Activity and Concentration, Transport Numbers and Boundary Potential

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A DISSERTATION

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
THE UNIVERSITY OF MICHIGAN, JUNE, 1915.

By

ALFRED LYNN FERGUSON

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The writer wishes to express his earnest appreciation for the kind advice and helpful assistance rendered by Professor R. C. Tolman, under whose direction some preliminary work was carried out, without which the present investigation would not have been possible.

It is with sincere gratitude that acknowledgment is here made to Professor S. L. Bigelow for the interest he has taken in this work and for his most valuable criticisms.

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ACTIVITY AND CONCENTRATION, TRANSPORT NUMBERS, AND BOUNDARY POTENTIAL[1]

Introduction

In this investigation of the relation between activity and concentration, a new form of cell was used which permits of two new methods for measuring transport numbers and a direct method for measuring boundary electromotive force.

There are various types of concentration cells, but the type which has excited the most interest and stimulated the greatest amount of experimental and theoretical investigation is that one in which the electrodes are of the same material, but dip into solutions of different concentrations of the same electrolyte. An extensive investigation of such cells was carried out by Hans Jahn. His primary object was to test the existing formulas and theories of solutions when applied to dilute and moderately concentrated solutions of strong electrolytes. From his work Jahn felt justified in concluding: (1) that conductivity measurements do not give satisfactory values for the degree of dissociation; and (2) that the mobility of the ions is a function of the concentration increasing with increasing concentration. These are remarkable conclusions and constitute a blow aimed directly at the formula $\alpha = \mu_v/\mu_\infty$ of Arrhenius for calculating the degree of dissociation. Naturally they provoked much discussion and criticism. The principal participants in this discussion were H. Jahn,[2] Arrhenius,[3] Nernst,[4] Lehfeldt,[5] Goebel,[6] Sand,[7] Planck,[8] and Kruger.[9]

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[1] Contribution from the Chemical Laboratory of the University of Michigan.

[2] Zeit. phys. Chem., 35, 1 (1900); 36, 453; 37, 490; 38, 125 (1901); 41, 257 (1907).

[3] Ibid., 36, 28; 37, 315 (1901).

[4] Ibid., 36, 596; 38, 487 (1901).

[5] Ibid., 35, 257 (1900).

[6] Ibid., 42, 54 (1902).

[7] Ibid., 36, 499 (1901).

[8] Ibid., 41, 212 (1902).

[9] Ibid., 36, 86 (1901).

As a result of this discussion, Jahn was forced to admit several mistakes in his reasoning, but he maintained to the end that the above stated conclusions were justifiable. For a while, however, his work was rather discredited, but within the past fifteen, and particularly within the last five years, results have been obtained supporting his conclusions: Such for instance, as the investigation of F. Flugel[1] on the freezing point lowering and conductivity of very dilute solutions. The study of concentration cells with thalium electrodes by Lewis and Von Ende.[2] The investigation, by Lewis and Edgar,[3] of the equilibrium between nitric acid, nitrous acid, and nitric oxide. The influence of one salt on the solubility of another as worked out by Bray.[4] The work of Washburn and MacInnes[5] on the freezing point lowering and conductivity of cesium nitrate. And an earlier investigation by the author in conjunction with R. C. Tolman[6] on the free energy of dilution of hydrochloric acid.

In this earlier investigation it was concluded that the ratio of concentrations of ions was in every instance greater than the ratio of their activities, while the concentration ratios for the undissociated acid were in every case less than the activity ratios. The variation was found to be much greater for the undissociated acid than for the ions. In all these calculations one concentration was tenth normal and the other was something less. A form of cell was used that eliminated transport numbers.

Theoretical

The application of thermodynamic theory to physicochemical measurements is rapidly increasing in importance and nowhere is it more important than in connection with such cells as form the subject of this investigation.

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[1] Zeit. phys. Chem., **79**, 577 (1912).

[2] Jour. Am. Chem. Soc., **32**, 737 (1910).

[3] Ibid., **33**, 292 (1911).

[4] Ibid., **33**, 1673 (1911).

[5] Ibid., **33**, 1686 (1911).

[6] Ibid., **34**, 232 (1912).

The work which a reversible cell is capable of furnishing must equal its electromotive force times the quantity of electricity passing through the cell. That is, $w = EF$ per equivalent, where F equals one Faraday and E equals electromotive force.

Suppose we consider a hydrochloric acid concentration cell with calomel electrodes and the acid on the two sides having the concentrations C_1 and C_2. When one equivalent of electricity passes through the cell, the following changes take place: On the concentrated side, one equivalent of Cl ion will be removed to combine with the equivalent of Ag ion formed; N_a equivalents of Cl ion will migrate in from the dilute side, where N_a represents the transport number for the Cl ion. On the dilute side one equivalent of Cl ion will form; N_a equivalent of Cl ion will migrate out to the concentrated side, and $1 - N_a$ equivalents of H ion will migrate in from the concentrated side. The net result is then the disappearance of N_a equivalents of HCl from the concentrated side and the appearance of N_a equivalents on the dilute side, or, in other words, the transfer of N_a equivalents of HCl from one concentration to another. The electromotive force of such a cell multiplied by one Faraday gives the free energy of dilution of N_a mols of HCl, so the free energy per mol is $\frac{EF}{N_a}$. This is the type of cell used by Jahn in his measurements of free energy. The objections to this type of cell have been pointed out in an earlier paper.[1]

Let us now consider the conception developed by Lewis[2], which he calls activity. This quantity is defined by the following conditions:

1. "The activity of a molecular species is the same in two phases when these phases are in equilibrium as regards the distribution of that species."

2. "The activity of a gas approaches the gas concentration as a limiting value if the gas is indefinitely rarefied."

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[1] Loc. cit.

[2] Proc. Am. Acad., 43, 257 (1907).

In an earlier paper[1] he developed another quantity which he called "escaping tendency."

In yet another[2] he uses the same conception but calls it, for brevity, "fugacity." The quantity fugacity has the dimensions of pressure while activity has the dimensions of concentration, and the two are connected by the formula $a = \frac{\psi}{RT}$, where a represents activity, ψ fugacity, R the gas constant and T the absolute temperature.

Let us apply this activity conception to a hydrochloric acid concentration cell. If the activities of undissociated HCl in the two solutions be represented by a'_{HCl} and a''_{HCl} and the activities of the ions by $a'_{\overset{+}{H}}$, $a''_{\overset{+}{H}}$, $a'_{\overset{-}{Cl}}$, $a''_{\overset{-}{Cl}}$ then by substituting in the equation for free energy

$$F = EF = RT\, ln \frac{a_2}{a_1}$$

we have for the free energy change, accompanying the transfer of one mol of HCl from one solution to the other

$$F = EF = RT\, ln \frac{a''_{HCl}}{a'_{HCl}} = RT\, ln \frac{a''_{\overset{+}{H}} \times a''_{\overset{-}{Cl}}}{a'_{\overset{+}{H}} \times a'_{\overset{-}{Cl}}}.$$

We may assume also that $a'_{\overset{+}{H}} = a'_{\overset{-}{Cl}}$ and that $a''_{\overset{+}{H}} = a''_{\overset{-}{Cl}}$, then

$$EF = 2RT\, ln \frac{a''_{\overset{+}{H}}}{a'_{\overset{+}{H}}} = 2RT\, ln \frac{a''_{\overset{-}{Cl}}}{a'_{\overset{-}{Cl}}} = RT\, ln \frac{a''_{HCl}}{a'_{HCl}}. \quad (1)$$

This equation applies to concentration cells without boundary potential.

For concentration cells having boundary potential, and reversible with respect to the anion, we have the well known formula,

$$E_1 = 2 \frac{N_c RT}{F} ln \frac{a''_{\overset{+}{H}}}{a'_{\overset{+}{H}}}. \quad (2)$$

If the cell is reversible with respect to the cation the formula becomes

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[1] Proc. Am. Acad., 36, 145 (1900).

[2] Ibid., 37, 49 (1901).

$$E_2 = 2\frac{N_a RT}{F}\, ln \frac{a''_{\overline{Cl}}}{a'_{\overline{Cl}}}. \qquad (3)$$

A combination of (1) and (2) gives $N_c = \frac{E_1}{E}$.

A combination of (1) and (3) gives $N_a = \frac{E_2}{E}$.

Since $N_c + N_a = 1$, we have a very good check on our work, as both of these can be determined. Also, since $N_c + N_a = \frac{E_1 + E_2}{E} = 1$, it is evident that $E_1 + E_2 = E$.

A consideration of these equations shows that all that is necessary, then, to measure the transference number of the hydrogen ion is to measure the electromotive force of a concentration cell with transference and without using hydrogen electrodes. The transference number of the chloride ion in the same solution could be determined in a similar way by using calomel electrodes.

It is a well known fact that the surface of contact between two solutions is a source of potential difference. This potential difference between solutions has been one of the greatest stumbling blocks in the way of potential measurements of concentration cells. Those who have made such measurements have attempted to avoid it in one way or another or dismissed it entirely with the statement that it was too small to consider.

The first investigator to give a reasonable explanation for this liquid potential was Nernst.[1] He based his explanation on the unequal velocities of migration of the ions. Suppose, for example, a concentrated and a dilute solution of hydrochloric acid are in contact. The hydrogen ions and the chloride ions of the concentrated solutions diffuse into the dilute side. But the hydrogen ions travel with a much greater velocity than the chloride ions and, since they carry positive charges and the chloride ions negative charges, the dilute solution becomes positive with reference to the concentrated. This separation cannot take place to any appreciable extent, however, because of the attraction between these electrostatic

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[1] Zeit. phys. Chem., **4**, 129 (1889).

charges. The result of this attraction is to increase the velocity of the chloride ions and lessen the velocity of the hydrogen ions till eventually both travel with the same velocity, with the hydrogen in the lead; thus an electrical double layer is formed with its accompanying difference in potential. Nernst not only gave this explanation for the phenomena but he also derived a formula for calculating the values of such potential differences. With activity substituted for concentration the formula derived by him takes the form

$$E = \frac{(1 - 2N_a)RT}{F} \ ln \frac{a_1}{a_2}.$$

A consideration of the HCl concentration cell, reversible with respect to the chloride ion, shows that the boundary potential acts in the same direction as the electrode potentials, while in the HCl concentration cell, reversible with respect to the hydrogen ion, the boundary potential is opposed to the electrode potentials. Thus it is evident that this boundary potential is equal to one-half the difference between the electromotive forces of such concentration cells, and, therefore, the measurement of contact potential between solutions differing only in concentration of the same electrolyte resolves itself simply into the simultaneous measurement of the electromotive force between electrodes which furnish the positive ions in the solution and the electromotive force between electrodes which furnish the negative ions. Or, in the case of hydrochloric acid, the measurement of the electromotive force of the hydrogen concentration cell and at the same time the measurement of the electromotive force of the calomel concentration cell.

The formula for the electromotive force of a concentration cell without boundary potential shows that the only variables are the activity ratio and the electromotive force. If one of these is measured the other may be calculated. The concentration ratio can be calculated from conductivity measurements. The expression for the ratio of ion concentrations is $\frac{c''^{+}_{H}}{c'^{+}_{H}} = \frac{\alpha'' n''}{\alpha' n'}$, where α'' and α' are the degrees of dissociation at normalities n'' and n'. The ratio of undissociated acid is $\frac{c''_{\text{HCl}}}{c'_{\text{HCl}}} = \frac{n''(1-\alpha'')}{n'(1-\alpha')}$.

As has been stated, the conclusion was drawn in an earlier paper that the ratios of ion concentrations calculated from conductivity measurements were in every instance greater than the measured ratios of activities, while the ratios for the undissociated acid were in every case less than the activity ratios. Many have realized that this great variation between observed and calculated values should be more thoroughly investigated. These discrepancies between the activity ratios and concentration ratios for both the ions and un-ionized acid can be accounted for in either of two ways. It may be that conductivity measurements give the true value for the degree of dissociation, in which case activity and concentration are not proportional. Or, it may be that activity and concentration are proportional, in which case conductivity measurements can no longer be considered a true measure for ion concentration. The fact that activity and concentration have been shown to be proportional for all ordinary solutions of nonelectrolytes and even for weak electrolytes makes the second of the above alternatives the more probable. In view of this, a careful investigation of the basis for Arrhenius' formula, $\alpha = \frac{\mu_v}{\mu_\infty}$, is likely to reveal something of interest.

The conductivity of a liquid is the current density under unit potential gradient and may be represented by

$$k = F\alpha C(U_a + U_c),$$

where F represents one Faraday, α the degree of dissociation, C the total concentration in gram equivalents per cubic centimeter, U_a the mobility of the anion and U_c the mobility of the cation.

If this specific conductivity is multiplied by the volume V containing one equivalent, it gives the equivalent conductivity which may then be represented by

$$\mu = F\alpha CV(U_a + U_c) = F\alpha(U_a + U_c).$$

As the dilution increases, it is an observed experimental fact that α increases up to a certain limiting value characteristic for each electrolyte. According to the dissociation theory, the explanation for this is that the dissociation becomes greater the greater the dilution up to a certain limit for each electrolyte where $\alpha = 1$. The formula for the equivalent conductivity at this point of complete dissociation would then become $\mu = F(U_a + U_c)$. By a combination of this formula with the one for the equivalent conductivity at any dilution, V, there is obtained an expression

$$\frac{\mu_v}{\mu_\infty} = \frac{F\alpha(U_c + U_a)}{F(U_c + U_a)} = \frac{\alpha(U_c + U_a)}{(U_c + U_a)}.$$

In the numerator of this fraction, U_a and U_c represent the mobilities of cation and anion at the dilution V, while in the denominator the same terms represent the mobilities at infinite dilution. It is evident then, in order that the formula of Arrhenius shall be true, that the mobilities of the ions must be independent of the concentration. It is this assumption that introduces the greatest doubt into this method for calculating ion concentration.

It was with the object of determining whether the ions change their mobility with concentration, that the author devised the method used in this work. This method consists in a combination of electromotive force measurements of concentration cells with contact potential, and without contact potential.

Apparatus and Materials

The Cells.—A variety of cells was tried out before an entirely suitable one was found. The nature of the problem made it desirable to be able to take series of measurements on four different combinations from the same set-up. These measurements were as follows: (1) The electromotive force between a hydrogen and calomel electrode in HCl of concentration C_1. (2) A similar measurement but with HCl of concentration C_2. (3) The electromotive force between the calomel electrode in concentration C_1 and the one in C_2. (4) A similar measurement for the hydrogen electrodes. From (1) could be calculated the free energy of formation of HCl from hydrogen and calomel in concentration C_1. From (2) a similar calculation for the case where the concentration is C_2. From the difference between (1) and (2) could be obtained the free energy of dilution of HCl from one concentration to the other. The difference between (1) and (2) would give also the E of Equation 1. The measurements in (3) would give the electromotive force of the concentration cell having boundary potential with calomel electrodes, or the value of E_1 in Equation 2. Similarly (4) would give E_2 in Equation 3.

The above data would make it possible to calculate the ratios $\frac{a''_{\overline{Cl}}}{a'_{\overline{Cl}}}$, $\frac{a''_{\overset{+}{H}}}{a'_{\overset{+}{H}}}$ and $\frac{a''_{HCl}}{a'_{HCl}}$; also the transference numbers for both—the hydrogen and chloride ions. Several other things had to be considered in the construction of these cells in order to be sure that the above electromotive force values represented accurately what they were supposed to. First of all, they should remain constant a reasonable length of time. This necessitated extreme caution to prevent diffusion between the solutions of different concentrations. As a result of an extensive study of the calomel electrodes, it was decided they must be in separate chambers from the hydrogen electrodes. Slight unavoidable movements of the connecting tube when this passed through the calomel to the mercury, as is generally the case, agitated the calomel and mercury in D (Fig. 1) and caused a change in the value of the electrode. To avoid this source of error it was thought advisable to make contact directly with the mercury. With these various requirements in mind a set-up of the type shown in Fig. 1 was finally used. Compartment A contains a calomel electrode in acid of concentration C_2; B contains a hydrogen electrode in acid of the same concentration; C contains a calomel electrode in acid of concentration C_1, and D contains a hydrogen electrode in acid of this same concentration. The various compartments are connected through the three-way stopcocks *a*, *b*, *c* and *d*. The rubber connections between B and D;

and A and C contain filter paper to reduce the diffusion; also the holes of the three-way stopcocks in *b* and *d* contain filter paper. The hydrogen inlet tubes are at *e* and *f*, and the outlet tubes at *g* and *h*. In each hydrogen compartment are two electrodes *i* and *i'*, and *j* and *j'*.

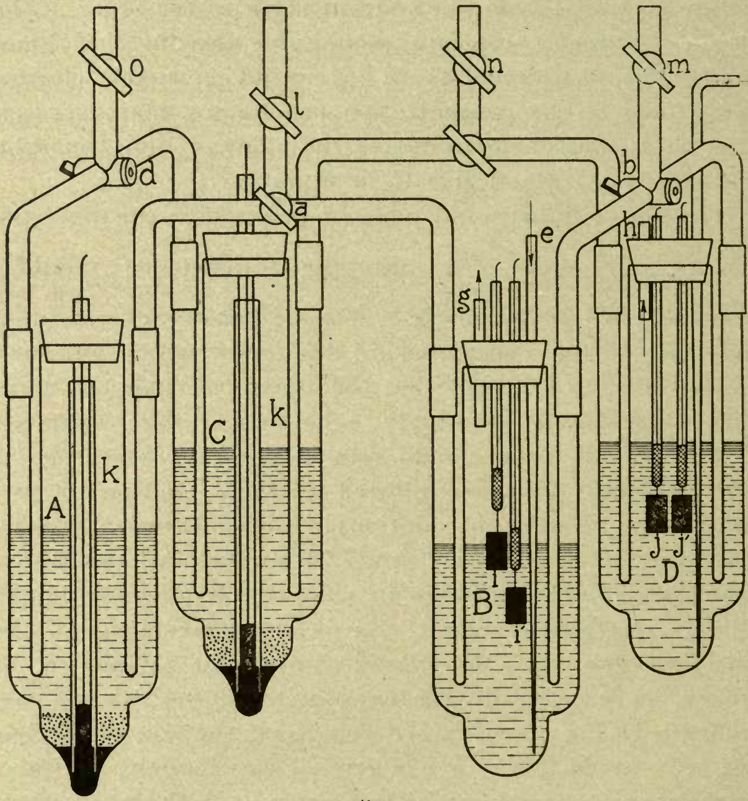

Fig. 1

The Hydrogen Electrodes.—An extended study of the hydrogen electrodes was made to settle the following points: the size and shape most suitable for our cells, ease of construction, effect of varying amounts of platinum black, the constancy when changed from a solution of one concentration to a solution of another concentration, reproducibility, and effect of exposure to air for several days. This study showed that the size and shape of the electrodes has no influence on their value. Those finally used in this work were made of platinum foil about one and one-half centimeters by two centimeters. As long as the coating had a black velvety appearance the electrodes remained constant; but after continued use they turned gray, became less sensitive, and fluctuated in value. The same electrodes were used several times before replatinizing. It was found inadvisable to have too much platinum black. As to constancy, they proved to be perfectly satisfactory. Electrodes were used in solutions of different concentrations, where they remained for several days, in some instances, and when they were returned to the stock solution they were found to have suffered no change. The degree of reproducibility is shown by the fact that when twelve of these electrodes were made and placed in a stock solution of very dilute acid and eleven were compared with the remaining one, eleven were exactly at the same potential and the twelfth showed a variation of only 0.01 mv. Over a period of eight days the greatest variation was 0.02 mv. Some of these electrodes were exposed to the air for several days without any permanent effect. An accident which happened to one of them shows they will stand much abuse. This electrode became unevenly covered with paraffin, and was left on a shelf for several months. To remove the paraffin the electrode was soaked in benzole, and to remove any other organic matter it was boiled in nitric acid and then several times in water. Again it was put through the platinizing and washing process and returned to the stock solution. A comparison showed it to be at exactly the same potential with the standard. This study shows that these hydrogen electrodes would make a better standard than the calomel electrodes. Nernst[1] was the first one to recognize the advantages of the hydrogen electrode and advocated its use as a standard in preference to the calomel electrode.

The Calomel Electrodes.—An investigation of the calomel electrodes, even more extensive than with the hydrogen elec-

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[1] Zeit. Elektrochemie, 7, 253 (1900).

trodes, was necessary because of the gradual and often rapid changes which took place in them.

They were all made from the same stock of Baker and Adamson analyzed calomel (Serial no. 3772) and twice distilled mercury. It was found better not to use mercury in making the paste. The calomel was mixed in a small beaker with a little of the solution to be used, until it was creamy, and then was washed three times by decantation with the same solution. A layer of calomel of considerable depth was found advisable. Connection with the electrode was made through the side arm (*k*), Fig. 1.

The first cells used had the calomel and hydrogen in the same compartment. Two, and often four, of these were made up at the same time. In a few minutes they would come together within a few hundredths of a millivolt. Soon after the hydrogen started to flow through the cell, the calomel electrodes began slowly to change. Some of the solutions, after there had been considerable change in the values of the cells, were titrated against barium hydroxide, and in every case increase in strength of acid was observed. The reason for this change in concentration has not yet been determined. This increase was roughly (not exactly) proportional to the change which had taken place in the electromotive force of the cell. Solutions taken from cells that remained constant gave the same analysis as the original solution. It was observed, moreover, that in the cells which had changed, the surface of the calomel appeared darker. In other cases, when freshly platinized electrodes were used, a few small specks of platinum black became loosened from the electrode by the action of the bubbles of hydrogen. In these cases the rate of change of electromotive force was greater. To prevent these particles of platinum black from reaching the calomel, the electrodes were covered with a filter paper bag, but this did not prove satisfactory. These facts offered an explanation for the changes that had been observed. There appeared to be close connection between the change in the electromotive force and the darkening of the calomel. Often the surface became nearly black; in such cases, a large increase in concentration of acid was found. To determine whether simply the passage of hydrogen through the cell would produce a change in concentration, a sample of calomel mercury paste was placed in each of two tubes and covered with $N/60$ acid. Through one of these, hydrogen was passed for two days while the other was left undisturbed. No change in color of the calomel was observed, and no appreciable change in concentration. These results are not sufficient to establish any conclusion, but they are enough to arouse the suspicion that the changes observed in the calomel electrodes are due to a change in concentration of the acid. This in turn is in some way connected with the combined action of hydrogen, platinum black and calomel. It might be stated, as a possibility, that the hydrogen, aided by the catalytic action of platinum black, decomposes the calomel with the formation of more HCl and free mercury. Much more work would be required before any definite statement could be made, but no difficulties were encountered when the form of cell in Fig. 1 was used.

The Thermostat.—In all earlier work the ordinary form thermostat heated by a gas flame, the size of which was regulated by the rising and lowering of a column of mercury, was used. This did not prove satisfactory. The variation in gas pressure, and the corroding of the mercury surface made close attention necessary and decreased the accuracy of regulation. To avoid these difficulties an electrically heated and regulated thermostat was constructed. In this new thermostat the regulation was so close that no change of temperature could be detected by a Beckman thermometer over a period of several days.

The Electrical Apparatus.—The electromotive forces were measured with an Otto Wolff 15,000 ohm potentiometer and suitable galvanometer. A certified Weston cell was used as a standard and was kept in the same thermostat in which the measurements were carried out.

The Hydrochloric Acid.—An approximately fifth-normal stock solution of hydrochloric acid (Baker & Adamson's analyzed hydrochloric acid C. P.) was prepared by dilution with conductivity water and its concentration determined by precipitation of AgCl. Five analyses showed per 1000 grams solution, 7.259, 7.266, 7.262, 7.263 grams of chlorine. The solutions used for measurement were $N/5$, $N/10$, $N/60$, $N/90$, $N/120$, $N/180$, and $N/300$, made from a weighed quantity of the stock solution by dilution at 18°, using flasks carefully calibrated with standardized weights.

The Hydrogen Generator.—The hydrogen used was generated electrolytically from a strong sodium hydroxide solution in a generator of the type described by Bodenstein.[1] The electrodes were of nickel wire.

In order to remove possible traces of oxygen, the gas was passed, before use, through a tube containing a platinum wire heated to incandescence by an electric current.[2] It was then passed through a wash bottle filled with distilled water, then bubbled from a fine capillary through acid of the same concentration and temperature as that in the cell, and finally allowed to bubble from a fine capillary through the solution surrounding the platinized electrodes and escape through a long tube into the air.

Method of Procedure and Experimental Results

In all of the measurements $N/30$ HCl was taken as the standard for comparison and they were all made at 18° C.[3] The cells constructed as described were, in most cases, set up at night, and by the next night the readings had become constant. Readings were taken at varying intervals over a period of several days.

The following uniform method was adopted: The stopcock *d*, Fig. 1, in the tube connecting the calomel electrode in concentration C_x with the one in C_{30} was opened, also the similar stopcock *b* between the hydrogen electrodes. After

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[1] Zeit. Elektrochemie, 11, 373 (1905).

[2] This precaution was really not necessary as no change in electromotive force could be detected when the wire was not heated.

[3] The bath temperature remained so constant that it was unnecessary to record it in the tables.

about five minutes the potentials were measured and the stopcocks closed. By producing a slight suction on the upward directed tube of the three-way stopcock *a* connecting the hydrogen chamber and calomel chamber of the *N*/30 solution, the liquid in the downward directed branches was drawn up till contact was made within the stopcock *a*; the stopcock *l* in the upward tube was then closed. After the reading was taken *l* was opened sufficiently to permit a separation of the liquid in *a*. The cell was left in this condition till the next reading. A similar procedure was then followed for the cell containing C_x acid.

The experimental data obtained in this work are included in eighteen tables of which Table I in this article is a sample. In column E_{30} is given the electromotive force between the hydrogen electrode and calomel electrode in *N*/30 HCl. Column E_{60}, E_{90}, —, —, etc., in the various tables contains the electromotive force measurements between the hydrogen and calomel electrodes in concentrations *N*/60, *N*/90, —, —, etc. Under E_2 are given the potentials between a hydrogen electrode in *N*/30 HCl and the hydrogen electrode in the other concentration being investigated; and under E_1 are given corresponding values for the calomel electrodes.

As was stated in the discussion above, $E_x - E_{30}$ should equal $E_1 + E_2$. The remarkable agreement found is shown by a comparison of the last two columns.

The slight variations observed between successive readings can be accounted for largely by changes in barometric pressure.[1] The effect of these changes is practically the same in acid of all concentrations, and as we are concerned with differences only, it is not necessary to make corrections for them.

A large number of preliminary experiments were performed before all of the disturbing elements were discovered and eliminated. After the proper conditions were secured, however, no further difficulties were experienced, and the eighteen tables contain all of the measurements that were taken.

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[1] Since there is considerable lag in the effect produced by pressure changes, the changes in electromotive force measurements do not correspond to these unless the changes in pressure were gradual.

TABLE I

No.	Date	Time	Bar.	E_{30}	E_{60}	E_2	E_1	$E_{60} - E_{30}$	$E_2 + E_1$
1	April 22	11 P.M.	—	0.45110	0.48575	—	—	0.03465	—
2	23	8.00 A.M.	744.2	082	432	—	—	350	—
3		1.00 P.M.	—	85	50	—	—	65	—
4		4.00 P.M.	—	98	56	—	—	58	—
5		5.00 P.M.	—	83	40	—	—	57	—
6		6.00 P.M.	—	78	40	—	—	62	—
7	24	12.00 M.	739.1	59	18	—	—	59	—
8		2.00 P.M.	—	61	16	—	—	55	—
9		7.25 P.M.	—	51	05	0.00575	0.02787	54	0.03362
10		8.30 P.M.	—	53	11	69	88	58	57
11	26	10.00 A.M.	735.3	45	395	83	64	50	47
12		11.00 A.M.	—	41	86	77	66	45	43
13		4.00 P.M.	—	49	94	78	64	45	42
14		7.00 P.M.	—	46	96	78	65	50	43
15	27	9.00 A.M.	737.0	57	403	70	77	46	47
			Av.,	0.45062	0.48420	0.00574	0.02776	0.03354	0.03350

Remarks: Cell was set up April 22, 10.00 P.M.

Discussion of Results

To facilitate the study of the results a summary of the values for E, E_1 and E_2 is presented in Tables II, III and IV.

TABLE II—SUMMARY OF VALUES FOR E

Conc. Diff.	Calculated		Measured		
	New formula	Old formula	By diff.	By sum.	Average
n/30 — *n*/5	0.08530	0.08702	0.08567	0.08558	0.08562
n/60 — *n*/30	0.03361	0.03414	0.03350	0.03347	0.03349
n/90 — *n*/30	0.05365	0.05423	0.05334	0.05333	0.05334
n/120 — *n*/30	0.06744	0.06828	0.06711	0.06705	0.06708
n/150 — *n*/30	0.07879	0.07955	0.07847	0.07847	0.07847
n/180 — *n*/30	0.08778	0.08858	0.08784	0.08772	0.08778
n/300 — *n*/30	0.11305	0.11400	0.11361	0.11361	0.11361

In Table II under the head "Old formula" are given the values calculated from the regular formula for concentration cells without boundary potential, namely $E = \frac{2RT}{F} \ln \frac{c_1}{c_2}$. In Tables III and IV in the columns headed "Old formula, $N_c = 826$," are given the values calculated from the formulas for concentration cells with boundary potential, namely, $E_2 = \frac{2RTN_a}{F} \ln \frac{c_1}{c_2}$ and $E_1 = \frac{2RTN_c}{F} \ln \frac{c_1}{c_2}$. In these calculations R was taken equal to 8.3160 joules, T equal to 291.09°, and F equal to 96490. The conductivity data given by Goodwin and Haskell[1] for HCl was plotted and, in the calculation of the degree of dissociation at the various concentrations used by the writer, the conductivity values were taken from this curve. The value for infinite dilution was taken equal to 380.

A comparison of the measured values with the calculated in these three tables shows fairly close agreement; in fact agreements much less close than these have been considered very satisfactory and used as a confirmation of the accuracy of the formulas. A careful inspection of these tables, however,

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[1] Phys. Rev., **19**, 386 (1904).

shows that the calculated values are in every instance greater than the measured and this was found to be the case, not only for these results, but also for similar measurements made by others.

TABLE III—SUMMARY OF VALUES FOR E_1

Conc. Diff.	Measured	Calculated			
		Old formula		New formula	
		$N_c = 832$	$N_c = 826$	$N_c = 832$	$N_c = 826$
n/30 — *n*/5	0.01397	0.01463	0.01512	0.01433	0.01484
n/60 — *n*/30	0.00571	0.00580	0.00594	0.00571	0.00585
n/90 — *n*/30	0.00888	0.00910	0.00943	0.00901	0.00933
n/120 — *n*/30	0.01130	0.01147	0.01187	0.01133	0.01173
n/150 — *n*/30	0.01315	0.01337	0.01384	0.01324	0.01371
n/180 — *n*/30	0.01475	0.01488	0.01541	0.01474	0.01527
n/300 — *n*/30	0.01898	0.01916	0.01984	0.01899	0.01967

TABLE IV—SUMMARY OF VALUES FOR E_2

Conc. Diff.	Measured	Calculated			
		New formula		Old formula	
		$N_c = 832$	$N_c = 826$	$N_c = 832$	$N_c = 826$
n/30 — *n*/5	0.07163	0.07140	0.07046	0.07282	0.07188
n/60 — *n*/30	0.02773	0.02789	0.02776	0.02833	0.02820
n/90 — *n*/30	0.04446	0.04463	0.04431	0.04511	0.04479
n/120 — *n*/30	0.05573	0.05611	0.05570	0.05681	0.05640
n/150 — *n*/30	0.06535	0.06555	0.06508	0.06618	0.06571
n/180 — *n*/30	0.07299	0.07304	0.07251	0.07370	0.07317
n/300 — *n*/30	0.09488	0.09406	0.09338	0.09484	0.09416

By substituting the measured values in the formula for the electromotive force of concentration cells without boundary potential, the activity ratios for the various concentration differences were calculated. These are presented in Table V, together with the concentration ratios for the same concentration differences calculated from conductivity measurements.

TABLE V—ACTIVITY AND CONCENTRATION RATIOS

Conc. Diff.	$\frac{a_{1\mathrm{H}}}{a_{2\mathrm{H}}}$	$\frac{c_{1\mathrm{H}}}{c_{2\mathrm{H}}}$	$\frac{a_{1\mathrm{HCl}}}{a_{2\mathrm{HCl}}}$	$\frac{c_{1\mathrm{HCl}}}{c_{2\mathrm{HCl}}}$
n/5 — *n*/30	5.507	5.664	30.311	12.881
n/60 — *n*/30	1.949	1.974	3.799	2.723
n/90 — *n*/30	2.895	2.946	8.375	4.784
n/120 — *n*/30	3.806	3.893	14.455	7.080
n/150 — *n*/30	4.776	4.880	22.793	10.570
n/180 — *n*/30	5.750	5.842	33.037	13.443
n/300 — *n*/30	9.621	9.687	92.449	29.500

This table again brings out the fact that the activity ratios for the ions are in every case less than the corresponding concentration ratios; but for the undissociated part of the acid the activity ratios are much greater than the concentration ratios, and as the dilution becomes greater the activity increases more rapidly than the concentration.

In view of the fact that for all non-electrolytes and even for weak electrolytes, the activity has been shown by others to be proportional to the concentration, the nature of these results is quite remarkable. They confirm the statement made in the consideration of the preliminary experiments, that either conductivity measurements do not give true values for the degree of dissociation or, else the concentration of the ions as well as the undissociated part of the acid is not proportional to the activity in the case of hydrochloric acid.

It will be remembered that Jahn, in his measurements with concentration cells having boundary potential, found his observed values to be less than those calculated from the Nernst equation. Table II shows the same relation for measurements with concentration cells without boundary potential. To explain these discrepancies between his observed and calculated values, Jahn suggested that conductivity is not an accurate method for determining the degree of dissociation. He doubted the validity of the assumption that the transport numbers do not change with concentration, and this assumption must be made when the degree of dissociation is calculated from conductivity data. It will be remembered that the investigation of the relation between transport numbers and concentration is one of the primary objects of this paper.

As was pointed out earlier in the discussion the measurements in this work give two new and distinct methods for calculating transport numbers. One is by the formula $N_c = \frac{E_1}{E}$ or $N_a = \frac{E_2}{E}$, (one serves as a check on the other) and the other by the formula for boundary potential $E = (1 - 2N_c) \frac{RT}{F} \ln \frac{c_1}{c_2}$. In the first method nothing is involved but the measurements of E_2, E_1 and E which can be made with a very high degree of accuracy. The second method, however, involves a formula which is possibly questionable, particularly the ratio $\frac{c_1}{c_2}$.

The results obtained by the application of these two formulas are presented in Table VI.

TABLE VI—SUMMARY OF TRANSPORT NUMBER N_c

Conc. Diff.	$\frac{E_1}{E}$	$1 - \frac{E_2}{E}$	Average	From boundary E. M. F.	
				Using $\frac{c_1}{c_2}$	Using $\frac{a_1}{a_2}$
n/30 — *n*/5	0.836	0.8377	0.837	0.831	0.837
n/60 — *n*/30	0.828	0.830	0.829	0.822	0.829
n/90 — *n*/30	0.833	0.833	0.833	0.827	0.833
n/120 — *n*/30	0.830	0.831	0.830	0.825	0.831
n/150 — *n*/30	0.833	0.832	0.832	0.830	0.835
n/180 — *n*/30	0.831	0.8315	0.831	0.829	0.831
n/300 — *n*/30	0.835	0.833	0.834	0.832	0.833

Final av., 0.832

It should be noted that E_2 and E_1 give practically identical values for N_c but these do not agree with the values calculated from the formula for boundary potential. According to the first method N_c remains constant at dilutions greater than *n*/90 and increases slightly between *n*/30 and *n*/5.

In Table VI, under the head $\frac{a_1}{a_2}$, are given the values for N_c calculated from boundary potentials by substituting the activity ratios from Table V in place of concentration ratios. This gives results nearly identical with those given by the other method. One of the most important features of these results is the argument they add to the view that the formula for calculating boundary potential is reliable and that the formula for calculating ionic concentration is unreliable.

To facilitate a comparison of the results of the various investigators who have measured the transport numbers of HCl the data obtained by them is presented in Table VII.

All of the recent investigators except one have used the Hittorf method, with variations to eliminate as far as possible the various sources of error. The wide variation between the different results of each investigator as well as the lack of agreement between the values of different investigators, shows that the method is not very reliable. Washburn[1] has expressed the belief that during such experiments water is transported, due to the hydration of the ions, from one electrode chamber to the other when the solutions are fairly concentrated. Buchböck also came to the same conclusion. Their evidence appears to be strong. If water is so transported then it is evident that transference numbers cannot be accurately determined by this method.

The moving boundary method for measuring transference numbers is not open to the same criticism, but so few measurements have been made on hydrochloric acid by it that scarcely anything can be said.

The two methods used in this present investigation appear to be entirely free from all the sources of error attending the Hittorf method. Their limitations have been discussed but they appear to give more consistent and reproducible values than have been obtained before.

In Table VIII is presented a summary of the measured values for boundary potential together with the calculated values when N_c is given the commonly accepted value 0.826 and also when N_c is given the value 0.832 found in this investi-

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[1] Jour. Am. Chem. Soc., 31, 322 (1909).

TABLE VII—COMPARISON OF VALUES FOR N_c

Volume in L. containing one equivalent	Hopfgartner 1898	Bein 1898	Jahn and Bogden 1901	Noyes and Sammet 1902	Buchböck 1906	Jahn and Joachim 1907	Noyes and Kato 1908	Riesenfeld and Reinhold 1908	Denison and Steele 1908	Drucker and Kranjavi 1908	Ferguson	
											from $\frac{E_2}{E}$	from boundary E. M. F.
0.4	—	—	—	—	824	—	—	—	—	—	—	—
1	—	—	—	—	842	—	—	845	—	—	—	—
1.1	841	—	—	—	—	—	—	—	—	—	—	—
1.25	843	—	—	—	—	—	—	—	—	—	—	—
2	833	—	—	—	—	—	—	845	—	—	—	—
5	836	—	—	—	—	—	—	—	—	—	837	837
5 to	20	829	—	—	—	—	—	—	—	—	—	—
10	833	825	—	—	—	—	—	839	835	—	—	—
20	—	—	—	836	—	—	—	—	—	—	—	—
30	—	—	823	—	—	835	—	—	—	830.6	—	—
50	—	—	828	—	—	—	—	—	835	—	—	—
60	—	—	—	834	—	833	—	—	—	—	829	829
70	—	—	823	—	—	—	—	—	—	—	—	—
80	—	—	827	—	—	—	—	—	—	—	—	—
90	—	—	—	—	—	832	—	—	—	—	833	833
103	—	—	828	—	—	—	—	—	—	—	—	—
110	—	—	825	—	—	—	—	—	—	—	—	—
120	—	—	—	—	—	834	—	—	—	—	830.5	831
150	—	—	—	—	—	833	—	—	—	—	833	835
180	—	—	—	834	—	—	—	—	—	—	829	831
300	—	—	—	—	—	—	—	—	—	—	832	833
500	—	—	—	—	—	—	831	—	—	—	—	—

gation. The table shows much better agreement between the measured values and those calculated with $N_c = 0.826$ than with $N_c = 0.832$. This is really a false agreement as can easily be shown. In the discussion of transference numbers it was pointed out that the values in Table VI, in the column headed $\frac{a_1}{a_2}$, were obtained by substituting in the formula activity ratios in the place of concentration ratios. This gave values which are in very close agreement with those determined from the ratio $\frac{E_2}{E}$. It is evident then that the error introduced by using $N_c = 0.826$ is approximately counterbalanced by the error introduced by using concentration ratios in the place of activity ratios, and thus causes a false agreement between measured and calculated values.

In Table VIII, in the column headed, $N_c = 0.832$ and $\frac{a_1}{a_2}$, are given the calculated values when, for N_c, the values measured from the ratio $\frac{E_1}{E}$ are used and for $\frac{a_1}{a_2}$ are used the measured activity ratios. The remarkable agreement between these calculated and measured values speaks for itself. There can remain little doubt concerning the exactness of the formula; but the grave necessity for accurate transference values and activity ratios is also made evident.

TABLE VIII—SUMMARY OF BOUNDARY E. M. F.

Conc. Diff.	Calculated			Measured
	$N_c = 0.826$ and $\frac{c_1}{c_2}$	$N_c = 0.832$ and $\frac{c_1}{c_2}$	$N_c = 0.832$ and $\frac{a_1}{a_2}$	
$n/30 - n/5$	0.02837	0.02930[1]	0.02893[1]	0.02883
$n/60 - n/30$	0.01113	0.01126	0.01112	0.01100
$n/90 - n/30$	0.01767	0.01800	0.01771	0.01771
$n/120 - n/30$	0.02226	0.02267	0.02226	0.02221
$n/150 - n/30$	0.02593	0.02641	0.02605	0.02610
$n/180 - n/30$	0.02887	0.02941	0.02914	0.02912
$n/300 - n/30$	0.03715	0.03783	0.03777	0.03785

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[1] In calculating this value N_c was taken equal to 0.837.

In the discussion of Tables II, III and IV it was pointed out that the calculated values for electromotive forces were invariably greater than the measured; and that the same is true of all similar measurements made by others. The most probable explanation for this is some constant source of error in the formula. One such source has been pointed out, namely, the formula calls for an activity ratio, but in place of this a concentration ratio, calculated from conductivity measurements, had to be substituted. After a careful study of the most probable changes within the cell, it appears to the writer that the formula does not exactly fit the case. The following discussion is an effort to make this point evident and to suggest an improvement.

The formula as it is commonly used has the form

$$W = EF = 2RT\, ln \frac{c_1}{c_2}.$$

This equation is supposed to represent the work required to transfer one electrochemical equivalent of electricity from one electrode to the other. If this is carried out in a double cell so that there can be no change at the boundary, it would result in the disappearance of one mol of HCl from the more concentrated side and the appearance of one mol in the dilute. The work involved then is that required to transfer a mol of HCl from one side to the other. In case of complete ionization this would mean the transfer of one equivalent of hydrogen ion and one equivalent of chloride ion, and would be represented by the expression $2RT\, ln \frac{c_1}{c_2}$. This is the same as the third member in the above equation. Under the conditions of complete dissociation then this equation is entirely applicable, but in no actual experiment is this the case. What would really take place if a faraday of electricity were passed through such a cell would be, (1) the transfer of an amount of chloride ion equal to the dissociation of the acid, (2) the transfer of an amount of hydrogen ion equal to the dissociation of the acid, (3) the transfer of an amount of undissociated acid equal to the undissociated part.

The work in (1) equals the work in (2) and may be represented by

$$W_1 = \alpha RT\, ln\, \frac{c_1}{c_2}.$$

The work in (3) may be represented by

$$W_2 = (1 - \alpha)\, RT\, ln\, \frac{c_1}{c_2}.$$

Now

$$c_{2_H} = c_2\alpha'' = c_{2_{\overline{Cl}}}$$

and

$$c_{1_H} = c_1\alpha' = c_{1_{\overline{Cl}}}$$

and

$$c_{2_{HCl}} = c_2(1 - \alpha'')$$

and

$$c_{1_{HCl}} = c_1(1 - \alpha').$$

Combining and substituting,

$$W = 2\alpha RT\, ln\, \frac{c_2\alpha''}{c_1\alpha'} + (1 - \alpha)\, RT\, ln\, \frac{c_2(1 - \alpha'')}{c_1(1 - \alpha')}.$$

This formula is not absolutely exact because of the uncertainty in α. The assumption is made that the dissociation is the same in both sides, but this evidently is not true; so the most likely value to use for α is $\frac{\alpha'' + \alpha'}{2}$.

The values for E, E_1 and E_2 have been recalculated according to this new formula and are recorded in Tables II, III and IV under the heading "New formula."

In Table IX are presented the differences ($\times 10^5$) between the measured and the calculated values by use of the old formula in one case and the new formula in the other.

It is evident from these differences that the new formula is an improvement.

TABLE IX—SUMMARY OF DIFFERENCES BETWEEN MEASURED AND CALCULATED VALUES

Conc. Diff.	E		E₁				E₂			
	New — meas.	Old — meas.	New — meas.	Old — meas.	New — meas.	Old — meas.	New — meas.	Old — meas.	New — meas.	Old — meas.
			N_c = 0.832		N_c = 0.826		N_c = 0.832		N_c = 0.826	
n/30 — *n*/5	—32	140	+7	23	87	115	—23	119	—117	25
n/60 — *n*/30	12	65	00	9	14	23	16	60	+ 3	47
n/90 — *n*/30	31	89	13	22	45	55	17	65	— 15	33
n/120 — *n*/30	36	120	3	17	43	57	38	108	— 3	67
n/150 — *n*/30	32	108	9	22	56	69	20	83	— 27	26
n/180 — *n*/30	00	80	—1	13	53	67	5	71	— 48	18
n/300 — *n*/30	—56	39	+1	18	69	86	—82	—2	—150	—72

Conclusion

From all this it is concluded: (1) that the transport numbers for hydrochloric acid remain constant for dilutions greater than $n/30$, and thus conductivity measurements give an accurate method for determining ion concentrations in dilutions greater than $n/30$, so far as any change in the velocity of the ions is concerned; (2) that the concentration is not proportional to activity; (3) that the Nernst equation cannot be applied to an actual concentration cell without some changes; (4) that the formula for calculating boundary electromotive force gives accurate results if the true transport numbers are used and if activity is substituted in the place of concentration.[1]

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[1] Since the completion of this investigation, an article by Duncan A. MacInnes and Karr Parker (Jour. Am. Chem. Soc., **37**, 1445 (1915)) on the KCl concentration cell has appeared in the literature. The KCl concentration cell is dealt with in much the same way as the present work deals with the HCl concentration cell. The values obtained for the transport numbers show practically no variation with concentrations between 0.5 and 0.005 *n*. It may be said, in general, that the conclusions arrived at in this investigation of HCl solutions agree remarkably well with those stated by MacInnes and Parker for KCl solutions.