in Fig. 3 correspond to 0.10%.) Through this range the smoothed molal conductance values of Randall and Vanselow correspond closely to the minimum $j$ values. With the use of values that appear to me to give the best smoothing, Equation 2 fits the data slightly better than Equation 1. In spite of the apparent discrepancy between $\sqrt{m} = 0.1$ and 0.2, the agreement of the data with the two curves above $\sqrt{m} = 0.1$ is practically the same, and in both cases within the experimental error.

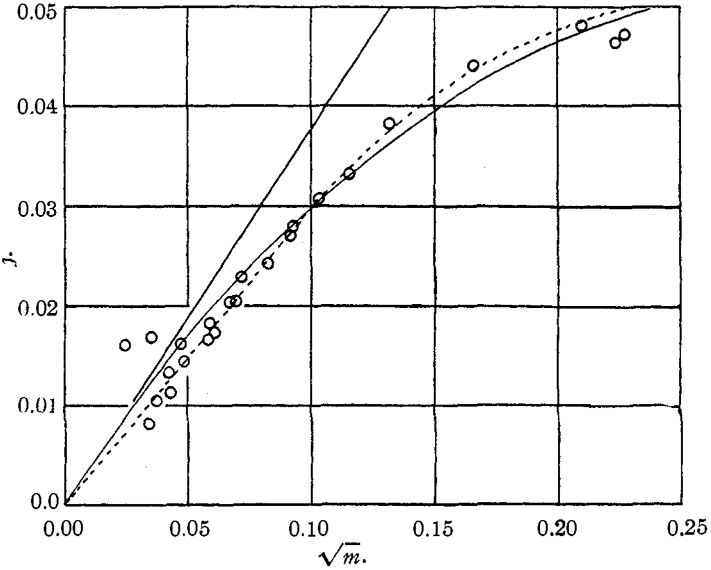

Fig. 3.—Freezing points of HCl. (Randall and Vanselow.)

The values of the activity coefficients calculated from Equations 1 and 2 are given in the third and fourth columns of Table II. Above 0.01 *M*, both the determination of $j$ and the computation of $\gamma$ are performed graphically. On the average the coefficients from Equation 1 are 0.6% greater than those from electromotive-force measurements, those from Equation 2 are 0.1% less. It is apparent that these latter values together with $E_0 = 222.6$ mv. would give a curve in Fig. 2 almost identical with that from the electromotive-force measurements.

The agreement of the values computed from the freezing-points by either formula with those from the electromotive-force measurements is very good, and the activity coefficients of the ions of hydrochloric acid can be considered to be determined within a few tenths of a per cent. It seems clear that the freezing-point measurements cannot determine the activity coefficient more closely than the difference between the results required by Equations 1 and 2. The values computed from electromotive-force measurements lie within this range and determine the most probable values still more accurately.

In conclusion I wish to express my gratitude to the National Research Council for its financial assistance, and to Professor F. G. Keyes and the other members of the staff of this Laboratory, especially to Professor D. A. MacInnes, for the suggestions and help they have given.

## Summary

1. The electromotive force at 25° of the cell, $Pt,H_2 | HCl,AgCl | Ag$, has been measured at several concentrations in the range 0.01–1.5 *M*, using a rocking hydrogen-electrode vessel designed for use in a water thermostat.

2. The mean activity coefficients of the ions have been calculated from these measurements and earlier ones on the same type of cells.

3. The coefficients are in very good agreement with those calculated from the freezing-point measurements of Randall and Vanselow.

4. The resulting activity coefficients at low concentrations are consistent within the experimental error with the limiting equation of Debye and Hückel, retaining the theoretical value of the constant of that equation.

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# THE ACTIVITIES OF STRONG ELECTROLYTES. II. A REVISION OF THE ACTIVITY COEFFICIENTS OF POTASSIUM, SODIUM, AND LITHIUM CHLORIDES, AND POTASSIUM HYDROXIDE[1]

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## I. Introduction

For a study of liquid-junction potentials, to be published later, values for the mean activity coefficient of the ions of potassium chloride more accurate than those available in the literature were necessary. In an attempt at accurate revision the activity coefficients of the salts named in the title were calculated from all available measurements of electromotive force, freezing point and vapor pressure.

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[1] Revised manuscript received December 11, 1924.

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