

bromide to bromo-acetone. The chloride is then determined gravimetrically as silver chloride.

2. The various errors of the process have been carefully studied.

3. On a 1-g. sample the accuracy of the procedure lies within 0.1%.

4. The rate at which a solution of bromo-acetone reacts with silver nitrate makes the nephelometric method inaccurate for small amounts of chloride.

5. By using a preliminary concentration method samples up to 10 g. can be employed for the accurate analytical testing of high grade reagents.

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THE TRANSFERENCE NUMBER OF BARIUM CHLORIDE AS A FUNCTION OF THE CONCENTRATION

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Introduction

According to the classical electrolytic dissociation theory of Arrhenius the transference number of the ions should be independent of the concentration, but there are numerous well-established exceptions to the old rule. It has been the common practice to explain away the known variation of the transference number with the concentration as due to the presence of complex ions or as due to hydration in amounts which vary with the concentration, but these speculations have as a rule been qualitative only, with little serious attempt to develop a consistent quantitative theory or to express the variation of the transference number quantitatively as a function of the concentration.

The newer theory of complete electrolytic dissociation of Debye and Hückel gives a new point of view for the study of transference numbers. The new theory, unlike the old, does not neglect the electrostatic forces between the ions. According to this theory, at finite concentrations, the interionic forces tend to maintain a space lattice distribution of the ions and to oppose any disturbance of this arrangement by an outside electric field from an electrode and thus decrease the mobility of the ions. Therefore, the velocity of motion of an ion is not proportional to the potential gradient due to the outside electrode alone regardless of the concentration but is a decreasing function of the concentration. Debye and Hückel¹ have derived from this standpoint an equation for the variation of the equivalent conductance of strong electrolytes as a function of the concentration. This equation fits the facts fairly well at extreme dilutions

¹ P. Debye and E. Hückel, *Physik. Z.*, **24**, 185 (1923); **24**, 305 (1923); E. Hückel, *Ergebnisse der Exakten Naturwissenschaften*, **3**, 199 (1924).

(under 0.01 *N*) but fails quantitatively at higher concentrations. Owing to the abundance of relatively reliable conductance data and the scarcity of reliable data on transference numbers, especially at high dilutions, the proponents of this new theory have apparently confined their attention to conductance data in testing the predictions of the theory in regard to ionic migration velocities. The newer theory, however, predicts that the influence of interionic attraction on the mobility is not proportionally the same for all ions but is a function of the size of the ion, of the temperature and of the dielectric constant of the solvent, and especially of the valence. Therefore the new theory, unlike the old, would predict that the transference numbers of ions should be a function of the concentration. So far as we know no one has yet published the derivation from these new premises of an expression for the variation of the transference number as a function of the concentration, valence and nature of the ions.²

The present paper records the first results of an attempt to study experimentally the variation of transference numbers with concentration and to determine the factors which influence this variation.

Experimental Part

Analytical Method.—The best available barium chloride was dissolved in hot water, filtered, precipitated by adding pure, freshly distilled alcohol, dried in a centrifuge, recrystallized from water, dried in a centrifuge and finally dried in an electric oven at 120°. Spectroscopic tests gave no evidence of the presence of strontium or calcium, although the original material when tested in a similar fashion showed the presence of strontium. Solutions were made up of approximately the concentration desired and the exact concentrations determined by analysis as described below.

The most exact determinations of the transference numbers of chlorides by the analytical method have been made by Washburn,³ whose technique is a distinct advance over that of all earlier experimenters, but in spite of his fundamental improvements Washburn's method is involved, difficult, laborious and time consuming, and considerable skill and practice are needed to obtain reliable results. It should be especially noted that evaporation of the solutions during the operations of separating the electrolyte into five portions and filtering out the silver-silver chloride mixtures composing the electrodes, changes the concentration of the solution and thus introduces an error. Every detail of manipulation must be planned to reduce this source of error as much as possible. The error due to unavoidable evaporation during manipulation can be minimized by using an apparatus of large volume of the anode and cathode chambers. For the anode Washburn recommends a Soxhlet extraction tube of filter paper filled with electrolytic silver crystals in which a coil of silver wire is buried. During the experiment silver chloride is formed on the silver wire and crystals, but contrary to Washburn's experience, we found that the silver chloride formed during electrolysis

² This has been done by the junior author, but since the conductivity data are also needed to evaluate the constants of the equation, the theoretical discussion is postponed until a subsequent paper when data on the conductivity and viscosity of barium chloride solutions will be presented and correlated with the transference data. See Malcolm Dole, Harvard Ph.D. "Dissertation," 1928.

³ E. W. Washburn, *THIS JOURNAL*, 31, 322 (1909).

cemented the crystals together. During the mechanical disintegration of the anode loss by evaporation was unavoidable and thus made the solution stronger than it should have been.

This difficulty was overcome by the invention of a more satisfactory form of anode. A silver wire gauze was attached to a silver wire and rolled into a cylindrical coil of three layers about 1 cm. long and slightly less than the glass tube in diameter. The gauze was covered with an adherent but spongy coating of metallic silver by the pyrogenetic decomposition of silver oxide, thus producing a much larger surface than is available in the Washburn form of electrode. These anodes would carry a current of 0.1 ampere for eight hours without the slightest formation of acid in the electrolyte due to the evolution of oxygen instead of the formation of silver chloride, provided the potential gradient in the electrolyte did not exceed one volt per centimeter. At the beginning of the experiment the lower end of the anode is attacked and as it becomes covered with silver chloride the zone of the reaction gradually moves upward and at the end of the experiment the upper portion is being used. The potential necessary to cause oxygen evolution is approximately one volt greater than that required to change silver to the chloride. Therefore if the potential gradient in the solution exceeds one volt per centimeter, oxygen may be formed at the lower edge of the anode instead of chloride being formed one centimeter higher up on the electrode. In our apparatus the distance between the electrodes was about 100 centimeters. We found that if 100 volts were used, gassing would occur on the lower edge of the electrode before the silver on the upper part of the electrodes had been covered with chloride. By restricting the voltage used to 70 volts there was an adequate margin of safety to avoid gassing at the anode until its capacity had been fully used. With the more concentrated solutions this limitation was of no consequence because we found it best to limit the current to 0.1 ampere to avoid excessive heating and to avoid gassing at the cathode and 70 volts was not necessary to give 0.1 ampere. With 0.1 molal and weaker solutions this limitation to 70 volts limited the current that could be used.

With our new form of anode no filter paper is required. The silver chloride formed during electrolysis adheres firmly to the anode and yet the anode remains porous so that the weak electrolyte within the anode can readily be mixed with the anode liquid without disintegrating the anode by shaking and diffusion and without opening the anode chamber. At the end of the experiment the anode chamber filled with anode and anode electrolyte was weighed, then the anode removed intact, washed with water and dried in an oven without the loss of silver chloride. The rest of the manipulation is similar to that of Washburn except that no filtration of the anode liquid is required and therefore the amount of evaporation is much less than in his procedure.

After the new form of anode had been developed and the experimental technique seemed to be satisfactory in other respects and we were getting results from the anode side which seemed to be reliable, the results from the cathode side continued to be erratic. For the cathode we were using a silver plate covered with a layer of precipitated silver chloride in accordance with Washburn's recommendation.⁴ We found that such an electrode would carry a current of 0.1 ampere without evolution of hydrogen or formation of alkali. Since we could find no evidence of any other abnormal reaction at this electrode we were at length forced to conclude that the difficulty was in the washing of the silver chloride for the cathode with the original solution and in the filling of the electrode chamber.

Repeated washing of the precipitate with the solution to be used improved the

⁴ S. A. Braley and J. L. Hall, *THIS JOURNAL*, **42**, 1770 (1920); S. A. Braley and R. F. Schneider, *ibid.*, **45**, 1121 (1923), who used Washburn's method without modification, were unable to get reliable results with the cathode portions.

results somewhat but did not solve the problem. After much experimentation two different procedures were adopted, one suitable for the more concentrated solutions and the other suitable for the more dilute solutions. We tried a form of cathode somewhat similar to those used by Dewey⁵ but modified so as to give a larger surface of silver. This larger surface of silver was obtained by decomposing silver oxide by heat. The first steps in making these cathodes were identical with the procedure used in making the anodes already described. Then the electrode was coated heavily with silver chloride by electrolysis in a chloride solution, washed and dried. These cathodes proved to be satisfactory for use with the dilute solutions (0.03 molal and under). With these solutions the current density was necessarily low on account of the high internal resistance and the necessity of limiting the potential gradient to one volt per centimeter as explained above. With the more concentrated solutions, however, these new cathodes failed because they would not carry the heavier currents needed without evolution of hydrogen. We were therefore forced to return to the Washburn type of cathode for use with the more concentrated solutions but were able to find a modification of the procedure which solved the difficulties described above.

The procedure finally adopted was as follows. A suitable quantity of silver nitrate was weighed out, dissolved in hot water, precipitated from hot solution by an excess of sodium chloride, thoroughly washed with hot water and then the supernatant water decanted. The damp precipitate was added to a glass-stoppered bottle containing all of the barium chloride solution to be used in the experiment and the whole thoroughly shaken. Of course, this changed the composition of the solution but no harm resulted, because it was later analyzed in the middle portions after the experiments. The bottle was allowed to stand until the precipitate had settled and most of the clear solution was decanted into a dry bottle. The precipitate was brought into suspension by shaking and the suspension poured into the cathode chamber through a funnel. The funnel was then withdrawn and the entire apparatus filled with clear solution and tightly closed. This procedure ensured that the barium chloride solution was uniform in composition throughout the entire apparatus. Certainly the agreement between the results obtained from the anode and cathode sides of the apparatus was greatly improved after this procedure was adopted. The five portions of the electrolyte were analyzed gravimetrically by precipitation of the chloride as silver chloride. This work must be done with great care because the errors in the analysis were magnified in the subsequent calculations, but this unusually accurate analytical method is so well known that it need not be described here.

The rest of the manipulation need not be described in detail since there were no significant variations from Washburn's procedure. In some cases the analyses of the anode middle and the cathode middle portions were omitted after it had been shown by measurements of the conductivity that these solutions were the same as the middle portion. During the electrolysis the apparatus was mounted in a thermostat at $25 \pm 0.02^\circ$.

The results are computed on the assumption that the water does not move under the influence of the current and are, therefore, "Hittorf" numbers rather than "true" transference numbers in the sense that these terms are used by Washburn.

In the following table are given all the results that we believe to be reliable. It was not until Expt. 16 that our improved technique in handling the cathode was adopted. All earlier results obtained from the cathode side are rejected. Some of the later experiments had to be rejected because variations in the procedure were tried which proved to be unsuccessful. A few were lost by accident in the analysis. Some of the

⁵ Jane Dewey, *THIS JOURNAL*, 47, 1927 (1925).

TABLE I
EXPERIMENTAL DATA

	Experiment no.									
	10	12	16	18	19	20	24	26	33	
Molality (gr. mol./liter)	0.99	1.035	0.24745	0.10025	0.04985	0.05079	0.02395	0.01000	0.4987	
Amperes	.1	.1	.1	.06	.03	.03	.015	.01	.10	
Volts	27	27	60	70	70	70	70	64	25	
Time in hours	7	7	7	10	8	8	7	5	7	
Ag deposited in coul. from anode side	3.0792	2.9699	2.6585	2.0971	0.9588	0.9223	0.4487	0.2010	1.6704	
From cathode side	3.0790	2.9694	2.6587	2.0972	.9586	.9230	.4487	.2010	1.6703	
Wt. of anode portion	55.70	51.54	121.58	119.68	122.87	125.25	126.06	128.53	128.52	
Wt. of cathode portion	71.09	73.45	121.80	121.06	Lost	123.90	120.83	120.83	133.61	
Per cent. BaCl ₂ in anode										
1st analysis	16.023	16.680	4.149	1.3658	0.7139	0.7521	0.3507	0.14253	9.1264	
2nd analysis	16.020		4.147	1.3666					9.1257	
Anode middle	17.570	Cond.	4.946	2.0546	1.0329	1.0505	Cond.	Cond.	9.5578	
Middle middle										
1st analysis	17.576	18.275	4.948	Lost	1.0323	1.0512	0.4983	0.20846	9.5565	
2nd analysis	17.571	18.282	4.946				.4984	Cond.	9.5574	
Cathode middle	17.576	Cond.	4.946	2.0563	1.0308	1.0518	Cond.			
Cathode										
1st analysis	18.590	19.329	5.747	2.7384	1.3434	1.3534	.65207	.27800	9.9655	
2nd analysis	18.579		5.745	2.7388					9.9744	
									9.9614	
									9.9672	
									9.9780	
									9.9769	
Wt. BaCl ₂ transferred										
From anode	1.0494	1.0073	1.0219	0.8428	0.3935	0.3786	.1871	.0849	0.6126	
To cathode	(0.8654)	(0.9449)	1.0259	.8433		.3785	.1867	.0850	.6105	
<i>t</i> _{Ba} from anode	.3530	.3514	0.3981	.4163	.4252	.4251	.4320	.4377	.3799	
<i>t</i> _{Ba} from cathode3996	.41654249	.4310	.4379	.3786	
Accepted results	.3530	.3514	.3988	.4164	.4252	.4250	.4315	.4378	.3792	
<i>t</i> computed from formula	.35317	.35119	.39878	.41612	.42525	.42504	.43202	.43748	.37928	
Deviation <i>t</i> _{comp.} - <i>t</i> _{obs.}	+ .00017	- .00021	- .00002	- .00028	+ .00005	+ .00004	+ .00052	- .00032	+ .00008	

missing numbers represent attempts to use 0.005 molal solutions but we were unable to obtain a reliable result with such dilute solutions. None of the results were rejected because they were not consistent with the new formula given below.

The Transference Number as a Function of Concentration.—The transference number, t , was plotted against the square root of the concen-

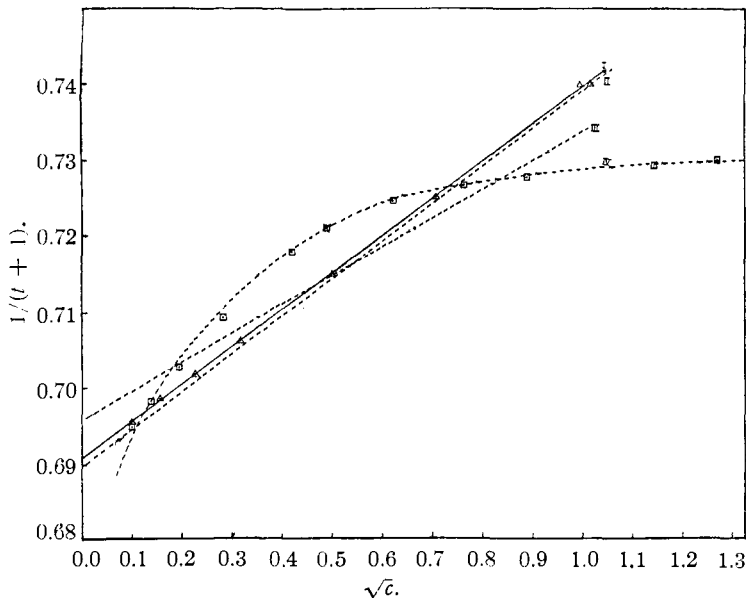


Fig. 1.—Reciprocal of transference number plus one, $1/(t + 1)$, against square of the concentration, \sqrt{c} . The straight line I with points in triangles represents our data by the analytical method and is plot of Equation 1. The results obtained by the electromotive force method are represented by broken lines. The straight line II represents our data based on Equation 20. The straight line III represents our interpretation of Lucasse's data based on Equation 21. Curve IV with points in squares represents Lucasse's interpretation of his own data.

tration, giving a smooth curve which was nearly straight but showed a definite curvature. It was then found that by plotting $1/(t + 1)$ against \sqrt{c} (Fig. 1, Curve I) a perfect straight line was obtained with all the experimental points falling on a straight line within the limit of error of the experiment. Then by the method of least squares the constants of the equation of this straight line were computed, giving

$$\sqrt{c} = \frac{20.6501}{t + 1} - 14.2655 \quad (1)$$

as the functional relationship between c and t . This is readily transferred into

$$(\sqrt{c} + 14.2655)(t + 1) = 20.6501 \quad (2)$$

This is the equation of a rectangular hyperbola between t and \sqrt{c} with the asymptotes displaced from the axes at -14.2655 and -1 . Another simple transformation gives

$$t = \frac{1.4476}{1 + 0.07010 \sqrt{c}} - 1 \quad (3)$$

The value of t at each concentration used in our experiments was then computed from this equation and is given in the second line from the bottom of Table I. The difference between the computed and observed values of t is given in the last line of Table I. As will be seen, the maximum deviation is $+0.00052$ in Expt. 24 and even here the computed result agrees exactly with the determination from the anode side, so that this deviation is clearly less than the possible experimental error. The average deviation is less than 0.0002 . In view of the fact that most experimenters on transference numbers record their results only to the third decimal place this agreement is highly satisfactory. It should be noticed that the greater deviations occur in the dilute solutions where the experimental error is the greatest. Moreover, this equation holds exactly over the entire range of concentration from 0.01 to 1.035 mole per liter with no indication of systematic deviations in the more concentrated solutions. An additional reason for satisfaction is that the form of the function is such that there is no rapid change in slope as c approaches zero. It may therefore be used with considerable confidence for interpolation to obtain the value of the transference number at rounded concentrations and for extrapolation to infinite dilution. The values thus obtained are recorded in Table II. The value at infinite dilution is 0.4476 .

TABLE II

TRANSFERENCE NUMBERS OF BARIUM IN BARIUM CHLORIDE SOLUTIONS AT 25° AT VARIOUS CONCENTRATIONS

c	0.000	0.001	0.005	0.01	0.025	0.05	0.10	0.25	0.5	1.0
t	0.4476	0.4444	0.4405	0.4375	0.4317	0.4253	0.4162	0.3986	0.3792	0.3528

Having discovered a new hyperbolic relationship between the transference number and the square root of the concentration which holds exactly in the case of barium chloride over a hundred-fold range in concentration, it becomes of much interest to determine whether or not this relationship is a general one. In the case of barium chloride one of the asymptotes of the hyperbola is at -1 , but this may not be the case with other salts. An examination of the available data on transference numbers reveals very few cases in which the transference numbers have been determined over a wide range of concentration by the same method and at the same temperatures and by the same experimenter so that the data are comparable. The principal exceptions are the work of MacInnes and Beattie⁶

⁶ D. A. MacInnes and J. A. Beattie, THIS JOURNAL, 42, 1117 (1920).

on lithium chloride, that of Lucasse⁷ on barium chloride, strontium chloride and calcium chloride, that of Pearce and Gelbach⁸ on barium chloride and that of Ferguson and Schlucter⁹ on sodium hydroxide, all computed from the electromotive force of concentration cells with and without liquid junction. The transference numbers computed by these authors from their data do not show the same hyperbolic relationship between the transference number and the square root of the concentration which we have found for barium chloride. The results of Lucasse on barium chloride are shown in Fig. 1, Curve IV and, as will be seen, are widely different from the results which we obtained by the analytical method.

Experimental

Electromotive-Force Method.—In order to determine, if possible, the cause of the discrepancy, we undertook to measure the electromotive force of concentration cells with liquid junction similar to those used by Lucasse. The cells were of the flowing junction type used by Lamb and Larson.¹⁰ In all of the experiments one-half of the cell contained 0.05 molal solution and the solution in the other half was varied in successive experiments from 0.001 to 1.000 molal. The electrodes were prepared by depositing silver chloride by a current of 1 milliamperes for ten hours on a foundation of spongy silver formed by the pyrogenous decomposition of silver oxide. Electrodes when prepared in this way, then allowed to stand for several hours in a solution of potassium chloride or of barium chloride, nearly always agree within 0.00001 volt. We found that these electrodes could be transferred from one solution to another of different concentration and after standing for about one hour they gave definite and reproducible results.

For our final measurements a set of four electrodes was used. Two electrodes remained in the 0.05 barium chloride solution and the other two were used successively in the other solutions. These electrodes were allowed to stand for at least twenty-four hours in the solution under investigation in a thermostat before measurements were made. The difference between the pair in the same solution never exceeded 0.00003 volt and rarely exceeded 0.00001 volt. After this long-continued use in many different solutions they were all four put into a 0.05 molal solution of barium chloride and then the maximum difference between any two of the four was only 0.00003 volt.

Computation of Transference Numbers from the Electromotive Force of Concentration Cells.—The results shown in Table III were used in

⁷ W. W. Lucasse, *THIS JOURNAL*, **47**, 743 (1925).

⁸ J. N. Pearce and R. W. Gelbach, *J. Phys. Chem.*, **29**, 1023 (1925).

⁹ A. L. Ferguson and A. W. Schlucter, *Trans. Am. Electrochem. Soc.*, **49**, 614 (1927).

¹⁰ A. B. Lamb and A. T. Larson, *THIS JOURNAL*, **42**, 229 (1920).

TABLE III
ELECTROMOTIVE FORCE OF BARIUM CHLORIDE CONCENTRATION CELLS WITH LIQUID JUNCTION AT 25°

c_2	c_1	$E_2 - E_1$			$E_2 - E_1,$ mean
		(1)	(2)	(3)	
0.001	0.05	+0.0583	+0.0585	+0.0584
.005	.05	+ .03317	+ .03333	+0.03329	+ .03326
.01	.05	+ .02273	+ .02277	+ .02275
.025	.05	+ .00940	+ .00944	+ .00942
.1	.05	- .00921	- .00923	- .00922
.25	.05	- .02127	- .02139	- .02133
.5	.05	- .03085	- .03077	- .03081
1.0	.05	- .04103	- .04101	- .04102

preparing Fig. 2, in which $E_2 - E_1$ is plotted against $\log c_2$ (points enclosed in circles). Then Lucasse's measurements (points enclosed in squares) were placed on the same plot by adding 0.02280 to each of his readings,

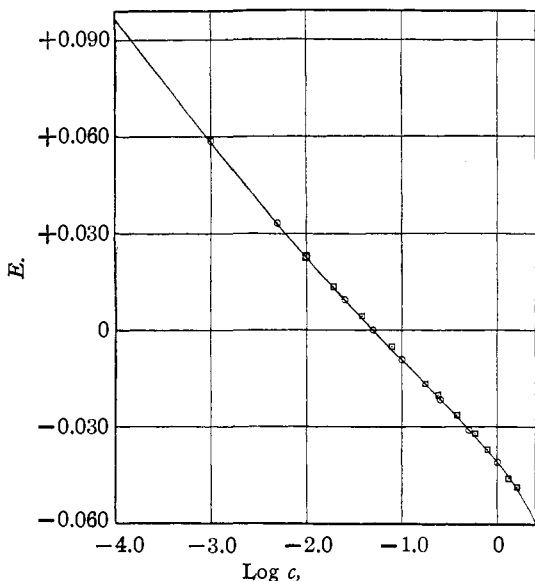


Fig. 2.—Electromotive force of barium chloride concentration cells with liquid junction, $E_2 - E_1$, against $\log c_2$, all measurements being made against a solution having $c_1 = 0.05$ mole per liter. Points in circles represent our data. Points in squares represent Lucasse's data. The solid curve is the plot of Equation 16 which is derived from Equation 15 by substituting values of A and B determined from our analytical data and the values of N and P determined from Lucasse's data on concentration cells without liquid junction.

which refers them to the same arbitrary reference electrode ($c = 0.05$) as was used in our measurements instead of $c = 0.009968$ used by Lucasse. As will be seen, both sets of data fall on the same curve so well that the deviations are barely noticeable even on a large plot 50 cm. square, although Lucasse's data do not fit the curve as well as ours. We thus find ourselves in substantial agreement with Lucasse as to the experimental data. We have not verified his data on cells without liquid junction but in view of subsequent developments this seemed to be unnecessary.

The next step was a critical study of the method of computing transference numbers from the electromotive force of concentration cells. Lucasse employed a method modeled on that of MacInnes and Beattie for lithium chloride but modified disadvantageously so as to make it more dependent on plotting and less dependent on algebraic analysis. Lucasse first used his data on the electromotive force of concentration cells without liquid junction of the type $\text{Ag}, \text{AgCl}, \text{BaCl}_2 (c_2), \text{BaHg}_x \text{---} \text{Hg}_x\text{Ba}, \text{BaCl}_2 (c_1), \text{AgCl}, \text{Ag}$ to prepare a plot of activity coefficient against the square root of the concentration. From this plot he obtained by interpolation the activity coefficient at each of the different odd concentrations which were used in the measurements on concentration cells with liquid junction. The activity, a , was then computed and hence the quantity, A , which is arbitrarily defined as $1000a$. Then the electromotive force of concentration cells with liquid junction was plotted against $\log A$. Up to this point he used the procedure of MacInnes and Beattie in principle, but with the difference that MacInnes and Beattie used identical concentrations in their cells with and without liquid junctions and therefore did not have to rely on values interpolated on plots. MacInnes and Beattie found that E could be expressed analytically as a binomial function of $\log A$. This on differentiation gave a linear relationship between the transference number, t , and $\log A$, which they used to compute t at any concentration within the range of their data. But this linear relationship cannot be applicable over the entire range of concentration because it leads to the result that as the concentration approaches zero the transference number must approach infinity.

Lucasse found that his curve between E and $\log A$ could not be expressed as a binomial and indeed was so complicated that he was unable to find the equation of the curve. He was therefore compelled to carry out by geometrical means the steps equivalent to those carried by MacInnes and Beattie by analytical methods. Lucasse measured the slope of his curves at various points and by dividing each value of the slope by the appropriate constant factor obtained a set of values for the transference number at various concentrations. These results are shown graphically in our Fig. 1 in the curve marked IV and, as will be seen, are not in agreement with our results obtained by the analytical method. Having con-

firmed the approximate reliability of Lucasse's measurements on the electromotive force of concentration cells with liquid junction, it seemed to us probable that the cause of the discrepancy was to be sought in errors introduced in the complicated method of plotting used by Lucasse. In this case the transference numbers must be inferred from the slope of the curves. The slope and especially the variation of the slope with concentration is greatly influenced by slight differences in judgment in drawing the complicated curves through the experimental points. We therefore undertook to develop an analytical procedure for computing transference numbers at any concentration from the data on electromotive force of concentration cells with and without liquid junctions.

The differential equation for the electromotive force of a concentration cell with liquid junction of the type Ag, AgCl, BaCl₂ ($c + dc$), BaCl₂(c), AgCl, Ag is

$$dE = - \frac{3RT}{2F} t d \ln a \quad (4)$$

where t is the transference number of the barium ion at the concentration c and temperature T and a is the geometric mean activity of the ions in the same solution. The problem therefore is to express t and a as functions of the concentration and then integrate the resulting equation between the limits of concentration used in the measurements of electromotive force of concentration cells with liquid junction. If the values so computed agree with the observed voltages over a considerable range of concentration, the reliability of the expressions for t and a as functions of c may be regarded as confirmed.

It has been shown that for barium chloride we may write

$$t = \frac{1.4476}{1 + 0.0701\sqrt{c}} - 1 \quad (3)$$

or in generalized¹¹ form that

$$t = \frac{A}{1 + B\sqrt{c}} - 1 \quad (5)$$

The determination of the activity, a , as a function of the concentration, c , may be based on the measurement of the electromotive force of concentration cells without liquid junction. In a very important paper Hückel¹² has attacked the general problem of the variation of activity coefficient with concentration. He derives an equation (his Equation 97) for the

¹¹ This form is not fully generalized, as it may be necessary with other salts to replace the term -1 by another constant. The introduction of another constant would complicate the ensuing mathematical derivation and computations but would introduce no change in principle.

¹² E. Hückel, *Physik. Z.*, **26**, 93 (1925). See also T. H. Gronwall, V. K. LaMer, and K. Sandved, *Physik. Z.*, **29**, 358 (1928), for another attempt to solve this general problem.

variation of activity coefficient with concentration which for a monovalent salt has the form

$$\log f = \frac{-0.354\sqrt{2c}}{1 + N\sqrt{c}} + Pc \quad (6)$$

where N and P are constants for any given salt.¹³ Hückel gives computations and curves showing that this formula is consistent with the data of Allmand and Polack¹⁴ on the electromotive force of sodium chloride concentration cells without liquid junction up to a concentration of 5.4 molal; and also consistent with similar data of MacInnes and Beattie⁶ on lithium chloride up to 3 molal. For a divalent salt Hückel's equation reduces to the form $\log f = -1.734\sqrt{c}/(1 + N\sqrt{c}) + Pc$. The first step is to endeavor to select values for N and P which would be consistent with Lucasse's actual data. As first approximations for N and P we have used the values $N' = 2.175$ (taken from Harned's paper)¹⁵ and $P' = 0.1475$.

The electromotive force of a concentration cell without liquid junction having a divalent salt such as barium chloride and electrodes reversible with respect to the anion such as Ag, AgCl electrodes is given by the equation

$$dE = -\frac{3RT}{2F} d \ln a = -\frac{3RT}{2F} 2.3026 d(\log c + \log f) \quad (7)$$

$$dE = -\frac{3RT}{2F} 2.3026 d\left(\log c - \frac{1.734\sqrt{c}}{1 + N\sqrt{c}} + Pc\right) \quad (8)$$

Integrating between the limits c_2 and c_1 gives

$$E_2 - E_1 = -3.4539 \frac{RT}{F} \left[\left(\log c_2 - \frac{1.734\sqrt{c_2}}{1 + N\sqrt{c_2}} + Pc_2 \right) - \left(\log c_1 - \frac{1.734\sqrt{c_1}}{1 + N\sqrt{c_1}} + Pc_1 \right) \right] \quad (9)$$

As a convenient abbreviation we will write $E = \phi(c, N, P)$, and refer to this as the Phi function. By the use of this equation $E_2 - E_1 = E_{\text{comp}}$.

¹³ There are in use three methods of defining the concentration: mole fractions, moles per 1000 g. of water and moles per liter—with corresponding definitions of the activity coefficient. In Hückel's Equation 97 the activity coefficient is on the mole fraction basis, but owing to the uncertainty in the polymerization of water the mole fraction basis is inconvenient for practical use. Hückel uses the moles per liter basis in his practical numerical calculations to test his general formulas and this is the basis which we have adopted. It is easy to show by the use of Hückel's Equation 30 that if the activity coefficient is defined as the activity divided by the concentration in moles per liter, no change in the form of Equation 97 is necessary and that the only change required is a slight change in the numerical value of the coefficient of the term containing the first power of c (our P). But P is an empirical constant anyway. The mathematical steps in this transformation must be omitted to save space. See Harned, *THIS JOURNAL*, **48**, 338 (1926), for some discussion of this question and for the corresponding transformation in terms of moles per 1000 g. of water.

¹⁴ A. J. Allmand and W. C. Polack, *J. Chem. Soc.*, 115, 1020 (1919).

¹⁵ H. S. Harned, *THIS JOURNAL*, **48**, 338 (1926).

was computed for the actual values of the concentration used by Lucasse (after changing from m to c by the use of the following equation for the density of barium chloride solutions at 25° based on our own measurements: $d = 0.99707 + 0.1821c - 0.00407c^2$). These computed values were near enough to the observed values, $E_{\text{obs.}}$, to be encouraging but they probably were not within the experimental error and the deviations $\Delta E = E_{\text{obs.}} - E_{\text{comp.}}$ were apparently systematic. This indicated that N and P should be changed by some finite amount, ΔN and ΔP , and these values were found as follows. The rate of change of E with change in N and in P can be found by taking the partial derivatives of

$$E_2 - E_1 = \phi(c, N, P)_{c_1}^{c_2} \quad (10)$$

with respect to N and to P . Then

$$\Delta E = \left[\frac{\partial \phi(c, N, P)}{\partial N} \right]_{c_1}^{c_2} \Delta N + \left[\frac{\partial \phi(c, N, P)}{\partial P} \right]_{c_1}^{c_2} \Delta P \quad (11)$$

Each cell measured thus gives a linear equation between ΔN and ΔP with numerical coefficients and these equations can be solved by the method of least squares for ΔN and ΔP . The second approximations for N and P are then given by $N'' = N' + \Delta N$, and $P'' = P' + \Delta P$.

The values of $E_2 - E_1$ may then be recomputed and if the deviations are reduced but still significant and systematic, the process outlined above may be repeated. In this particular case the deviation equation takes the form

$$\Delta E = - \frac{3 \times 2.3026RT}{2F} \left[\left(\frac{1.734\sqrt{c_2}}{(1 + N\sqrt{c_2})^2} - \frac{1.734\sqrt{c_1}}{(1 + N\sqrt{c_1})^2} \right) \Delta N + (c_2 - c_1) \Delta P \right] \quad (12)$$

In this manner (using the points up to $m = 0.97$, only) we found $\Delta N = +0.052$ and $\Delta P = +0.0052$ and hence $N'' = 2.175 + 0.052 = 2.227$ and $P'' = 0.1475 + 0.0052 = 0.1527$. A repetition of the calculations gave $\Delta N = +0.0048$ and $\Delta P = -0.00004$ and hence $N''' = 2.227 + 0.0048 = 2.2318$ and $P''' = 0.1527 - 0.00004 = 0.15266$. Then f and E were computed with the equation $\log f = -1.734\sqrt{c}/(1 + 2.2318\sqrt{c}) + 0.15266c$, with the results shown in the following table.

TABLE IV

TEST OF HÜCKEL'S ACTIVITY FUNCTION FOR BARIUM CHLORIDE SOLUTIONS AT 25°

$$\log f = \frac{-1.734\sqrt{c}}{1 + 2.2318\sqrt{c}} + 0.15266c$$

Data by Lucasse on Electromotive Force of Cells without Liquid Junction

m	c	\sqrt{c}	$E_c - E_{0.01}$, obs.	$E_c - E_{0.01}$, comp.	ΔE volts	f
0.01	0.009968	0.09984	0	0	0	0.7244
.03016	.030048	.17334	0.03548	0.03612	-0.00064	.6136
.1004	.09984	.31597	.07420	.07406	+ .00014	.4942
.2978	.29452	.54270	.10921	.10914	+ .00007	.4163
.9710	.94073	.96992	.15322	.15325	- .00003	.4094
1.521	1.4459	1.2024	.17183	.17359	- .00176	.4516
1.650	1.5615	1.24962	.17713	.17759	- .00046	.4640

Having a new exact relationship between t and c from our own measurements by the gravimetric method and Hückel's relationship between a and c , we are in a position to integrate the fundamental differential equation. Neither of these relationships was known at the time when MacInnes and Beattie published their important improvement over Nernst's method of computing transference numbers from the electromotive-force data.

$$dE = -\frac{3RT}{2F} t \, d \ln a \quad (4)$$

but

$$t = \frac{A}{1 + B\sqrt{c}} - 1 \quad (5)$$

and

$$\ln a = \ln c + \ln f = 2.3026(\log c + \log f) = 2.3026 \left(\log c - \frac{1.734\sqrt{c}}{1 + N\sqrt{c}} + Pc \right) \quad (13)$$

$$-\frac{2F}{6.9078RT} dE = \left(\frac{A}{1 + B\sqrt{c}} - 1 \right) d \left(\log c - \frac{1.734\sqrt{c}}{1 + N\sqrt{c}} + Pc \right) \quad (14)$$

By substituting $x = \sqrt{c}$, which simplifies the form of the integral, and integrating between the limits $x_2 = \sqrt{c_2}$ and $x_1 = \sqrt{c_1}$

$$E_2 - E_1 = \frac{3RT \times 2.3026}{2F} \left[-\frac{2APx}{B} + Px^2 - (2A - 2) \log x + \left(\frac{2A}{2.3026} + \frac{1.734AB}{(N-B)^2} + \frac{2AP}{B^2} \right) 2.3026 \log(1 + Bx) - \left(\frac{1.734A}{N-B} - \frac{1.734}{N} \right) \left(\frac{1}{1 + Nx} \right) - \frac{1.734AB}{(N-B)^2} 2.3026 \log(1 + Nx) \right]_{x_1}^{x_2} \quad (15)$$

As a convenient abbreviation we will write $E = \psi(x, A, B)$ and refer to this as the Psi function.

This equation, although complicated, is as rigid as the equations connecting t and a with c . If we substitute at 25° $3RT/2F = 2.3026 = 0.088731$ and $A = 1.4476$, $B = 0.07010$, $N = 2.2318$ and $P = 0.15266$; Equation 15 reduces to

$$E_2 - E_1 = +0.088731 \left[-6.30489x + 0.15266x^2 - 0.89512 \log x + 210.082 \log(1 + 0.0701x) - \frac{0.38420}{1 + 2.2318x} - 0.0867026 \log(1 + 2.2318x) \right]_{x_1}^{x_2} \quad (16)$$

$E_2 - E_1$ was then computed for each of the barium chloride concentration cells with liquid junction measured by us and by Lucasse with the results shown in Tables V and VI.

These computed values against 0.05 molal barium chloride were then plotted ($E_2 - E_1$ against c_2) and are shown in the solid curve drawn in Fig. 2. This method of plotting was chosen because it gives a curve which is approximately a straight line, but when it is drawn on a large scale it is easily apparent that it is concave for small values of c , has a point of inflection near the middle and is convex for the higher values of c . As will be seen from Fig. 2, our experimental points and those of Lucasse

TABLE V
BARIUM CHLORIDE CONCENTRATION CELLS WITH LIQUID JUNCTION AT 25°. COMPARISON
OF OUR OBSERVED VOLTAGE WITH THAT COMPUTED BY EQUATION 15

c_2	c_1	$E_2 - E_1, \text{obs.}$	First approximation, $A = 1.4476, B = 0.07010$			Second approximation, $A = 1.450, B = 0.07135$	
			$E_2 - E_1, \text{comp.}$	$\Delta E, \text{obs.-comp.}$	$E_2 - E_1, \text{comp.}$	ΔE	
0.001	0.05	+0.0584	+0.05825	+0.00015	+0.05855	-0.00015	
.005	.05	+ .03326	+ .03292	+ .00034	+ .03308	+ .00018	
.01	.05	+ .02275	+ .02256	+ .00019	+ .02267	+ .00008	
.025	.05	+ .00942	+ .00946	- .00004	+ .00951	- .00009	
.05	.05	0	0	0	0	0	
.10	.05	- .00922	- .00918	- .00004	- .00922	+ .00000	
.25	.05	- .02133	- .02114	- .00019	- .02123	- .00010	
.5	.05	- .03081	- .03066	- .00015	- .03078	- .00003	
1.0	.05	- .04102	- .04094	- .00008	- .04109	+ .00007	
			$\Sigma \Delta E = +0.00018$		$\Sigma \Delta E = -0.00004$		

TABLE VI
BARIUM CHLORIDE CONCENTRATION CELLS WITH LIQUID JUNCTION AT 25°. COMPARISON
OF LUCASSE'S OBSERVED VOLTAGE WITH THAT COMPUTED BY EQUATION 15

m	c_2	$E_2 - E_1, \text{obs.}$	$c_1 = 0.09968$ First approximation, $A = 1.4476, B = 0.07010$			Second approximation, $A = 1.4372, B = 0.05409$	
			$E_2 - E_1, \text{comp.}$	$\Delta E, \text{obs.-comp.}$	$E_2 - E_1, \text{comp.}$	ΔE	
0.01	0.009968	0	0	0	0	0	
.01923	.01916	-0.00927	-0.00941	+0.00014	-0.00925	-0.00002	
.03815	.03800	- .01852	- .01890	+ .00038	- .01859	+ .00007	
.07977	.07937	- .02804	- .02874	+ .00070	- .02834	+ .00030	
.1791	.1777	- .03941	- .03929	- .00012	- .03884	- .00057	
.2426	.2403	- .04277	- .04330	+ .00053	- .04282	+ .00005	
.3927	.3873	- .04907	- .04972	+ .00065	- .04926	+ .00019	
.5971	.5854	- .05475	- .05550	+ .00075	- .05512	+ .00037	
.8122	.7909	- .05995	- .05993	- .00002	- .05964	- .00031	
1.372	1.311	- .06872	(- .06795)	(- .00077)	(- .06791)	(- .00081)	
1.715	1.619	- .07134	(- .07158)	(+ .00024)	(- .07170)	(+ .00036)	
			$\Sigma \Delta E = + .00224$		$\Sigma \Delta E = - .00009$		

fit the theoretical curve closely and follow the complicated curvature throughout the entire range in a way which supports the validity of our new function and shows that there is no real discrepancy between our data on the transference of barium chloride and by the analytical method and the electromotive-force data.

Although the deviations between the observed and computed voltages (ΔE of Tables V and VI) are so small as to be scarcely visible on a plot 50 cm. square, nevertheless computation shows that there are deviations which are apparently greater than the experimental error of the electromotive-force measurements. It will be seen from Table V that our deviations are apparently systematic, being positive in dilute solutions, negligible in middle concentrations and negative in the concentrated solutions, and that those of Lucasse are predominantly positive and larger than ours.

It now becomes of interest to reverse the computation described above and compute transference numbers from electromotive force alone and compare the results with the transference numbers obtained analytically. The numerical value of N and P is first computed from the voltage of concentration cells without liquid junction in the manner described above. Then as a matter of mathematical theory it would only be necessary to measure two different cells with liquid junction to make it possible to compute A and B and hence compute t at any concentration. But in practice it will be advisable to measure many cells covering the desired range of concentration and this requires that the data be treated by the method of least squares to find the best values of A and B . Moreover, the form of the function is so complicated that a simple numerical solution is not feasible. The problem can be solved, however, in a manner similar to that indicated above. First assume some value of A' and B' as a first approximation. Then compute $E = \psi(x, A', B')$ for each value of x used in the experiments and hence the deviation $\Delta E = E_{\text{obs.}} - E_{\text{comp.}}$. Then

$$\Delta E = \left[\frac{\partial \psi(x, A', B')}{\partial A'} \right]_{x_1}^{x_2} \Delta A + \left[\frac{\partial \psi(x, A', B')}{\partial B'} \right]_{x_1}^{x_2} \Delta B \quad (17)$$

Each cell measured thus gives a linear numerical equation with two unknowns, ΔA and ΔB , and these equations can be solved by the method of least squares. This gives a second approximation: $A'' = A' + \Delta A$ and $B'' = B' + \Delta B$.

This process can be repeated as often as is necessary, but unless the first approximation were greatly in error the third approximation will not differ from the second by a significant amount. In this particular case the partial derivatives take the form shown below

$$\begin{aligned} \Delta E = & + \frac{3RT}{2F} 2.3026 \left[-\frac{2Px}{B} - 2 \log x + \left(\frac{2}{2.3026} + \frac{1.734B}{(N-B)^2} + \frac{2P}{B^2} \right) 2.3026 \log(1+Bx) \right. \\ & \left. - \frac{1.734}{(N-B)(1+Nx)} - \frac{1.734B}{(N-B)^2} 2.3026 \log(1+Nx) \right]_{x_1}^{x_2} \Delta A \\ & + \frac{3RT}{2F} 2.3026 \left[+ \frac{2APx}{B^2} + \left(\frac{1.734A}{(N-B)^2} + \frac{2 \times 1.734AB}{(N-B)^3} - \frac{4AP}{B^3} \right) 2.3026 \log(1+Bx) \right. \\ & \left. + \left(\frac{2A}{2.3026} + \frac{1.734AB}{(N-B)^2} + \frac{2AP}{B^2} \right) \frac{x}{1+Bx} - \frac{1.734A}{(N-B)^2(1+Nx)} \right. \\ & \left. - \left(\frac{1.734A}{(N-B)^2} + \frac{2 \times 1.734AB}{(N-B)^3} \right) 2.3026 \log(1+Nx) \right]_{x_1}^{x_2} \Delta B \quad (18) \end{aligned}$$

By substituting $A' = 1.4476$, $B' = 0.0701$, $N = 2.2318$ and $P = 0.15266$, this reduces to the form

$$\begin{aligned} \Delta E = & +0.088731 \left[-4.35554x - 2 \log x + 145.129 \log(1+0.0701x) - \frac{0.802146}{1+2.2318x} \right. \\ & \left. - 0.059896 \log(1+2.2318x) \right]_{x_1}^{x_2} \Delta A + 0.088731 \left[+89.9424x - 5907.46 \right. \\ & \left. \log(1+0.0701x) + \frac{91.2374x}{1+0.0701x} - \frac{0.537147}{1+2.2318x} - 1.31704 \log(1+2.2318x) \right]_{x_1}^{x_2} \Delta B \quad (19) \end{aligned}$$

By using the values of ΔE from Column 5 of Table V and solving the resulting deviation equations by the method of least squares, it was found that $\Delta A = +0.00240$ and $\Delta B = +0.00125$. Hence $A'' = 1.4476 + 0.00240 = 1.4500$ and $B'' = 0.07010 + 0.00125 = 0.07135$. Then, using these second approximations for A and B , the values for $E_2 - E_1$ were recomputed by means of Equation 15, with the results shown in Table V. The corresponding deviations are shown in Col. 7. The average deviation, disregarding the sign, is only 0.09 millivolt. The only deviations exceeding 0.1 millivolt are for the 0.005 and 0.001 molal solutions and these solutions are so dilute that the measurements are not so reliable as for the more concentrated solutions, as will be apparent from Table II. Moreover, the deviations are about equally positive and negative, so that the sum, including the sign, is only -0.00004 volt. This equation was plotted in Fig. 1, Line II. The deviations being now within the experimental error, there is nothing to be gained by further computations by the method of successive approximations. Therefore our data on the electromotive force of barium chloride concentration cells with liquid junction and Lucasse's data on concentration cells without liquid junction lead to the conclusion that the transference number of the barium ion in barium chloride solutions at 25° is

$$t = \frac{1.4500}{1 + 0.07135\sqrt{c}} - 1 \quad (20)$$

The hyperbolic form of the function $(t + 1)(\sqrt{c} + 1/B) = A/B$, which was found to be in accord with our data by the analytical method, is confirmed by the electromotive-force method and extended down to $c = 0.001$. The values of the transference number obtained by the electromotive-force method agree with those obtained by the analytical method to within 0.0024 throughout the entire range of concentration up to 1.0 molal. However, we believe that the results obtained by the analytical method are the more accurate.

In an exactly analogous manner the calculations were carried out with Lucasse's data on cells with transference and the results are shown in Table VI. The first deviations computed with $A' = 1.4476$ and $B' = 0.07010$ (based on the analytical data) are substantially greater than the corresponding deviations in our work and are predominantly positive. Then by the method described above it was computed that $\Delta A = -0.0104$, and $\Delta B = -0.01601$; hence $A'' = 1.4476 - 0.0104 = 1.4372$, and $B'' = 0.07010 - 0.01601 = 0.05409$. In these calculations the values for cells in which c is greater than 1 were not used because Hückel's formula for the activity does not hold above 1 molal. Line III in Fig. 1 gives the corresponding plot of this equation.

The values for $E_2 - E_1$ computed with these values of A and B are shown in Table VI. The deviations, although larger than in Table V,

are no longer systematic and the plus and minus deviations offset each other so nearly that no significant improvement can be made by repeating the calculations by successive approximations. Lucasse's data lead to the conclusion that the transference number is given by the equation

$$t = \frac{1.4372}{1 + 0.05409\sqrt{c}} - 1 \quad (21)$$

Line III in Fig. 1 gives the plot showing our interpretation of Lucasse's data. Curve IV in this figure is drawn by using the values of the transference number computed by Lucasse from the same data that were used in drawing Line III. We believe that Lucasse's computations of transference numbers from his data are erroneous and that when his data are properly interpreted they support rather than contradict our new hyperbolic relationship between the transference number and the square root of the concentration.

Further experiments on other salts to test the generality of our new hyperbolic relationship are under way.

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Summary

1. Improvements have been made in the details of Washburn's analytical method for the determination of transference numbers of chlorides which make it more precise, especially with dilute solutions.

2. The transference number of the barium ion in barium chloride solutions has been measured by the analytical method at 25° at many different concentrations in the interval from 0.01 to 1.035 molal and found to vary from 0.4378 to 0.3514 over this range.

3. The results can be expressed within the limits of the experimental error by a hyperbolic equation between the transference number of the barium ion, t , and the square root of the concentration, \sqrt{c} , as follows: $(t + 1)(\sqrt{c} + 14.2655) = 20.6501$, or its equivalent form

$$t = \frac{1.4476}{1 + 0.07010\sqrt{c}} - 1$$

4. The limiting value of the transference number of the barium ion in barium chloride solutions at infinite dilution at 25° is 0.4476.

5. The mean activity coefficient of the ions of barium chloride solutions varies with the concentration in accordance with the equation

$$\log_{10} f = \frac{-1.734\sqrt{c}}{1 + 2.2318\sqrt{c}} + 0.15266c$$

This function has the form derived by Hückel.

6. The computation of transference numbers from the electromotive force of concentration cells with and without liquid junction is discussed.

7. Measurements have been made on the electromotive force of

concentration cells with liquid junction containing barium chloride covering the range from 0.001 molal to 1.0 molal. These data when combined with Lucasse's data on concentration cells without liquid junction lead to the conclusion that

$$t = \frac{1.4450}{1 + 0.07135\sqrt{c}} - 1$$

Transference numbers computed by this formula agree with those obtained by the analytical method within 0.0024 over the entire range of concentration up to 1.0 molal.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

THE SYSTEMS: STRONTIUM OXIDE-PHOSPHORUS PENTOXIDE-WATER, AND BARIUM OXIDE-PHOSPHORUS PENTOXIDE-WATER AT 25° (ACID REGION)

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No investigation of the systems SrO-P₂O₅-H₂O and BaO-P₂O₅-H₂O has been reported in the literature. Investigation of the closely related system CaO-P₂O₅-H₂O has been made by Cameron and his co-workers² and by Bassett.³ Fairhall⁴ has studied the system PbO-P₂O₅-H₂O.

Each system is one of three components. By working at a constant temperature, such a system may be made univariant, in which case the existence of a single solid phase is indicated by a variation in the composition of the solution. The formation of a second solid phase produces an invariant system, the solution being constant. Analyses of the solid and liquid phases of a series of empirical mixtures which have been permitted to attain equilibrium afford the data necessary for defining the conditions under which the different compounds exist in solid form.

For this investigation only those conditions under which at least three phases—gas, solid and solution—exist in equilibrium were of interest and the isotherms at 25° were determined. The composition of the solid phases was found by extrapolation, using Schreinemaker's⁵ residue method. Analyses were made of the saturated solution and of the solid residue together with the adhering mother liquor. The values from the two analyses when plotted on a coordinate system lie on straight line, which when projected passes through a point representing the composition of

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² (a) Cameron and Seidell, *THIS JOURNAL*, **27**, 1503 (1905); (b) Cameron and Bell, *ibid.*, **27**, 1512 (1905).

³ (a) Bassett, *Z. anorg. chem.*, **59**, 1 (1908); (b) *J. Chem. Soc.*, 111, 620 (1917).

⁴ Fairhall, *THIS JOURNAL*, **46**, 1593 (1924).

⁵ Schreinemaker, *Z. physik. Chem.*, **11**, 81 (1893).