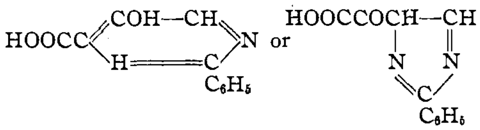
The Chloropyrimidine.—The product from benzaldehyde, glyoxal and *m*-tolenylamidine refluxed with a PCl_5-$POCl_3$ mixture for several hours gave a gum insoluble in water. This, after boiling with water several hours, was dissolved in alcohol. After several days a small yield of yellow crystals was obtained which, recrystallized from alcohol several times, melted at 285.5° (bloc Maquenne).

Anal. Calcd. for $C_{17}H_{13}N_2Cl$: Cl, 12.63. Found: Cl, 12.83, 12.89.

Phenylpyrimidine Carboxylic Acid.—The mother liquor from the benzamidine glyoxal product, after several weeks (red color) was neutralized with hydrochloric acid giving an orange-red precipitate which was separated mechanically from the red gum. Boiling with dilute potassium hydroxide and charcoal several times, reprecipitation with acid and recrystallization from dilute alcohol, gave flesh-colored crystals (m. p. 310°, electrical bloc Maquenne, 250° capillary tube).

Anal. Calcd. for $C_{11}H_8N_2O_3$: C, 61.11; H, 3.70; N, 12.95. Found: C, 61.50; H, 3.90; N, 12.82, 13.15.

Since "polyglyoxal" (Schuchardt) contains a small amount of glyoxylic acid, this has evidently reacted with the addition product to form



This acid is an isomer of an acid obtained by Pinner.[6]

Summary

1. A series of addition products of aromatic amidines and glyoxal has been prepared, analyzed and formulas determined. The hydrochloride of the benzamidine–glyoxal addition product has been prepared and analyzed.

2. A series of diphenylhydroxypyrimidines (benzoylphenylglyoxalines) have been prepared, analyzed and presumptive formulas ascribed to them.

3. A chloropyrimidine from phenyl-*m*-tolenylhydroxypyrimidine has been prepared and analyzed.

4. A phenylpyrimidine carboxylic acid has been prepared and analyzed.

BOULDER, COLORADO RECEIVED APRIL 29, 1935

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

The Determination of Activity Coefficients from the Potentials of Concentration Cells with Transference. I. Sodium Chloride at 25°

BY ALFRED S. BROWN[1] AND D. A. MACINNES

In the determination of the activities of electrolytes in solution the method depending upon the measurement of concentration cells has certain decided advantages over the other available methods, which are, it will be recalled, the determinations of freezing points, of boiling points or of vapor pressures. The concentration cell method is superior to the first two of these alternative methods in that the measurements are isothermal and that they may be made at any temperature at which the existence of the cell is possible. The concentration cell method is also better than the other procedures mentioned in that the precision of the measurements does not decrease rapidly as the concentrations of the solutions are lowered. There is, however, a distinct limitation to a method depending upon the determination of electromotive forces in that reversible electrodes are necessary for the ion constituents involved. Thus, for sodium chloride solutions, a concentration cell without liquid junction, of which the following is a typical example

Ag; AgCl, NaCl (C_1): $NaHg_x$ – $NaHg_x$; NaCl (C_2), AgCl; Ag (A)

involves electrodes reversible to the chloride and sodium ion constituents, in this case silver–silver chloride and sodium amalgam electrodes. Amalgam electrodes, however, require elaborate experimental technique and are limited in the concentration range in which they can be used.

Although it is rarely possible to find electrodes for both ions of a binary electrolyte which are reversible and at the same time convenient to work with experimentally, suitable electrodes for one of the ion constituents are much more frequently available. With such electrodes, cells with liquid junctions can be set up. A cell of this type and the one that is the subject of this research is the following

Ag; AgCl, NaCl (C_1): NaCl (C_2), AgCl; Ag (B)

If the transference number t_i is a constant in the concentration range C_1 to C_2 the activity ratio can be computed from the equation

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[1] National Research Council Fellow during the progress of this research.

$$E_l = -\frac{2t_lRT}{F}\log\frac{a_1}{a_2} \qquad (1)$$

in which E_l is the potential of a cell of type B and a_1 and a_2 are the mean ion activities at the concentrations C_1 and C_2. In general, however the transference number is a function of the concentration, in which case equation (1) must be replaced by

$$E_l = -\frac{2RT}{F}\int_{\mathrm{I}}^{\mathrm{II}} t_l d\log a \qquad (2)$$

the integration being from solution I to solution II.

Although equation (2), or the differential form of it, has been used to obtain transference numbers from e. m. f. data by MacInnes and Beattie, Jones and Dole, Jones and Bradshaw,[2] and others, it does not appear to have been used for the purpose of obtaining activity coefficients from e. m. f. and transference data. This is undoubtedly due to the fact that determinations of transference numbers of adequate accuracy have not been available. The recent development, mainly in this Laboratory, of the moving boundary method has, however, placed at our disposal transference numbers of high precision, measured over a range of concentrations.[3] Furthermore, it has been shown that transference numbers obtained by the moving boundary method agree with the more recent results obtained by the Hittorf method.[4]

Values of the transference number at concentrations so low that direct measurement is inconvenient or impossible can be obtained by interpolating between the measured values and a limiting value at infinite dilution obtained with the aid of Kohlrausch's law of independent ion mobilities. Using a method of extrapolation, the details of which are given elsewhere,[5] which is in accord with the assumption that the Onsager[6] equation is valid for very dilute solutions of electrolytes, the same value for the limiting conductance of the chloride ion, $\Lambda_{0\mathrm{Cl}}$, was obtained from conductance and transference data on solutions of four chlorides. The limiting value of the transference number, $t_{0\mathrm{Cl}}$, is, of course, given by the ratio $t_{0\mathrm{Cl}} = \Lambda_{0\mathrm{Cl}}/\Lambda_{0\mathrm{MCl}}$ in which $\Lambda_{0\mathrm{MCl}}$ is the limiting conductance of the salt MCl. In addition Longsworth[7] has developed an equation, connecting the observed transference number with the concentration, which is useful for interpolation and which gives an extrapolation to infinite dilution in accord with the same assumptions.

It should be recalled that the potential of a cell containing a liquid junction of the type

$$\mathrm{NaCl}\,(C_1) : \mathrm{NaCl}\,(C_2)$$

is independent of the manner in which the junction is made, and has a definite constant value. This has been tested recently by Scatchard and Buehrer,[8] who, as a matter of fact, found a very small change of potential (of the order of 0.03 mv.) when a flowing junction between 7.3 and 0.1 N hydrochloric acid was allowed to become diffuse by stopping the flow. This slight effect they attribute to temperature gradients in the flowing boundary due to dilution caused by the relatively rapid diffusion. The potentials of the stationary boundaries were found to be constant within the small experimental error. New experimental evidence concerning the constancy and reproducibility of the cell potentials will be discussed later in this article.

Apparatus

The apparatus used in measuring the potentials of cells of type B is shown, in position for filling, in Fig. 1. The two half-cells, A and B, containing the concentrated and dilute solutions, respectively, are made of Pyrex glass. These half-cells are filled through the tubes C and C′. Rinse solutions and excess pass out through tubes D and D′. The half-cell B and the tube D are fitted through holes in the plate glass disk F, and A and D′ pass through holes in the disk G. The electrodes E and E′, of a special form to be described below, are supported in rubber stoppers which fit snugly into the tops of the two half-cells. Air remaining in the upper portions of the half-cells can be removed through holes (not shown) in the rubber stoppers. These holes are normally fitted with glass plugs. After filling the apparatus, the tubes C and C′ are closed with small cork stoppers, and the liquid junction is formed by rotating the upper plate glass disk F until half-cell B is directly over half-cell A. The plate glass surfaces are lubricated with a mixture of vaseline, paraffin and para rubber which had been repeatedly extracted with conductivity water.

With the clean dry apparatus in the position shown in the figure the two cells were each rinsed five times with the appropriate solution. The electrodes were then inserted and the tubes C and C′ were connected to the solution containers to be described below. Each half-cell was then filled with the solution. This was replaced with nitrogen,

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[2] MacInnes and Beattie, THIS JOURNAL, **42**, 1117 (1920); Jones and Dole, *ibid.*, **51**, 1073 (1929); Jones and Bradshaw, *ibid.*, **54**, 138 (1932).

[3] (a) Longsworth, *ibid.*, **54**, 2741 (1932); (b) MacInnes and Longsworth, *Chem. Rev.*, **11**, 171 (1932). The last mentioned paper gives a comprehensive review of the method.

[4] MacInnes and Dole, THIS JOURNAL, **53**, 1357 (1931); also see (3) Ref. b, p. 213, where it is shown that the recent moving boundary results on lithium chloride agree closely with the careful measurements with the Hittorf method on the same salt made by Jones and Bradshaw, THIS JOURNAL, **54**, 138 (1932).

[5] MacInnes, Shedlovsky and Longsworth, *ibid.*, **54**, 2758 (1932).

[6] Onsager, *Physik. Z.*, **28**, 277 (1927).

[7] Longsworth, THIS JOURNAL, **54**, 2741 (1932).

[8] Scatchard and Buehrer, *ibid.*, **53**, 574 (1931).

the cell again refilled and allowed to stand for thirty minutes, before the final replacement with nitrogen and refilling.

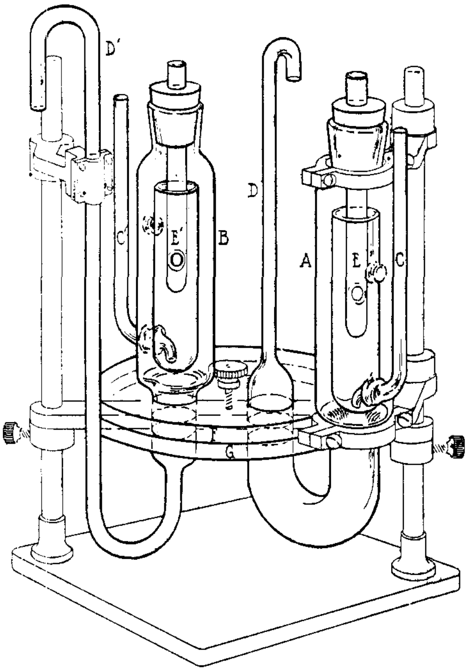

Fig. 1.

The electrodes were made by the electrolytic formation of chloride on silver-plated platinum wires. The details of this process and the reproducibility of the resulting electrodes are discussed in a recent paper from this Laboratory.[9] It was found, however, that the electrodes are much affected by any mechanical disturbance of their active surfaces. To overcome this difficulty the electrodes were mounted as shown in Fig. 2. The inner tube a and the outer tube b held mercury which served for electrical connection with the electrodes e and e'. The active surfaces of these electrodes were protected by an extension of the outer tube b. Holes were, however, provided in this tube as shown to permit free access of solution to the electrodes.

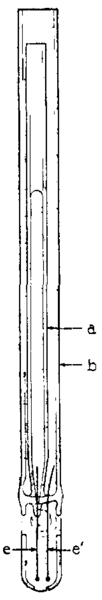

Fig. 2.

The solutions were made up by weight to approximately round molalities in one-liter Pyrex flasks fitted with ground-glass stoppers. These flasks had been carefully cleaned and then subjected to prolonged steaming. A certain amount of contamination (presumably due to carbon dioxide) from the laboratory air was unavoidable. Repeated tests showed that the effect on the specific conductance of various sources of contamination could be reduced to about $3 \times 10^{-7}\ \Omega^{-1}$ by passing a stream of carefully purified nitrogen through the solutions from twenty to thirty minutes. This produced an average increase in concentration of 0.02%, as was shown by conductivity measurements. The arrangement by which this sweeping out of the solutions could be accomplished, and the cell shown in Fig. 1 filled, without exposing the solutions to laboratory air, is shown in Fig. 3. The ground-glass stopper carrying the various tubes is interchangeable with the regular stopper of the flask. Nitrogen is passed into the system by means of the tube marked N_2, and the exit tube A is connected by means of a short piece of para rubber tubing with one of the tubes C or C' of Fig. 1. With the stopcock S open, nitrogen passes through the solution and through the cell. With this stopcock closed, solution is forced into the cell through the tube A. The tube R is furnished as an exit for either solution or nitrogen, and is normally fitted with a rubber tube and pinchcock. It will be observed that with this arrangement solution need not come in contact with lubricating grease either at the flask stopper or the stopcock. This is important as we have found that the silver–silver chloride electrodes are very sensitive to traces of such grease, which may be carried to them by the solution.

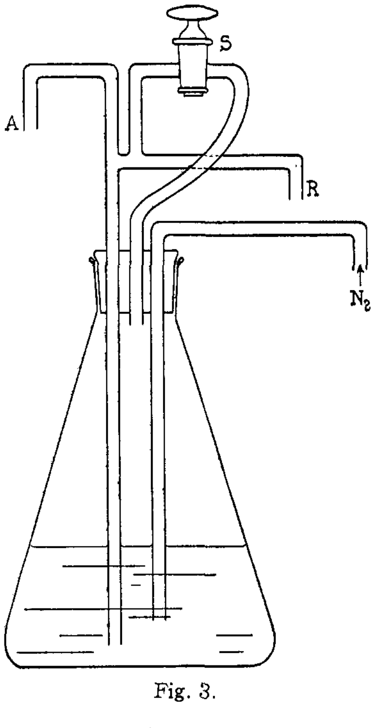

Fig. 3.

The potentiometer used was of the Leeds and Northrup "Type K" form, and had been calibrated with the aid of a Mueller bridge certified by the Bureau of Standards. The "one-tenth" scale range was used in all the measurements. The standard cell used was compared at intervals with five Weston saturated cells which had been standardized by the same Bureau.

The apparatus was immersed in an oil thermostat which was maintained at 25 ± 0.02°. The thermometer was compared with a platinum resistance thermometer that had been calibrated at the ice, steam and sulfur points by Dr. Shedlovsky of this Laboratory.

Materials

A high grade of commercial sodium chloride was further purified by precipitation with hydrogen chloride gas.

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[9] Brown, THIS JOURNAL, 56, 646 (1934).

This was followed by several washings with conductivity water and filtration through sintered glass. After a preliminary drying in an electric oven the resulting salt was fused in a modified Richards bottling apparatus.[10] Stock solutions (0.3 to 0.4 *N*) were prepared by weight. These solutions were neutral to bromothymol blue.

Conductivity water was used in preparing all the solutions. As collected from the still it had a specific conductance of 1 to 3 × $10^{-7}\ \Omega^{-1}$.

Experimental Results

The potential of the concentration cell was determined twice for each pair of solutions used. During the first determination a pair of electrodes, which we will call 1 and 2, was in the dilute solution and the pair of electrodes, 3 and 4, was in the concentrated solution. In the second determination the pairs of electrodes were in the reverse positions. Typical readings for one pair of solutions are given in Table I. In separate determinations the mean deviation from the average was about 0.002 mv. The average difference between determinations with electrodes in reversed positions was about 0.02 mv. If the electrodes retain their potentials relative to each other when transferred from one solution to another, which seems to be the case, this method of averaging the results should, almost completely, eliminate the effect of individual deviations of the electrodes. During each determination the potentials were followed until they did not vary more than 0.001 mv. per hour over a two-hour period, which required from three to six hours.

TABLE I

MEASUREMENTS AT 25° OF THE POTENTIAL OF THE CONCENTRATION CELL

Ag; AgCl, NaCl (0.099533): NaCl (0.0069785), AgCl; Ag

First determination		Second determination		Average
Electrodes	Potential, mv.	Electrodes	Potential, mv.	potential, mv.
1–3	−49.892	3–1	−49.927	−49.910
1–4	−49.883	4–1	−49.935	−49.909
2–3	−49.897	3–2	−49.924	−49.910
2–4	−49.887	4–2	−49.932	−49.910

The results of all the determinations are collected in Table II. The first two columns give the concentrations (gram equivalents per liter of solution at 25°) of the solutions. The measured potentials are given in the third column. The concentrations in Table II were obtained from measurements of the conductances of the solutions as they were introduced into the concentration cell. Actually, the solutions were first prepared, close to a round value of the molality, by careful weighing of the salt and water. On sweeping out the resulting solution with nitrogen, however, it was shown by conductance measurements that a slight change of concentration, of the order of 0.02%, had occurred, and these corrected concentrations appear in the table. The conductance data, at short intervals of concentration, so that precision interpolation was possible, have been published elsewhere.[11]

TABLE II

POTENTIALS AT 25° OF THE GALVANIC CELL

Ag; AgCl, NaCl (C_1): NaCl (C_2), AgCl; Ag

C_1	C_2	Observed potential, mv.
0.099548	0.079666	− 4.05$_6$
.099554	.059766	− 9.31$_4$
.099570	.049833	−12.69$_2$
.099559	.039882	−16.80$_6$
.099554	.029885	−22.19$_3$
.099570	.019937	−29.80$_4$
.099537	.0099654	−43.04$_5$
.099555	.0099672	−43.04$_0$
.099570	.0099654	−43.02$_5$
.099533	.0069785	−49.91$_0$
.099537	.0049829	−56.46$_0$
.049826	.0099697	−30.34$_9$

Since the potentials given in Table II are to be used to compute the thermodynamic activity coefficients of sodium chloride, it was important to find out whether, as the theory of the mechanism of the cells would indicate, such potentials are independent of the method of forming the liquid junction and of diffusion after the junction is formed. The predictions of the theory are, as a matter of fact, entirely fulfilled. The evidence is as follows. (a) The reproducibility of the cell measurements is of the same order as that of the silver–silver chloride electrodes, *i. e.*, 0.01 mv., and the potentials of individual cells were constant, within a few thousandths of a millivolt, for many hours. (b) The potentials are additive. Thus, for instance, the sum of the potentials, from Table II, for the molality ranges 0.1 to 0.05 and 0.05 and 0.01 is 43.041 mv., whereas the potential for the range 0.1 to 0.01 is −43.029 mv. (c) Using an apparatus we will not take the space to describe, it was possible to set up cells having the composition

Ag; AgCl, NaCl (0.1 *M*): NaCl (0.2 *M*): NaCl (0.04 *M*), AgCl; Ag

Ag; AgCl, NaCl (0.1 *M*): NaCl (0.1 *M*): NaCl (0.04 *M*), AgCl; Ag

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[10] Richards and Parker, *Proc. Am. Acad. Sci.*, **32**, 59 (1896).

[11] Shedlovsky, Brown and MacInnes, *Trans. Am. Electrochem. Soc.*, **66**, 165 (1934).

These two cells gave the same potential within 0.003 mv. (d) At the conclusion of some of the measurements the liquid junctions were disturbed by applying an intermittent gas pressure to the filling tubes C and C′ of Fig. 1. The changes of potential observed were of the order of 0.003 mv. It would appear therefore that the potential of the type of concentration cell that we are dealing with depends only on the concentrations of the solutions in contact with the electrodes and is independent of the distribution of the concentration gradients in the connecting solution.

Discussion

Before using the data in Table I for interpretation in terms of the Debye–Hückel theory it was important to investigate and correct for effect of the slight but unavoidable contaminations of the solutions. By means of the manipulations outlined earlier in this article such contaminations were kept down to a point at which they accounted for increases in the specific conductance of the solutions of only $3 \pm 1 \times 10^{-7}$ Ω^{-1}. This was estimated by treating pure conductivity water in the same manner as the solutions, and also by the comparison of solutions, made up as described earlier in this article, with another series of conductance measurements going on in the laboratory at the same time. The contamination is principally due to minute traces of salts since the solutions as used were found to be neutral to isohydric indicators, carbon dioxide having been swept out by means of purified nitrogen.

For the purpose of estimating the effect of impurities on the potential of a concentration cell of the type we are studying, equation (2) may be modified as follows

$$-E^a = \int \frac{RT}{F} [t_{\mathrm{Na}}{}^a \, \mathrm{d} \ln a_{\mathrm{Na}} + (1 - t_{\mathrm{Cl}}{}^a) \, \mathrm{d} \ln a_{\mathrm{Cl}} + t_{\mathrm{i}}{}^+ \, \mathrm{d} \ln a_{\mathrm{i}}{}^+ - t_{\mathrm{i}}{}^- \, \mathrm{d} \ln a_{\mathrm{i}}{}^-] \quad (3)$$

In this expression E^a is the measured potential of the cell, $t_{\mathrm{Na}}{}^a$ and $t_{\mathrm{Cl}}{}^a$ are the actual transference numbers of the sodium and chloride ions, and $t_{\mathrm{i}}{}^+$ and $t_{\mathrm{i}}{}^-$ the transference numbers of the positive and negative ions of the contaminating salt, assumed to consist of univalent ions. These contaminating ions are assumed, further, not to react at the electrodes. The last two terms are small and tend to cancel, the main effect of the presence of the impurities being that of influencing the values of $t_{\mathrm{Na}}{}^a$ and $t_{\mathrm{Cl}}{}^a$. If the impurity is assumed to be a heterionic salt the actual transference numbers can be obtained with sufficient accuracy by $t_{\mathrm{Na}}{}^a = t_{\mathrm{Na}}(\kappa/\kappa^a)$ and $t_{\mathrm{Cl}}{}^a = t_{\mathrm{Cl}}(\kappa/\kappa^a)$ in which κ^a represents the specific conductance of the actual solution, and κ that of the pure solution. Thus equation (3) becomes

$$-E^a = \int \frac{RT}{F} \left[t_{\mathrm{Na}} \frac{\kappa}{\kappa^a} \mathrm{d} \ln a_{\mathrm{Na}} + \left(1 - \frac{\kappa}{\kappa^a} t_{\mathrm{Cl}}\right) \mathrm{d} \ln a_{\mathrm{Cl}} \right] \quad (4)$$

If E is the potential of the corrected (uncontaminated) cell then the correction ΔE_{i} is

$$\Delta E_{\mathrm{i}} = E - E^a = \frac{RT}{F} \int_{a_1}^{a_2} \left[\left(1 - \frac{\kappa}{\kappa^a}\right) t_{\mathrm{Na}} \, \mathrm{d} \ln a_{\mathrm{Na}} - \left(1 - \frac{\kappa}{\kappa^a}\right) t_{\mathrm{Cl}} \, \mathrm{d} \ln a_{\mathrm{Cl}} \right] \quad (5)$$

Setting $\kappa^a = \kappa + \kappa_{\mathrm{i}}$, where κ_{i} is the specific conductance due to the contamination

$$\Delta E_{\mathrm{i}} = -\frac{RT}{F} \int \frac{\kappa_{\mathrm{i}}}{\kappa_a} [t_{\mathrm{Na}} \, \mathrm{d} \ln a_{\mathrm{Na}} - t_{\mathrm{Cl}} \, \mathrm{d} \ln a_{\mathrm{Cl}}] \quad (6)$$

Replacing activities by concentrations and setting C_{Na} and $C_{\mathrm{Cl}} = 1000 \, \kappa^a/\Lambda$ and assuming an average value of $\Lambda = 120$ and $t_{\mathrm{Na}} - t_{\mathrm{Cl}} = -0.214$ then

$$\Delta E_{\mathrm{i}} = \kappa_{\mathrm{i}} \times 47 \left[\frac{1}{C_1} - \frac{1}{C_2}\right] \text{millivolts} \quad (7)$$

For a value of κ_{i} of 3×10^{-7} the maximum correction to be applied to a measurement is that of +0.003 mv. to the potential of the cell having the concentration range 0.1 to 0.005, and the corrections are, of course, progressively smaller as the concentration of the more dilute solution is increased. Though this just reaches the experimental error, we feel that it is important to demonstrate the fact. The correction will become increasingly important when more dilute solutions are studied.

Similar reasoning indicates that (a) an impurity consisting of a sodium salt other than a chloride has practically the same effect on the potential as a heterionic salt, (b) that the effect of the presence of a small amount of another chloride than sodium is nearly zero, and (c) that if the impurity is sodium chloride the effect on the potential is −0.20 and +0.20 mv. for 1% increase in concentration, respectively, for the dilute and concentrated solutions. This last result can be used to correct the observed potentials in Table II for small deviations from round values of the molality. These small corrections and the solvent correction have been made to the e.m.f. values in the third column of Table III. The largest value of the total of these corrections is only 0.012 mv. for the cell containing the most dilute solution.

As explained in the introduction to this paper the purpose of this investigation was to obtain activity coefficients from data on the potentials of concentration cells "with transference." The essential data for the computation are gathered in Table III. The molalities are given in the first column and the corresponding normalities (volume concentrations) in the second column. The transference numbers at each concentration were obtained from the data of Longsworth,[12] using in the interpolation and extrapolation an equation given by that author.

According to equation (2) the potential of the cell

Ag; AgCl, NaCl (C_1): NaCl (C_2), AgCl; Ag

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[12] Longsworth, THIS JOURNAL, **54**, 2741 (1932).

is the integral of

$$\begin{aligned} dE &= -(2RT/F)\,t_{\text{Na}}\,d\log a \qquad (8)\\ &= -(2RT/F)\,t_{\text{Na}}\,(d\log C + d\log f) \end{aligned}$$

in which C is the salt concentration, f the mean activity coefficient, and t_{Na} the transference number of the sodium ion constituent. The use of this equation for the determination of the activity coefficients from the electromotive force data is complicated by the fact that the transference number t_{Na} varies with the concentration C. It would, of course, be possible to express both t_{Na} and E as analytic functions of C, but the resulting equations are unwieldy. We have therefore used the following method of computation, for which we are indebted to Dr. L. G. Longsworth.

The transference number at any concentration may be expressed by

$$t_{\text{Na}} = t_1 + \Delta t$$

t_1 being the transference number at some reference concentration, in this case 0.1 N. If the potentials are stated in millivolts at 25° equation (8) becomes

$$dE = -2 \times 59.144\,(t_1 + \Delta t)\,(d\log C + d\log f) \qquad (9)$$

Expanding and rearranging we obtain

$$-dE/118.29\,t_1 = d\log C + \Delta t/t_1 \cdot d\log C + d\log f + \Delta t/t_1 \cdot d\log f \qquad (10)$$

Integrating and again rearranging yields

$$\Delta\log f = \log f_2 - \log f_1 = \frac{-E}{118.29\,t_1} - (\log C_2 - \log C_1) - \frac{1}{t_1}\int_1^2 \Delta t\,d\log C - \frac{1}{t_1}\int_1^2 \Delta t\,d\,\Delta\log f \qquad (11)$$

Of the four terms on the right-hand side of this equation the first two are computed directly from the data. The third term is obtained by graphical integration, using a plot of Δt values against values of log C. The fourth term, of relatively small magnitude, is obtained by graphical integration using preliminary values of Δ log f, obtained by adding the first three terms of the equation, and plotting against Δt. This process could be repeated with more accurate values of $\Delta \log f$ but a further approximation was not found to be necessary. The resulting values of Δ log f are given in the fifth column of Table III.

To provide a basis for the activity coefficients, f, such that they will approach unity as the concentration is progressively decreased, use can be made of the familiar equation of the Debye–Hückel theory

$$-\log f = \alpha\sqrt{C}/(1 + \beta\sqrt{C}) \qquad (12)$$

in which α depends upon the temperature, the dielectric constant and universal constants, and β depends upon these factors, and, in addition, upon the distances of closest approach of the ions. This equation is valid for dilute solutions containing relatively large ions. To use this equation (12) with the data in Table III the following procedure was found to be convenient. We may set

$$\log f = A - \Delta\log f \qquad (13)$$

in which A is a constant. Combining equations (12) and (13) and rearranging terms

$$\Delta\log f - \alpha\sqrt{C} = A + \beta(A - \Delta\log f)\sqrt{C} \qquad (14)$$

Thus, through the range of validity of equation (12) a plot of $\Delta\log f - \alpha\sqrt{C}$ against $(A - \Delta\log f)\sqrt{C}$ should be a straight line with intercept A and slope β. The constant A is obtained by means of a short series of approximations. Using a value of $\alpha = 0.5056$ at 25° this computation yields a value of A of -0.1081 and of β of 1.463. This value of β corresponds to a distance of closest approach of 4.45 Å., which is sufficiently large for the higher terms of the extended theory of Gronwall, La Mer and Sandved[13] to be negligible.

Another method for carrying out the extrapolation has been suggested by Hitchcock,[14] which consists in the use of the equation

$$-\log f = +\alpha\sqrt{C} - BC \qquad (15)$$

instead of equation (12). A combination of this equation with equation (13) indicates that, if valid, a plot of $\Delta\log f - \alpha\sqrt{C}$ against C should be linear, the intercept and slope giving the parameters A and B, respectively. However, when the data in Table III are treated in this way the resulting line shows a distinct curvature throughout its whole length, making an accurate extrapolation impossible. The plot also shows that equation (15), which is obtained from equation (12) by expanding and neglecting higher terms, does not represent the data in the lower concentration range with sufficient accuracy.

In columns 6 and 7 of Table III are given the observed activity coefficients and those computed from equation (12). It will be observed that the agreement of the corresponding values is excellent up to a concentration of 0.04 or 0.05, above which there is a progressive deviation. For solutions of higher concentrations Hückel[15] has proposed an equation of the form

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(13) Gronwall, La Mer and Sandved, *Physik. Z.*, **29**, 358 (1928).

(14) Hitchcock, THIS JOURNAL, **50**, 2076 (1928).

(15) Hückel, *Physik. Z.*, **26**, 83 (1925).

TABLE III

THE COMPUTATION OF ACTIVITY COEFFICIENTS OF SODIUM CHLORIDE AT 25°

Molality m	Normality C	E. m. f., mv.	Trans. no. t_{Na}	Log activity coeff. ratio, $\Delta \log f$	Activity coefficients		
					f (obsd.)	f (computed equation (12))	f (computed equation (17))
0.005	0.0049849	−56.450	0.39304	−0.0758	0.9283	0.9281	0.9281
.007	.0069786	−49.907	.39249	− .0705	.9171	.9171	.9169
.01	.0099670	−43.029	.39183	− .0640	.9034	.9036	.9034
.02	.0199344	−29.804	.39024	− .0489	.8726	.8726	.8724
.03	.029897	−22.181	.38914	− .0382	.8513	.8515	.8515
.04	.039855	−16.818	.38828	− .0300	.8354	.8354	.8354
.05	.049810	−12.695	.38760	− .0230	.8221	.8221	.8224
.06	.059762	− 9.317	.38700	− .0176	.8119	.8110	.8115
.08	.079655	− 4.056	.38609	− .0079	.7940	.7925	.7938
.1	.099533	0	.38545	0	(.7796)	.7779	.7796

$$\log f = -\frac{\alpha\sqrt{C}}{1+\beta\sqrt{C}} + DC \qquad (16)$$

in which D is an additional constant. Using this extra term, agreement between observed and computed values of the activity coefficient is obtained as high as the measurements were made, which was up to 0.1 molar. This can be seen by comparing the values of columns 6 and 8 of Table III. The differences in the observed and computed values are of the order of 0.0002. The more complete equation connecting the activity coefficient and the concentration is

$$\log f = -\frac{0.5056\sqrt{C}}{1+1.315\sqrt{C}} + 0.047\ C \qquad (17)$$

However, as can be seen, to attain this agreement between the observed and computed values of the activity coefficient it was necessary to change the value of β from 1.463 to 1.315. Equally good agreement between observed and computed activity coefficients may be obtained with a range of values of the constants β and D, a decrease in one of them compensating for an increase of the other.

Harned and Nims[16] have recently published data on activity coefficients of sodium chloride solutions based on measurements of concentration cells without liquid junctions, involving amalgam electrodes. Due to the uncertain behavior of these electrodes in dilute solutions the measurements were made in the relatively high concentration range of 0.05 to 4.0 molar. If the results of these measurements are adjusted to the same basis as ours by making them coincide at 0.1 *N*, all the data fall upon a smooth curve, and equation (17) is valid for Harned and Nims' data up to about 0.5 normal. These authors have computed constants for the Hückel equation with which it closely fits their data. These constants are, however, quite different from those we have found for the more dilute solutions.

We expect to continue this work to include other salts for which accurate transference data are available. The relation of activity coefficients determined at 25° by the method described above to coefficients obtained from freezing point measurements will be considered in another paper.

Summary

Accurate values of the activity coefficients of the ions of sodium chloride in aqueous solution at 25° have been determined by a method involving transference numbers and the potentials of concentration cells with transference. The resulting activity coefficients have been found to follow the Debye–Hückel theory to high precision, up to 0.05 *N*, with a "distance of closest approach" of 4.45 Å.

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[16] Harned and Nims, THIS JOURNAL, **54**, 423 (1932).