

DETERMINATION OF THE ELECTRIC CONDUCTIVITY OF CERTAIN SALT SOLUTIONS.

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Introduction.

DURING the last few years a great deal of work has been done in the line of determining the electric conductivity of certain salts in their water solutions. Two objects are accomplished by means of such observations; namely, the determination of the velocities of the so-called ions, and the gaining of some insight into the condition of the salts when in solution. It is true that the same objects may be accomplished by observations of the depression of the freezing-point, but owing to the ease and accuracy of making the observations, the following method seems to be preferable.

The following determinations fill in a few vacancies in the list of results heretofore obtained for salts of the alkaline earths and acetates.

Apparatus.

The resistance bottles used were the same as those employed by Professor Kohlrausch in his work.

As the solutions varied in strength from $m=0.0001$ to $m=1.00$ (m denotes the gram equivalent in the liter of solution), it was necessary to employ two resistance bottles, one for the solutions from $m=0.0001$ to $m=0.01$, and the other for the remaining ones.

In measuring the most dilute solutions I employed a Becher glass of 80 mm. diameter and 130 mm. high: the edge was ground off even and fitted with a hard rubber cover 10 mm. thick and 110 mm. across. By means of three small pieces of rubber on the under side all lateral movement was avoided. Three holes were bored through the cover: two of them were situated on either

side of the center at a distance of 25 mm. from the same, and through them passed heavy copper wires. At the upper end of these wires binding posts were placed, while at the lower end were fastened large platinum wires ending in the electrodes of heavy platinum foil, 40 mm. square. The wire and foil were fastened together by welding and soldering, and were afterwards platinized in the usual manner. The third hole contained the thermometer, which entered the solution midway between the electrodes on a line connecting the outer edge.

With a normal filling of 500 cc. the electrodes dipped about 20 mm. under the surface of the liquid. The glass was entirely surrounded by felt.

The thermometer used was graduated to 0.°2, thus giving readings to 0.02°. The thermometer was tested by comparison with one from the Reichsanstalt. The bottle used for the other solutions consisted of two small glass bottles joined by a tube about 6 mm. in diameter. The bottles were provided with glass stoppers. After being filled, the bottle was placed in a water bath and the thermometer hung next to the connecting tube. Owing to the heat produced by the passage of the current the bridge readings were made as rapidly as possible. It was always necessary to wait until the temperature of the solution was the same as that of the bath before the readings were taken. The Kohlrausch roller bridge which was used was supplied with resistances of 1, 10, 100, and 1000 ohms, but for the most part only the 100 and the 1000 were used, their actual value being carefully determined by comparison with a normal instrument. By the use of a rheostat having resistances up to 4000 ohms the bridge wire was calibrated for every $\frac{1}{100}$ of its length. Whenever it was possible the resistances were determined by the use of both the 100 and 1000 ohms, and the middle taken as the true value. If the two values did not agree within 0.2 per cent, the bridge was again calibrated. Twelve calibrations in all were made during the course of the work. At one end of the wire the corrections remained quite constant, while at the other end there was a variation between the beginning to the completion of my work equivalent to about 0.0005 of the entire length of the wire.

Resistance Capacity of the Bottles.

The resistance capacities of the two bottles were determined by the use of normal and part normal solutions of KCl and NaCl. Before the solutions were used they were carefully tested by comparing their conductivity and specific gravity with existing data.

The capacity of the larger bottle was found by the use of solutions having a strength $m=0.05$, $m=0.02$, $m=0.01$, the conductivity of these solutions at 18° being, according to Kohlrausch, 5415, 2246, and 1147 respectively for KCl, and 4485, 1876, and 962 for NaCl (Hg.=1). These values are to be multiplied by 10^{-10} . For the solutions used in calibrating the smaller bottle the values of m were 1.00, 0.5, and 0.1.

The mercury capacities thus found for the larger bottle were as follows:—

Salt	$m =$	0.05	0.02	0.01
NaCl		1073.9	1072.5	1073.2
KCl		1071.0	1075.0	1073.0
Middle $1073 \cdot 10^{-8}$ ohms.				

For the smaller bottle:—

Salt	$m =$	1.00	0.5	0.1
KCl		1652.4	1653.0	1650.1
NaCl		1650.7	1651.3	1653.0
Middle $1651.7 \cdot 10^{-6}$ ohms.				

Making the Solutions.

Whenever it was possible the solutions were made by weighing out the required amount of the pure salt, dissolving it in water, and then diluting to a liter of solution. When this was not possible, a concentrated solution was made and then brought to the normal strength by the specific gravity method. To accomplish this it was necessary to use tables giving the relation between the specific gravity and the per cent of salt. The following tables

were used: from Kohlrausch for SrCl_2 and $\text{Ca}(\text{NO}_3)_2$, from Franz for $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$, and from Hager for $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$.

The normal solutions thus obtained were tested by comparing with tables of the specific gravity from other authors, and, when possible, with tables of the electric conductivity.

The values thus found for the specific gravity of the normal solutions were as follows:—

Salt.	Sp. Grav. $\frac{18}{4}$	Salt.	Sp. Grav. $\frac{18}{4}$
$\frac{1}{2}$ CaCl_2	1.0435	$\frac{1}{2}$ SrCl_2	1.06765
$\frac{1}{2}$ $\text{Ca}(\text{NO}_3)_2$	1.0611	$\frac{1}{2}$ $\text{Sr}(\text{NO}_3)_2$	1.0816
$\frac{1}{2}$ $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$	1.0386	$\frac{1}{2}$ $\text{Sr}(\text{C}_2\text{H}_3\text{O}_2)_2$	1.0669
$\frac{1}{2}$ $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$	1.0843	$\frac{1}{2}$ $\text{K}_2\text{C}_2\text{O}_4$	1.0575

The solutions of $m=0.5$ to $m=0.05$ were made by diluting the normal solutions in quantities of 100 cc. (The smaller bottle held about 40 cc.) For the more dilute solutions I used a method suggested by Professor Kohlrausch,¹ which is as follows: The Becher glass was first filled with 500 cc. of water and its conductivity determined. Then I drew out 9.5 cc. of water, and using very exact pipettes added successively 0.5 cc., 0.5 cc., 2.0 cc., and 2.0 cc., of the solution for which $m=0.1$, determining the conductivity after each addition. Then 0.5 cc., 2.0 cc., and 2.0 cc. of the solution for which $m=1.0$ were added in the same way. After each addition the pipettes were rinsed out three or four times.

In this manner I obtained solutions having the following strengths:—

After the addition of the solution $m=0.1$:—

0.5 cc.	$m = 0.0001018$
0.5	0.0002034
2.0	0.0006079
2.0	0.0010090

From solution $m=1.0$:—

0.5 cc.	$m = 0.002016$
2.0	0.006024
2.0	0.010000

¹ Wied. Ann. XXVI., 175, 1885.

The conductivity was determined for eleven (11) degrees of concentration between the values $m = 1.0$ and $m = 0.0001$.

In order to compute the molecular conductivity from the conductivity of the solution, the latter was diminished by the conductivity of the water, and this difference was divided by the values for m as given above.

As the resistance in the Becher glass depended upon the amount of solution, it was necessary to know the variation in the capacity for different degrees of filling. Instead of making new determinations I employed the values obtained by Professor Kohlrausch for the same glass and the same degrees of filling.

Filling	460 cc.	470	480	490	500	510	520
Capacity	1.0685	1.0489	1.0314	1.0155	1.000	0.9855	0.9715

The value for 500 cc. (Hg. at 0°) was determined as given above.

Temperature and Temperature Coefficient.

With very little difficulty the observations were all made at 18°. The room in which I worked had the sun only for a short time in the morning.

If the solution in the bottle became too warm, it was cooled from the outside by means of a piece of ice, or by moistening the outside and thus cooling by evaporation. If the solution became too cool, it was warmed by the hand until the correct temperature was obtained. I am sure that the variation in the temperature was never greater than 0.02° from 18°, as the thermometer could be read to this degree of exactness. In two or three cases I began with a temperature of 18°, and after forty minutes there was no perceptible change.

To avoid parallax I used a vision line drawn on the window, its position being determined in the usual manner. The temperature coefficients were determined from the normal solutions.

Salts Investigated.

The following salts were investigated: Calcium sulphate, calcium chloride, calcium nitrate, calcium acetate, strontium chloride, strontium nitrate, strontium acetate, barium acetate, silver acetate, potassium oxalate.

The following methods were employed for making the individual solutions:—

CaSO_4 : The water of crystallization was first driven off and then the required amount of salt weighed out. Owing to the insolubility of the salt, only solutions having strengths of $m=0.01$ and under were investigated. 0.3400 g. was weighed out and then diluted to $\frac{1}{2}$ liter.

CaCl_2 : The salt was first heated for two hours above 200° in order to drive off the water of crystallization, then cooled in a desiccator. 27.713 g. were weighed out and diluted to $\frac{1}{2}$ liter.

$\text{Ca}(\text{NO}_3)_2$: Made according to specific gravity. Spec. Grav. of the original solution 1.1141. According to Kohlrausch this denotes 13.822 g. of salt in 100 g. of solution. Since a normal solution requires 82.04 g. salt in a liter, 593.02 g. of the solution were weighed out and diluted to a liter.

$\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$: Made according to specific gravity. Spec. Grav. of the original solution 1.1443. According to Hager this denotes 27.234 g. of salt in 100 g. of solution. Normal requires 79.01 g. of salt in a liter of solution. So 289.86 g. were weighed out and diluted to a liter.

SrCl_2 : Made according to specific gravity. Spec. Grav. of original solution 1.1343. According to Kohlrausch this denotes 13.922 g. salt in 100 g. of solution. Normal requires 79.20 g. in a liter. So 568.38 g. were weighed out and diluted to a liter.

$\text{Sr}(\text{NO}_3)_2$: The salt was first recrystallized, dried at $75-80^\circ$, and then 105.79 g. were weighed out.

$\text{Sr}(\text{C}_2\text{H}_3\text{O}_2)_2$: The amount of water of crystallization was estimated and found to be 4.1 per cent, thus denoting the presence of $\frac{1}{2}$ molecule of water. Then 107.2595 g. were weighed out.

$\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$: Made according to specific gravity. Spec. Grav. of original solution 1.1724. According to Franz this denotes 22.349 g. of salt in 100 g. of solution. Normal solution requires 127.509 g. of salt in a liter of water. 570.03 g. of the solution were weighed out and diluted to a liter.

$\text{K}_2\text{C}_2\text{O}_4$: The salt was first well dried over H_2SO_4 , and then 92.113 g. were weighed out. (Reckoning 1 mol. of water.)

$\text{AgC}_2\text{H}_3\text{O}_2$: The salt was weighed out directly. Owing to its

slight solubility, solutions from $m=0.01$ and under were the only ones investigated. (The salt is soluble 1 part in 98 of water.) An attempt was made to make a solution $m=0.05$, but after this had stood in a dark room for three days a precipitate began to form, and so the attempt was abandoned. All the investigations with this salt were made in a room illuminated by gaslight only. For the solution $m=0.01$, 0.8347 g. of the salt was weighed out and diluted to $\frac{1}{2}$ liter. The specific gravities of the normal solutions are given above.

The Water Used.

The water for the very dilute solutions was obtained by triple distillation, the last two distillations being made in a tinned copper boiler having a tin cooler. The boiler was heated by a large Bunsen flame, and the products of combustion were led off into the chimney. The required purity was attained in about an hour and a half after the water began to boil; then for about three hours water was obtained having a conductivity between $0.75 \cdot 10^{-10}$ and $1.5 \cdot 10^{-10}$. In a few cases the conductivity was only $0.68 \cdot 10^{-10}$, so that its average conductivity was about $1.00 \cdot 10^{-10}$.

The water was kept in glass stoppered bottles covered by a bell jar.

It has been noticed by others, as well as by myself, that after the water has stood for a few days the conductivity has decreased from what it was directly after distilling. For example, water distilled May 5 had a conductivity of $1.095 \cdot 10^{-10}$. On the 12th it was $1.019 \cdot 10^{-10}$, and on the 18th $0.997 \cdot 10^{-10}$.

Results.

Professor Kohlrausch having investigated the solutions of CaCl_2 , $\text{Ca}(\text{NO}_3)_2$, and SrCl_2 , for values of $m=1.00$ and above, I used only those having a less value. His work was based upon per cent of salt, and not upon the gram equivalent, and so his values for the normal solutions and their multiples are interpolated. In the case of $\text{Ca}(\text{NO}_3)_2$ a slight difference occurred, in that he found $K=541.0 \cdot 10^{-8}$ (K =molecular conductivity), while I found $536.4 \cdot 10^{-8}$.

The first columns in the following table contain the values for

m ; the second the observed conductivity diminished by the conductivity of the water. All the observations were made at 18° unless otherwise indicated.

TABLE I.

$\frac{1}{2} \text{CaSO}_4$.		$\frac{1}{2} \text{CaCl}_2$.	
m	$k_{18} \cdot 10^{10}$.	m	$k_{18} \cdot 10^{10}$.
water	(1.465)	water	(1.603)
0.0001	10.789	0.0001018	10.983
0.0005	51.234	0.0002034	21.686
0.0010	97.714	0.0006079	64.084
0.0050	402.30	0.001009	105.17
0.0100	719.81	0.002016	208.69
0.0100	(815.42)	0.006024	594.35
	($t = 23^\circ.77$)	0.01	964.67
		0.05	4341.6
		0.10	8218.0
		0.50	35008.0
		1.0	63310.0
		2.0	108300.0
		3.0	138900.0
		4.0	158300.0
		5.0	166600.0
		6.0	164400.0
$\text{AgC}_2\text{H}_3\text{O}_2$.		$\frac{1}{2} \text{Ca(NO}_3)_2$.	
water	(1.206)	water	(1.663)
0.0001053	8.395	0.0001018	11.138
0.0002083	16.687	0.0002034	22.058
0.0006000	48.108	0.0006079	64.499
0.0009615	76.844	0.001009	105.99
0.0050	388.68	0.002016	208.11
0.0100	750.40	0.006024	597.59
		0.01	963.3
		0.05	4266.0
		0.10	7948.0
		0.50	31711.0
		1.0	53640.0
		2.0	81800.0
		3.0	94600.0
		4.0	98300.0
		5.0	94600.0
		6.0	84500.0
$\frac{1}{2} \text{Ca(C}_2\text{H}_3\text{O}_2)_2$.		$\frac{1}{2} \text{Ca(C}_2\text{H}_3\text{O}_2)_2$.	
water	(1.345)	water	(1.345)
0.0001018	7.387	0.0001018	7.387
0.0002034	14.417	0.0002034	14.417
0.0006079	42.154	0.0006079	42.154
0.001009	69.084	0.001009	69.084
0.002016	135.44	0.002016	135.44
0.006024	383.61	0.006024	383.61
0.01	616.34	0.01	616.34
0.05	2596.9	0.05	2596.9
0.10	4663.6	0.10	4663.6
0.50	15972.0	0.50	15972.0
1.0	23708.0	1.00	23708.0
2.0	(28120.0)	1.00	(28120.0)
3.0	($t = 26^\circ.00$)	2.00	29752.0
4.0		3.00	27108.0
5.0			
6.0			

TABLE I. (*continued*).

$\frac{1}{2}$ SrCl ₂ .		$\frac{1}{2}$ Sr(NO ₃) ₂ .	
<i>m</i>	<i>k</i> ₁₈ · 10 ¹⁰ .	<i>m</i>	<i>k</i> ₁₈ · 10 ¹⁰ .
water	(1.024)	water	(1.095)
0.0001018	11.449	0.0001018	10.623
0.0002034	22.564	0.0002034	21.056
0.0006079	65.769	0.0006079	61.652
0.001009	107.90	0.001009	101.37
0.002016	212.05	0.002016	198.74.
0.006024	608.34	0.006024	568.26
0.01	986.62	0.01	919.98
0.05	4404.7	0.05	4009.0
0.10	8492.0	0.10	7462.8
0.50	35396.0	0.50	28858.0
1.0	63890.0	1.0	47837.0
2.0	108200.0	1.0	(56820.0)
3.0	138700.0		(<i>t</i> = 26.°∞)
3.5	149900.0	3.00	80530.0
$\frac{1}{2}$ Sr(C ₂ H ₃ O ₂) ₂ .		$\frac{1}{2}$ Ba(C ₂ H ₃ O ₂) ₂ .	
water	(1.222)	water	(1.019)
0.0001018	7.837	0.00009990	7.699
0.0002034	15.626	0.0001996	15.373
0.0006079	46.367	0.0005964	45.260
0.001009	76.356	0.0009901	74.266
0.002016	149.02	0.001978	145.84
0.006024	426.97	0.005911	415.84
0.01	687.53	0.009814	670.09
0.05	2936.6	0.05	2939.2
0.10	5328.7	0.10	5390.6
0.50	18920.0	0.50	19754.0
1.0	29126.0	1.0	(31169.0)
2.0	36577.0	1.0	(<i>t</i> = 26.°∞)
3.0	34976.0	2.0	42203.
$\frac{1}{2}$ K ₂ C ₂ O ₄ .			
<i>m</i>	<i>k</i> ₁₈ · 10 ¹⁰ .	<i>m</i>	<i>k</i> ₁₈ · 10 ¹⁰ .
water	(0.997)	0.01	1054.67
0.0001018	11.926	0.05	4693.4
0.0002034	23.368	0.10	8839.1
0.0006079	69.648	0.50	37570.0
0.001009	114.75	1.0	68783.0
0.002016	226.57	1.5	95900.0
0.006024	650.73		

In Table II. the gram equivalents m and the molecular conductivity $\frac{k}{m}$ are given.

TABLE II.

$\frac{1}{2}$ CaSO ₄ .		$\frac{1}{2}$ CaCl ₂ .		$\frac{1}{2}$ Ca(NO ₃) ₂ .	$\frac{1}{2}$ Ca(C ₂ H ₃ O ₂) ₂ .
m	$\frac{k}{m} \cdot 10^8$.	m	$\frac{k}{m} \cdot 10^8$.	$\frac{k}{m} \cdot 10^8$.	$\frac{k}{m} \cdot 10^8$.
0.0001	1079.0	0.0001	1078.9	1094.1	725.6
0.0005	1025.0	0.0002	1066.2	1084.5	708.8
0.001	977.1	0.0006	1054.2	1061.0	693.4
0.005	804.6	0.001	1042.3	1050.5	684.7
0.01	719.8	0.002	1035.2	1032.3	671.8
$\text{AgC}_2\text{H}_3\text{O}_2$.		0.006	986.7	992.0	636.8
		0.01	964.7	963.3	616.3
0.0001	797.2	0.05	868.3	853.2	519.4
0.0002	801.1	0.1	821.8	794.8	466.4
0.0006	801.8	0.5	700.2	634.2	319.4
0.001	799.2	1.0	633.0	536.4	237.1
0.005	777.4	2.0	541.0	409.0	148.8
0.01	750.4	3.0	463.0	315.0	90.4
		4.0	396.0	246.0	
		5.0	333.0	189.0	
		6.0	274.0	141.0	
$\frac{1}{2}$ SrCl ₂ .		$\frac{1}{2}$ Sr(NO ₃) ₂ .	$\frac{1}{2}$ Sr(C ₂ H ₃ O ₂) ₂ .	$\frac{1}{2}$ Ba(C ₂ H ₃ O ₂) ₂ .	$\frac{1}{2}$ K ₂ C ₂ O ₄ .
m	$\frac{k}{m} \cdot 10^8$.	$\frac{k}{m} \cdot 10^8$.	$\frac{k}{m} \cdot 10^8$.	$\frac{k}{m} \cdot 10^8$.	$\frac{k}{m} \cdot 10^8$.
0.0001	1124.7	1043.5	769.8	770.7	1171.5
0.0002	1109.4	1035.2	768.3	770.2	1148.9
0.0006	1081.9	1014.2	762.7	758.9	1145.7
0.001	1069.4	1004.7	756.8	750.1	1137.4
0.002	1051.8	985.8	737.4	737.3	1123.9
0.006	1009.9	943.3	708.8	703.5	1080.2
0.01	986.6	920.0	687.5	682.8	1054.7
0.05	880.9	801.8	587.3	587.8	938.7
0.1	849.2	746.3	532.9	539.1	883.9
0.5	707.9	577.2	378.4	395.1	751.4
1.0	639.0	478.0	291.2	311.7	688.0
1.5	588.0				639.0
2.0	541.0		182.8	211.0	
2.5	500.0				
3.0	462.0	268.4	116.6		
3.5	428.0				

Graphic Reproduction of the Molecular Conductivity.

In the curves shown in Fig. 1, the values for $\frac{k}{m}$ are used as ordinates and the values for $m^{\frac{1}{2}}$ as abscissæ. Thus we can represent the course of the curve for all possible degrees of concentrations in a comparatively small space. The curves are constructed directly from the results obtained, excepting in a few cases where they are made a little more regular than the observations give, although the change is very slight.

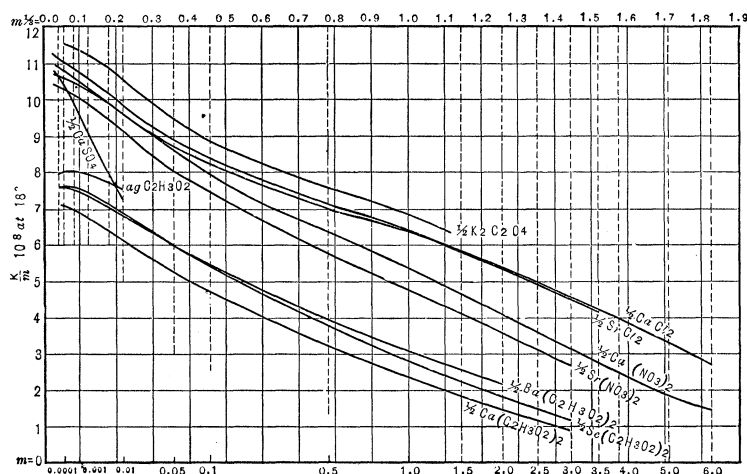


Fig. 1.

Temperature Coefficient.

The following tables contain the temperature coefficient for the normal solutions excepting for CaSO_4 , where the value is for $m=0.01$.

The values for CaCl_2 , $\text{Ca}(\text{NO}_3)_2$, and SrCl_2 are those obtained by Professor Kohlrausch.

TABLE III.

Salt.	$\frac{\Delta k}{k_{18}}$	Salt.	$\frac{\Delta k}{k_{18}}$
$\frac{1}{2}$ CaSO ₄	0.023	$\frac{1}{2}$ SrCl ₂	0.0212
$\frac{1}{2}$ CaCl ₂	0.0213	$\frac{1}{2}$ Sr(NO ₃) ₂	0.0224
$\frac{1}{2}$ Ca(NO ₃) ₂	0.0219	$\frac{1}{2}$ Ba(C ₂ H ₃ O ₂) ₂	0.022
$\frac{1}{2}$ Ca(C ₂ H ₃ O ₂) ₂	0.023	$\frac{1}{2}$ K ₂ C ₂ O ₄	0.0209

General Remarks.

The curves giving the molecular conductivity are, for the most part, entirely regular, and even in the most dilute solutions there is no tendency in the curve to change from its upward course.

In the case of AgC₂H₃O₂ three separate determinations were made, and each time the curve changed from an upward to a downward course. Professor Kohlrausch assisted in one of the series at which the dilutions were carried to $m=0.00001$, and then we obtained the value $\frac{k}{m}=782 \cdot 10^{-8}$. This change in direction is quite characteristic for free acids or bases, but why it should occur with AgC₂H₃O₂, never having been observed with any other salt, is something I am unable to explain.

The salt had almost no odor of acetic acid. Perhaps a more thorough study of the acetates will explain this peculiarity.

The curve for CaSO₄ agrees in form very nearly with the curves for MgSO₄, ZnSO₄, and CuSO₄, as given by Professor Kohlrausch.