ing and crystallizing the acid perchlorate or zirconyl perchloric acid separates.

3. The basic zirconyl chlorate formed is crystalline and corresponds to the formula $ZrO(OH)_2.3ZrO(ClO_3)_2$. It is easily decomposed.

CHAPEL HILL, N. C.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

STUDIES IN CONDUCTIVITY. V. NOTES ON THE MEASUREMENT OF THE CONDUCTIVITY OF SOLUTIONS.

BY H. I. SCHLESINGER AND F. H. REED.[1]

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During the past few years a series of very thorough and valuable papers by Washburn and his associates[2] on the methods and apparatus for measuring the conductivity of solutions has been published. ,Other papers by Acree and his students[3] have also added greatly to our knowledge of the subject. Nevertheless a number of difficulties which we have encountered in the measurements required for our work on formic acid solutions have either not been touched on at all or have received only very scant attention as will be pointed out below. Since we have developed simple criteria for detecting the difficulties in question and simple methods for overcoming them, it has been suggested to us that the publication of a résumé of these points would be of value to other workers in this field.

The resistance of the solutions was measured by the Wheatstone-Kohlrausch method, using a Siemens and Halske high frequency generator, a rotary bridge, and a standardized Curtis coil resistance box. The connections and the methods of shielding the apparatus are those recommended by Washburn and Bell.[4] In conjunction with the high frequency circuit we used a Leeds and Northrup condenser which permits of placing equal capacities in series with the two lines of the circuit; by means of a two-way switch this condenser could be eliminated and readings taken without any capacity in the high frequency circuit. It was observed that the introduction of the condenser, while it improved the sharpness of the minimum, decidedly shifted its position and that the shift thus produced depended on the type of resisting medium and the magnitude of

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[1] The work reported in this and the following paper of this series has been presented to the Faculty of the Ogden Graduate School of Science of the University of Chicago by F. H. Reed in part fulfillment of the requirements for the degree of Doctor of Philosophy. The work was completed in the fall of 1916.

[2] THIS JOURNAL, **38**, 2431 (1916); **39**, 235 (1917).

[3] Acree and Taylor, *Ibid.*, **38**, 2396 (1916).

[4] THIS JOURNAL, **35**, 177 (1913). An excellent résumé of the Washburn apparatus is given in the Leeds and Northrup *Catalog* **48** (1915).

the resistance. The shift was particularly large when the usual Wheatstone bridge set-up, that is with the current entering at the ends of the bridge, was used. Thus, the introduction of the condenser did not shift the minimum when a resistance coil of approximately 300 ohms was measured against 300 ohms in the Curtis box, but with 400 ohms the minimum shifted from 0.5001 to 0.5005, and when a 1000 ohm coil was measured against a 1000 ohm Curtis coil from 0.5001 to 0.5013. It is seen therefore that when the type of the resisting medium remains the same the shift in the minimum increases with the resistance to be measured. But there is another factor involved, for when the coil resistance is replaced by a cell containing 0.01 *N* solution of potassium chloride, larger shifts are obtained even with smaller resistances. Thus in a cell in which the solution had a resistance of approximately 880 ohms, the bridge reading shifted from 0.2540 to 0.2589 with the condenser, while in another cell in which the resistance of the same solution was 1387 ohms, the reading shifted from 0.2238 to 0.2320. It is to be noted that even where the shift is very large, each reading was very sharp, the maximum error of setting being not greater than 0.0001.

It is of course necessary to eliminate such shifts. To do this we first determined the arrangements of the bridge, etc., which gave correct readings when two standardized Curtis coils (each of 1000 ohms) were placed in the two remaining arms of the bridge, and it was found that the results without capacity in the high frequency circuit were correct, whereas the use of the condenser produced the sort of shift described. In order to retain the advantages of having resonance on the circuit, and at the same time to avoid the difficulty described, we investigated the matter from an experimental point of view and found the following: (1) The shift could be completely eliminated by having capacities in the two sides of the circuit which were not identical. When, for example, the two capacities were, respectively, 0.0245 and 0.0225 microfarad, the shift was greatly decreased but not entirely eliminated. No further changes in capacity which could be produced by our Leeds and Northrup condenser made further improvement, but by using a small variable Clapp-Eastham air condenser in parallel with the smaller capacity we eliminated the divergence for all cases investigated. The setting of this condenser for our purpose made the total capacity for this side about 0.0228 microfarads. There is, however, a disadvantage in using this method of avoiding the difficulty; for when the capacities are adjusted to give correct readings for the case in which the shift is fairly great, the setting is also correct for any case where the divergence is smaller, but not necessarily so where it is greater. This condition necessarily leads to uncertainty in the results. (2) It was further found that when the bridge was arranged to have the telephone at the ends of the slide wire the shift was very much reduced. We shall call this arrangement "set-up A" while the arrangement usually used is called "set-up B." Thus, in the case in which with set-up B the bridge reading with equal capacities was 0.2320 and without capacity was 0.2238, the corresponding readings were 0.2234 and 0.2238, respectively, for set-up A; and where set-up B gave smaller shifts than this, set-up A gave identical results with, or without, capacity. Furthermore, in the case of set-up A, when the capacities in the high frequency circuit were 0.0245 and 0.0225, respectively, instead of equal, the introduction of the condenser into the circuit no longer produced any shift in the minimum and gave the correct reading for every type and value of resistance measured by us. Small changes, such as would be produced by introducing the air condenser, have no effect on the readings with set-up A. This arrangement has, however, the disadvantage that a larger amount of current flows through the cell than with set-up B, and more heating of the solution results. This difficulty can be completely overcome by making an approximate setting, waiting until the solution returns to the bath temperature, and then making the final reading very quickly. It is also helpful to use a resistance in the box somewhat smaller than the resistance in the solution.[1]

The explanation of the results described can doubtless be found in some dissymmetry in the high frequency circuit[2] before it reaches the bridge. We were unable to locate it and made no extended efforts to do so as we eliminated the difficulty by the method described. The reason why set-up A gives smaller deviations than does set-up B is probably because the arrangement of the bridge in the former is more nearly symmetrical and consequently produces more nearly equal energy losses in the various arms of the bridge.

There is another source of possible error in measuring resistances of solutions which has not received the attention which it deserves in the treatment of the subject. In the papers to which reference is made above the fact that the minimum may be perfectly sharp and yet may not be correct has been mentioned, but no stress has been laid on this important point. Acree, for example, has stated that one of the criteria for the reliability of a cell is that it must give for the ratio of the resistance of two solutions measured in it the same value as is found in some other cell. This may be put in other words by the statement that the cell constant

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[1] That the readings as usually taken by us and the readings at the center of the bridge give identical results, with the set-up used, was repeatedly proven. We also found that the capacity of approximately 0.024 microfarads in the condenser was the amount required to produce resonance, and that making the capacities in the two sides of the circuit unequal did not materially decrease the current obtained.

[2] That the difficulty did not lie in an inequality of the capacities of the two sides of the condenser was shown by a rough measurement of the capacities and by substituting two standardized capacities for the one we had been using.

must be the same no matter what standard solution is used to determine it. It is of course the usual procedure to determine the cell constant with more than one solution. But more than this is necessary to make certain that the cell in question is suited to the solutions whose conductivities are to be determined in it. It is essential that the standard solutions used to determine the cell constant have in the cell a range of resistance completely covering the range of the solutions to be measured in it. That this is not usually understood is demonstrated by the fact that the specific conductivities determined by Kohlrausch, which are usually employed as standards for the determination of cell constants, are not well enough distributed to cover satisfactorily every possible range of resistance. The data presented below will make this point clear.

In previous work on anhydrous formic acid a special form of Arrhenius cell, with fixed electrodes, adapted to the measurement of fairly dilute solutions, has been employed.[1] These cells have cell constants of approximately 0.2, as determined with both 0.02 *N* and 0.01 *N* solutions of potassium chloride. Since these cells are not well adapted to the measurement of concentrated solutions, without the use of fairly large capacities in parallel with the bridge circuit, no further determinations of the cell constants were made at that time as the only other Kohlrausch standards are fairly concentrated solutions. The more accurate measurements of the formate solutions required for the work to be reported in later papers gave reason to doubt the reliability of these cells and measurements of the cell constant with a larger number of solutions were carried out. For this purpose we used 0.01, 0.02, 0.05 and 0.2 *N* solutions of potassium chloride and made the equivalent conductivities of A. C. Melcher, reported in the paper of Noyes and Falk,[2] the basis of the calculation of the cell constant. The data obtained for one of these "Arrhenius type" cells as well as for the two cells referred to by the symbols H_1 Fig. 1, and H_3 are given in Table I. The latter are cells of the kind which have been constructed for the later work on formic acid solutions. Their construction will be sufficiently clear from Fig. 1. The electrodes are platinized. The cells are particularly well adapted to work where only a small volume of solution is available since 20 cc. of solution brings its level so high above the electrodes that the addition or removal of 1 cc. or slight tilting of the cell does not change the observed resistance. Furthermore, the

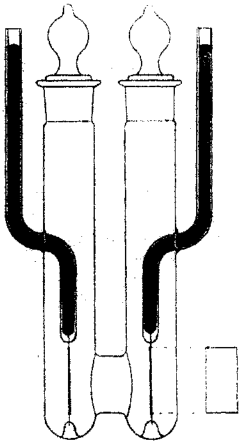

Fig. 1.

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[1] This Journal, **36**, 1589 (1914).

[2] *Ibid.*, **34**, 454 (1912).

readings are very sharp over wide ranges of concentration and only small capacities are required in parallel with the bridge circuit in order to obtain excellent minima.[1] Throughout a period of more than a year in which the cells were constantly in use the cell constants did not change, which shows that the support for the electrodes is sufficiently rigid. In the table mentioned above, the solutions used, the measured resistance (*R*) in ohms and the cell constant (*C*), calculated from the latter for each of the 3 cells are given. The resistances are in each case the averages of very closely agreeing duplicates made with different solutions prepared from different samples of potassium chloride which had been recrystallized several times from conductivity water with all due precautions and had then been ignited.

TABLE I.

The Variation of Cell Constant with Increasing Resistance of the Solution in the "Arrhenius" Cell.

KCl solution.	Arrhenius cell.		Cell H1.		Cell H3.	
N.	*R.*	*C.*	*R.*	*C.*	*R.*	*C.*
0.01	142.38	0.2015	1391.1	1.9684	883.37	1.2501
0.05	30.25	0.2021	294.49	1.9682	187.12	1.2506
0.2	8.21	0.2040	79.25	1.9686	50.35	1.2509
0.02	72.77	0.2018	710.40	1.9707	451.21	1.2517

Leaving out of consideration for the moment the results obtained with the 0.02 *N* solution, we see that the cell constant of Cell H1 does not vary and that the variation in Cell H3 is only 0.06%. Hence we may conclude that we may use H3 for solutions whose resistance in the cell lies between 79 and 1400 ohms and H_3 for resistances between 50 and 880 ohms. As a matter of fact, it is only the lower limit which is of importance. For some reason, which we are unable to explain, the 0.02 *N* solutions give divergent results; the only suggestion which we can offer is that there may be an error in the equivalent conductivity reported by Noyes and Falk. If we now examine the data for the "Arrhenius" cell we see that the cell constant undergoes an apparent change of over 1% in the same range of concentrations which gave a maximum variation of only 0.06% in the other cells, even although each reading in the "Arrhenius type" cell was very sharp, quite as sharp in fact as in the other cells. It is clear, therefore, that the "Arrhenius" cell is not adapted to the whole range of resistance covered by these solutions, although there is nothing in the individual readings to indicate this fact. The following data show, furthermore, that although the cell constant may be the same when calculated from the results obtained with solutions of different concentration

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[1] In the "Arrhenius type" cells, for example, a capacity of 0.18 microfarad had to be used in parallel with the bridge circuit to obtain a good minimum for small resistances, while for the type of cell here described the maximum capacity required for our solutions was less than 0.01 microfarad.

the cell may, nevertheless, not be satisfactory unless the standard solutions cover the correct range of resistance. In the cells H1 and H3, the average of the ratio of the resistance of the 0.01 N to that of the 0.02 N potassium chloride solution is 1.9580. In the "Arrhenius" cell the ratio is 1.9566, which differs from the one obtained in the other cells by only 0.07%. In other words, the cell constant of the "Arrhenius" cell calculated from the resistance of the 0.01 N solution would differ hardly at all from that calculated from the resistance of the 0.02 N solution and the unreliability of the cell would have been overlooked had only these two solutions been used.[1]

Summary.

It has been pointed out that even though the minima obtained in the measurement of the resistance of solutions by the usual method may be perfectly sharp, the results may nevertheless be incorrect and criteria for determining the reliability of the measurements and methods for overcoming some of the difficulties encountered have been suggested.

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[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY.]

CONCENTRATED THALLIUM AMALGAMS: THEIR ELECTROCHEMICAL AND THERMOCHEMICAL BEHAVIOR, DENSITIES AND FREEZING POINTS.

BY THEODORE W. RICHARDS AND FARRINGTON DANIELS.

Received August 1, 1919.

More than twenty years ago a series of investigations on the thermodynamics of amalgams was begun in Harvard University.[2] Recently, similar investigations have been conducted by G. A. Hulett.[3] The further interesting contributions of Joel H. Hildebrand concerning the vapor pressure of amalgams have added important auxiliary information.[4]

Nevertheless, the complete understanding of the electrochemical, thermochemical, and osmotic performance of these interesting metallic solutions has not been attained. This is unfortunate, since the nature of amalgams renders them more susceptible to varied investigation than that of many other types of solutions. It might reasonably be hoped that knowledge gained from these might be transferred by analogy to

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[1] Errors of the kind found in the case of the "Arrhenius" cells are doubtless due to polarization.

[2] T. W. Richards and G. N. Lewis, *Proc. Am. Acad.*, **34**, 87 (1898); T. W. Richards and G. S. Forbes, *Carnegie Inst. Publications*, **56**, 1 (1906); T. W. Richards and J. H. Wilson and R. N. Garrod-Thomas, *Ibid.*, 118, 1 to 72 (1908); T. W. Richards and F. Daniels, *Trans. Am. Electrochem. Soc.*, **22**, 343 (1912).

[3] G. A. Hulett and DeLury, THIS JOURNAL, 30, 1805 (1908).

[4] J. H. Hildebrand and E. D. Eastman, *Ibid.*, 36, 2020 (1914); **37**, 2452 (1915).