

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE ELECTRICAL CONDUCTANCE OF AQUEOUS SOLUTIONS OF BARIUM CHLORIDE AS A FUNCTION OF THE CONCENTRATION

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Introduction

This is the third of a series of papers on the properties of solutions of barium chloride and is part of an extensive experimental investigation of the properties of these solutions covering a wide range of concentration which was undertaken in the hope that the data when studied in the light of the new Debye-Hückel theory of electrolytes would reveal new laws for the variation of these properties with the concentration or new relationships between the properties. Barium chloride is well adapted for this purpose because the theory and the known facts indicate that the influence of interionic attraction increases greatly with the valence. The first paper¹ in this series records data on the transference numbers of the barium ion covering the range 0.01 to 1.0 molal which resulted in the discovery of a new law for the variation of the transference numbers with the concentration. The second paper² contains new data on the viscosity of these solutions covering the range 0.005 to 1.0 molal and a new general law for the variation of the viscosity of solutions of electrolytes with the concentration. In this paper are recorded data on the conductance of this salt covering the range 0.001 to 1.0 molal which have suggested an equation for the variation of the conductance with concentration. All of these properties of these solutions turn out to be functions of the square root of the concentration.

Experimental Part

The barium chloride was purified as already described.³ To prepare neutral solutions of known composition the salt was dried by heating to a low red heat in a current of hydrochloric acid in a Richards⁴ bottling apparatus, and cooled in a vacuum. The solutions were made by weight, using conductivity water of known conductance. After the salt had dissolved and had been well mixed by shaking, a portion was withdrawn to test its neutrality. It was found that methyl red when added to solutions of barium chloride was sensitive to a trace either of hydrochloric acid or of barium hydroxide. Therefore, methyl red was added to the sample of the solution prepared as described above and also to a solution of approximately the

¹ Grinnell Jones and Malcolm Dole, *THIS JOURNAL*, **51**, 1073 (1929).

² Grinnell Jones and Malcolm Dole, *ibid.*, **51**, 2950 (1929).

³ Grinnell Jones and Malcolm Dole, *ibid.*, **51**, 1074 (1929).

⁴ T. W. Richards and H. G. Parker, *Proc. Am. Acad.*, **32**, 59 (1896).

same composition prepared from crystallized unheated barium chloride and the solution was rejected if the two could be distinguished. After the proper technique of drying the salt had been developed the solutions always gave the same color.

The stopper was then replaced by a special ground-glass stopper provided with two tubes, one of which extended to the bottom of the bottle and was connected by a ground joint with the conductivity cell. Air which had been bubbled through a barium chloride solution of approximately the same concentration was then blown into the bottle through the other tube, thus forcing the solution into and through the conductivity cell until the cell was well rinsed without danger of changing the composition of the solution by evaporation. The cell was then tightly closed by its own glass stoppers and placed in the thermostat at 25.00° and its resistance measured. It was then refilled and measured again. Only rarely was any change noted and in such cases the rinsing was repeated until successive fillings gave concordant results. The density of the solution was then determined by an Ostwald pycnometer to permit calculation of the concentration in moles per liter. The resistance measurements were made by the special bridge already described by Jones and Josephs⁵ using all precautions recommended in that paper. The results with 1100 cycles and with 2500 cycles agreed within 0.01%.

All solutions more dilute than 0.01 molal were prepared by dilution by weight of a 0.01 molal solution.

Three different cells of the Washburn pipet type with cell constants of 144.65, 51.4953 and 1.2326 were used. The cell constants of the first two were determined by means of a 0.01 *N* solution of potassium chloride in accordance with the suggestion of Kraus and Parker.⁶ The cell constant of the third cell was found by intercomparison with the second. The standard reference solution had 7.4945 g. of potassium chloride dissolved in 1000.00 g. of water (both weighed in air uncorrected to vacuum). The specific conductance of this solution was taken to be 0.0128988 plus the specific conductance of the water used. This value corrects for a slight inconsistency in Kohlrausch's figures for the *N* KCl and the 0.1 *N* KCl standards of reference but it is based on Kohlrausch's absolute measurements.

We are aware that H. C. Parker and E. W. Parker⁷ have concluded as the result of a careful investigation that the absolute measurements of the specific conductance of the standardizing solutions by Kohlrausch are in error by more than 0.1%. Parker and Parker have utilized fully the best of the earlier technique and have made important improvements in the details of procedure and valuable suggestions as to definitions of units,

⁵ Grinnell Jones and R. C. Josephs, *THIS JOURNAL*, **50**, 1049 (1928).

⁶ C. A. Kraus and H. C. Parker, *ibid.*, **44**, 2422 (1922).

⁷ H. C. Parker and E. W. Parker, *ibid.*, **46**, 312 (1924).

but their bridge assembly has since been shown to be imperfect,⁸ and the pipet cells of the type used show an apparent variation of cell constant with the resistance of the solution being measured, which was discovered by H. C. Parker⁹ and Randall and Scott.¹⁰ This Parker effect is ascribed by him to absorption at the electrodes and walls but he did not succeed in finding a practical means of avoiding the effect. Parker and Parker believe that this effect was present in the cells used in their absolute measurements (Ref. 7, p. 324), and although they attempt to minimize this error by the device of subtracting the measured resistance of two cells, they show a commendable lack of enthusiasm for this procedure, which is based on the unproved (and in our judgment unprovable) assumption that the electrode effects cause an equal error in the resistance of two cells of different cell constant and design. It therefore seemed to us premature to adopt the figures of Parker and Parker for the specific resistance of solutions of potassium chloride as a basis for determining the cell constant unless and until their results are confirmed by an independent investigation. Our opinion in this matter is not altered by the fact that the figures of Parker and Parker are used as the basis for conductance data in Vol. VI of the "International Critical Tables," which has been published during the final stages of the preparation of the manuscript of this paper.

It is believed that uncertainty of greater than 0.02% in the data on barium chloride solutions due to the Parker effect⁹ was avoided by always selecting a cell which would give a resistance of above 1000 ohms and by the use of the Jones and Joseph's bridge.¹¹

The data are recorded in Table I, in which each horizontal row represents a different solution and in which the columns give in order (1) the concentration in gram molecules (BaCl_2) per liter, c , based on weights *in vacuo* (the molecular weight of barium chloride being taken as 208.284); (2) the square root of the concentration, \sqrt{c} ; (3) the density, d , absolute with vacuum corrections applied; (4) density computed from the formula given below; (5) the difference between the observed and computed density; (6) the measured molecular conductance, Λ obs.; (7) a correction to give the conductance at the nearest round concentration, $\Delta\Lambda$; (8) the corrected values at the round concentration indicated, Λr . The density

⁸ Compare Parker and Parker, Ref. 7, p. 314, with Jones and Josephs, *THIS JOURNAL*, **50**, 1058-1062, 1070-1074 (1928).

⁹ H. C. Parker, *ibid.*, **45**, 1366, 2019 (1923).

¹⁰ M. Randall and G. N. Scott, *ibid.*, **49**, 636 (1927).

¹¹ The question of the cause and cure for the Parker effect has been investigated further in this Laboratory since the experimental work described in this paper was completed. This later work has disclosed that although the cells used in the research described in this paper embodied all principles of good design known at the time, they are not as free from Parker effect as some cells built in this Laboratory subsequently. A paper on cell design including a discussion of the Parker effect is now in preparation.

data when treated by the method of least squares gave $d = 0.99707 + 0.18224c - 0.00421c^2$. The maximum deviation between the observed results and computed results is 0.00006 and the average deviation is 0.00003.

TABLE I

MOLECULAR CONDUCTANCE OF BARIUM CHLORIDE SOLUTIONS AT 25°

Gram moles per liter	\sqrt{c}	Density, d , obs.	Density computed	Difference	Λ obs., con- ductance	$\Delta\Lambda$ Correction to round concn.	Λ Conductance at round concn.
0.0009827	0.031348	0.99725	264.70	-0.13	264.57
.0009701	.03114699725	264.72	-0.23	264.49
						Mean Λ at $c = 0.001$	264.53
.0024547	.04954599752	256.46	-0.19	256.27
.0024969	.04996999753	256.25	-0.01	256.24
						Mean Λ at $c = 0.0025$	256.25
.0049940	.070668	0.99801	.99798	+0.00003	248.14	-0.02	248.12
.0051560	.071805	(.99801)	247.70	+0.40	248.10
						Mean Λ at $c = 0.005$	248.11
.009999	.099995	0.99890	.99889	+ .00001	238.273	-0.001	238.27
.009999	.099995	(.99889)	238.274	-0.001	238.27
						Mean Λ at $c = 0.01$	238.27
.025002	.15812	1.00163	1.00163	223.25	-0.00	223.25
.025000	.15811	(1.00163)	223.24	0.00	223.24
						Mean Λ at $c = 0.025$	223.25
.049986	.22358	210.656	-0.005	210.65
.049998	.22360	1.00621	1.00617	+ .00004	210.652	-0.001	210.65
						Mean Λ at $c = 0.05$	210.65
.100009	.31624	1.01531	1.01525	+ .00006	197.358	+0.002	197.36
.099995	.31623	(1.01525)	197.370	-0.001	197.37
						Mean Λ at $c = 0.10$	197.36
.250044	.50004	1.04240	1.04238	+ .00002	178.388	+0.004	178.392
.249992	.49999	1.04236	1.04237	- .00001	178.398	-0.001	178.397
						Mean Λ at $c = 0.25$	178.39
.50000	.70715	1.08711	1.08714	- .00003	161.184	+0.000	161.184
.50000		1.08708	1.08714	- .00006	161.226		161.226
						Mean Λ at $c = 0.50$	161.20
.97476	.98730	1.17066	1.17071	+ .00005	137.982	-1.039	137.94
1.00527	1.00263	1.17601	1.17602	- .00001	137.764	+0.217	137.98
						Mean Λ at $c = 1.0$	137.96

The uncorrected data shown in Col. 6 are represented in Fig. 1 by the center points of the circles. In most cases the two independent determinations on solutions of nearly the same concentration are shown by a single circle because the slight differences are not visible on the scale which can be printed.

The corrections to bring the values to round concentrations were determined by plotting Λ against \sqrt{c} , the slope of the curve $d\Lambda/d\sqrt{c}$ was found at each point and the correction $\Delta\Lambda = (d\Lambda/d\sqrt{c})\Delta\sqrt{c}$ computed and applied. It will be noticed that after correction to a common round concentration each pair of solutions of similar concentration agree very well, the average deviation being only 0.025 ohm. These differences are greater in the most dilute solutions, as is to be expected on account of the greater experimental difficulties in working with dilute solutions.

Interpretation of the Data

Having obtained a set of data covering a wide range of concentration it becomes of interest to attempt to find an equation for the molar conductance as a function of the concentration which is in harmony with the data and of a form which is as simple as possible and which shows no abnormal or improbable behavior as the concentration approaches zero; and to use the best equation which can be found to estimate the limiting conductance at zero concentration. It seemed hardly necessary to carry out the laborious

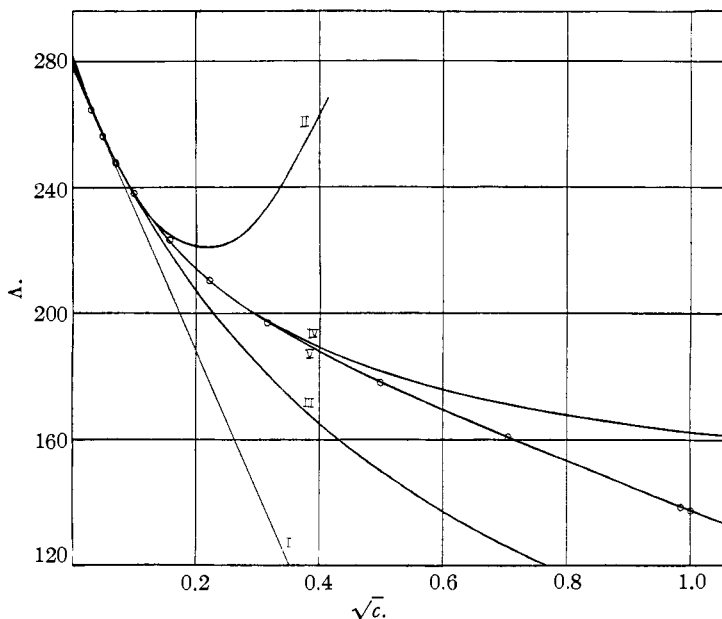


Fig. 1.—I, Kohlrausch, $\Lambda = 278.75 - 449.9 \sqrt{c}$; II, Debye-Hückel-Onsager, $\Lambda = 280.64 - 550.12 \sqrt{c} + 1265.1 c$; III, Walden, $\Lambda = 278.69 / (1 + 1.715 \sqrt{c})$; IV, Lattay, $\Lambda = 281.22 - [602.8 \sqrt{c} / (1 + 4.069 \sqrt{c})]$; V, Jones and Dole, $\Lambda = 282.13 - [636.3 \sqrt{c} / (1 + 4.628 \sqrt{c})] - 31.13 c$.

calculations with all of the numerous equations which have been proposed because nearly all of the empirical equations which antedate the Debye-Hückel theory are now known to be inaccurate or to be in harmony with the facts only within a quite limited range of concentration.

Recently Debye and Hückel¹² have proposed a theory of electrolytes based on the hypothesis that ionization is substantially complete and that the electric forces between the ions which Arrhenius assumed to be negligible play a significant role.

The mathematical complexities of deriving definite equations on this

¹² P. Debye and E. Hückel, *Physik. Z.*, **24**, 185 (1923); **24**, 305 (1923); E. Hückel, *Ergebnisse der Exakten Wissenschaften*, **3**, 199 (1924).

basis are very great and compel them to neglect some known physical factors in the problem and to introduce some relatively simple approximate mathematical relationships instead of using the rigid but more complicated functions. Their conclusion is that the equation

$$\Lambda = \Lambda_0 - A\sqrt{c} \quad (I)$$

is the limiting law to which the measured conductance will approach more and more closely as the concentration approaches zero. The constant A has a very complicated theoretical significance, being dependent upon the dielectric constant of the solvent, the temperature, the mobilities at infinite dilution and valence of all of the ions present, as well as several universal constants. However, the value of A as well as Λ_0 is in practice chosen to fit the data. It should be noted, however, that the theory predicts that the most important factor in determining the variation of A from salt to salt is the valence type and this prediction is borne out in practice. Indeed it has long been known that the conductance-concentration curves of all salts of the same valence types (in the absence of abnormalities such as complex formation) tend to run parallel and near together, whereas the curves for salts of different types diverge markedly.

This Equation I was discovered long ago by Kohlrausch,¹³ was much used by him in extrapolating to zero concentration and is commonly called Kohlrausch's square root law. The most convenient way to test the validity of this law is to plot the observed values of the conductance against the square root of the concentration and observe how closely the points fall on a straight line. A straight line (I in Fig. 1) having the equation $\Lambda = 278.75 - 449.9\sqrt{c}$, passes through the values of Λ at 0.001 and 0.0025, but this line deviates greatly from the data at all higher concentrations. Kohlrausch's law can, therefore, only be regarded as a limiting law which is approximately obeyed in very dilute solutions. This is evident from Col. 5 of Table II and from Fig. 1, in which our data are plotted as points within the circles and Curve I represents the equation given above. Space does not permit a detailed recapitulation and analysis of the evidence from other cases in the literature but much can be found. The case of barium chloride cited from our own data is typical rather than exceptional or peculiar.

But although Kohlrausch's law can only be regarded as a limiting law, the experimental evidence in its favor and the theoretical support which it receives from the work of Debye and Hückel make it extremely probable that the true equation expressing the conductance as a function of the concentration when plotted Λ against \sqrt{c} will be asymptotic at $c = 0$ with a straight line having finite negative slope. In attempting to find an

¹³ F. Kohlrausch and M. E. Maltby, *Wiss. Abh. Phys. Techn. Reichsanstalt*, **3**, 156-227 (1900); F. Kohlrausch and E. Grüneisen, *Berl. Ber.*, 1215-1222 (1904); F. Kohlrausch, *Z. Elektrochem.*, **13**, 336 (1907); **13**, 645 (1907); F. Kohlrausch, "Gesammelte Abhandlungen," 1911, Vol. II, pp. 901, 1083, 1127, 1148.

equation which is valid up to as high a concentration as possible, we have applied this criterion and rejected all forms of the function which do not meet this test.

TABLE II
CALCULATED AND OBSERVED VALUES

Concn. c	\sqrt{c}	Obs. conductance	I Kohlrausch		II Debye-Hückel	
			$\Lambda = 278.75 - 449.9 \sqrt{c}$ Λ comp.	$\Delta\Lambda$	$\Lambda = 280.64 - 550.12 \sqrt{c} + 1265.1c$ Λ comp.	$\Delta\Lambda$
0.001	0.031623	264.53	264.53	+0.00	264.51	+0.02
.0025	.05	256.25	256.25	+0.00	256.30	-0.05
.005	.070711	248.11	246.94	+1.17	248.07	+0.04
.01	.1000	238.27	233.76	+4.51	238.28	-0.01
.025	.15811	223.25	207.61	+15.64	225.29	-2.04
.05	.22361	210.65	178.15	+32.50	220.89	-10.24
.1	.31623	197.36	136.48	+60.88	233.19	-35.83
.25	.50000	178.39	53.80	+124.59	321.86	-143.46
.50	.70711	161.20	-39.38	+200.58		
1.00	1.00000	137.96	-171.15	+309.11		

Concn.	\sqrt{c}	Obs. conductance	III Walden		IV Lattey		V Jones and Dole	
			$\Lambda = \frac{278.69}{1 + 1.715 \sqrt{c}}$ Λ comp.	$\Delta\Lambda$	$\Lambda = 281.22 - \frac{602.8 \sqrt{c}}{1 + 4.069 \sqrt{c}}$ Λ comp.	$\Delta\Lambda$	$\Lambda = \frac{282.13 - 636.3 \sqrt{c}}{1 + 4.828 \sqrt{c}} - 31.13c$ Λ comp.	$\Delta\Lambda$
0.001	0.031623	264.53	264.25	+0.28	264.33	+0.20	264.55	-0.02
.0025	.05	256.25	256.65	-0.44	256.16	+0.09	256.22	+ .03
.005	.070711	248.11	248.56	-0.45	248.10	+0.01	248.03	+ .03
.01	.1000	238.27	237.89	+0.38	238.37	-0.10	238.32	- .05
.025	.15811	223.25	219.24	+4.01	223.22	+0.03	223.26	- .01
.05	.22361	210.65	201.44	+9.21	210.64	+0.01	210.65	+ .00
.1	.31623	197.36	180.69	+16.67	197.86	-0.50	197.36	+ .02
.25	.50000	178.39	150.04	+28.35	181.90	-3.51	178.35	+ .04
.50	.70711	161.20	125.95	+35.25	171.28	-10.08	161.26	- .06
1.00	1.00000	137.96	100.03	+37.93	162.30	-24.34	137.94	+ .02

The next form of the conductance function to be considered was a modification of Kohlrausch's law having the form

$$\Lambda = \Lambda_0 - A\sqrt{c} + Bc \tag{II}$$

This equation obviously meets the asymptotic test given above. It was first suggested by Debye and Hückel in their early paper and used as a means of extrapolating to infinite dilution, but since the last term has no theoretical basis it may be regarded as an empirical equation. Debye and Hückel chose values of Λ_0 , A and B empirically to fit the data. Onsager¹⁴ points out that the space lattice arrangement postulated by Debye and Hückel must be disturbed by Brownian movement and has worked out a mathematical technique to make allowance for this disturbance and to take account of the combined relaxation of the ionic atmospheres due to the

¹⁴ L. Onsager, *Physik. Z.*, **27**, 388 (1926); **28**, 277 (1927); *Trans. Faraday Soc.*, **23**, 341 (1927).

diffusion of the ions in respect to one another and to enable the effect of electrophoresis to be calculated without a knowledge of ionic radii. Onsager's derivation leads to an equation of the form of Kohlrausch's square root law in which the slope Λ is a complicated but explicit function of the dielectric constant and viscosity of the solvent, the temperature and the valencies and mobilities at infinite dilution of all of the ions present, as well as several universal constants. Ionic radii are, however, not involved directly. Assuming the conductance of the ions at infinite dilution to be known, Onsager has computed the slope of the $\Lambda-\sqrt{c}$ curves for many salts with results which agree within about 10% with the slopes found experimentally; but although this does not solve the problem of extrapolation to infinite dilution, because for this purpose we need to know the slope with an uncertainty of much less than 10% in order to find the limit of the conductance at infinite dilution, nevertheless it is of much interest.

Onsager recognizes that an equation of the form of Kohlrausch's law which he has derived is only valid as a limiting law and in order to extend its range of validity he follows Debye and Hückel in adding a term, $+Bc$, linear with the concentration. The equation

$$\Lambda = \Lambda_0 - A\sqrt{c} + Bc \quad (\text{II})$$

is an improvement over the Kohlrausch equation but no claim is made by its proponents that it is valid above 0.01 molal. We have found that an equation of this form

$$\Lambda = 280.64 - 550.12\sqrt{c} + 1265.1c$$

fits our data on barium chloride fairly well up to 0.01 molal (see Curve II in Fig. 1 and Cols. 6 and 7 in Table II) but it fails badly in higher concentrations. This is the equation of a parabola (when plotted Λ against \sqrt{c}) with a minimum value of Λ at $\sqrt{c} = 0.217$ or $c = 0.048$, whereas the data show no indication of the occurrence of a minimum. Beyond this minimum this equation gives grossly erroneous results. It is quite evident from the curves and computations that the term $+Bc$ is at fault.

The complicated and difficult derivations of this equation evidently and admittedly fail to account adequately and fully for all of the factors in the problem. In these circumstances we thought it best to attempt to find a valid equation by inductive methods from the data themselves rather than by deductive reasoning from hypotheses.

Walden¹⁵ has proposed an equation of the form

$$\Lambda = \frac{\Lambda_0}{1 + N\sqrt{c}} \quad (\text{III})$$

and has presented considerable evidence in its support, especially for non-aqueous solutions. It is easy to show by differentiation that this equation conforms to the asymptotic test described above. The Walden equation

¹⁵ P. Walden, *Z. physik. Chem.*, **108**, 341 (1924).

can be readily transformed into $1/\Lambda = 1/\Lambda_0 + N/\Lambda_0 \sqrt{c}$, which permits its validity to be tested by plotting $1/\Lambda$ against \sqrt{c} , and the coefficients to be readily determined. We used our data on barium chloride at $c = 0.01$ and below to evaluate the constants and thus obtained $\Lambda = 278.69/(1 + 1.715\sqrt{c})$. This equation comes much nearer to the experimental values at the higher concentrations than either of the forms already discussed but, nevertheless, it is not within the experimental errors either at low or high concentrations and indeed is not as good at low concentrations as Equation I or II (see Curve III in Fig. 1 and Cols. 8 and 9 in Table II).

Lattey¹⁶ has recently suggested the form

$$\Lambda_0 - \Lambda = \frac{A}{V^{1/2} + N}$$

where $V = 1/c$ and A and N are dependent on the salt chosen and the temperature. This may be readily transformed into

$$\Lambda = \Lambda_0 - \frac{A\sqrt{c}}{1 + N\sqrt{c}} \quad (\text{IV})$$

Lattey in a brief paper gives calculations showing that an equation of this form, $\Lambda = 130.01 - [89.47 \sqrt{c}/(1 + 1.82 \sqrt{c})]$, agrees with the data of Kohlrausch and Maltby on potassium chloride up to 1 molal. He states that he has tested it on many other univalent salts and finds that it conforms to the facts up to 0.1 molal, but does not publish the proof in detail. His paper contains no indication that he has tested his equation on salts of higher valence types. This equation is obviously asymptotic to $\Lambda = \Lambda_0 - A\sqrt{c}$ as \sqrt{c} approaches zero. We then applied the method of least squares to the data on barium chloride up to 0.05 to determine the best values of the coefficients with the result $\Lambda = 281.22 - [602.8 \sqrt{c}/(1 + 4.069 \sqrt{c})]$. As will be seen from Cols. 10 and 11 of Table II and Curve IV in Fig. 1, this equation is a very substantial improvement over the other forms already discussed. The Lattey equation agrees with the data within the experimental error up to 0.05 molal, but if the constants are chosen so as to give good agreement at these concentrations the computed values of Λ at the higher concentrations are too great.

We noticed that these deviations of the Lattey equation seemed to be proportional to the concentration and this suggested to us that they might be remedied by adding a term, $-Bc$ giving an equation of the form

$$\Lambda = \Lambda_0 - \frac{A\sqrt{c}}{1 + N\sqrt{c}} - Bc \quad (\text{V})$$

The constants of this equation were determined by the method of least squares to be

$$\Lambda = 282.13 - \frac{636.3\sqrt{c}}{1 + 4.628\sqrt{c}} - 31.13c, \text{ or}$$

$$\frac{\Lambda}{282.13} = 1 - \frac{2.1845\sqrt{c}}{1 + 4.628\sqrt{c}} - 0.1103c$$

¹⁶ R. T. Lattey, *Phil. Mag.*, [7] 4, 831 (1927).

This equation fits the data within 0.06 mho at all points from 0.001 to 1.0 molal. The average deviation is only 0.014%. Curve V in Fig. 1 is the graph of this equation and the experimental points are the centers of the circles. The deviations are much too small to be apparent in the graph on the scale which can be printed but are shown numerically in the last column of Table II.

A discussion of the general validity of Equation V will be postponed until new data on many salts covering a wide range of concentration can be obtained. In view of the fact that important improvements in the design of cells for the measurement of conductance have recently been effected in this Laboratory, it seems inadvisable to undertake the laborious calculations necessary to test this equation by means of the data existing in the literature. The correlation of these conductance data with our transference data will be discussed in a separate paper by the junior author.

The Viscosity Correction

In the above theoretical treatment no attempt has been made to apply to the conductance data a viscosity correction.¹⁷ During the course of the experimental work, measurements were made to determine the viscosity of barium chloride solutions. These results have already been published.² Although these data were originally obtained in the expectation of using them to correct the conductance values for the viscosity changes, a careful consideration of the question suggests that a large part if not all of the viscosity correction should not be applied. By studying our viscosity data we discovered that the relative fluidity (ϕ) of the solution could be expressed accurately by an equation of the form

$$\phi = 1 - A\sqrt{c} - B(c) \quad (\text{VI})$$

or for viscosities in dilute solutions

$$\eta = 1 + A\sqrt{c} + (B + A^2)(c) + \dots \quad (\text{VII})$$

A and B are constants chosen to fit the data. For barium chloride solutions at 25°, $A = 0.02013$ and $B = 0.20087$. The square root term suggested to us that this part of the viscosity increase might be due to the electric forces existing between the ions.

Falkenhagen and Dole¹⁸ have deduced from the Debye theory of interionic attraction that the distortion of the symmetrical ionic arrangement by means of viscous flow increases the macroscopic viscosity of the solution in proportion to the square root of the concentration; but the friction encountered by an ion moving in an electric field is determined by the microscopic viscosity of the water molecules in its immediate path and this microscopic viscosity is probably not identical with the macroscopic viscosity as determined in a viscometer.

¹⁷ See C. A. Kraus, *THIS JOURNAL*, **36**, 35 (1914), for a historical review of this question.

¹⁸ H. Falkenhagen and M. Dole, *Physik. Z.*, **30**, 611 (1929).

If the electric forces between the ions really change the microscopic viscosity, then this would influence the motion of the ions and would need to be taken into account in considering the variation of conductance with concentration. In such a case it would be fallacious to use Stokes' law without allowing for the change in viscosity. But if the microscopic viscosity is unaffected by the interionic attraction, it would be erroneous to apply a viscosity correction to the data for the change in macroscopic viscosity due to the interionic attraction represented in our viscosity equation (VII) by the term $A\sqrt{c}$.

This may also be true for the Bc term of Equation VI. Thus MacInnes and Cowperthwaite¹⁹ have found that the conductance of the chloride ion is exactly the same in 0.1 normal solutions of sodium chloride and of potassium chloride although the measured macroscopic viscosities differ by 2%. This identity of the mobility of the chloride ion in the two solutions indicates that the effective or microscopic viscosity of the medium in the path of the moving ion may be the same in the two solutions.

This evidence against applying any viscosity correction is not entirely unambiguous since the junior author has discovered in some unpublished work that ions apparently affect macroscopic viscosities quite independently of each other, at least as regards the B terms of Equation VI. If this is true, then it is possible for the chloride ion to migrate in an environment whose microscopic viscosity is determined only by the chloride on itself, and thus have the same conductance either in sodium or potassium chloride. However, new experiments must be carried out before this question can be entirely settled.

Grateful acknowledgment is made for an appropriation from the Milton Fund of Harvard University for the expenses of this work.

Summary

1. Measurements of the density and electrical conductance of aqueous solutions of barium chloride at 25° covering the range 0.001 to 1.0 molal are recorded.

2. Numerous functions which have been suggested to express the variation of the conductance with the concentration are discussed and a new function having the form, $\Lambda = \Lambda_0 - [A\sqrt{c}/(1 + N\sqrt{c})] - Bc$ is shown to be in harmony with the facts in this case, over the range 0.001 to 1.0 molal.

3. The propriety of applying a viscosity correction to measurements of conductance is discussed.

4. In this and the preceding papers of this series it is shown that the properties of aqueous solutions of barium chloride at 25° can be expressed as a function of the concentration up to 1 molal by the equations

¹⁹ D. A. MacInnes and I. A. Cowperthwaite, *Trans. Faraday Soc.*, **23**, 400 (1927).

Activity coefficient	$\log f = \frac{-1.734\sqrt{c}}{1 + 2.2318\sqrt{c}} + 0.15266c$
Transference number of the barium ion	$t = \frac{1.4476}{1 + 0.07010\sqrt{c}} - 1$
Relative fluidity	$\varphi = 1 - 0.02013\sqrt{c} - 0.20087c$
Density	$d = 0.99707 + 0.18224c - 0.00421c^2$
Molal conductance	$\Lambda = 282.13 - \frac{636.3\sqrt{c}}{1 + 4.628\sqrt{c}} - 31.13c$

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THE OXYGEN ELECTRODE: AN ADSORPTION POTENTIAL

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The problem of the oxygen electrode arose, for the most part, from the study of the Grove cell: Pt, HNO₃, H₂SO₄, Zn. This cell gives, when freshly made, a potential of 1.6 to 1.7 volts. It is extremely sensitive to polarization effects, which change the potential over a considerable range and render it irreproducible. The cause of this polarization was supposed to be some reaction involving the transfer of oxygen from the gaseous to an ionic or combined state. The outcome was that the study of the oxygen electrode was approached from the standpoint of polarization reactions.

One very prevalent explanation of the behavior of this electrode is the formation of various oxides of platinum and their hydrates; the so-called "oxide theory."¹ Another theory is that the potentials are due to the formation of unstable products in the electrolyte about the electrode.² The experimental work described in the literature just cited affords abundant evidence that the oxygen electrode is irreversible, and cannot be classed with the hydrogen electrode or metal electrodes against solutions of their ions. As a matter of fact, there is no experimental evidence to show that there is any chemical reaction at the electrodes.

Recently, efforts based upon purely empirical considerations have been made to use the oxygen electrode in electrometric titrations involving oxidizing solutions.³

¹ G. Grube, *Z. Elektrochem.*, **16**, 621-632 (1910); R. Lorenz and co-workers *ibid.*, **15**, 206-212, 293-297, 349-355 (1909); F. Foerster, *Z. physik. Chem.*, **69**, 236-271 (1910); Spielman, *Trans. Faraday Soc.*, **5**, 88-102 (1909); G. Grube and B. Dulk, *Z. Elektrochem.*, **24**, 237-248 (1918); E. P. Schoch, *J. Phys. Chem.*, **14**, 665-677 (1910).

² F. Haber, *Z. Elektrochem.*, **7**, 441-448 (1901); E. Bose, *Z. physik. Chem.*, **34**, 726-730 (1900); E. Bose, *ibid.*, **38**, 23-26 (1901); Bornemann, *Z. Elektrochem.*, **15**, 673-679 (1910); G. N. Lewis, *THIS JOURNAL*, **28**, 164 (1906).

³ N. H. Furman, *ibid.*, **44**, 2685-2697 (1922); Tilley and Ralston, *Trans. Am. Electrochem. Soc.*, **44**, 31 (1923); A. K. Goard and E. K. Rideal, *Trans. Faraday Soc.*, **19**, 740-747 (1924); W. T. Richards, *J. Phys. Chem.*, **32**, 990-1005 (1928).