THE DETERMINATION OF ACTIVITY COEFFICIENTS FROM THE POTENTIALS OF CONCENTRATION CELLS WITH TRANSFERENCE

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The usefulness of Lewis' conceptions of "activity" and "activity coefficients" in the theory of solutions is now generally conceded. As is well known, activities replace concentrations in thermodynamic equations involving the law of mass action if the components are not perfect solutes. Also the variation of an activity coefficient of a component of a solution from unity is a convenient measure of the departure of that component from the behavior of a perfect solute. A very considerable progress was made when these empirical functions were expressed, by Debye and Hückel, in terms of the electrical state of the solution. According to their theory the variation, from unity, of the activity coefficients of the ion constituents of electrolytes is due to attractions and repulsions of oppositely and like charged particles. Charged particles will tend to arrange themselves, if undisturbed, in regular geometrical order, giving a "lattice structure." Such an arrangement will, however, be continuously disordered by the thermal vibration of the particles. The result of these two opposing effects is that the Gibbs free energies of the ion constituents will be smaller than if the ions were uncharged, and the activity coefficients will, accordingly, be less than unity. Although there remains little doubt that the fundamental assumptions of Debye and Hückel are correct, there is a comparatively small amount of experimental data suitable for testing the theory, particularly in the region of low ion concentrations where their equations are expected to be valid. In dilute solutions complicating secondary effects, not considered in the theory, are most likely to be absent.

Of the various methods available for obtaining activity coefficients, the one depending upon the determination of the potentials of concentration cells is, when applicable, the most convenient and accurate. In contrast to freezing points or boiling points, the measurements are isothermal, and can be carried out at any temperature at which the existence of the cell is physically possible. The concentration cell procedure is superior to these and the vapor pressure method, 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 the electromotive force method, in that reversible electrodes are necessary for the ion constituents of the solute electrolyte. Thus, for sodium chloride solutions, a concentration cell without liquid junction, of which the following is a typical example

$$\text{Ag; AgCl, NaCl}(C_1)\text{; NaHg}_x - \text{NaHg}_x\text{; NaCl}(C_2)\text{, AgCl; Ag} \qquad \text{(Cell A)}$$

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, concentration cells with liquid junctions can be set up. A cell of this type is the following

$$\text{Ag; AgCl, NaCl}(C_1) : \text{NaCl}(C_2)\text{, AgCl; Ag} \qquad \text{(Cell B)}$$

Another cell of this kind is

$$\text{Ag; AgNO}_3(C_1) : \text{AgNO}_3(C_2)\text{; Ag} \qquad \text{(Cell C)}$$

For silver nitrate as solute a concentration cell without liquid junction is impossible, since no electrode reversible to the nitrate ion is available. The experimental work so far carried out has been on cells B and C at 25°C.

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

$$E = -\frac{2tRT}{F} \log \frac{a_1}{a_2} \tag{1}$$

in which E is the potential of a cell of the type represented by B and C, 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

$$E = -\frac{2RT}{F} \int_{\text{I}}^{\text{II}} t \, \mathrm{d} \log a \tag{2}$$

the integration being from solution I to solution II.

The validity of equation 2 will be evident from the following considerations. If the cell

$$\text{Ag; AgCl, NaCl}(\mu) : \text{NaCl}(\mu + \mathrm{d}\mu)\text{, AgCl; Ag} \qquad \text{(Cell D)}$$

is set up its potential dE is

$$-F\,\mathrm{d}E = t_{\mathrm{Na}}\mathrm{d}\mu$$

Here NaCl (μ) represents a solution of sodium chloride, the chemical potential of the solute of which is μ, and t_{Na} is the number of equivalents per faraday transferred from the higher to the lower concentration during the reversible operation of the cell. It will be noted that the operation of cell D is, differentially and reversibly, the opposite of the usual process for determining the Hittorf transference number t_{Na}. If now a second cell is made as follows

$$\text{Ag; AgCl, NaCl}(\mu + \mathrm{d}\mu) : \text{NaCl}(\mu + \mathrm{d}\mu + \mathrm{d}\mu'),\ \text{AgCl; Ag} \qquad \text{(Cell E)}$$

its potential dE' can be obtained from

$$-F\mathrm{d}E' = t'_{\mathrm{Na}}\mathrm{d}\mu'$$

in which t'_{Na} may have a slightly different value from t_{Na}. If cells D and E are put in series the potentials of the electrodes in contact with solutions of like chemical potential will cancel, and the resulting cell will have the same potential as one having the composition

$$\text{Ag, AgCl, NaCl}(\mu),\ \text{NaCl}(\mu + \mathrm{d}\mu + \mathrm{d}\mu'),\ \text{AgCl, Ag} \qquad \text{(Cell F)}$$

Such a series of cells could, of course, be continued indefinitely, from which it follows that

$$\sum - \mathrm{d}E = \int - \mathrm{d}E = -\frac{1}{F}\int t_{\mathrm{Na}}\,\mathrm{d}\mu = \frac{2RT}{F}\int t_{\mathrm{Na}}\,\mathrm{d}\log a$$

the last term following from the conventional definition of mean ion activity.

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 (4, 5, 8), 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 (7, 10). 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 (9).

Values of the transference number of the chloride ion in sodium chloride 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 (11), which is in accord with the assumption that the Onsager (12) equation is valid for very dilute solutions of electrolytes, the same value for the limiting conductance of the chloride ion, Λ_{0Cl}, was obtained from conductance and transference data on solutions of four chlorides. The limiting value of the transference number, t_{0Cl}, is, of course, given by the ratio $t_{0Cl} = \Lambda_{0Cl}/\Lambda_{0MCl}$ in which Λ_{0MCl} is the limiting conductance of the salt MCl. In addition Longsworth (6) 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. For the transference number of the nitrate ion in silver nitrate solutions the limiting value was obtained from Kohlrausch's law, and a simple linear equation was found to hold for this and all the measured values.

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

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

where two solutions of the same electrolyte but at different concentrations meet at the boundary, is independent of the manner in which the junction is made, and has a definite constant value. This has been tested by Scatchard and Buehrer (13), 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.

EXPERIMENTAL

For the determination of the potentials of concentration cells with liquid junction involving silver nitrate as solute (type C), the vessels shown in figure 1 were used. The more dilute solution filled the half-cell B and the more concentrated the half-cell A. The electrodes e and e′ were formed from platinum wires plated with silver. The wires were sealed through narrow tubing, leaving about 1 cm. exposed. Electrical contact was made with mercury. Comparisons of the electrodes in the same silver nitrate solution showed variations of about ±0.02 mv. The data given in table 1 were obtained in this laboratory by Dr. Philip G. Colin. Each reading for an electromotive force is the average of nine readings, using the various possible combinations of electrodes in the two half-cells. After making the liquid junction by bringing the two solutions into contact, the cell reached its final potential immediately and held it with variations of the order of ±0.01 mv. for three hours or longer. The results are additive within the same limit of accuracy. Thus the potential of the combination 0.01 N–0.002 N is 42.56 mv., whereas the sum of the potentials for the

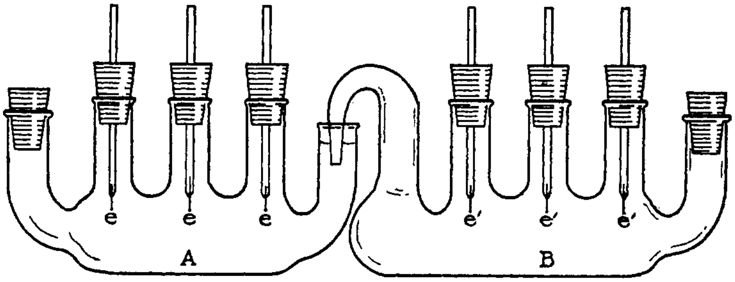

Fig. 1

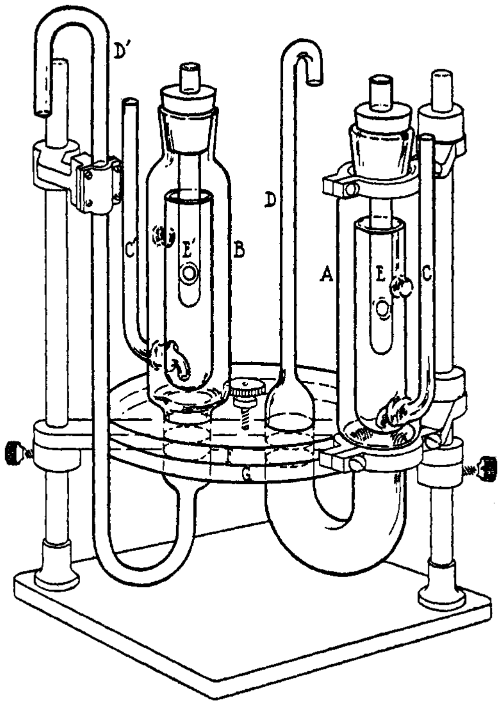

Fig. 2

combinations 0.01 N–0.005 N and 0.005 N–0.002 N is 42.55 mv. Measurements on cells of type C have been made by earlier workers. Their results are, however, very scattered and inaccurate.

A considerable advance in experimental technique was made for the measurement of the concentration cells with liquid junction involving sodium chloride as solute (cells of type B). Since the improved technique has been described in a recent article (1) it will be merely outlined in this place. The apparatus used is shown in figure 2, in position for filling with the solutions. This filling is carried out without bringing the solutions into contact with air, through the tubes C and C′. Contact between the two solutions is produced by rotating the disk F, in a counter-clockwise direction, over the disk G. The potentials are then measured between the electrodes E and E′. For the methods for avoiding contaminations that would affect the results, and for correcting for the unavoidable small amounts of such contaminations, the reader is referred to the original article. Dr. Theodore Shedlovsky has devised a much simpler type of cell which will replace that shown in figure 2 in our future work, which will include measurements on most of the commoner electrolytes. A confirmatory series of determinations of the potential of the silver nitrate concentration cells will shortly be made, using the modified technique.

THE COMPUTATION OF THE ACTIVITY COEFFICIENTS

To compute activity coefficient ratios from cells with transference, it is necessary to perform the indicated integration of equation 2 which may be written in the form:

$$E = -\frac{2RT}{F}\int_{\mathrm{I}}^{\mathrm{II}} t\,(\mathrm{d}\log C + \mathrm{d}\log f) \tag{3}$$

in which C is the salt concentration, f the mean activity coefficient, and t the transference number of the ion to which the electrodes are *not* reversible. This integration has been carried out (a) by introducing E and t as empirical functions of C, and (b) by a method which is partly graphical. Method a cannot conveniently be used unless the empirical equations are relatively simple. For the case of cells involving silver nitrate, simple equations represent the data with accuracy, so that the method can be used as well as method b, which is general. The empirical equations for the sodium chloride data are unwieldy, so that method b only is available.

Method a. The potentials of the silver nitrate concentration cells, given in table 1, may be expressed with an accuracy of ±0.02 mv. by an equation of the form

$$E = 2t_0\frac{RT}{F}\log C + AC^n + K \tag{4}$$

with the following numerical coefficients

$$0.001E = 0.063373 \log C + 0.02374C^{0.42} + 0.17279 \tag{5}$$

In these equations t_0 is the limiting value of the transference number of the nitrate ion, and E is the "summed up" potential for the concentration 0.002 N to C. Thus E corresponding to 0.1 N consists of the sum of the potentials for the cells containing the solutions 0.002 N to 0.01 N and 0.01 N to 0.1 N. The measured values of E and the corresponding values from equation 5 are given in the second and third columns of table 2.

TABLE 1

The potentials of silver nitrate concentration cells at 25°C.

C_1	C_2	E.M.F.
moles per liter	*moles per liter*	*mv.*
0.10	0.05	16.78
0.05	0.01	41.03
0.05	0.02	23.04
0.02	0.01	17.99
0.01	0.005	18.15
0.01	0.002	42.56
0.005	0.002	24.40

TABLE 2

Computations of the activity coefficients of silver nitrate in aqueous solution at 25°C.

C	$E_{\text{obsd.}}$	$E_{\text{calcd.}}$	f/f_0 BY METHOD a	$f/f_{0.1}$ BY METHOD b	$f_{\text{obsd.}(a)}$	$f_{\text{obsd.}(b)}$	$f_{\text{calcd.}}$ EXTENDED THEORY
moles per liter	*mv.*	*mv.*					
0.002	0.00	0.00	0.939	1.295_2	0.949	0.950	0.950
0.005	24.40	24.40	0.911	1.257_7	0.922	0.922	0.922
0.01	42.56	42.61	0.883	1.216_6	0.894	0.892	0.894
0.02	60.55	60.53	0.848	1.170_3	0.857	0.858	0.857
0.05	83.59	83.59	0.785	1.083_4	0.794	0.795	0.794
0.10	100.37	100.39	0.725	1.000_0	0.734	0.733	0.735

The transference number of the nitrate ion in silver nitrate can be expressed by the empirical equation

$$t = t_0 - bC \tag{6}$$

$$t = 0.5357 - 0.039C \tag{7}$$

as is shown in table 3, in which the measured transference numbers obtained in this laboratory by Dr. Irving A. Cowperthwaite are given in the second column and the values from equation 7 are given in the third column.

With the use of equations 4 and 6, equation 3 can be put in the form

$$\frac{dE}{t} = 2R' \, d \log Cf = \frac{2t_0R' \, dC}{2.303(t_0 - bC)C} - \frac{nAC^{n-1}}{(t_0 - bC)} dC \tag{8}$$

where R' replaces RT/F. After expanding the second term on the right-hand side, integrating between the limits C and zero, introducing the numerical coefficients from equations 5 and 7 and solving for $\log f/f_0$, we have the equation

$$-\log f/f_0 = \log (1 - 0.07280C) + 0.3746(C^{0.42} + 0.021533C^{1.42} + 0.0008733C^{2.42}) \tag{9}$$

Equation 9 cannot be used for extrapolation, since equation 5 is valid only over the concentration range investigated. Log f_0 is an integration constant which would be zero if the equation held to $C = 0$. The ratios f/f_0 for silver nitrate, given in the fourth column of table 2, were obtained from equation 9.

TABLE 3

Transference numbers for the nitrate ion in silver nitrate solutions

C	$t_{\text{obsd.}}$	$t_{\text{calcd.}}$
moles per liter		
0.10	0.5318	0.5318
0.05	0.5336	0.5337
0.02	0.5348	0.5349
0.01	0.5352	0.5353
0.00	[0.5357]	0.5357

Method b. For our data on sodium chloride concentration cells and transference numbers, given in the first three columns of table 4 (1), the following more general method devised by Dr. L. G. Longsworth for computing the activity coefficients was used. The transference number, t_{Na}, at any concentration may be expressed by

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

t_1 being the value at some reference concentration, in this case 0.1 N. If the potentials are stated in millivolts at 25°C. equation 3 becomes

$$dE = -2 \times 59.144(t_1 + \Delta t)(d \log C + d \log f) \tag{10}$$

Expanding and rearranging we obtain

$$-dE/118.29\, t_1 = d \log C + \Delta t/t_1 \cdot d \log C + d \log f + \Delta t/t_1 \cdot d \log f \tag{11}$$

Integrating and again rearranging yields

$$\Delta \log f = \log f_2 - \log f_1 = \frac{-E}{118.29 t_1} - (\log C_2 - \log C_1)$$

$$- \frac{1}{t_1} \int_{\mathrm{I}}^{\mathrm{II}} \Delta t \; \mathrm{d} \log C - \frac{1}{t_1} \int_{\mathrm{I}}^{\mathrm{II}} \Delta t \; \mathrm{d} \, \Delta \log f \qquad (12)$$

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 $\Delta \log f$, 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 $\Delta \log f$ for sodium chloride are given in the fourth column of table 4.

TABLE 4

The activity coefficients of sodium chloride at 25°C.

NORMALITY C	E.M.F. IN MV.	TRANSFERENCE NO. t_{Na}	LOG ACTIVITY COEFFICIENT RATIO, $\Delta \log f$	ACTIVITY COEFFICIENTS		
				f (obsd.)	f (computed from equation 13)	f (computed from equation 17)
0.004984_9	-56.45_0	0.3930	−0.0758	0.9283	0.9281	0.9281
0.006978_6	-49.90_7	0.3925	−0.0705	0.9171	0.9171	0.9169
0.009967_0	-43.02_9	0.3918	−0.0640	0.9034	0.9036	0.9034
0.019934_4	-29.80_4	0.3902	−0.0489	0.8726	0.8726	0.8724
0.02989_7	-22.18_1	0.3891	−0.0382	0.8513	0.8515	0.8515
0.03985_5	-16.81_8	0.3883	−0.0300	0.8354	0.8354	0.8354
0.04981_0	-12.69_5	0.3876	−0.0230	0.8221	0.8221	0.8224
0.05976_2	-9.31_7	0.3870	−0.0176	0.8119	0.8110	0.8115
0.07965_5	-4.05_6	0.3861	−0.0079	0.7940	0.7925	0.7938
0.09953_3	0	0.3855	0	(0.7796)	0.7779	0.7796

In the fifth column of table 2 values of $f/f_{0.1}$ (i.e., the antilogs of $\Delta \log f$) are given. These were obtained by method *b* from the data on silver nitrate.

THE INTERPRETATION OF THE ACTIVITY COEFFICIENT RATIOS

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

$$- \log f = \alpha \sqrt{C} / (1 + \beta \sqrt{C}) \qquad (13)$$

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 13 with the data in table 4 the following procedure was found to be convenient. We may set

$$\log f = A - \Delta \log f \tag{14}$$

in which A is a constant. Combining equations 13 and 14 and rearranging terms

$$\Delta \log f - \alpha\sqrt{C} = A + \beta(A - \Delta \log f)\sqrt{C} \tag{15}$$

Thus, through the range of validity of equation 13 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°C., 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 (2) to be negligible.

In columns 5 and 6 of table 4 are given the observed activity coefficients and those computed from equation 13. 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 (3) has proposed an equation of the form

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

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 5 and 7 of table 4. 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

$$\log f = -\frac{0.5056\sqrt{C}}{1 + 1.315\sqrt{C}} + 0.047\,C \tag{17}$$

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. It is evident that the Hückel equation is useful for expressing the data, at least in this case, although it is in large measure empirical. The activity coefficients for sodium chloride and their relation to the limiting law

$$-\log f = \alpha\sqrt{C}$$

are shown in figure 3, where the values of $\log f$ are plotted as ordinates against the square root of the concentration as abscissas.

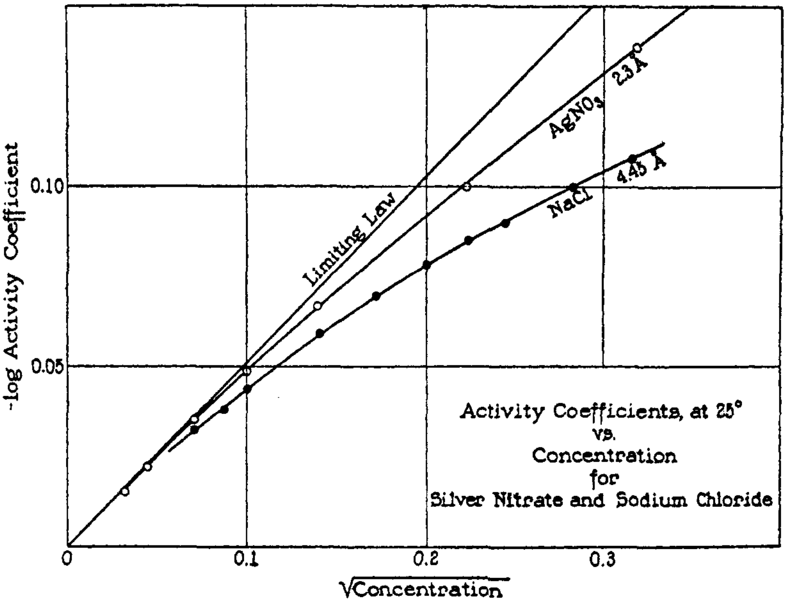

FIG. 3

For the data on silver nitrate equation 13 will express the data with a distance of closest approach of 2.0 Å. However, if that parameter is as small as this preliminary value would indicate, the computations should be made with the more complete theory in the form given it by Gronwall, La Mer, and Sandved (2), who have extended it to include higher terms omitted in the mathematical development in its earlier form. For the details of the calculation the reader is referred to the original article. With the aid of that theory a value of f_0 or $f_{0.1}$ necessary for converting the activity ratios, obtained by methods a and b, respectively, was obtained. The resulting activity coefficients are given in columns 6 and 7 of table 2. It will be observed that the two methods of computation yield practically the same results. Column 8 contains the activity coefficients calculated directly from the extended theory, using a distance of closest approach of 2.3 Å. The agreement between the observed and computed values is excellent. The activity coefficients for silver nitrate are also plotted in figure 3.

SUMMARY

Using a method involving the determination of the potentials of concentration cells with liquid junctions, and of transference numbers, accurate values of the activity coefficients of sodium chloride and of silver nitrate in aqueous solution at 25°C. have been determined. The method requires a type of electrode reversible to only one of the constituents of a binary electrolyte, and thus greatly extends the range of electrolytes for which the concentration cell method is available for obtaining the thermodynamic properties of the substances in solution.

The data on the activity coefficients for sodium chloride follow the Debye-Hückel relations in their original form up to a concentration of 0.05 normal, with a distance of closest approach of 4.45 Å. For the activity coefficients of silver nitrate, however, the extended theory of Gronwall, La Mer, and Sandved should be used. The extended theory accurately expresses the data for that substance if the distance of closest approach of 2.3 Å. is used.

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DISCUSSION

DR. HILDEBRAND: There used to be a great deal of discussion about different methods of setting up a liquid-liquid junction; will you tell us the present answer to the question?

DR. MACINNES: I can give a decisive answer only for the type of junction involved in the cells of the kind discussed in our paper. These, it will be recalled, are of the form:

$$\text{NaCl}(C_1) : \text{NaCl}(C_2) \qquad \text{(Cell A)}$$

in which two solutions *of the same electrolyte* meet at the boundary. It has been found by repeated and careful experiments that potentials of cells involving such liquid junctions are quite independent of the way they are made. There are two qualifications to this statement. One is that the mixed solutions must not reach the electrodes. The other is that large heat effects due to mixing of the solutions at the junction must not occur. We have found that a junction, initially sharp, can be stirred without changing the cell potential. Also we have found that the potential of the cell:

$$\text{Ag; AgCl, NaCl } (0.1\ M) : \text{NaCl } (0.04\ M)\text{, AgCl; Ag} \qquad \text{(Cell B)}$$

was equal within 0.001 mv. to the cell:

$$\text{Ag; AgCl, NaCl } (0.1\ M) : \text{NaCl } (0.2\ M) : \text{NaCl } (0.04\ M)\text{, AgCl; Ag} \qquad \text{(Cell C)}$$

Here it is seen that in cell C a strong solution is interposed between the two solutions in cell B, but that all three solutions are of the same electrolyte.

Theoretically this constancy is due to the fact that the transference number t and the activity a in equation 2 are both functions of the concentration C. From the point of view of the liquid junction, all computations of the potentials of such junctions start from the equation (for uni-univalent electrolytes):

$$FE_j = -RT \int \sum_i t_i \, \mathrm{d} \log a_i$$

in which E_j is the liquid junction potential, t_i and a_i are, respectively, the transference number and the (hypothetical) single ion activity of the ion species i. The summation is over all the ion species present and the integration is from values of the variables corresponding to one of the solutions to those in the other. For liquid junctions of type A, t_i and a_i

are single valued functions of the concentration C for all mixtures of the two solutions in contact, and the integration will therefore be independent of the spatial arrangement of these mixtures. This is not true of junctions of the type

$$\text{NaCl} : \text{HCl} \qquad \text{(D)}$$

for instance. Here the transference numbers and activities will depend upon the way that the two solutions are brought together. This theoretical deduction is also supported by experiment. The potentials of cells involving junctions of type D are dependent upon whether they are sharp, as with a flowing junction, or whether appreciable diffusion has taken place.