

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Conductance of Aqueous Solutions as a Function of the Concentration. I. Potassium Bromide and Lanthanum Chloride

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More than thirty different equations to express the conductance of aqueous solutions as a function of the concentration have been published but none of them have been shown to be valid for electrolytes of varied types over a wide range of concentration.

In 1900 Kohlrausch¹ proposed the equation $\Lambda = \Lambda_0 - A\sqrt{c}$ which he found inductively by a study of his data on dilute solutions. But in spite of the great reputation of its sponsor this square root law received scant attention at the time because the current theoretical views gave no ground for regarding the conductance as a function of the square root of the concentration. It does not conform to the data except at extreme dilutions.

Twenty-three years later this law was derived theoretically by Debye and Hückel from the fundamental postulates of the interionic attraction theory.² The derivation was soon revised and improved by Onsager,³ who gave it the form $\Lambda = \Lambda_0 - (\alpha\Lambda_0 + \beta)\sqrt{c}$ where for binary salts α and β are complicated but explicit functions of several universal constants, the dielectric constant and viscosity of the solvent, the temperature, and the valences of the ions. For non-binary salts the coefficient α is also a function of the limiting conductance of the separate ions. This represents a substantial advance in spite of the fact that the limiting conductances of the ions cannot be measured directly but must be estimated by an extrapolation of conductance and transference data.

If the Onsager equation is transformed by using molar concentrations (gram molecules per liter) and molar conductances instead of equivalent concentrations and conductances, and by introducing the appropriate numerical values for water at 25°, namely, $\eta = 0.008949$, $D = 78.57$ and $T = 298.1$, the Onsager equation becomes

$$\Lambda = \Lambda_0 - [0.27446w\Lambda_0 + 21.138 z_1 z_2 (z_1 + z_2)] \sqrt{z_1 z_2 (z_1 + z_2) c}$$

(1) F. Kohlrausch, *Wiss. Abhandl. physik.-tech. Reichsanstalt.* **3**, 219 (1900).

(2) P. Debye and E. Hückel, *Physik. Z.*, **24**, 185, 305 (1923); P. Debye, *ibid.*, **25**, 97 (1924).

(3) L. Onsager, *ibid.*, **27**, 388 (1926); **28**, 277 (1927).

$$w = \frac{2gz_1 z_2}{1 + g}$$

$$g = \frac{z_1 z_2 \Lambda_0}{(z_1 + z_2) \{ \Lambda_0 + (z_2^2 - z_1) \Lambda_1^0 + (z_1^2 - z_2) \Lambda_2^0 \}}$$

At 0° substitution of $T = 273.1$, $\eta = 0.017938$ and $D = 88$ gives

$$\Lambda = \Lambda_0 - [0.26406w\Lambda_0 + 10.4105 z_1 z_2 (z_1 + z_2)] \sqrt{z_1 z_2 (z_1 + z_2) c}$$

This equation may be abbreviated to

$$\Lambda = \Lambda_0 - (\alpha\Lambda_0 + \beta)\sqrt{c}$$

If the Onsager equation were valid it would have the great merit that the conductance could be computed without the use of any parameters chosen arbitrarily to fit the data except the conductance of the two ions at infinite dilution (for binary salts for which $z_1 = z_2$, only the sum of the conductances of the two ions is required). But the Onsager equation has the form of the Kohlrausch square root law $\Lambda = \Lambda_0 - Ac^{1/2}$, which has long been known to be invalid except for extreme dilution. The great drawback of the Onsager formula is that at best it is only an approximation because in its derivation only terms proportional to the square root of the concentration have been retained and terms proportional to c or to a higher power of c have been rejected. Therefore if we plot Λ against \sqrt{c} , the Onsager equation gives a line which is tangent to the true conductance curve at zero concentration.

Nevertheless if, in spite of this limitation, the Onsager equation gives the true limit of the slope at infinite dilution it will be a great aid in the extrapolation necessary to obtain the values of the conductance of salts and ions at infinite dilution. The question whether the limiting slope computed from the Onsager equation is correct or not can only be determined by comparison with the data. For this purpose reliable data at high dilutions are necessary and such data are scarce in the literature. Onsager and other authors have given such comparisons. For a discussion of these attempts to test the Onsager equation and for the references the books of Davies and of Falkenhagen should be consulted.⁴ In general

(4) Cecil W. Davies, "The Conductivity of Solutions," J. Wiley and Sons, New York, 1933, 2d ed., pp. 78-92; Hans Falkenhagen, "Elektrolyte," S. Hirzel, Leipzig, 1932, pp. 191-197.

these comparisons indicate that the computed and observed slopes agree within about 10% for uni-univalent salts in aqueous solutions, and even this degree of concordance is rightly regarded by most commentators as a triumph for the theory. However, the question whether these discrepancies are due to experimental error or to an incompleteness or inaccuracy in the formula remains open. One of the objects of the present investigation is to supply new evidence on this question.

Another important result of Onsager's analysis is that it makes it extremely probable that when the long sought general law expressing the conductance as a function of the concentration is found it will have such a mathematical form that the value of $\partial\Lambda/\partial\sqrt{c}$ will approach a negative constant as c approaches zero. Many of the equations which have been proposed, including the Ostwald dilution law, the Storch equation and other modifications of Ostwald's law do not satisfy this test.

In 1930 Grinnell Jones and Malcolm Dole⁵ made a critical comparison of the more promising of the formulas which have hitherto been proposed by means of their new data on barium chloride and found the Lattey equation⁶ to be the best of the older equations. They were able to make a substantial improvement by modifying the Lattey function by the addition of a negative term proportional to the concentration. The Jones and Dole equation has the form

$$\Lambda = \Lambda_0 - \frac{A\sqrt{c}}{1 + N\sqrt{c}} - Bc$$

This equation was shown to be in agreement with their data within a few hundredths of a per cent. over the entire range from 0.001 to 1.0 molar. This equation meets the test referred to above since $\partial\Lambda/\partial\sqrt{c}$ approaches $-A$ when c approaches zero. However, it has the great drawback that it contains four constants chosen to fit the data. The theoretical significance of the Λ_0 term is clear and the A coefficient is presumably given in principle at least by Onsager's analysis, but the significance of the N and B terms is still obscure. The N term possibly involves the radius of the ion and the B term the viscosity effect.

Recently Shedlovsky⁷ has tested the Onsager equation by computing the values of Λ_0 by the

(5) Grinnell Jones and Malcolm Dole, *THIS JOURNAL*, **52**, 2245 (1930).

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

(7) T. Shedlovsky, *THIS JOURNAL*, **54**, 1405 (1933).

use of new very precise data of his own on several uni-univalent salts. He found that the computed values of Λ_0 were not constant, thus proving that the deviations between the actual conductance and the Onsager equation were beyond the experimental errors even at extreme dilutions. Shedlovsky then found empirically that if he added a term $-Bc$, giving the equation

$$\Lambda_0 = \frac{\Lambda + \beta\sqrt{c}}{1 - \alpha\sqrt{c}} - Bc$$

he obtained an equation which agreed with his data on several uni-univalent salts up to about 0.1 normal, although it failed for potassium nitrate and for some other salts. Since the coefficients α and β are not arbitrarily chosen to fit the data but are computable by Onsager's formulas and for the binary salts are definite for a specified solvent and temperature, this equation of Shedlovsky has only two parameters chosen to fit the data, namely, Λ_0 and B , and therefore is a great advance if it has the proper mathematical form to be generally valid. For salts in which the valence of the anion differs from that of the cation the conductance of each ion is needed instead of the sum of these conductances, in addition to the parameter B .

Although Shedlovsky only claims that his equation is valid for uni-univalent salts, it is of interest to test it for salts of other valence types.

It has long been known that the shape of the conductance-concentration curve is greatly influenced by the valence type of the salt. According to the Onsager equation the limiting slope is chiefly dependent on the valences of the ions. In order to test the validity of the equations which have been proposed, data on many salts of varied valence types, covering as wide a range of concentration as possible and of a high precision, are evidently needed.

As a preliminary to this investigation the electrical part of the technique has been critically examined in this Laboratory, and improvements in the bridge and its accessories and in the cells have been devised. The absolute values of the conductance of several standard solutions have been redetermined to serve as a basis for the calibration of cells.⁸

In this paper are recorded new measurements on solutions of potassium bromide and of lan-

(8) Grinnell Jones and R. C. Josephs, *THIS JOURNAL*, **50**, 1049 (1928); Grinnell Jones and G. M. Bollinger, *ibid.*, **51**, 2407 (1929); **53**, 411, 1207 (1931); Grinnell Jones and B. C. Bradshaw, *ibid.*, **55**, 1780 (1933).

thanium chloride at both 25 and 0°. Lanthanum chloride was chosen because it was expected that it would be less hydrolyzed than any other salt of a trivalent metal. Further work on other salts is in progress.

The electrical part of the technique and the temperature control are believed to be so reliable that the greatest source of error is in the preparation of the solutions. All solutions were prepared by dissolving a weighed amount of salt in water of low measured conductivity and determining the weight of the solution. After determining the conductivity, the density was determined so that the concentration in gram molecules per liter could be computed.

The potassium bromide used was prepared by Dr. Sven Baekström in this Laboratory for another investigation. It was fused in dry, oxygen-free nitrogen. A saturated solution gave no indication of alkalinity when tested with phenolphthalein.

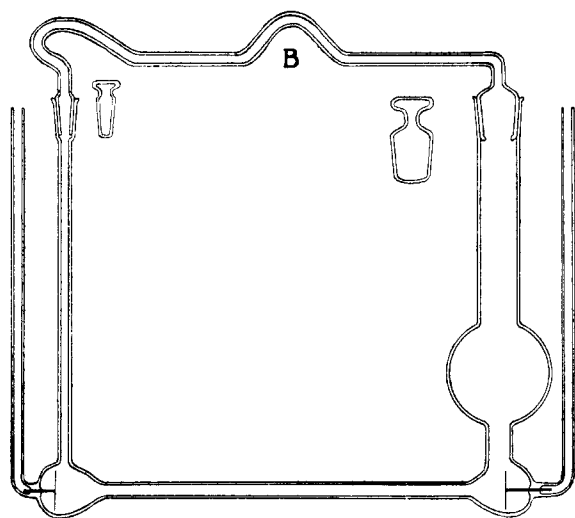


Fig. 1.—Cell Q.

The lanthanum chloride used had been prepared by the late Professor Charles James. A spectroscopic examination kindly carried out for us by Professor G. P. Baxter showed that it was essentially free from other rare earth salts but contained traces of other impurities. These impurities were removed by precipitating the lanthanum chloride from a concentrated aqueous solution with pure hydrogen chloride in the cold. The precipitated crystals were dried centrifugally. These steps were then repeated. A preliminary heating freed the crystals from the greater part of their water content, although a little basic salt was formed. An appropriate quantity for each experiment was dried in a modified quartz Richards bottling apparatus at 600° in a current of pure dry hydrogen chloride gas. After cooling, the hydrogen chloride was removed by exhausting and admitting dried purified air, repeatedly.

No insoluble material was found after this treatment. The boat containing the salt was then enclosed in a bottle and weighed. A micro balance was used for weighing the small amounts required for making the dilute solutions.

For the concentrated solutions (0.1 to 3.75 molar potassium bromide and 0.05 to 1.0 molar lanthanum chloride) combined cells and solution flasks of the type shown in Fig. 1 were used. Several of these cells differing in volume and cell constant were available. They were made of Jena 16 III glass. A suitable quantity of salt was dried and weighed as described above in a boat which would pass through the larger opening. The amount of water needed was then computed. The cell having been dried and weighed to milligrams was rinsed out with conductivity water. Then the water was flushed through the cell into the water cell by means of suitable connections not shown in the figure and its conductivity measured. If these measurements showed the water to be of suitable quality, the weight of water in the cell was adjusted to within a few centigrams of the amount desired by removing the excess and the final weight determined to milligrams. The boat containing the salt was then placed in the flask and the mixing tube B inserted. The ground joints were sealed on the outside with melted beeswax and the whole apparatus rocked until the salt was dissolved and the solution thoroughly mixed by circulation through the mixing tube. The solutions were perfectly clear. The mixing tube was then removed and quickly replaced by ground stoppers because the film of solution in the mixing tube acted as a shunt across the electrodes and gave erratic results. The cell was placed in an oil thermostat at $25 \pm 0.002^\circ$ and its resistance measured with the bridge built by Mr. Josephs. Measurements were always made with at least two frequencies (about 1090 and 2280 cycles per second) and if a significant difference was found the cause of the discrepancy was discovered and remedied.

The cell was then immersed in oil in a water-tight metal box which was completely surrounded by ice and water in a well insulated container. After stirring the oil slowly for about two hours, or until its temperature was within a few hundredths of a degree of 0° the stirring was stopped because the friction of the stirring heated the oil. The shaft of the stirrer was made of wood to minimize conduction of heat into the oil. After waiting for about twelve hours the temperature was within 0.01 of 0°. The resistance was then measured and observed at intervals for several hours.

The dilute solutions were prepared in Pyrex flasks provided with suitable connections which made it possible to bubble purified carbon dioxide-free air through the water and force the solution into the conductance cells and pycnometers without contact with the laboratory air. Blank experiments using an empty boat showed no significant gain in conductivity during the manipulation required for the preparation of the solutions and their transfer to the conductance cells and pycnometers. None of the solutions were prepared by dilution of a more concentrated solution but in all cases the salt and solution were weighed to determine the concentration. The water used for the dilute solutions had a specific conductivity at 25° within the range of 0.1 to 0.3×10^{-6} . The specific conductance of the water used was subtracted from that of

the solutions before computing the molar conductance. The cell constants were determined by means of standard potassium chloride solutions using the values of the specific conductance determined by Jones and Bradshaw.⁸

No corrections were applied to the data on lanthanum chloride to compensate for changes in conductance due to hydrolysis. The best estimate of the effect of hydrolysis which we could make indicated that it is negligible in comparison with the unavoidable experimental errors in the concentration range studied. The effect of hydrolysis increases with dilution but so do the experimental errors. Sadolin⁹ reports P_H values for lanthanum chloride solutions determined by the electromotive force method ranging from 6.1 to 7.0. Kleinheksel and Kremers¹⁰ found that a 0.495 normal solution of lanthanum chloride had a P_H of

11.5 (especially ferric salts) by the use of glass electrodes. He says in regard to lanthanum chloride "The P_H values obtained below 0.009 N were greater than 6, which indicates, we believe, negligible hydrolysis. . . . It is certain that the hydrolysis is so small as not to affect the conductance seriously down to very low concentrations." Jacques measurements were made on a part of the same preparation of lanthanum chloride as was used for this investigation.¹²

At each round concentration at least two but usually three or four independent solutions were prepared. However, the actual concentrations were always slightly different from the round concentration desired so that a small correction was required to bring the results to the round concentration. The detailed data on each solution and the

TABLE I
COMPARISON OF THE EXPERIMENTAL DATA FOR CONDUCTANCE WITH THE VALUES COMPUTED BY VARIOUS EQUATIONS
POTASSIUM BROMIDE AT 25°

c	d 25°	Aobs.	Not corrected for viscosity			Corrected for viscosity					
			Onsager Λ_0	Shedlovsky $\Lambda_{comp.}$	$\Delta\Lambda$	Jones and Dole $\Lambda_{comp.}$	$\Delta\Lambda$	η	$\Lambda\eta_{obs.}$	Jones and Dole $\Lambda\eta_{comp.}$	$\Delta\Lambda\eta$
0.00025	(0.99709)	150.16	151.65	150.16	0.00	150.24	-0.08	1.00006	150.17	150.18	-0.01
.00036	(.99710)	149.87	151.66	149.88	-.01	149.93	-.06	1.00007	149.88	149.89	-.01
.0005	(.99711)	149.55	151.66	149.57	-.02	149.61	-.06	1.00008	149.56	149.58	-.02
.00075	(.99713)	149.12	151.70	149.12	.00	149.13	-.01	1.00009	149.13	149.12	.01
.001	.99715	148.78	151.76	148.75	.03	148.74	.04	1.00010	148.80	148.74	.06
.0016	(.99721)	148.02	151.79	148.02	.00	147.98	.04	1.00011	148.04	148.00	.04
.002	.99725	147.64	151.86	147.62	.02	147.56	.08	1.00010	147.65	147.59	.08
.005	.99746	145.47	152.14	145.46	.01	145.36	.11	1.00009	145.48	145.44	.04
.01	.99793	143.15	152.60	143.19	-.04	143.11	.04	0.99997	143.14	143.20	-.06
.02	.99877	140.26	153.66	140.25	.01	140.25	.01	.99973	140.22	140.31	-.09
.05	1.00129	135.44	156.68	135.36	.08	135.51	-.07	.99863	135.25	135.38	-.13
.1	1.00553	131.19	161.73	131.19	.00	131.27	-.08	.99678	130.77	130.80	-.03
.2	1.01397	126.59	170.69	127.61	-1.02	126.62	-.03	.99287	125.69	125.59	.10
.5	1.03912	120.35	193.79	127.33	-6.98	120.23	.12	.98180	118.16	117.96	.20
1.0	1.08061	115.46	226.83	135.36	-19.90	115.50	-.04	.96795	111.76	111.74	.02
2.0	1.16255	109.37	285.86	155.30	-45.93	110.98	-1.61	.95744	104.72	104.95	-.23
3.0	1.24328	103.55	341.69	171.93	-68.38	108.39	-4.84	.96879	100.32	100.46	-.14
3.75	1.30331	98.70	383.25	180.96	-82.26	106.96	-8.26	.99181	97.89	97.70	.19

Kohlrausch: $\Lambda = 151.46 - 85.03 \sqrt{c}$
 Onsager: $\Lambda_0 = (\Lambda + 59.790 \sqrt{c}) / (1 - 0.2274 \sqrt{c})$
 Shedlovsky: $\Lambda = 151.63 - 94.27 \sqrt{c} + 100.96 (1 - 0.2274 \sqrt{c})$
 Jones and Dole: $\Lambda = 151.84 - \frac{103.77 \sqrt{c}}{1 + 1.8953 \sqrt{c}} - 0.492c$
 Jones and Dole: $\Lambda\eta = 151.70 - \frac{98.22 \sqrt{c}}{1.5815 \sqrt{c}} - 1.916c$

3.375, which would indicate substantial hydrolysis. On the other hand, Kolthoff and Elmquist¹¹ say "The P_H of the 0.1 molar solution (of $LaCl_3$), determined colorimetrically with adjusted brom thymol blue as indicator in carbon dioxide-free water as solvent is 6.2." We have tested a number of our solutions as prepared for the conductance measurements by means of chlor phenol red and found values which confirm the results of Sadolin and of Kolthoff and Elmquist instead of Kleinheksel and Kremers. Simultaneously with our work Mr. A. G. Jacques was engaged in this Laboratory in an extensive study of hydroly-

correction to round concentration are omitted. From the original data preliminary values of the coefficients of the Jones and Dole equation were determined and then by the use of this equation the values of $\partial\Lambda/\partial \sqrt{c}$, which is the slope of the $\Lambda - \sqrt{c}$ curve, were computed for each concentration and these values used to compute the slight correction to the round concentration. These corrections only amounted to a few hundredths of one per cent. The new data are given in the first three columns of Tables I-IV. Concentrations are expressed in gram molecules per liter.

Interpretation of the Data

Potassium Bromide at 25°.—The equation $d = 0.99707 + 0.08555c - 0.002006c^{3/2}$, which

(9) E. Sadolin, *Z. anorg. Chem.*, **160**, 136 (1927).
 (10) J. H. Kleinheksel and H. C. Kremers, *THIS JOURNAL*, **50**, 959 (1928).
 (11) I. M. Kolthoff and R. Elmquist, *ibid.*, **53**, 1217 (1931).

(12) A. G. Jacques, Dissertation, Harvard, 1931, p. 344.

TABLE II
COMPARISON OF EXPERIMENTAL DATA FOR CONDUCTANCE WITH THE VALUES COMPUTED BY VARIOUS EQUATIONS
POTASSIUM BROMIDE AT 0°

c	d	Aobs.	Onsager Λ_0	Shedlovsky Acomp. $\Delta\Lambda$	Jones and Dole Acomp. $\Delta\Lambda$
0.00025	(0.99989)	82.57	83.324	82.57 0.00	82.62 -0.05
.00036	(.99990)	82.43	83.335	82.43 .00	82.46 -.03
.0005	(.99991)	82.26	83.325	82.27 -.01	82.30 -.04
.00075	(.99994)	82.04	83.345	82.05 -.01	82.05 -.01
.001	(.99996)	81.87	83.38	81.86 .01	81.85 .02
.0016	(1.00001)	81.48	83.39	81.49 -.02	81.47 .01
.002	1.00004	81.32	83.45	81.29 .03	81.25 .07
.005	1.00029	80.20	83.57	80.21 -.01	80.15 .05
.01	1.00076	79.06	83.84	79.07 -.01	79.02 .04
.02	1.00165	77.61	84.38	77.65 -.04	77.60 .01
.05	1.00430	75.25	86.04	75.21 .04	75.29 -.04
.1	1.00869	73.23	88.67	73.24 -.01	73.29 -.06
.2	1.01746	71.22	93.54	71.70 -.48	71.26 -.06
.5	1.04356	69.08	106.35	72.34 -3.26	69.01 .07
1.0	1.08635	68.15	124.92	77.66 -9.51	68.18 -.03
2.0	1.17014	67.39	157.87	90.19 -22.80	69.07 -1.68
3.0	1.25218	65.85	188.19	100.96 -35.07	70.93 -5.04
3.75	1.31286	64.01	209.98	107.25 -43.24	72.59 -8.58

Kohlrausch: $\Lambda = 83.23 - 43.03 \sqrt{c}$

Shedlovsky: $\Lambda = 83.313 - 47.67 \sqrt{c} + 53.874c (1 - 0.21875 \sqrt{c})$

Onsager: $\Lambda_0 = (\Lambda + 29.445 \sqrt{c}) / (1 - 0.21875 \sqrt{c})$

Jones and Dole: $\Lambda = 83.43 - \frac{52.956 \sqrt{c}}{1 + 1.9157 \sqrt{c}} + 2.915c$

TABLE III
COMPARISON OF EXPERIMENTAL VALUES FOR CONDUCTANCE WITH THE VALUES COMPUTED BY VARIOUS EQUATIONS
LANTHANUM CHLORIDE AT 25°

c	d	Aobs.	Onsager Λ_0	Shedlovsky Acomp. $\Delta\Lambda$	Jones and Dole Acomp. $\Delta\Lambda$
0.00025	(0.99713)	414.61	437.47	411.20 3.41	415.11 -0.50
.00036	(.99715)	410.11	437.54	407.20 2.91	410.31 -.20
.0005	.99718	405.64	437.98	403.02 2.62	405.40 .24
.00075	(.99724)	398.83	438.46	397.15 1.68	398.54 .29
.001	.99727	393.48	439.28	392.13 1.35	393.10 .38
.0025	.99762	372.84	445.66	372.80 0.04	372.67 .17
.005	.99820	354.33	458.49	354.38 -0.05	354.32 .01
.01	.99932	333.74	484.40	333.72 0.02	334.14 -.40
.025	1.00274	305.90	559.52	307.80 -1.90	306.12 -.22
.05	1.00839	284.86	677.82	294.30 -9.44	284.80 .06
.1	1.01960	263.68	917.78	282.42 -18.74	263.38 .30
.25	(1.05292)	231.99	1908.11	167.48 64.51	232.09 -.10
.5	1.10756	200.03	9853.84	-369.86 569.89	200.33 -.30
1.0	1.21455	153.44	-3483.00	-2538.44 2691.88	150.54 +2.90

Kohlrausch: $\Lambda = 435.57 - 1336 \sqrt{c}$

Onsager: $\Lambda_0 = (\Lambda + 878.69 \sqrt{c}) / (1 - 1.29633 \sqrt{c})$

Shedlovsky: $\Lambda = 432.70 - 1439.6 \sqrt{c} + 5168.3c (1 - 1.29633 \sqrt{c})$

Jones and Dole: $\Lambda = 442.97 - \frac{1996.9 \sqrt{c}}{1 + 8.4889 \sqrt{c}} - 81.98c$

has the form suggested by Root,¹³ expresses the densities of these solutions within a few hundredths of one per cent. up to 3.75 normal.

Figure 2 shows a plot of Λ against \sqrt{c} with the experimental values shown as the centers of the circles for the more concentrated solutions and as

points in the dilute range. When the data for the dilute solutions are plotted on a large scale it is apparent that the $\Lambda - \sqrt{c}$ plot, although nearly straight, nevertheless has a definite positive curvature even at the most extreme dilutions studied. If we put the best straight line through the points up to 0.005 *N*, as suggested by Kohl-

(13) W. C. Root, THIS JOURNAL, 55, 850 (1933).

TABLE IV
COMPARISON OF THE EXPERIMENTAL VALUES OF CONDUCTANCE WITH THE VALUES COMPUTED BY VARIOUS EQUATIONS
LANTHANUM CHLORIDE AT 0°

c	d	Aobs.	Onsager Δ_0	Shedlovsky Acomp.	$\Delta\Delta$	Jones and Dole Acomp.	$\Delta\Delta$
0.00025	(0.99993)	216.47	227.74	215.17	1.30	216.81	-0.34
.00036	(.99996)	214.36	227.88	213.20	1.16	214.46	-.10
.0005	(.99999)	212.15	228.09	211.13	1.02	212.06	.09
.00075	(1.00005)	208.93	228.47	208.17	0.76	208.71	.22
.001	1.00009	206.29	228.86	205.76	.53	206.05	.24
.0025	1.00044	196.21	232.10	196.22	-.01	196.05	.16
.005	1.00104	187.15	238.46	187.13	.02	187.07	.08
.01	1.00225	176.98	251.09	176.98	.00	177.18	-.20
.025	1.00575	163.23	287.48	164.51	-1.28	163.42	-.19
.05	1.01152	152.85	344	158.83	-5.98	152.94	-.09
.1	1.02297	142.62	457	157.10	-14.57	142.39	.13
.25	(1.05709)	127.04	890	115.0	12.0	126.92	.12
.5	1.11273	111.12	3170	-109.7	221	111.14	-.02
1.0	1.22092	86.31	-2275	-1062	1148	86.33	-.02

Kohlrausch: $\Lambda = 226.6 - 643.6 \sqrt{c}$

Onsager: $\Lambda_0 = (\Lambda + 432.76 \sqrt{c}) / (1 + 1.22813 \sqrt{c})$

Shedlovsky: $\Lambda = 225.78 - 710.05 \sqrt{c} + 2531.6c (1 - 1.22813 \sqrt{c})$

Jones and Dole: $\Lambda = 230.42 - \frac{975.0 \sqrt{c}}{1 + 8.454 \sqrt{c}} - 40.96c$

rausch, the result is $\Lambda = 151.46 - 85.03 \sqrt{c}$. This equation is represented in Fig. 2 by the line K. As is evident from the figure, it fails badly at all higher concentrations.

The Onsager equation may be written $\Lambda_0 = (\Lambda + \beta \sqrt{c}) / (1 - \alpha \sqrt{c})$, and is represented in Fig. 2 by the straight line O. For aqueous solutions of uni-univalent salts at 25°, $\alpha = 0.2274$ and $\beta = 59.790$. The values of Λ_0 thus computed are shown in Table I and are clearly not constant even up to 0.001 N. We have followed Shedlovsky's suggestion in plotting these values against c and find that for potassium bromide at 25° the resulting plot is straight up to 0.1 N, which agrees with Shedlovsky's experience with several other uni-univalent salts. Shedlovsky's equation for this case becomes $\Lambda = 151.63 - 94.27 \sqrt{c} + 100.96c (1 - 0.2274 \sqrt{c})$. This equation agrees with these data up to 0.1 N better than any other equation known to us but fails completely at higher concentrations as shown by the curve S in Fig. 2 and in Table I.

We have also used the data to test the Jones and Dole equation. The values of the parameters were found by the method of least squares using all of the points up to 1.0 N, inclusive, giving

$$\Lambda = 151.84 - \frac{103.77 \sqrt{c}}{1 + 1.8953 \sqrt{c}} - 0.492c$$

Curve J in Fig. 2 is the plot of this equation. Up to 1 N the agreement is so good that the

deviations are not apparent on a scale that can be printed. The deviations are shown in the last column of Table I. The average deviation over the range 0.00025 to 1.0 N is only 0.07 and the maximum deviation 0.12, which is much better agreement than can be obtained over such a wide range of concentration by any other

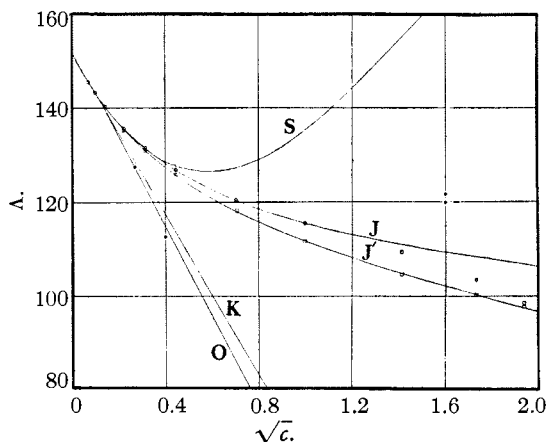


Fig. 2.—KBr at 25°.

equation. However, the equation gives too high values at 2 N and above, and there are some indications that the equation requires too great a curvature at extremely low concentrations. The value Λ_0 given by this equation is appreciably higher than that given by either the Kohlrausch or Shedlovsky method of extrapolation, and the limiting slope given by this equation, -103.77 ,

is about 10% greater than computed by Onsager's method -94.27 .

We have reliable data¹⁴ for the viscosity of potassium bromide at 25° which were determined in this Laboratory for the purpose and are, therefore, able in this case to test the various equations which have been proposed both with and without a viscosity correction. We have analyzed the Λ_η data by the same methods as the Λ data and obtained the equations

$$\begin{aligned} \text{Kohlrausch: } \Lambda_\eta &= 151.48 - 85.28 \sqrt{c} \\ \text{Shedlovsky: } \Lambda_\eta &= 151.64 - 94.274 \sqrt{c} + 98.61c \\ &\quad (1 - 0.2274 \sqrt{c}) \end{aligned}$$

The tables of deviations and curves are not printed because the essential conclusions are not changed by the slight numerical variations from the results shown in Table I.

These equations for Λ_η are only slightly different from the equations for Λ given above because they are based entirely on the data for dilute solutions and the viscosity correction only amounts to 0.01% up to 0.0005 N and to 0.32% at 0.1 N . But in concentrated solutions the application of the viscosity correction considerably modifies the form of the curve as is shown in Fig. 2 by the points within the squares, which represent the values of Λ_η . The uncorrected data give a curve of Λ against \sqrt{c} with a point of inflection at about 1 normal, whereas the curve of Λ_η against \sqrt{c} has no point of inflection up to the highest concentration studied, $c = 3.75$, and therefore is a simpler form of curve which should be easier to fit to an equation. We have found that the equation

$$\Lambda_\eta = 151.70 - \frac{98.22 \sqrt{c}}{1 + 1.5815 \sqrt{c}} - 1.916c$$

(Curve J', Fig. 2) fits the equation almost within the limit of experimental error through the entire range from 0.00025 to 3.75 N .

It should be noted that by the use of the viscosity-corrected data the limiting slope comes out to be -98.22 , which is in much better agreement with the value -94.27 computed by Onsager's method, and that the deviations in the dilute solutions are substantially reduced. The value for Λ_0 is reduced from 151.84 to 151.70. These results indicate that in this case at least the relationships are simplified by the application of the viscosity correction. Unfortunately we do not as yet have suitable viscosity data to be used

(14) Grinnell Jones and S. K. Talley, *THIS JOURNAL*, **55**, 4124 (1933).

in conjunction with the other new conductance data to be discussed below.

Potassium Bromide at 0°.—The densities of the potassium bromide solutions at 0° can be expressed by the equation $d = 0.99987 + 0.089674c - 0.003210c^{3/2}$.

The data for potassium bromide at 0° have been analyzed in a similar manner and the results are shown in Table II, but the curves representing these data are not printed because except for the difference in scale they are quite similar to the curves for 25° shown in Fig. 2. The Kohlrausch equation is $\Lambda = 83.23 - 43.03 \sqrt{c}$. It fails badly above 0.005 N . The Onsager equation for aqueous solutions at 0° is $\Lambda = \Lambda_0 - (0.21875 \Lambda_0 + 29.445) \sqrt{c}$. The values of Λ_0 computed by this equation are not constant even up to 0.001 N . The Shedlovsky method of extrapolation gives $\Lambda_0 = 83.313$, which makes the Onsager limiting slope -47.67 . The Shedlovsky equation for this case becomes $\Lambda = 83.313 - 47.67 \sqrt{c} + 53.874c (1 - 0.21875 \sqrt{c})$. As is shown in Table II this equation agrees with the data up to 0.1 N better than any other equation but fails badly at higher concentrations.

The Jones and Dole equation for this case is

$$\Lambda = 83.43 - \frac{52.956 \sqrt{c}}{1 + 1.915 \sqrt{c}} + 2.915c$$

This equation is not quite as good as Shedlovsky's equation up to 0.1 N but is better for the concentrated solutions. Just as at 25° it gives a higher value for Λ_0 than either Kohlrausch's or Shedlovsky's equation and a higher value for the limiting slope than is predicted by Onsager's method. The equation fails above 1 N when applied to the data uncorrected for viscosity just as it did at 25°. Unfortunately we do not as yet have the viscosity data for 0° and therefore cannot determine whether or not the application of the viscosity correction would make the equation applicable up to 3.75 N as was the case for 25°. It is curious that the coefficient of the linear term comes out to be positive in this case. In all other cases so far studied this term has been negative. In all other respects the interpretation of the data for potassium bromide at 0° is entirely analogous to the interpretation of the data for the same salt at 25°.

Lanthanum Chloride at 25°.—The densities of lanthanum chloride solutions up to 1 molar can be expressed by the equation: $d = 0.99707 + 0.22928c - 0.01179c^{3/2}$.

Figure 3 shows a $\Lambda - \sqrt{c}$ plot for 25°. The slope is greater and curvature is more pronounced than it is for potassium bromide but the curve becomes approximately straight at extreme dilution. The best straight line put through the points up to and including $c = 0.001$ in accordance with the recommendation of Kohlrausch is:

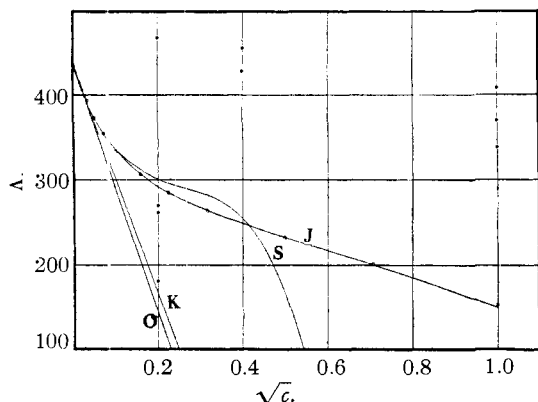


Fig. 3.—LaCl₃ at 25°.

$\Lambda = 435.57 - 1336 \sqrt{c}$ (Fig. 3, line K). This method of extrapolation, therefore, gives a value for Λ_0 of 435.57 and a slope in the dilute range of -1336 . It is obvious from Fig. 3 that the Kohlrausch equation fails seriously at $c = 0.0025$ and above.

The values of α in Onsager's equation $\Lambda = \Lambda_0 - (\alpha\Lambda_0 + \beta) \sqrt{c}$ cannot be computed directly by Onsager's method except for uni-univalent salts without assuming an estimated value for Λ_0 . However, the values of α are only slightly dependent on Λ_0 and therefore mutually consistent values for α and Λ_0 could be found easily by the method of successive approximation if the Onsager equation really held for the range of concentrations for which accurate experimental data are obtainable. The next step is to compute the values of $\Lambda_0 = (\Lambda + \beta\sqrt{c}) / (1 - \alpha\sqrt{c})$, which should give a constant if Onsager's equation is valid. Values thus computed are shown in Table III and as will be seen are not constant but show a systematic trend even over the range from 0.00025 to 0.001 molar. It is therefore evident that Onsager's equation is not in accord with the data

even in this extremely dilute range. To obtain a true value of Λ_0 some method of extrapolation not dependent solely on Onsager's equation must be adopted. We have followed the procedure suggested by Shedlovsky in plotting these values against the concentration as is shown on an enormously reduced scale in Fig. 4. But, contrary to Shedlovsky's results with most of the uni-univalent salts which he studied, the resulting plot is unquestionably curved, with a positive curvature at low concentration, and a point of inflection at about 0.005 molar. The curve is approximately straight from 0.0025 to 0.01 but has a negative curvature above this point up to about 0.1 molar. Dr. Shedlovsky has informed us that he has new unpublished data on the chlorides of the alkaline earths which give similar curves. Above 0.1 molar the curve becomes extremely erratic, rising to infinity as \sqrt{c} approaches $1/\alpha$ (about $c = 0.6$ in this case) and having negative values when $\sqrt{c} > 1/\alpha$ (see Table III). If we attempt to find a value of Λ_0 by extending the straight portion of the curve as was done by Shedlovsky for the uni-univalent salts, we obtain $\Lambda_0 = 432.7$. Using this value of Λ_0 , α becomes 1.29633 and since $\beta = 878.69$ for a tri-univalent salt at 25° the limiting slope computed

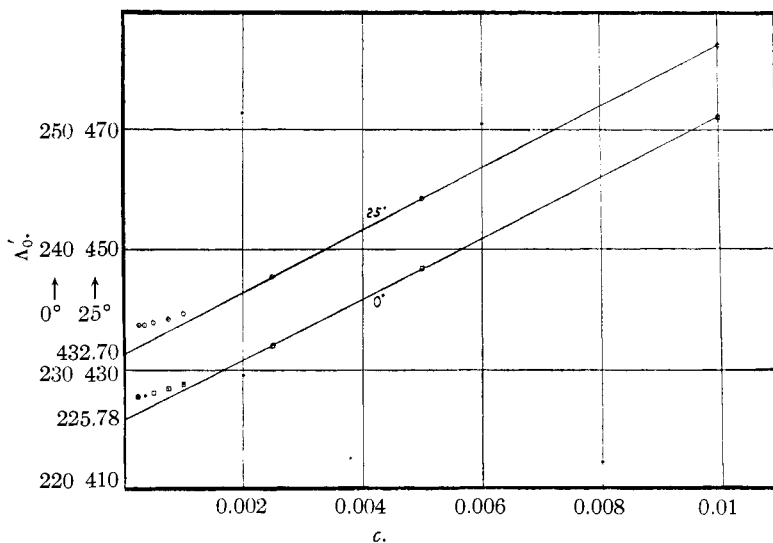


Fig. 4.—LaCl₃, Shedlovsky plot.

by Onsager's method is $-(\alpha\Lambda_0 + \beta) = -1439.6$. The data for the 0.0025, 0.005 and 0.01 molar solutions, which plot on a straight line by Shedlovsky's method, were used to determine the remaining parameter in Shedlovsky's equation, giving $\Lambda = 432.70 - 1439.6 \sqrt{c} + 5168.3c (1 -$

1.29633 \sqrt{c}). As will be evident from Table III and Fig. 3, this equation fails badly at all other concentrations. It is therefore evident that Shedlovsky's equation is not valid for lanthanum chloride. The value $\Lambda_0 = 432.7$ given by this method is evidently too low since it makes no allowance for the experimentally demonstrated curvature in the Shedlovsky plot at low concentrations. Any extrapolation along a curve is dangerous unless the mathematical form of the curve is known so that the change in curvature can be computed. In this case if we assume that the Onsager equation is valid as a limiting law for extreme dilutions, this curve should straighten out and enter the axis horizontally. This assumption gives $\Lambda_0 = 437.4 \pm 0.1$, which is the best estimate we can make from these data on the assumption that Onsager's equation gives the true limiting slope. It should be noted that this value is 25 units greater than the conductance of the most dilute solution studied ($c = 0.00025$), which is a considerably greater extrapolation than is necessary for the uni-univalent salts. Using this value Λ_0 , α becomes 1.3046 and the limiting slope $-(\alpha\Lambda_0 + \beta) = -1448.8$.

The data were also used to test the Jones and Dole equation. The values of the four parameters were found by the method of least squares (omitting the data for 0.5 and 1.0 molar), giving

$$\Lambda = 442.97 - \frac{1996.9 \sqrt{c}}{1 + 8.4889 \sqrt{c}} - 81.98c$$

The agreement of the values computed by this equation with the data is shown in Table III and in Fig. 3, in which the curve J is the plot of this equation and the experimental points are shown by the point within the circles. The agreement is so good that the deviations are not apparent on a scale which can be printed. The actual deviations as shown in Table III are appreciably greater than were found for barium chloride by Jones and Dole and for potassium bromide up to 1 molar in this investigation.

The value for Λ_0 given by this method, 442.97, is appreciably greater than that given by Kohlrausch's method, 435.57, or by Shedlovsky's method, 432.7, and the limiting slope, -1997 , is greater than that computed by Onsager's method, -1449 . It is apparent that the Jones and Dole equation is in much better conformity with these data at high concentrations than any of the other equations discussed or than any

equation known to us. But a careful study of the curves gives some indications that it may give too great curvature at low concentrations and therefore may give too high a value for Λ_0 .

Lanthanum Chloride at 0°.—The density of lanthanum chloride solutions at 0° can be expressed by the equation $d = 0.99987 + 0.23673c - 0.01567c^{3/2}$.

The interpretation of the data for the conductance of lanthanum chloride at 0° is entirely analogous to the interpretation at 25°. The best straight line put through the points up to and including 0.001 molar in accordance with Kohlrausch's recommendation is $\Lambda = 226.6 - 643.6 \sqrt{c}$.

Again we find that Λ_0 as computed by Onsager's equation is not constant even up to 0.001 molar, as is shown in Table IV. Shedlovsky's method of analysis gives $\Lambda_0 = 225.78$ and hence $\alpha = 1.22813$ and $\beta = 432.76$ and $-(\alpha\Lambda_0 + \beta) = -710.05$. Hence Shedlovsky's equation becomes $\Lambda = 225.78 - 710.05 \sqrt{c} + 2531.6c(1 - 1.22813 \sqrt{c})$. This equation, however, fails badly at both low and high concentrations, as is shown in Table IV.

If we extrapolate along the curve assuming that Onsager's equation is valid as a limiting law, we obtain $\Lambda_0 = 227.6$, which makes $\alpha = 1.2323$ and $-(\alpha\Lambda_0 + \beta) = -713.2$.

The Jones and Dole equation becomes

$$\Lambda = 230.42 - \frac{975.0 \sqrt{c}}{1 + 8.454 \sqrt{c}} - 40.96c$$

The deviations are smaller than at 25°. Just as at 25° the Jones and Dole equation gives a greater limiting slope (-975.0) than is computed by the Onsager equation (-710) and a higher value for Λ_0 (230.4) than is given by either the Kohlrausch (226.6) or Shedlovsky (225.78) method of extrapolation. It should be noted that the equation can be made to fit the data at 0.5 and 1.0 molar concentration better than at 25°.

These data show the temperature coefficient of conductivity is much less in concentrated solutions than in dilute solutions for both of the salts studied and greater for lanthanum chloride than for potassium bromide. A more detailed analysis of these data will be postponed until we have viscosity data on these solutions.

Grateful acknowledgment is made for an appropriation from the Milton Fund of Harvard University for use in this investigation.

Summary

1. The electrical conductance and density of solutions of potassium bromide from 0.00025 to 3.75 molar and of lanthanum chloride from 0.00025 to 1.0 molar have been determined at both 0° and 25°.

2. The densities may be expressed by equations having the form suggested by Root throughout the range of concentration studied.

3. The Shedlovsky conductance equation fits the data for potassium bromide up to 0.1 *N*

better than any other equation, but this equation is not applicable to the data on lanthanum chloride.

4. The Jones and Dole equation fits the data on both salts and at both temperatures up to high concentrations better than any known equation. This equation gives higher values for Λ_0 than either the Onsager or Shedlovsky method of extrapolation and a greater limiting slope than is predicted by the Onsager equation.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MOUNT HOLYOKE COLLEGE]

Derivatives of Normal Pentane and Normal Heptane. III. Dipole Moments of the Bromoethoxy and the Dibromo Derivatives

BY MARY L. SHERRILL, MARTHA E. SMITH AND DOROTHY D. THOMPSON¹

Previously one of the authors^{1a} has measured the dielectric constants and determined the electric moments of a series of derivatives of normal heptane. The dielectric constant and moment were found to be considerably smaller for the halogen derivatives with the substituent in the 1-position than for those with the substituent in the 2-, 3- or 4-positions. The moments of the latter are the same although the dielectric constants of these differ somewhat from each other.

In connection with an investigation of unsaturated hydrocarbons, a series of bromoethoxy derivatives and the corresponding dibromo derivatives of *n*-pentane and *n*-heptane have been prepared and their physical constants determined. It seemed that an accumulation of dielectric constant and electric moment data covering parallel series of compounds should ultimately be valuable in the field of molecular structure and their dielectric constants have been measured. The boiling points, refractive indices and densities of the compounds, including the density of the benzene solutions used in the dielectric constant measurements, were determined by methods given in a previous paper.² The dielectric constants were determined by the resonance method. The apparatus consisted of two heterodyne oscillators, connected by a resistance-coupled amplifier and a calibrated condenser.

The capacity measurements of the pure compounds were of a precision of 1 part in 500. The condenser used for the capacity measurements of the benzene solutions at 25 ± 1° was a Type 222-S Precision Condenser (General Radio Company). The calibration of this condenser was accurate to one-tenth of a micro-microfarad. The wave length was 100 meters. The condenser used for measuring the capacity of the liquids is a nickel cell with an adjustable plate. The probable error in the dielectric constant is 0.5%.

Experimental

Preparation of Compounds

β -Ethoxyalkyl Bromides, $\text{RCHBrCHOC}_2\text{H}_5\text{R}'$.—These compounds have been synthesized according to the method used by Boord and co-workers.³ The method involved the synthesis of the α -chloroalkyl ethyl ether, the bromination of the ether and the reaction of the α,β -dibromoalkyl ethyl ether thus formed with a Grignard reagent, $\text{R}'\text{MgX}$. The best yields of both crude and purified β -ethoxyalkyl bromides were obtained when an excess (0.5 mole) of the Grignard reagent was used. The repeated distillation of the bromo ethers with alkali, suggested by Boord and co-workers, while removing any excess of the dibromo ether has been found to form some of the unsaturated ether, $\text{RCH}=\text{COC}_2\text{H}_5\text{R}'$.⁴ Therefore the bromo ethers were purified by distillation in vacuo until products of constant densities and refractive indices were obtained. The positions of the bromine and the ethoxy groups were confirmed by the transformation of each bromo ether into the corresponding olefin.

(1) Holder of a Skinner Fellowship, Mount Holyoke College, 1931–1932.

(1a) Jacques Errera and Mary L. Sherrill, *THIS JOURNAL*, **52**, 1993 (1930).

(2) Mary L. Sherrill, *ibid.*, **52**, 1982 (1930).

(3) Swallen and Boord, *ibid.*, **52**, 651 (1930); Dykstra, Lewis and Boord, *ibid.*, **52**, 3396 (1930); Shoemaker and Boord, *ibid.*, **53**, 1505 (1931).

(4) Lauer and Spielman, *ibid.*, **53**, 1533 (1931); Soday and Boord, *ibid.*, **55**, 3293 (1933).