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THE ELECTRICAL CONDUCTANCE OF SOLUTIONS OF THE ALKALI HALIDES IN ACETOPHENONE

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Introduction

The increasing interest in the study of the laws of solution, the value of the conductance method for such a study, and the lack of quantitative experimental conductance data in non-aqueous solvents makes an investigation of the properties of such systems as these of importance.

The work described in this paper, the conductances of the solutions in the dark, was undertaken as preliminary to an investigation of the same systems when under the influence of the radiations of a mercury-quartz lamp, the outcome of which will be presented in a later paper.

The only results in the literature available for solutions of the alkali halides in acetophenone are those of Nicollier (working with Dutoit)[1] of sodium iodide and lithium bromide. These results, however, are quite evidently burdened with considerable error, the sources of which, according to Dutoit, are the use of platinized electrodes and the changes in concentration due to adsorption, together with the changes due to the photochemical reactions, and impurities in the solvent.

Since the conductance value of the purest fractions of acetophenone used by Nicollier was 2.2×10^{-7} reciprocal Siemens units, which, by the conversion factor 1.063, gives in reciprocal ohms a value of 2.34×10^{-7}, and since we have found the value for the conductance of pure acetophenone to be 8.43×10^{-9} reciprocal ohms, it seemed desirable, because of this source of error alone, to repeat these measurements for sodium iodide and lithium bromide and to extend the measurements to those other halides, namely potassium iodide and lithium chloride, which are sufficiently soluble to warrant the effort. Furthermore, inasmuch as there have been many improvements in the bridge assembly since Nicollier's work, and since the cells designed and the procedure developed for the handling of the cells by the authors,[2] together with the development of the detail for working in the dark, would eliminate more of the errors, it seemed quite probable that improvements in the results in other directions could be made.

Purification of Materials

Acetophenone.—The purification of this substance is described in a preceding paper.[3] The solvent from the solutions, frequently containing free iodine, is best re-

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[1] Nicollier, *Thèse* (Dutoit), Lausanne. (Professor Kraus was good enough to place his copy of this at our disposal.) Dutoit, *Z. Elektrochem.*, **12**, 640 (1906).

[2] Morgan and Lammert, THIS JOURNAL, **45**, 1692 (1923).

[3] Morgan and Lammert, *ibid.*, **46**, 881 (1924).

covered by shaking the solution with an aqueous solution of sodium thiosulfate, drawing off the acetophenone layer and distilling. However, as by this method hydrogen sulfide is formed, the distillate should be shaken with an aqueous solution of copper sulfate, and then redistilled from anhydrous copper sulfate. The freezing point of this product is usually about normal, and only a few recrystallizations are needed to bring it to this constant value.

Water.—The conductivity water was prepared by redistilling ordinary distilled water from alkaline permanganate, the distillate being condensed in a block tin condenser so cooled that some of the water escaped as steam. The first and last fractions were discarded. The specific conductance of the water used in making up the standard solutions of potassium chloride was 1×10^{-6} reciprocal ohm, or less.

Air.—The air was furnished by a water pump and purified and dried by passage successively through solutions of sulfuric acid and potassium hydroxide, through water, soda lime and finally through a number of towers of calcium chloride.

Nitrogen.—The nitrogen used in purifying the salts was compressed nitrogen purified in the same way as the air.

Alkali Halides.—The salts used were the purest obtainable and further purified as follows.

Potassium Chloride.—The potassium chloride, "T. P.," was recrystallized four times by precipitation with hydrogen chloride and twice without the hydrogen chloride. It was then fused in platinum, bottled and kept in a desiccator, and small amounts fused again just before they were used.

Potassium Iodide and Sodium Iodide.—The sodium iodide, "Pure," was recrystallized from ordinary distilled water five or six times, the potassium iodide, "C. P.," once. In order to obtain perfectly colorless samples free from iodine, four or five further recrystallizations were made in a flask in an atmosphere of nitrogen. The crystals were heated for several days in platinum above 150° in a stream of purified nitrogen. Even when kept in a weighing bottle in a desiccator these salts turned slightly yellow after several months, and consequently all samples were kept in small tubes enclosed in larger tubes filled with nitrogen and sealed. Samples prepared in this way remained perfectly colorless for longer than a year. As the salts were needed, a tube was opened and the contents emptied into a weighing bottle and heated for several hours in the stream of nitrogen.

Lithium Bromide.—The lithium bromide, "Pure," was recrystallized seven or eight times from ordinary distilled water to relieve it of a large quantity of a dark brown, greasy impurity. It was then precipitated with hydrogen bromide. The excess of acid was removed without decomposition by heating in a flask in an atmosphere of nitrogen. The sample was then recrystallized four or five times from conductivity water in the atmosphere of nitrogen and finally heated for several days above 160° in platinum in a stream of nitrogen. Although lithium bromide does not seem to decompose at room temperature, when heated to a higher temperature in air a light brown layer forms on the surface. In nitrogen, however, such decomposition is avoided and perfectly white crystals of the salt are obtained. The lithium bromide was kept in sealed tubes until ready for use as in the case of the sodium iodide.

Lithium Chloride.—Although a number of methods have been suggested for the the purification of lithium chloride, it has been pointed out by Richards and Willard,[4] and by Lamb and Lee[5] that the best method is the repeated recrystallization from water. The lithium chloride, "Pure," was recrystallized several times from ordinary distilled water, then precipitated with hydrogen chloride two or three times and finally crys-

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[4] Richards and Willard, THIS JOURNAL, **32**, 4 (1910).

[5] Lamb and Lee, *ibid.*, **35**, 1666 (1913).

tallized twice from conductivity water; it was heated above 120° in nitrogen and kept in sealed tubes.

Lithium Iodide and Ammonium Iodide.—These salts are soluble in acetophenone; the lithium iodide much more so than any of the other salts, the ammonium iodide to about the same extent as the potassium iodide. Both salts are extremely difficult to purify because of their tendency to liberate free iodine. Preliminary experiments indicate, however, that pure lithium iodide can be prepared by a large number of recrystallizations in an atmosphere of nitrogen by starting with a large quantity of the salt, and by taking special precautions to eliminate traces of oxygen from the nitrogen. Ammonium iodide can be purified by sublimation in a vacuum; up to this time the samples of these salts obtained were not sufficiently pure to justify our reporting the conductances of their solutions with those of the purer salts.

The other alkali halides are so insoluble in acetophenone that attempts to dissolve very small quantities of the salts by allowing them to stand in contact with the solvent for over a year, with frequent agitation, were unsuccessful.

Apparatus

The bridge assembly, cells and the technique of cleansing and drying the latter have been described in an earlier paper.[2]

The water-bath, regulating at 25° ± 0.002°, was provided with curtains of a heavy black rubberized material, supported on a wooden frame built over the bath; in this way it was possible to keep the solutions in the dark while the conductance measurements were being made. These curtains carried sleeves through which any adjustments of the leads could be made; from the curtains to the reading glass on the thermometer was a tube through which the temperature of the bath could be observed by switching on momentarily a red light suspended from the ceiling of the frame. The tube was again capped at the outer end as soon as the reading was made.

Cell Constants.—Since the completion of the experimental results presented in the following sections, the articles by Kraus and Parker[6] have appeared on the calibration of cells for conductance measurements. A successful calibration of such cells involves the accurate measurement of two types of solutions, a primary standard solution whose specific conductance is known and which is sufficiently concentrated to yield precise results with comparative ease in manipulation, and a number of comparison solutions having lower specific conductances and so prepared that they too can be transferred and measured with precision. The possible necessity for the redetermination of the absolute specific conductance of the calibrating potassium chloride solutions has been pointed out by a number of investigators, but until further investigations among the various phases of the modern conductance method have been undertaken to extend and to determine the limits of accuracy *in all directions*, in the manipulation as well as in the design of the apparatus, it would seem advisable to report all values in terms of *one* of the usual standards. A successful re-evaluation of that standard would then necessitate only a simple recalculation of the conductance based upon it; were a

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[6] Kraus and Parker, (a) THIS JOURNAL, **44**, 2422; (b) 2429 (1922). (c) Parker, *ibid.*, **45**, 1366 (1923).

weighted average of a number of values used, the conversion would not be so simple. It is, therefore, with the accurate measurement of the comparison solutions and with the methods for procuring dependably relative results that the discussion which follows is concerned. Parker [6c] has given some interesting data and curves showing a variation of the cell-constant ratio of two cells with the resistance. The striking difference between the curves for the non-platinized and the platinized electrodes, the shape of the former curve, and the magnitude of the changes suggested to us the possibility that such changes in the cell-constant ratio could readily be attributed to the fact that the electrodes used were too small to give results free from those errors which manifest themselves in a change of resistance with a change in frequency. Schlesinger and Reed[7] had previously given some data on the comparison of cell constants, which made it quite evident that, even with *platinized* electrodes, at least with small electrodes at low resistances, there were disturbing influences which necessitated a more rigid examination of the cells; as to just *which* cell is at fault cannot be conclusively determined from the incomplete experimental detail given.

An examination of the data in our paper on cell design for Cells 2, 4 and 6, which have electrodes very little smaller than Parker's, will show that if the differences in the resistances at the two frequencies were plotted against the resistances, curves similar to Curve I of Parker's Fig. 4 would be obtained throughout the range covered by his measurements, and would bend back beyond 10,000 ohms. We have made no extended measurements with platinized electrodes. Parker's data though incomplete at present, corroborate, qualitatively at least, Haworth's[8] throughout the limited range covered by the latter. If Haworth's results (obtained with two cells having electrodes of nearly the same area and distance apart, one containing two platinized electrodes, the other two unplatinized), for the changes in resistance apparent when the frequency is changed from 100 cycles to 1000 cycles, are plotted against the resistances at 1000 cycles the curves shown in Fig. 1 are obtained, Curve I giving the plot of the results with the non-platinized electrodes, Curve II the plot of the results with the platinized electrodes. The similarity to Fig. 4 in Parker's paper is indeed striking. In Haworth's results the magnitude of the effect is brought out by the large variation in frequency and the measurements at very low resistances. If the value of the lowest resistance in Curve I, burdened and increased as it is above the true resistance by an error the magnitude of which depends upon the particular frequency at which it is measured, is divided by a number selected so as to represent as nearly as possible the true resistance of another cell, the ratio obtained would be comparable to one of the first points on Parker's Curve I. A larger

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[7] Schlesinger and Reed, THIS JOURNAL, **41**, 1727 (1919).

[8] Haworth, *Trans. Faraday Soc.*, **16**, 365 (1921).

resistance value, burdened with less error and divided by the value, burdened with no error, of the resistance of the second cell would give a smaller ratio. Obviously a plot of these ratios against the resistances would follow along a line similar to Curve I *as long as the value in the denominator represented the true resistance of the comparison cell.* Similarly one would expect the ratios obtained with the values of a platinized cell of the same dimensions to follow along a line similar to Curve II. When therefore the constant of a cell with non-platinized electrodes, too small to eliminate the effect observed with a change of frequency, is being determined by comparison with a cell containing similar platinized electrodes, that constant would of necessity be burdened with an error of about the same order as the individual resistance readings of the cell with the non-platinized electrodes, the divergence from that order, particularly at the higher and lower resistances, depending upon the possible errors in the individual resistance readings of the cell with platinized electrodes. The constancy of a "cell-constant ratio" in a given range, then, is not an adequate criterion for the use of the cell in that range since such constancy might be the result of balancing errors in the two cells, whereas the individual resistance measurement made later would be burdened only with the error inherent in the one cell; and the calculated conductance of the solution would still be burdened with some error. It is only when the constant of the one cell is known to be correct throughout the entire range used for comparison that a constant error will be balanced out. Placing the emphasis then upon the constancy of the "cell-constant ratio" rather than upon the accuracy of the individual resistance readings might lead to errors large enough to affect the final results; this would depend upon the desired precision and the inter-relation of resistances between the two cells compared.

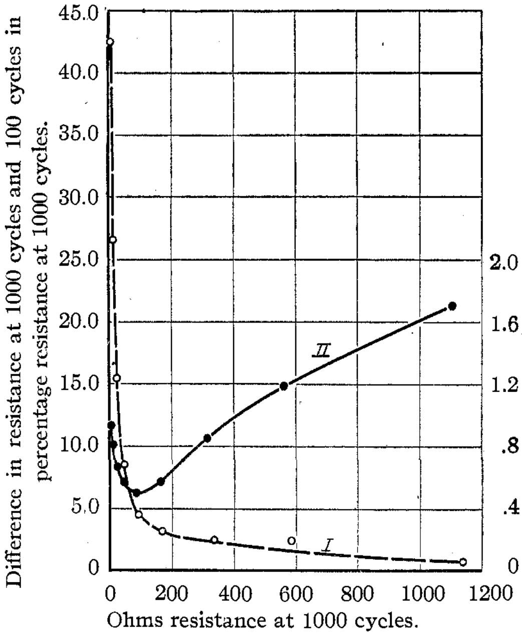

Fig. 1.—Curve I: non-platinized electrodes; vertical scale to left. Curve II: platinized electrodes; vertical scale to right.

Throughout this and Parker's discussion, the first cell to which the others have been compared has been a platinized one in which the errors are comparatively small and therefore a general drift in the "cell-constant ratio" is to be expected and has been observed. However, in investigations involving the determination of the conductances of non-aqueous solutions, where platinized electrodes cannot be used because of the effect on the solvent, an inter-comparison naturally would be made among cells all of which carried bare platinum electrodes. One would expect here not the gradual change observed with the cells with platinized electrodes where the errors are smaller, but changes depending even more upon the inter-relation among the cells. Such an intercomparison was made among the unplatinized Washburn cells over an extended range of resistances, and a series of seemingly very erratic cell constants obtained, the differences among which could not be ascribed entirely to experimental error. Among the new cells we have described with the larger electrodes, deviations of such magnitude were not evident.

Kraus and Parker have indicated the error in the calculations for the standard weight-normal solutions of potassium chloride, the conductance values of which are given by Kohlrausch and Holborn,[9] but they find no errors in the directions for making up the volume-normal solutions. The cell constant of DB1 (having electrodes of 50mm. diameter) based upon the assumption that *(74.555 ÷ 50)·g. of potassium chloride (weights in air) in 1 liter of solution at 18° has at 25° a specific conductance of 0.002765 reciprocal ohm, was found to be 1.37859 + 0.011%.* By using the alcoholic comparison solutions prepared and handled as previously described, the cell constant of DB2 (with electrodes of 50mm. diameter) was found to be 0.25442 and that of the Washburn Type A, our Cell 3 (electrode diameter 38 mm.) 0.017279. In Table I are given the more detailed data showing the inter-relationship of the resistances: in the first column is the resistance of a given solution in one cell, in the fourth column is the resistance of the same solution in the other cell. Each value given is the mean of a number of values; this number appears in the second and fifth columns. Usually three separate fillings of each cell were made with each solution, and three different bridge readings taken with a time allowance between every two for the maintenance of temperature equilibrium. The third and sixth columns give the certainty with which each resistance reading is known, that is, the mean error of the mean; in the seventh column is given the cell constant calculated from each set of values in terms of the cell constant of DB1.

It is evident that in these cells there is no general drift in the cell constants in any one direction; the irregular deviations from the mean values,

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[9] Kohlrausch and Holborn, "Leitvermögen der Elektrolyte," B. G. Teubner, Leipzig, 1898, pp. 87, 204.

namely, 0.25442 and 0.017279, can be accounted for by the apparent errors; the greater the deviations the larger the average deviation from the mean in a given set of readings. Over the same range of resistances in the cells with the smaller electrodes there were large discrepancies in the cell constants. In Cell 3 the smaller resistances measured at a given voltage make the temperature control more difficult; furthermore, it will be remembered that this cell was the more difficult to clean and in which to duplicate readings.

TABLE I

INTER-RELATION OF RESISTANCES

Resistance DB1	Number of values	Av. dev. from the mean, %	Resistance DB2	Number of values	Av. dev. from the mean, %	Constant DB2
6664.0	9	0.012	1229.7	9	0.005	0.25439
6881.6	11	.006	1269.9	10	.006	.25440
13273.0	9	.002	2449.9	9	.009	.25446
DB2			Cell 3			Cell 3
9119.7	9	.006	619.36	9	.014	.017283
10512.6	6	.007	714.20	6	.017	.017284
11018.8	9	.014	748.04	12	.022	.017273

It would seem, therefore, that instead of this drift being a surprising effect aside from the change in resistance with a change in frequency it is the natural concomitant of such a change; that in all probability when the cause of the one error is discovered so also will be that of the other, and that until that time, whatsoever the cause, the elimination of decrease of such a change in resistance with a change in frequency will result in the elimination or decrease of the drift in the cell constants. At any rate, in the event that there is another drift in the cell constants aside from the one expected from this one cause, such a change of resistance should either be eliminated or disposed of in some way before a second drift can conclusively be demonstrated.

Preparation of the Solutions.—Because of the very hygroscopic nature of both the solvent and the solute and the sparing solubility of the latter in acetophenone, it was impossible to make up and transfer the solutions in the usual way. For the third series, where a larger quantity of solution of one concentration was made up, the salt was transferred directly from a long-necked weighing bottle such as those used by Kendall and Landon[10] to a carefully dried, weighed flask and the acetophenone forced in from the stock bottle with a pressure of dried, purified air, the outlet of the system being protected by a calcium chloride tube. For the determination of the conductance of the solutions in the dark where not more than 100 cc. of solution at each concentration was needed, the required weight of the salt was too small to be weighed directly with ac-

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[10] Kendall and Landon, THIS JOURNAL, **42**, 2181 (1920).

curacy; these were prepared by diluting weighed portions of the mother solutions. An apparatus which was found to be very convenient for this purpose is shown in Fig. 2. The mother solution is run into the flask A, into which is fitted immediately the ground stopper carrying the 2-way stopcock B, and the buret C. Connecting the buret with the flask and with the outside are tubes, the 3-way stopcock D, and the 2-way stopcock E. By forcing air through E and opening B to the flask, the solution in A is made to fill the buret; B is then closed and D so turned that the air pressure forces the liquid from the buret when B is opened to the tube F. From F were drawn into weighed flasks the portions of the mother solution of the approximate volumes desired as read on the buret. By reversing the stopcocks the buret could be refilled and drained quickly, with very little exposure of the solution to the air or duplication in the concentration, since the volumes taken out could be estimated closely. This was an important factor in view of the fact that both solvent and solutes were expensive and difficult to purify.

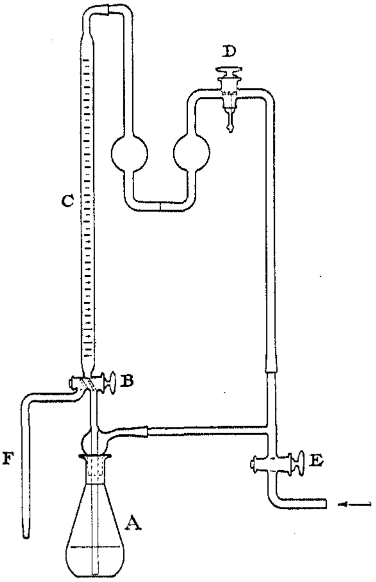

Fig. 2.

All of these mother solutions were made up by weight in a dark-room lighted with ruby bulbs; they were prepared and transferred only on the driest days, all of the transferring of either acetophenone or the solutions into the cells or into bottles and flasks being made through glass tubing with a pressure of dried air, the outlet of the systems being protected with calcium chloride tubes. The weights were calibrated against a set of weights standardized by the Bureau of Standards; two Becker balances were used, the smaller sensitive to 0.05 mg. at maximum load, the larger to 0.1 mg. All of the weights were corrected for air buoyancy using the following constants: 0.0012 as the average weight of a cubic centimeter of air; densities of brass and platinum 8.5 and 21.5, respectively; densities of the solid salts: LiBr, 3.464; LiCl, 2.068; KI, 3.115; NaI, 3.655; the densities of the solutions were those found by the equations given below; the international atomic weights for 1921 were used.

Densities of the Solutions in Acetophenone.—The densities of the salt solutions were calculated from the following empirical equation: $d_4^{25} = 1.02382 + 0.871 \times$ (g. of salt per g. of solution).

The values obtained in this way agreed for the limited range of concentrations measured, to within the accuracy needed for the conversion of the weight-normal concentrations to the volume-normal concentrations desired, with the experimental values determined with a pycnometer using for the volume of the apparent weight of 1 g. of water the value 1.00400 cc. at 25°.

NaI Solutions

Calc:	1.0318	1.0313	1.0275	1.0245	1.0242
Obs:	1.1317	1.0315	1.0275	1.0244	1.0243

LiBr Solutions				LiCl Solutions			
Calc.:	1.0275	Obs.:	1.0274	Calc.:	1.0240	Obs.:	1.0241

Results

In Table II are given the experimental results for the electrical conductance of these solutions; in Fig. 3 are given the plot constructed from this table of the experimental values and, for comparison, those of Nicollier. *All* of the experimental values obtained are given in Table III and plotted; the numbers of those values which, either because the solutions are so dilute that the conductance of the solvent becomes appreciable, or because they are, as indicated by the plot, burdened with a large error, are marked * (rejected); these values could not be expected to follow any dilution law, and carrying them through the calculations would simply lead to confusion. The different series occur as the result of the dilution of different mother solutions; all of the solutions of Series III, sodium iodide, however, were made by direct weighing of the salt. The results

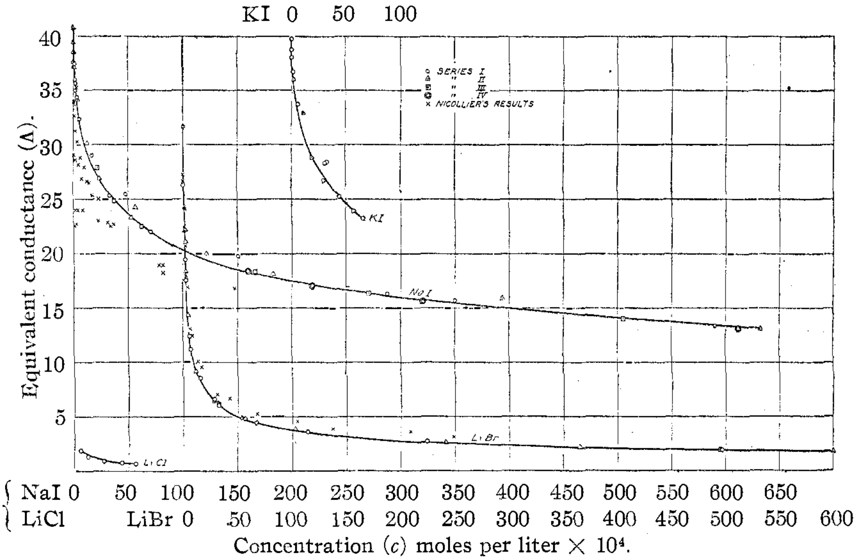

Fig. 3.

in any one series are given in the order of increasing concentration, a division within the series into stronger and weaker solutions being made for convenience in the later calculations.

TABLE II

CONDUCTANCE DATA FOR SOLUTIONS OF ALKALI HALIDES IN ACETOPHENONE

Temperature 25°±0.002°. International Atomic Weights for 1921. "Cell Constant" based upon the value 0.002765 reciprocal ohms for the specific conductance at 25° of a solution composed of 74.555 ÷ 50 g. of potassium chloride (weight in air) in one liter of solution at 18°. Electrode diameters between 38 and 50 mm.

Series	No.	Concentration Gram formula weights (in a vacuum) per liter	Density G. per ml. in a vacuum	Specific conductance $\times 10^6$ mhos	Λ Equivalent conductance Mhos	$100\ \gamma$ Percentage ionization	$10^4 \cdot \frac{c\gamma^2}{1-\gamma}$
SODIUM IODIDE							
$\Lambda_0 = 38.22$		$K = 24.82 \times 10^{-4}$	$D = 0.14$		$m = 0.698$		
A. Solutions Following the Mass Law							
I							
	1*	0.0001432	1.0238	5.357	37.41	....	....
	2*	.0001477	1.0238	5.157	34.92	....	....
	3	.0002004	1.0239	7.129	35.58	93.09	25.13
	4	.0003127	1.0239	10.73	34.31	89.77	24.63
	5	.0005314	1.0239	17.20	32.36	84.66	24.84
II							
	14*	.000004697	1.0238	0.1850	39.40	....	....
	15*	.000008099	1.0238	0.3299	40.74	....	....
	16*	.00002664	1.0238	1.001	37.54	....	....
	17*	.00002968	1.0238	1.144	38.55	....	....
	18*	.0001028	1.0238	3.812	37.07	....	....
	19	.0001719	1.0238	6.172	35.90	93.93	25.00
	20	.0002320	1.0239	8.154	35.14	91.95	24.36
	21	.0003457	1.0239	11.82	34.17	89.42	26.11
B. Remaining Solutions							
I							
	6	.001663	1.0240	48.17	28.96	75.76	39.40
	7	.003275	1.0242	82.91	25.32	66.24	42.57
	8*	.004788	1.0244	121.7	25.41	....	....
	9	.007014	1.0247	154.3	22.00	57.56	54.77
	10*	.01507	1.0258	297.8	19.78	....	.....
	11	.02870	1.0274	467.3	16.28	42.60	90.72
	12	.03499	1.0283	548.8	15.68	41.04	99.93
	13	.05903	1.0314	787.4	13.34	34.90	110.43
II							
	22	.001265	1.0240	38.09	30.11	78.78	37.00
	23	.002368	1.0241	63.65	26.88	70.34	39.49
	24	.005264	1.0245	122.5	23.27	60.89	49.90
	25*	.005615	1.0245	136.4	24.29	....	....
	26	.01214	1.0254	242.5	19.97	52.25	69.42
	27	.01824	1.0262	330.2	18.11	47.38	77.77
	28*	.03937	1.0289	626.6	15.92	....	....
	29	.06324	1.0319	827.3	13.08	34.23	112.7

TABLE II (*Continued*)

Series	No.	Concentration Gram formula weights (in a vacuum) per liter	Density G. per ml. in a vacuum	Specific conductance $\times 10^6$ mhos	Λ Equivalent conductance Mhos	100 γ Percentage ionization	$10^4 \frac{c\gamma}{1-\gamma}$
III							
	30	.002194	1.0241	61.10	27.85	72.86	42.91
	31	.003660	1.0243	90.80	24.81	64.91	43.94
	32	.006130	1.0246	138.1	22.53	58.95	51.90
	33	.01654	1.0259	302.9	18.32	47.93	72.95
	34	.02704	1.0273	441.6	16.33	42.73	86.18
	35	.05051	1.0302	704.1	13.94	36.47	105.8
IV							
	36	.01593	1.0258	293.2	18.41	48.16	71.26
	37	.02187	1.0265	372.3	17.02	44.54	78.24
	38	.03204	1.0278	499.5	15.59	40.79	90.04
	39	.06119	1.0314	800.3	13.08	34.22	108.93

Potassium Iodide

$\Lambda_0 = 37.52$ $K = 51.65 \times 10^{-4}$

A. Solutions Following the Mass Law

Series	No.	Concentration	Density	Specific conductance	Λ	100 γ	$10^4 \frac{c\gamma}{1-\gamma}$
I							
	40*	0.000003398	1.0238	0.1352	39.79	....	....
	41*	.000007924	1.0238	0.3072	38.76	....	....
	42*	.00001621	1.0238	0.6276	38.73	....	....
	43*	.00004143	1.0238	1.577	38.06	....	....
	44*	.00006732	1.0238	2.612	38.79	....	....
	45	.0001358	1.0239	4.974	36.68	97.76	57.74
	46	.0005344	1.0339	18.044	33.76	89.98	43.18
II							
	50	.0001626	1.0238	5.850	35.97	95.87	36.16
	51	.0005867	1.0239	19.83	33.80	90.08	47.93
	52*	.001030	1.0240	33.90	32.91	....	....
	53	.001821	1.0241	52.47	28.81	76.79	46.36
	54	.002951	1.0242	78.67	26.66	71.06	51.46

B. Remaining Solutions

Series	No.	Concentration	Density	Specific conductance	Λ	100 γ	$10^4 \frac{c\gamma}{1-\gamma}$
I							
	47*	.003009	1.0242	85.12	28.29	....	....
	48	.004329	1.0244	109.30	25.25	67.30	59.93
	49	.006540	1.0247	151.9	23.23	61.91	65.82
II							
	55*	.003224	1.0243	91.73	28.46	....	....
	56	.005659	1.0246	135.1	23.88	63.65	63.08

Lithium Bromide

$\Lambda_0 = 39.60$ $K = 0.92 \times 10^{-4}$

A. Solutions Following the Mass Law

Series	No.	Concentration	Density	Specific conductance	Λ	100 γ	$10^4 \frac{c\gamma}{1-\gamma}$
I							
	57	.00005649	1.0238	1.483	26.26	66.31	0.74
	58	.0001903	1.0238	3.693	19.41	49.01	.90
	59	.0002460	1.0238	4.308	17.52	44.24	.86
	60	.0005957	1.0239	7.339	12.32	31.11	.84
	61	.007313	1.0239	8.151	11.15	28.15	.81

TABLE II (*Concluded*)

Series	No.	Concentration Gram formula weights (in a vacuum) per liter	Density G. per ml. in a vacuum	Specific conductance $\times 10^4$ mhos	Λ Equivalent conductance Mhos	$100\ \gamma$ Percentage ionization	$10^4 \frac{c\gamma^2}{1-\gamma}$
	62	.001548	1.0239	13.23	8.549	21.59	.92
	63	.002848	1.0240	18.66	6.551	16.54	.93
	64	.003222	1.0241	19.40	6.021	15.203	.89
	65	.005633	1.0242	27.11	4.813	12.153	.95
	66	.006685	1.0243	29.55	4.421	11.163	.94
II							
	70	.00003802	1.0238	1.205	31.69	80.02	1.22
	71	.0001212	1.0238	2.690	22.19	56.03	0.87
	72	.0001477	1.0238	3.111	21.06	53.18	.89
	73	.0002187	1.0238	4.007	18.32	46.26	.87
	74	.0004778	1.0239	6.846	14.33	36.18	.98
	75	.001164	1.0239	10.64	9.140	23.08	.81
	76	.002859	1.0240	18.25	6.383	16.12	.89
	77	.003142	1.0241	19.34	6.157	15.55	.90
	78	.005409	1.0242	26.17	4.838	12.22	.92

B. Remaining Solutions

Series	No.	Concentration Gram formula weights (in a vacuum) per liter	Density G. per ml. in a vacuum	Specific conductance $\times 10^4$ mhos	Λ Equivalent conductance Mhos	$100\ \gamma$ Percentage ionization	$10^4 \frac{c\gamma^2}{1-\gamma}$
I							
	67	.01142	1.0246	35.65	3.565	9.002	1.017
	68	.02240	1.0254	59.64	2.662	6.722	1.085
	69	.04970	1.0274	94.08	1.893	4.780	1.181
II							
	79	.01024	1.0246	39.08	3.818	9.640	1.054
	80	.02407	1.0256	61.85	2.570	6.489	1.084
	81	.03651	1.0265	79.87	2.188	5.525	1.180
	82	.06005	1.0281	104.66	1.743	4.401	1.217
III							
	83	.04954	1.0274	93.37	1.885	4.760	1.178

LITHIUM CHLORIDE

$\Lambda_0 = 40.00$ $K = 0.0133 \times 10^{-4}$

A. Solutions Following the Mass Law

Series	No.	Concentration Gram formula weights (in a vacuum) per liter	Density G. per ml. in a vacuum	Specific conductance $\times 10^4$ mhos	Λ Equivalent conductance Mhos	$100\ \gamma$ Percentage ionization	$10^4 \frac{c\gamma^2}{1-\gamma}$
I							
	84	.0005786	1.0238	1.071	1.851	1.53	0.01299
	85	.001250	1.0239	1.592	1.273	1.80	.01308
	86	.002730	1.0239	2.359	0.8642	2.16	.01303
	87	.004039	1.0240	2.917	0.7221	3.18	.01341
	88	.005616	1.0240	3.449	0.6141	4.63	.01345

The most extensive consideration of the theoretical importance of the field of non-aqueous solutions has been undertaken by Kraus and Bray[11] but no attempt has been made to apply any law to solutions in acetophenone except in the case of sodium iodide, and that only very incompletely. Consequently, since it was evident from the experimental curves that

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[11] Kraus and Bray, THIS JOURNAL, **35**, 1315 (1913). Kraus, "The Properties of Electrically Conducting Systems," A. C. S. Monograph Series, The Chemical Catalog Company, **1922**.

these results were sufficiently precise to lend themselves to quantitative treatment, calculations have been made for the application of the Ostwald dilution law, and for the general equation proposed by Kraus and Bray, which approaches the Ostwald dilution law in the more dilute solutions, and the Storch equation in the more concentrated ones. Some of the results of these calculations are found in Table II.

That our repetition of Nicollier's work was justified can be seen by a comparison of the results in the plot (Fig. 3). This plot of the equivalent conductance against equivalent concentration, volume normal, the data for which are given in Table II, was made on a large scale in order to eliminate the points burdened with large experimental errors before any attempt was made to treat them theoretically. This was particularly desirable since, due to the very hygroscopic nature of the solutions, large errors were inadvertently introduced if the greatest uniformity in technique was not most scrupulously observed. Such errors would result in an abnormally high value for the equivalent conductance.

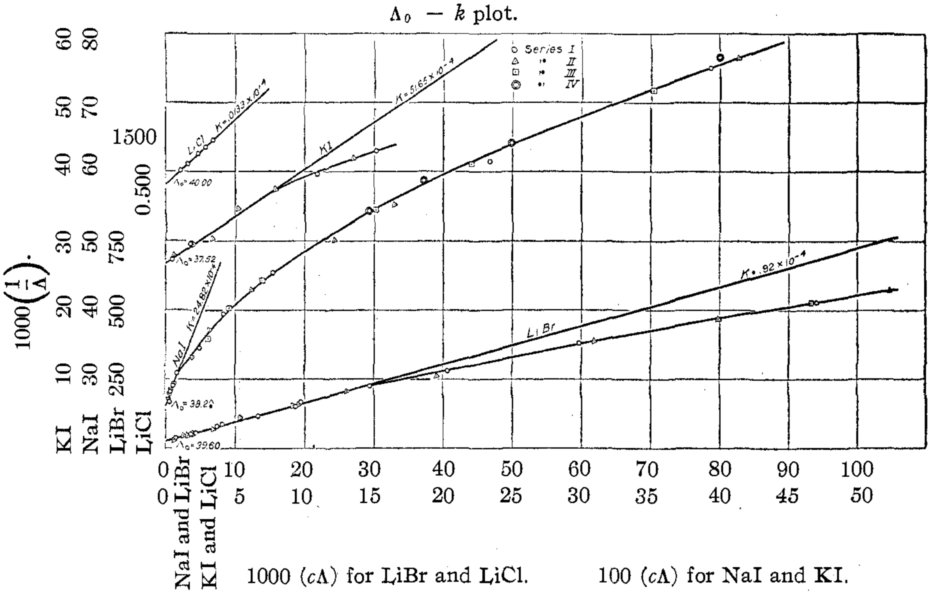
Λ_0 — *k* plot.

Fig. 4.

In Fig. 4 are given the plots for the four salts used, showing the approach of the experimental curve to the straight line representing the law of mass action, that is, the Ostwald dilution law. Quite evidently as Kraus has pointed out in other cases, the law of mass action holds over a range of dilute solutions. The intercept of this straight line on the axis ($c\Lambda$) = 0 should give a value representing the reciprocal of the equivalent conductance at infinite dilution. From such so-called Λ_0-K plots, made on a large scale, the following values for Λ_0 were obtained graphically: NaI, 38.22; KI, 37.52; LiBr, 39.60; LiCl, 40.00. Setting the graphically determined tangents of these curves equal to the reciprocal of $K\Lambda_0^2$, the following values for K were calculated: NaI, 24.82×10^{-4}; KI, 51.65×10^{-4}; LiBr, 0.92×10^{-4}; LiCl, 0.0133×10^{-4}. From these results the values for the degree of ionization, γ, defined experimentally by the ratio Λ/Λ_0, are calculated and given in the seventh column of Table II. In Col. 8 are given the values of the Ostwald constant calculated from these values of γ. In view of the fact that an error of 0.1% in the value of Λ produces an error of about 2.0% in the value of K, the agreement in the case of sodium iodide, lithium bromide and chloride is good; the potassium iodide results are not so good among themselves and therefore larger deviations in K are to be expected. It is to be noticed that the difference in the magnitude of K among the salts is of the same order as that found for these same electrolytes in acetone.[11]

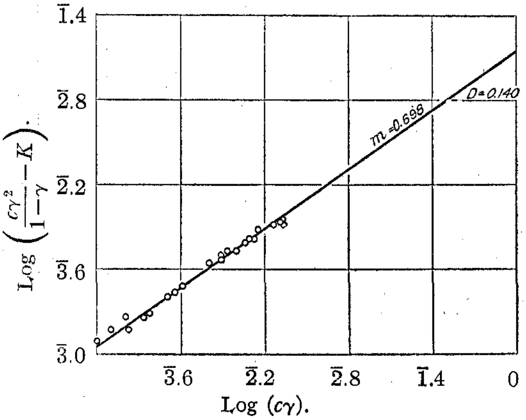

Fig. 5.—m-D plot, NaI.

Solutions of lithium chloride obey the law of mass action over the entire range of concentration possible with its limited solubility, while lithium bromide, and sodium and potassium iodides follow the law to a concentration of about 0.007 M, 0.0005 M and 0.003 M, respectively. Inasmuch as sodium iodide, the most soluble halide, deviated most widely from the mass law, it seemed well to use this system for the application of the general dilution law of Kraus and Bray. The constants m and D were evaluated graphically, using only the values required for those concentrations which do not follow the Ostwald law. This plot is shown in Fig. 5. The intercept of the straight line drawn as a mean through the points 6–13 of Series I, 22–29 of Series II, 30–35 of Series III, and 36–39 of Series IV, inclusive, on the axis log $(c\gamma) = 0$ gives for D the value 0.140 and the tangent of this line the value 0.698 for m. The straight line drawn on the K-D plot, Fig. 6, from the values for these same points given in Cols. 8 and calculated gave for the intercept on the axis $(c\gamma)^m = 0$ and for the tangent of the line the same values for K and D, respectively, that were obtained from the other plots. The final equation, then, which in general terms is $c\gamma^2/1-\gamma = K + D(c\gamma)^m$ becomes for sodium iodide in acetophenone $c\gamma^2/1-\gamma = 24.82 \times 10^{-4} + 0.140\ (c\gamma)^{.698}$.

In the K-D plot it is evident that this equation must hold up to a concentration of about 0.05 M, but that the last four points on the more concentrated end deviate distinctly from the straight line. Kraus and Bray explain a similar deviation in the system potassium amide in ammonia as due to viscosity effects in the more concentrated solutions.

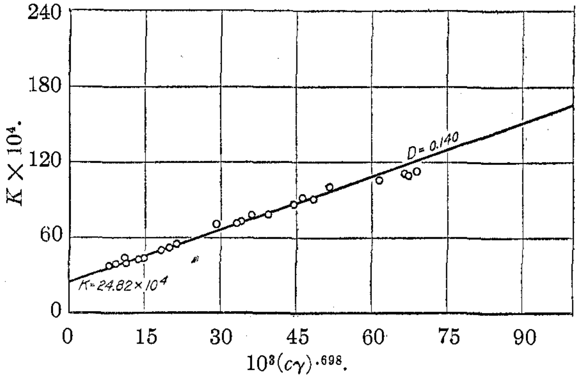

Fig. 6.—K-D plot, NaI.

In the case of lithium bromide and potassium iodide the points which deviate from the law of mass action are so few in number and the difference between the constant obtained and the Ostwald constant is so small that accurate evaluations of m and D would be possible only through a larger number of determinations in this very small range of concentration. However, the values used to determine these constants are given for these points in the table from which an approximate value for m and D can be obtained.

Summary

The conductances of solutions of sodium iodide, potassium iodide, lithium bromide and lithium chloride in acetophenone have been measured in the dark throughout a range of concentrations determined by the solubility of the salts in the solvent. Calculations have been made to show the approach of the equilibrium to the law of mass action and, for those concentrations which do not follow this law, for the general dilution law of Kraus and Bray. The following constants have been evaluated: for sodium iodide, $\Lambda_0 = 38.22$, $K = 24.82 \times 10^{-4}$, $m = 0.698$, $D = 0.0140$; for potassium iodide, $\Lambda_0 = 37.52$, $K = 51.65 \times 10^{-4}$; for lithium bromide,

$\Lambda_0 = 39.60, K = 0.92 \times 10^{-4}$; for lithium chloride, $\Lambda_0 = 40.00, K = 0.0133 \times 10^{-4}$. The general dilution law for sodium iodide in acetophenone then becomes: $c\gamma^2/1-\gamma = 24.82 \times 10^{-4} + 0.140 \times (c\gamma)^{.698}$.

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TERNARY SYSTEMS. II. SILVER PERCHLORATE, ANILINE AND WATER

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The high solubility of silver perchlorate in many organic liquids[2] which are themselves not soluble in water has suggested its use in the study of several ternary systems consisting of the salt, an organic liquid and water; such systems can usually be studied without great difficulty from the low temperature of the ternary eutectic point up to temperatures above the melting point of the organic liquid and water, so that nearly all possible phase complexes involving solid and liquid phases in three-component systems can be assembled without the requirement of a very large temperature range. The system consisting of silver perchlorate, benzene and water has been so studied at an earlier date.[2d] The system containing aniline, here reported on, adds a number of features not found in the system containing benzene, of which the most interesting are the occurrence of a number of additive compounds of silver perchlorate and aniline, the striking insolubility of some of these in water, the existence at various temperatures of four distinct composition areas in which liquid phases appear (although the co-existent liquids are never more than two in number) and the anomalous distribution of silver perchlorate between water and aniline; the salt is found wholly in the aniline phase, thus reversing the distribution relations which it shows between benzene and water,[2c] in which case it is found wholly in the water phase up to considerable concentrations.

The silver perchlorate was made from silver nitrate by precipitation as hydrous silver oxide, solution in perchloric acid and recrystallization. The aniline was prepared from a good grade of commercial material by distillation, the fraction distilling within 0.2° being taken and stored in brown bottles over solid potassium hydroxide. The melting point, as given in Table I, was —6.15°; samples used in other parts of the work were slightly less pure, melting at —6.25° to —6.3°. The analysis of solutions for silver perchlorate content was conducted according to Volhard's method, weighed samples being acidified and titrated with standardized ammonium thiocyanate solution in the

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[1] The material of this paper was contained in the thesis submitted by Rudolph Macy in partial fulfilment of the requirement for the degree of Doctor of Philosophy at New York University.

[2] (a) Gomberg, *Ber.*, **40**, 1867 (1905); (b) *Ann.*, **370**, 160 (1909). Hill, (c) THIS JOURNAL, **43**, 254 (1921); (d) **44**, 1163 (1922); (e) **45**, 1151 (1923).