The more stable perchlorate does not appear to be formed. The relative amounts of the products vary with the conditions under which the decomposition takes place.

A mixture of ammonium chloride and potassium chlorate, unless perfectly dry, decomposes in a similar manner.

Summary

1. The rate of the spontaneous decomposition of ammonium chlorate is autocatalytically accelerated when the products of decomposition are not quickly removed.

2. The solid residue from the decomposition is ammonium nitrate with no chloride.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CLARK UNIVERSITY, I, 17]

THE CALIBRATION OF CELLS FOR CONDUCTANCE MEASUREMENTS

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In carrying out an investigation on the electrical conductance of dil. aqueous solutions of iodic acid, the constants of the cells used were determined by comparison with an auxiliary cell whose constant was obtained by means of a solution of 0.1 N potassium chloride made up according to the weight method, following directions given in Kohlrausch and Holborn.[1] In order to secure a check on the value obtained, the auxiliary cell was also standardized with reference to a 0.01 N potassium chloride solution which was similarly made up according to the directions of Kohlrausch and Holborn. The determination with respect to the 0.1 N solution gave a value 3.42316 and that with respect to the 0.01 N solution 3.40693, the difference amounting to 0.48%. Since no sources of error of this order of magnitude were apparent in connection with the calibration procedure, the directions given in Kohlrausch and Holborn were examined and found to be in error. This led to a somewhat more extended investigation of the data underlying the methods of calibrating cells for conductance measurements according to the weight method. In view of the desirability of having the results of various investigators expressed in terms of comparable units, the results are given below in some detail.

The standard solutions for the purpose of calibrating conductance

[1] Kohlrausch and Holborn, "Leitvermögen der Elektrolyte," Teubner, Leipzig, **1898**, p. 76. See also Kohlrausch, Holborn and Diesselhorst, *Ann. Physik*, **64**, 440 (1898).

cells are made up most conveniently and accurately according to the weight method. In this method, the necessity of calibrating a large amount of volumetric apparatus is avoided and numerous other sources of error, such as reproducible drainage, temperature control, etc., are eliminated. Furthermore, when more dilute solutions are employed for the purpose of calibration, various errors due to contamination are liable to be introduced by the volume method which are readily avoided if solutions are made up according to weight. In what follows, only the weight method of making up solutions will be described. As a matter of fact, the method of making up solutions according to volume has already been described in sufficient detail by Kohlrausch and his associates.

Kohlrausch, Holborn and Diesselhorst have determined the absolute value of the specific conductance of various solutions. Among these, solutions of potassium chloride of known concentration are most readily prepared and are best adapted for purposes of calibration. Unfortunately, data relating to solutions having a concentration below 1.0 N are incomplete. In determining the value of the constant of cells employed in measuring the conductance of very dilute solutions, it is desirable to calibrate by means of solutions having a concentration as low as 0.1 N, or lower. Even under these conditions, it is necessary to use an auxiliary cell which may be directly calibrated against 0.1 N potassium chloride solutions. If the attempt were made to employ more concentrated solutions as standards for this purpose, the resistance of the cells would fall to such low values that errors would arise in the measurements owing to the influence of polarization.

The most extensive comparison of the absolute value of the specific conductance of various potassium chloride solutions has been made by Kohlrausch, Holborn and Diesselhorst. Unfortunately, the precision of these measurements does not exceed 0.1% and, since at the present time conductance measurements may be carried out with a precision approaching 0.01%, it is obvious that these values are inadequate. The most reliable data available on the specific conductance of potassium chloride solutions at different concentrations, which have been obtained by direct comparison with primary standards, are those of Kohlrausch and Maltby. They, however, do not give the necessary data for making up the solutions according to the weight method. In fact, the only writers who give such data for making up a solution of potassium chloride according to weight in air are Kohlrausch and Holborn, who give the correct values for making up such solutions of normal concentration. Their directions for making up 0.1, 0.02 and 0.01 N solutions, however, are in error, as stated above. According to these authors: "Tenth normal potassium chloride solution. Dissolve (weighed in air) 7.455 g. to one liter of solution, or 7.430 g. to 1000 g. solution." The first figure is cor-

rect, but the second is not. No value for the density of the solution is given. The density of 0.1 N potassium chloride at 18° has been determined for the purpose of these calculations by reading the value from a smooth curve, the data for which are derived from Kohlrausch and Maltby,[2] Archibald,[3] Grüneisen[4] and Röntgen and Schneider.[5] This gives a value 1.00343 for the density of the solution at 18°. Hence, one liter of solution at 18° weighs 1003.43 g. in a vacuum. The factor for reducing this to the weight in air (brass weights) is 1.00106,[6] and dividing by this factor we obtain 1002.37 for the weight in air of the solution at 18°. Then dividing 7.455, the weight of salt in air, by 1.00237, we obtain 7.4374 g. of salt (weight in air) to be added to water to make up 1000 g. of solution, weighed in air. The value given by Kohlrausch and Holborn is thus in error by 0.10%.

Kohlrausch and Holborn further state: "Fiftieth and hundredth normal solution. The weighing of 1.4860 and of 0.743 g., respectively, becomes inconvenient. Dilution in the volume ratio 1 : 50 and 1 : 100, respectively, ... is the usual method." It is immediately evident on inspection that in assuming the values 1.486 and 0.743 g. for the 0.02 and 0.01 N solutions the density change from 0.1 N to 0.02 and 0.01 N, respectively, has been neglected, while the error present in the 0.1 N solution has been retained. Going through the calculations in the same way as before we find, using the value 0.99911 for the density of 0.01 N potassium chloride solution and a factor 1.00106 for the reduction from weight in a vacuum to weight in air, that, to make up a 0.01 N solution, 0.74701 g. is required per 1000 g. of solution, both weighed in air. The error thus introduced in following the directions of Kohlrausch and Holborn amounts to 0.54%. The difference in error between the 0.1 N and 0.01 N solutions is thus 0.44%, which agrees very closely with the value initially found by the present authors as given in the first paragraph of this paper.[7]

As a matter of fact, there is no advantage in making up the solutions by volume as Kohlrausch and Holborn state. No great difficulty is experienced in weighing out salt and solvent in the proportions required, particularly if several liters of solution are made up at one time.

Many of the conductance measurements given in the literature cannot be interpreted with certainty, owing to uncertainties in the methods

[2] Kohlrausch and Maltby, *Wiss. Abh. Phys.-Tech. Reichsanst.*, **3**, 180 (1900).

[3] Archibald, *Trans. Nov. Scot. Inst.*, **9**, 335 (1897).

[4] Grüneisen, *Abh. Phys.-Tech. Reichsanst.*, **4**, 237 (1905).

[5] Röntgen and Schneider, *Ann. Physik*, **29**, 165 (1886).

[6] Landolt-Börnstein, "'Physikalisch-Chemische Tabellen," Springer, Berlin, **1912**, p. 15.

[7] The weights of salt as above calculated are based on values of the atomic weights used by Kohlrausch, Holborn and Diesselhorst. The correct weights based on the atomic weights used by Kohlrausch and Maltby are given below.

employed in calibrating the conductance cells. Thus, Weiland,[8] in his very careful work on the conductance of aqueous solutions of potassium chloride, determines his cell constant by means of 0.1 N solutions of potassium chloride made up by weight according to the directions of Kohlrausch and Holborn. He found that the value obtained for the cell constant, as determined between 0° and 25° according to the data of Kohlrausch and Holborn, differs by 0.2% between the two temperatures. He apparently assumed that the cell constant between these two temperatures varies as a linear function of the temperature, since the value which he employed at 18° corresponds with this assumption. In this case, various errors have evidently canceled each other since at 0.001 N his results agree closely with those of Kohlrausch and Maltby.

There is also considerable uncertainty as to the absolute value of the specific conductance of N potassium chloride solutions as determined originally by Kohlrausch. Newbery[9] has re-determined the absolute specific conductance of N potassium chloride at 25° by means of a direct-current method and found a value for the specific conductance, which is 0.6% higher than that of Kohlrausch at the same temperature. His value for a sodium chloride solution saturated at 25° is 0.3% higher than that of Kohlrausch. Eastman[10] used a somewhat similar direct-current method. In this case the cell was standardized by directly comparing with mercury and the results were checked by means of an alternating current; N potassium chloride solutions and maximum sulfuric acid solutions were tested at 25°. The values obtained by direct current were found to be, respectively, 0.11% and 0.18% lower than those of Kohlrausch, while with the alternating-current method the values obtained were approximately 0.03% lower than those of Kohlrausch. It is evident that the absolute values of the specific conductance of standard solutions are at the present time affected by errors which are in excess of the errors affecting conductivity measurements as carried out according to the most improved methods. Under the circumstances, it would appear advisable to accept as primary standard the value of the specific conductance of 0.1 N potassium chloride solutions, as determined by Kohlrausch and Maltby.[11] If this were done, then any measurements obtained could subsequently be corrected, when the absolute values of the specific conductance of these standard solutions have been re-determined.[12]

In Table I are given the necessary data for making up potassium chlor-

[8] Weiland, This Journal, **40**, 136 (1918).

[9] Newbery, *J. Chem. Soc.*, **113**, 701 (1918).

[10] Eastman, This Journal, **42**, 1648 (1920).

[11] Ref. 2, p. 157.

[12] Such a re-determination is now being undertaken by one of the present authors (Parker).

ide solutions of 1.0, 0.1, and 0.01 N concentration according to the weight method. The density data are those referred to above.

TABLE I

CONSTANTS OF AQUEOUS SOLUTIONS OF POTASSIUM CHLORIDE OF DIFFERENT CONCENTRATIONS[13]

Conc. of KCl N	Density 18°	Wt. of KCl to 1000 g. sol. G.	Wt. of KCl to 1000 g. H_2O G.	Specific cond. K. and M. 18°	Spec. cond. at 25°
1.0	1.04492	71.430	76.9247	0.09827	.....
0.1	1.00343	7.4388	7.4945	0.011203	0.0128988
0.01	0.99911	0.74710	0.74766	0.0012243	.....

The values of the specific conductance given in the fifth column are those of Kohlrausch and Maltby. The value for the 0.1 N potassium chloride solution at 25° was determined in this Laboratory.

In order to check the correctness of the calculations involved in the above table, the constant of a cell was determined by means of both the 0.1 N and the 0.01 N potassium chloride solution. The mean for the 0.1 N solution gave the value 3.41002, while that for the 0.01 N solution gave 3.41056, a difference of 0.016%, which comes just about within the limit of the experimental error. The value given for the specific conductance is that due to the salt alone. At concentrations of 0.1 and 0.01 N, the observed conductance of the solution must be corrected for the conductance due to the solvent.

In determining the cell constant by means of the 0.1 N solution, great accuracy may be attained. In a series of determinations, with 4 independent solutions, the constant of a cell of the pipet form was determined with an average deviation from the mean of only 0.002%.

The procedure employed in order to obtain an accuracy of this order may be briefly outlined. The conductivity water was kept in 4-liter bottles, and the specific conductance of this water was determined before pouring out by means of dipping electrodes which could be slipped into the water and stirred around while the resistance was being taken. It is necessary to obtain this resistance only within two places for the purpose of the correction in question. Approximately 1000 g. of this water was then poured out into a Pyrex flask and weighed, the flask having previously been cleaned with a cleaning mixture and live steam and thereafter rinsed repeatedly with distilled water. The weight of water was then multiplied by the factor 0.0074945, given in the fifth column of Table I, which gave the weight of potassium chloride required. The potassium chloride employed was twice recrystallized from conductivity water by filtering a boiling, saturated solution and cooling in ice water. It was placed in a porcelain crucible and heated over a Meker flame, after which it was

[13] The concentrations are based on the atomic weights employed by Kohlrausch and Maltby. K=39.15, Cl=35.45.

cooled over phosphorus pentoxide. In this process, about half of the potassium chloride melts while that at the top forms a crust to which the melt clings. Thus the potassium chloride comes out in a mass which is crumbly at the top and solid at the bottom. This was weighed out quickly on a watch glass to the exact quantity calculated. It was then added to the water and the flask kept stoppered. This solution was sucked out of the flask into the pipet cell whose constant was being determined. It was found that, after about 8 cells' full of the solution had been withdrawn, the specific conductance of the solution began to rise, showing that contamination had taken place, and a new solution was required.

In order to use the data at 18°, it is necessary to employ a thermostat operating at that temperature. Since most conductance measurements at the present time are carried out at 25°, it appeared worth while to carry out specific-conductance determinations of the 0.1 N solution at 25°, which was readily accomplished after the cell constant had been determined at 18°. The specific conductance at 25° was determined from the ratio of the resistances of the solutions in the cell at the two temperatures.[14] Two cells and 3 independent solutions were employed. Three samples of analyzed potassium chloride from different manufacturers were employed in making up the solutions, the salt being recrystallized twice from conductivity water and treated as described above. The resulting data are given in Table II. In the second column is given the value of the

TABLE II

COMPARISON OF THE SPECIFIC CONDUCTANCE OF 0.1 N POTASSIUM CHLORIDE SOLUTION AT 18° AND 25°

No.	Cell constant at 18°	Spec. cond. of solution 25°	Spec. cond. of H_2O	True spec. cond. at 25°
1	5.71549	0.0129014	1.7×10^{-6}	0.0128997
	5.47751	0.0129003		0.0128986
2	5.71499	0.0129009	1.5×10^{-6}	0.0128994
	5.47713	0.0129004		0.0128989
3	5.71477	0.0128999	1.5×10^{-6}	0.0128984
	5.47691	0.0128994		0.0128979

cell constant at 18°; in the third column is given the specific conductance at 25°, as measured; in the fourth column, the value of the specific conductance of the water employed in making up the solution; and in the last column, the true specific conductance due to the salt, after correcting for the specific conductance of the water. The resistances at 18° and 25° were obtained within an interval of 30 minutes between determinations. The mean value obtained for the specific conductance of the 0.1 N potassium chloride solution at 25° is 0.0128988 with a maximum variation from the mean of 0.007%.

[14] The measurements were carried out by Dr. Parker in this Laboratory while working under a Fellowship grant from the National Research Council.

According to these measurements, the ratio of the specific conductance of 0.1 N potassium chloride solution at 25° and 18° is 1.15130.[15] The value of this ratio according to the earlier measurements of Kohlrausch, Holborn and Diesselhorst, which are given only to the fourth place, is 1.15103. The value as above determined is evidently in agreement with the earlier determination of Kohlrausch, Holborn and Diesselhorst within the limit of precision of their measurements.

In the above determination, it has been assumed that the cell constant is independent of the temperature. This assumption is evidently justified, for the coefficient of expansion of the glass and of the platinum is 9.3×10^{-6}. The conductance varies directly as the cross section and inversely as the length of the conducting column or, in other words, as the first power of the linear dimensions. For a temperature change of 7°, therefore, the correction due to this effect would be of the order of 0.0065%, which may obviously be neglected.

The means employed for establishing the temperatures, as well as a description of the apparatus used and the precautions observed in making measurements, are given in detail in the succeeding paper and may be omitted here.

Summary

The necessary data for making up standard potassium chloride solutions, according to the weight method, for calibrating conductance cells are correctly given by Kohlrausch and Holborn for 1.0 N solutions only, and their directions for making up standard solutions of concentrations 0.1, 0.02 and 0.01 N are in error. For the 0.1 N solution the error is 0.10% and for the 0.01 N solution 0.54%.

The conductance data as given by Kohlrausch and Holborn do not have sufficient precision for present purposes and it is suggested that the values obtained by Kohlrausch and Maltby be employed. The necessary data are given for making up 1.0 N, 0.1 N and 0.01 N solutions of potassium chloride by the weight method.

The specific conductance of 0.1 N (at 18°) potassium chloride has been determined at 25° in terms of its value at 18°. Assuming for the specific conductance at 18° the value 0.011203, as determined by Kohlrausch and Maltby, there is obtained for the specific conductance at 25° the value 0.0128988. This value may serve for the purpose of calibrating cells at 25°, thus avoiding the necessity of making determinations at 18°.

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[15] This solution is 0.1 N at 18°. At 25° its concentration will differ from this value as a result of the expansion of the solution.