IV. In order to ascertain the magnitude of the concentration change due to the adsorption of the salt on the walls of the cell, the specific adsorption of potassium chloride was determined by the use of a large quantity of quartz fragments. This was accomplished by observing the conductivity of 0.001 N to 0.0005 N solutions of potassium chloride in a special quartz cell before and after the addition of a definite quantity of well cleaned quartz fragments.   Knowing the magnitude of the surface of the fragments and the surface of the cell, the maximum concentration change resulting from adsorption has been calculated and found to be negligible.

V. The values of Λ_c at round concentrations have been tabulated over the concentration range 0.00001 N to 0.001 N Table VII. The value of Λ_0 was found to be 129.64 $\times$ 0.02 as an average of four determinations.

VI. The Mass-Action "constant" K_E has been found to approach a constant value as the solution becomes sufficiently dilute. The limiting value at zero concentration was found to be 0.020 $\times$ 0.001.   The relative increase of K_E for a tenfold increase in concentration over different regions of the concentration range is shown graphically in Fig. 14.

VII. The empirical equations of Bates and of Kraus, employed to express the relation between equivalent conductance and concentration, have been tested between the concentrations zero and 0.005 N and have been found not to be capable of expressing the conductivity data throughout this range.

The author wishes to express his thanks and gratitude to Professor E. W. Washburn under whose direction this investigation has been carried out.   At all times his visits to the laboratory have been a source of help and inspiration.

Thanks are also due him together with his associates J. E. Bell, C. J. Baker and Karr Parker who contributed materially in solving the preliminary difficulties of this problem, without which it could not have been carried to a successful conclusion.

URBANA, ILL.

THE EQUIVALENT CONDUCTANCE OF ELECTROLYTES IN DILUTE AQUEOUS SOLUTION.
IV. TWO LAWS GOVERNING THE IONIZATION EQUILIBRIUM OF STRONG ELECTROLYTES IN DILUTE SOLUTIONS AND A NEW RULE, BY MEANS OF WHICH THE EQUIVALENT CONDUCTANCE AT INFINITE DILUTION CAN BE DETERMINED FROM A SINGLE CONDUCTANCE MEASUREMENT.

BY EDWARD W. WASHBURN.

CONTENTS.—1. Statement of the Two Laws. 2. The First Law. 3. The Second Law. 4. A General Rule for Determining Λ_0 Values from a Single Conductance

Measurement. 5. Strong Acids and Bases and Salts of Weak Acids and Bases. 6. Ion Conductances.

1. **Statement of the Two Laws.**—With the aid of the conductance data for potassium chloride presented in the preceding paper, together with a study of the most accurate of the conductance data for other salts, obtained by Kohlrausch and his associates, it becomes possible to establish two general laws with reference to the behavior of strong electrolytes in dilute solutions. These laws may be stated as follows:

1. In sufficiently dilute solution (*i. e.*, for most practical purposes below $C = 0.0001$ N, the increase of K_E between 0 and 0.0001 N being only 1.05 fold) all uni-univalent salts of strong acids and bases obey the Mass-Action law and all of them have the same ionization constant.

2. In sufficiently dilute solution the values of the Mass-Action expression (and hence also the degrees of ionization) for all such salts are identical, the identity in the case of any two salts persisting up to higher concentrations the more nearly the salts under comparison resemble each other, and in any case persisting, within the experimental error of the data now available, up to $C = 0.0002$ N for all salts which have been carefully measured below this concentration. In the case of two salts such as potassium chloride and bromide for example, which resemble each other very closely, this identity persists up as high as 0.005 N.

2. **The First Law.**—Direct and unequivocal evidence that strong electrolytes obey the law of Mass Action in aqueous solutions in portions of the concentration range open to direct measurement is given for the first time by the data presented in the preceding paper.[1] It has been held by several observers that strong electrolytes would obey the Mass-Action law in sufficiently dilute solutions, in fact this statement has been explicitly made by Kraus and Bray, by Arrhenius, by Drucker, Tarle and Gomez and by Muller and Romann, although it seems to the writer that in none of these instances was the evidence employed by the investigators of a very decisive character.

The author's reasons for regarding as indecisive the evidence offered

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[1] The theoretical basis of the Mass-Action law for a sufficiently dilute solution being almost purely thermodynamic in character, there would seem to be no necessity for additional evidence as to its validity for *all* classes of electrolytes at extreme dilutions. Such a view seems to the writer entirely sound and the value of the long desired "direct demonstration" furnished by the present investigation is not so much its conclusive evidence regarding the fact as it is its value as a discovery of the actual concentration range over which the law holds true within comparatively small known limits. As far as direct evidence of the fact that there was nothing in the behavior of strong electrolytes which would justify the view held by Kohlrausch and others to the effect that these substances would *not* obey the Mass-Action law even at high dilutions is concerned, it seems to the writer that this evidence is very clearly furnished by such figures as the first four ratios in the last column of Table VIII of the preceding paper.

by Kraus and Bray, insofar as it concerned aqueous solutions, have already been given in the second paper of this series. While indecisive and quantitatively quite erroneous in the case of aqueous solutions, the evidence presented by Kraus and Bray as to the behavior of electrolytes in other solvents than water, nevertheless pointed strongly to the conclusion that the behavior of salts in aqueous solution would be found to differ only in degree and not in kind from the behavior of such electrolytes in solvents of lower dielectric constant.

In the paper[1] already referred to, Arrhenius reached the conclusion that uni-univalent salts obey the Mass-Action law up to about 0.0002 N and that they all have the same ionization constant, basing his conclusion upon some measurements of Kohlrausch and Maltby with very dilute solutions of sodium chloride and nitrate. After applying a metathesis correction to these data he found that the values so corrected obeyed the law of Mass Action. It seems to the writer, however, that his conclusion is quite unjustified by the evidence which he presents, for the following reasons: First, The metathesis corrections which he applied were incorrect both in magnitude *and in sign* is explained in the second paper of this series. Second, The metathesis corrections at these high dilutions are very much smaller than the accidental experimental errors of the data themselves and consequently could not be significant in any case. Third, The Λ_0 value employed by Arrhenius was incorrect as was also, consequently, the K_E values computed from it.[2]

Wegscheider's attempt[3] to show that salts obeyed the Mass-Action law up to about 0.03 N involved the use of an erroneous infinity value and the rejection of certain conductance values which are now known to be correct. Morever, salts actually do not obey the law over the concentration interval given by Wegscheider but only over an interval entirely outside of that covered by any data accessible to him. Substantially the same statement may be made concerning the reasoning of Drucker, Tarle and Gomez[4] and of Muller and Romann.

3. The Second Law.—The second law is an extension of the first one in that it postulates for different electrolytes the identity of the values of K_E (and hence also of α) even above the concentration range within which the Mass-Action law is obeyed. In other words, according to this law, those influences, which in case of strong electrolytes cause them to depart from the Mass-Action law at the higher concentrations, begin to be prac-

[1] *Loc. cit.*, pp. 11, 12.

[2] On the basis of the second and third reasons just stated, Kendall (*Loc. cit.*) also points out that the evidence which Arrhenius presents cannot be considered as supporting his conclusion.

[3] *Z. physik. Chem.*, **69**, 624 (1909).

[4] Drucker, Tarle and Gomez, *Z. Elektrochem.*, **19**, 11 (1913); Muller and Romann, *Compt. rend.*, **157**, 400 (1913).

tically identical in their effects in the case of the different electrolytes before they disappear entirely.[1] This fact has considerable practical importance in that it enables us to derive a very convenient rule by means of which it is possible to calculate correct Λ_0 values from a conductance measurement at one concentration. The evidence upon which the two laws formulated above is based is obtained by deriving the rule in question and testing it in the case of all salts for which data are available.

4. A General Rule for Determining Λ_0 Values from a Single Conductance Measurement.—The second law stated above is expressed mathematically by the equation

$$\frac{\Lambda_c^2 C}{\Lambda_0 (\Lambda_0 - \Lambda_c)} = K_E \tag{60}$$

where the value of K_E is independent of the nature of the salt and can therefore be read off from the curve in Fig. 13, or taken from Table VII of the preceding paper (or preferably from a similar curve or table for a salt resembling as closely as possible the one under examination). Solving this expression we find

$$\Lambda_0 = \Lambda_c(1 + \Lambda_c C/\Lambda_0 K_E) \tag{61}$$

or with sufficient accuracy

$$\Lambda_0 = \Lambda_c(1 + C/K_E), \tag{62}$$

an expression by means of which the value of Λ_0 for any salt can be computed from a single value of Λ_c for that salt. Or since $1 + C/K_E = \alpha$ and equality of K_E values also implies equality of α values, the above equation may also be written

$$\Lambda_0 = \Lambda_c/\alpha \tag{63}$$

where α is independent of the nature of the salt.

It is evident that this method of calculating Λ_0 gives a result which possess exactly the same percentage accuracy as that possessed by the Λ_c value employed.

A convenient value of C to employ generally for this purpose is $C = 0.0001\ N$ and for this concentration and $18°$ the above expressions become

$$\Lambda_0 = 1.00475\ \Lambda_{0.0001} \tag{64}$$

or stated in words: *The Λ_0 value for every uni-univalent salt of a strong acid and base at $18°$ is 0.475% greater than its equivalent conductance at $0.0001\ N$.*

In order to demonstrate the validity of the assumption that in sufficiently dilute solutions all uni-univalent salts have identical values for their equilibrium expressions, it is only necessary to show for a sufficient number of

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[1] Cf. Noyes and Falk, *Loc. cit.*, pp. 475 and 476, where the approximate (*i. e.*, to about 0.5%) identity of the α values for uni-univalent salts is pointed out. The identity of the K_E values postulated above, however, involves a *very much* closer identity of α values than that comtemplated in the statement of Noyes and Falk.

TABLE IX.

Illustrating the calculation of Λ_0 values for typical uni-univalent salts by means of the general relation $\Lambda_0 = \Lambda_c(1 + C/K_E)$ and demonstrating the identity of the K_E values of all such salts up to $C = 0.0001\ N$. (Measurements by Kohlrausch and Maltby, corrected ($+0.02\%$) for metathesis but not for atomic weights.)

$C \times 10^4$. Equivalents per liter.	NaCl.		KNO$_3$.		LiCl.		LiNO$_3$.	
	Λ_c.	Λ_0.	Λ_c.	Λ_0.	Λ_c.	Λ_0.	Λ_c.	Λ_0.
1.037	108.20 108.11 108.04	108.72 108.63 108.57	125.48 125.54	126.09 126.15	98.17 98.11	98.63 98.57	94.48 94.44	94.92 94.88
$K_E = 0.0212$	Mean,	108.64 $\pm$ 0.05	Mean,	126.12 $\pm$ 0.03	Mean,	98.60 $\pm$ 0.01	Mean,	94.90 $\pm$ 0.02
2.053	107.83 107.82 107.82	108.65 108.64 108.64	125.16 125.22	126.11 126.17	97.85 97.86	98.58 98.59	94.16 94.14	94.90 94.88
$K_E = 0.0268$	Mean,	108.64 $\pm$ 0.01	Mean,	126.14 $\pm$ 0.03	Mean,	98.59 $\pm$ 0.01	Mean,	94.89 $\pm$ 0.01
0.5212 $K_E = 0.02017$	108.41	108.69						

salts that the Λ_0 values calculated from Equation 62 or 63 are independent of the concentration employed, for at least two concentrations sufficiently removed from each other.   In order to make this test of the law the conductance data of Kohlrausch and Maltby for four salts at the two lowest concentrations measured were employed to calculate Λ_0 values, with the results shown in Table IX.   These results show that within the experimental error the rule gives for these salts the same Λ_0 value for the two concentrations 0.0001 N and 0.0002 N respectively, and in one instance where such measurements were available also for the concentration 0.00005 N .   In this table the *individual conductance values* for the different concentrations have been employed instead of the rounded values obtained from a smooth curve, in order to show the degree of concordance of the measurements among themselves, and consequently the degree of concordance which might be expected for the Λ_0 values.

Using interpolated values at round concentrations and 1911 atomic weights as given by Noyes and Falk, a similar table has also been prepared

TABLE X.

Illustrating the calculation of Λ_0 values for typical uni-univalent salts by means of the relation, $\Lambda_0 = c(\Lambda\ 1 + (C/K_E))$.   The data employed are taken from the tables compiled by Noyes and Falk (THIS JOURNAL, **34,** 461 (1912)).   A metathesis correction[1] of +0.02% has been applied for concentrations 0.0001 and 0.0002 and one of +0.01% for concentrations 0.0005 and 0.001 N.   The values of Λ_c given below have also been corrected for viscosity where this correction is appreciable.   The values in parenthesis in the first column have been selected as the "best" Λ_0 values.   Salts in which either the acid or base is "weak" are excluded because the Λ_c values recorded in the literature are incorrect.

Salt.	$\frac{C \times}{10^4}$	Λ_c.	$\Lambda_0 - \Lambda_c$.	Λ_0.	Salt.	$\frac{C \times}{10^4}$	Λ_c.	$\Lambda_0 - \Lambda_c$.	Λ_0.
NaCl	1	108.05	0.513	108.56	NaNO₃	1	104.47	0.50	104.97
(108.57)	2	107.77	0.806	108.576	(104.95)	2	104.11	0.78	104.89
	5	107.12	1.33	108.45		5	103.54	1.29	104.83
	10	106.44	1.99	108.43		10	102.76	1.92	104.68
	20	105.50	2.83	108.33		20	101.81	2.72	104.53
	50	103.76	4.39	108.15		50	99.99	4.24	104.25
LiCl	1	97.98	0.464	98.44	KNO₃	1	125.42	0.59	126.01
(98.42)	2	97.69	0.734	98.42	(126.02)	2	125.10	0.94	126.04
	5	97.02	1.206	98.23		5	124.35	1.55	125.90
	10	96.36	1.80	98.16		10	123.56	2.31	125.87
	20	95.47	2.55	98.02		20	122.50	3.29	125.78
	50	93.82	3.96	97.78		50	120.38	5.12	125.48
RbCl	1	132.3	0.63	132.9	LiNO₃	1	94.32	0.44	94.76
(132.9)	2	(131.9)	0.99	132.9	(94.78)	2	94.01	0.71	94.72
	5	(131.2)	1.63	132.8		5	93.38	1.17	94.55
	10	130.3	2.44	132.7		10	92.74	1.73	94.47
						20	91.84	2.46	94.30
						50	90.26	3.82	94.08

[1] Cf. the first paper of this series, Sec. 8, p. 119.

TABLE X (continued).

Salt.	$C \times 10^4$	Λ_c	$\Lambda_0 - \Lambda_c$	Λ_0.	Salt.	$C \times 10^4$	Λ_c	$\Lambda_0 - \Lambda_c$	Λ_0.
CsCl	1	132.2	0.63	132.8	AgNO₃	1	115.03	0.54	115.57
(132.90)	2	131.9	0.99	132.9	(115.6)	2	114.58	0.86	115.44
	5	131.25	1.63	132.88		5	113.89	1.41	115.30
	10	130.55	2.45	132.90		10	113.15	2.12	115.27
	20	129.38	3.49	132.87		20	112.07	3.01	115.08
	50	127.33	5.43	132.76		50	110.03	4.66	114.69
KBr	1	131.07	0.62	131.69	KClO₃	1	118.65	0.56	119.21
(131.71)	2	130.78	0.98	131.76	(119.25)	2	118.37	0.89	119.26
	5	130.06	1.62	131.68		5	117.69	1.46	119.15
	10	129.29	2.42	131.71		10	116.93	2.19	119.12
	20	128.22	3.46	131.68		20	115.84	3.10	118.94
	50	126.31	5.39	131.70		50	113.84	4.81	118.65
KI	1	129.78	0.62	130.40	KBrO₃	10	109.9	2.06	111.96
(130.65)	2	129.52	0.97	130.49	(112.0	20	108.7	2.92	111.62
	5	128.98	1.61	130.59	±0.1)	50	106.9	4.54	111.4
	10	128.24	2.41	130.65					
	20	127.19	3.43	130.62					
	50	125.28	5.35	130.63					
KSCN	1	120.15	0.57	120.72	NaIO₃	1	76.71	0.36	77.07
(120.8)	2	119.95	0.90	120.85	(77.05)	2	76.46	0.57	77.03
	5	119.30	1.48	120.78		5	75.84	0.94	76.78
	10	118.56	2.22	120.78		10	75.20	1.40	76.60
	20	117.57	3.16	120.73		20	74.33	1.98	76.31
	50	115.73	4.99	120.72		50	72.69	3.04	75.73
KIO₃	1	97.66	0.464	98.12	LiIO₃	1	66.68	0.31	66.99
(98.12)	2	97.36	0.73	98.09	(66.92)	2	66.45	0.50	66.95
	5	96.73	1.20	97.93		5	65.88	0.82	66.70
						10	65.29	1.21	66.51
						20	64.47	1.71	66.18
						50	62.99	2.67	65.66

for all uni-univalent salts of strong acids and bases for which reliable data are available, the calculations being carried up as high as $C = 0.005 \ N$ in many cases. The results are shown in Table X. It will be seen that in every instance, with the possible exception[1] of silver nitrate there are at least two concentrations which give within the experimental error the same Λ_0 values. The values of K_E upon which the table is based are those for potassium chloride and it will be noticed that in the case of potassium bromide, potassium chloride, rubidium chloride and potassium thiocyanate the identity of the K_E values persists up as high as 0.005 N in several cases.

[1] In view of the Bureau of Standards' investigation of the behavior of this salt and its solutions (Bur. Standards, Scientific Paper 285), I think the accuracy of the conductivity data for AgNO₃ may be fairly questioned.

In the case of potassium iodide the table also indicates a strong probability that the conductance data given for this salt below 0.001 N are too low.

An example may also be given of the calculation of Λ_0 when the largest Λ_c available is that for $C = 0.001$ N. Suppose it is desired to calculate the Λ_0 value of lithium iodate from the conductance value, $\Lambda_{0.001} = 65.29$. The K_E value for potassium chloride cannot be employed here as the concentration is too high. Instead we will base the calculation upon the α value of sodium iodate at 0.001 N which we can calculate from the data in Table X and find to be 75.30/77.05. Whence from Equation 63 we find Λ_0 for lithium iodate to be 66.93 as against 66.92 given in Table X. Such a calculation as this is of course only trustworthy when the comparison salt resembles very closely the one whose Λ_0 value is being sought.

5. Strong Acids and Bases and Salts of Weak Acids and Bases.— The reason why strong acids and bases themselves as well as salts of weak acids and bases have not been included within the scope of the laws formulated above is not because there is any reason to suppose that these substances form exceptions to the laws, but merely because there exist no reliable data for testing the laws in any of these cases, nor can such data be secured except by employing ultra-pure conductivity water, as explained in Sec. 9 and 11 of the first paper of this series. In view of the great importance of securing reliable Λ_0 values for acids and bases it is highly desirable that the work begun with potassium chloride should be extended to these substances as well as to salts of weak acids and bases and to salts of higher valence types. The availability of ultra-pure conductivity water opens an entirely new field to accurate investigation and it is practically certain that the extension of the work would yield for the above classes of substances results and laws fully as important and interesting as those obtained by the study of potassium chloride. The special Conductivity Laboratory in the new chemistry building at the University of Illinois was designed and equipped especially for this work and its equipment is probably not equaled anywhere else at the present time. Unfortunately, however, there seems to be no present prospect that the work will be continued.

TABLE XI.

Illustrating Kohlrausch's law of the independent migration of ions. Differences in ion conductances for four pairs of ions, as calculated from the "best" Λ_0 values shown in Table X.

Salts.	$\Lambda_1 - \Lambda_2$.	Salts.	$\Lambda_1 - \Lambda_2$.	Salts.	$\Lambda_1 - \Lambda_2$.	Salts.	$\Lambda_1 - \Lambda_2$.
KCl-NaCl	21.07	NaCl-NaNO₃	3.62	KCl-LiCl	31.22	NaCl-NaIO₃	31.52
KNO₃-NaNO₃	21.07	KCl-KNO₃	3.62	KNO₃-LiNO₃	31.24	KCl-KIO₃	31.52
KIO₃-NaIO₃	21.07	LiCl-LiNO₃	3.64	KIO₃-LiIO₃	31.20	LiCl-LiIO₃	31.50
Mean,	21.07	Mean,	3.63	Mean,	31.23	Mean,	31.51

6. Ion Conductances.—From the "best" values given in Table X the differences in ion conductances for the four pairs of ions shown in Table XI have been calculated. From the mean values of these differences, together with the other Λ_0 values given in Table X, the set of ion conductances shown in Table XII has been calculated. These values are based upon 0.4960 as the cation transference number for potassium chloride.

TABLE XII.

Ion Conductances at 18°.

Ion	K.	Na.	Li.	Rb.	Cs.	Ag.	Cl.	NO₃.
Λ	64.30	43.23	33.07	67.6	67.56	53.9	65.34	61.71

Ion	IO₃.	Br.	I.	SCN.	ClO₃.	BrO₃.		
Λ	33.83	67.41	66.35	56.5	54.95	47.7		

URBANA, ILL.

EQUILIBRIUM DATA ON THE POLYBROMIDES AND POLYIODIDES OF POTASSIUM.

BY G. A. LINHART.

I. The Equilibrium between Bromine and Potassium Bromide Solutions at Different Temperatures.

In connection with an investigation dealing with the polyiodides of potassium, it was of interest to calculate for comparison the values for the equilibrium constants of the polybromides from Worley's data[1] at 26.5° and compare them with those obtained by Jones & Hartmann[2] at 0°. From these values at 0° and 26.5°, were then calculated equilibrium constants for 32.6° and compared with those calculated from Worley's data for 32.6°. In Table I are given Worley's data at 26.5° and the equilibrium constants calculated from them with the aid of the following relations:

$$\frac{(Br^-)}{\gamma} + \frac{(Br_3^-)}{\gamma} + \frac{(Br_5^-)}{\gamma} = \Sigma(KBr), \quad (1);$$

$$\frac{(Br_3^-)}{\gamma} + \frac{2(Br_5^-)}{\gamma} + (Br_2) = \Sigma(Br_2), \quad (2);$$

$$\frac{(Br_3^-)}{(Br^-)(Br_2)} = K', \quad (3); \qquad \frac{(Br_5^-)}{(Br_3^-)(Br_2)} = K'', \quad (4)$$

Combining (2) and (4) we have,

[1] *J. Chem. Soc. (London)*, **87**, 1107 (1905).

[2] *Trans. Am. Electrochem. Soc.*, **30**, 295 (1916).