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THE DESIGN AND USE OF CONDUCTANCE CELLS FOR NON-AQUEOUS SOLUTIONS

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Introduction

In the course of an investigation involving the precise measurement with non-platinized electrodes of the electrical conductance of solutions in non-aqueous solvents, it has been found necessary to take certain precautions in the selection and use of the conductance cell. Since the difficulties necessitating such precautions are those which would be encountered by others attempting to determine the conductance of non-aqueous solutions within the range from 2×10^{-3} to 2×10^{-7} reciprocal ohms, with an accuracy of 0.1% or less, the experimental method followed is given in some detail.

Washburn[1] from the theory of the Wheatstone bridge, has derived equations relating for aqueous solutions the minimum allowable area of the cross section between the electrodes and the distance between them; Taylor and Acree[2] have taken up in some detail the difference in the results obtained using non-platinized electrodes with varying frequency and voltage, and have given an experimental criterion for good cells; Schlesinger and Reed[3] have also emphasized this point; Haworth[4] investigating the variation of the resistance with frequency, using a different type of Wheatstone bridge, has confirmed Taylor and Acree's results, as have also Kraus and Parker.[5]

It is the object of this paper to correlate the work of these previous investigators with the results of this research in the hope that the cell design and technique developed will give comparable results from all different investigators working with non-platinized electrodes.

Bridge Assembly.—The bridge assembly was made up of standard commercial instruments of the usual type now recommended for precision work; the source of current was a Vreeland oscillator operating at a frequency of either 500 or 1000; the roller-type of Wheatstone bridge was used, and 2 dial resistance boxes, the smaller 1, 10 and 100 dials, bifilar wound with an aggregate resistance of a thousand ohms, and the larger a 1000- and 10,000-dial box of the Curtis[6] type; 2 variable air condensers were employed with a maximum capacity of 0.005 mfd. and 0.00125 mfd.,

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[1] Washburn, This Journal, **38**, 2431 (1916).

[2] Taylor and Acree, *ibid.*, **38**, 2403, 2415 (1916).

[3] Schlesinger and Reed, *ibid.*, **41**, 1727 (1919).

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

[5] Kraus and Parker, This Journal, **44**, 2429 (1922).

[6] Curtis and Grover, *Bur. Standards Bull.*, **8**, 3 (1911).

respectively. The telephone was a Baldwin head piece, Type F, with an impedance of 2000 ohms.

Both bridge and resistances were calibrated in the Ernest Kempton Adams Precision Laboratory using direct current and a D'Arsonval galvanometer; the resistances by direct comparison with resistances calibrated at the Reichsanstalt loaned by the Columbia University Department of Physics; the bridge by the Kohlrausch method.[7]

A water-bath regulated at 25° ± 0.002° by the method of D. J. and J. J. Beaver[8] was used for most of the work. An oil-bath regulated in the same way was used for the higher resistances when necessary.

The usual grounding and shielding between different parts of the apparatus and of the leads was used. Furthermore, the Vreeland oscillator, which was in the same room but at some distance from the assembly, was shielded and the shield grounded in such a way that no stray currents could be heard in the telephone. The bridge was placed close to the baths with the leads of such length in either arm of the set-up that no lead correction was necessary, the leads being connected to the cells in the way recommended by Washburn.

Comparison Solutions.—The first difficulty encountered in this work was the lack of a suitable solution for comparing the cell constants, one with the other. In any work requiring more than one conductance cell, liquids for the purpose of comparing the relative constants of the cells are as necessary and important as the standard solution employed to find the absolute constant of any one of them. The customary method of simply diluting with water the liquid used for calibrating the cell was found to be unsatisfactory, for the solutions would have to be so dilute (0.0002 *M*) as to make it difficult to keep them free from contamination in handling as well as in measuring in glass cells.

The most convenient and satisfactory comparison solutions we have found are those obtained by diluting the calibrating solution of potassium chloride with 95% alcohol. Such a solution was forced into the cell by a pressure of purified air. The air, furnished by a water pump and purified by passage successively through solutions of sulfuric acid, potassium hydroxide, through water, and through soda lime, was then bubbled through some of the alcoholic solution of like concentration to give it the same pressure of vapor there as in the air above the solution. By filling the cell, in this way conductances of the same solution could be duplicated exactly throughout the entire range.

Variation of Resistance with Frequency.—Taylor and Acree have found with bare platinum electrodes (1) that the difference in the resistance

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[7] Kohlrausch and Holborn, "Leitvermögen der Elektrolyte," Leipzig, B. G. Teubner, **1898**, p. 47.

[8] Beaver and Beaver, *J. Ind. Eng. Chem.*, **15**, 359 (1923).

of a solution at frequencies of 1000 and 600 decreases as the diameter of the electrode increases, (2) that for a given electrode this difference decreases as the resistance of the solution increases from 11.492 to 534.4 ohms, (3) that the resistance of a cell decreases as the frequency is increased from 60 to 2000 cycles. To obtain then the "true electrical resistance" of the solution the authors suggested one of the following methods: (1) an extrapolation of the resistances to infinite frequency, which involves the measurement of each resistance at several frequencies; (2) the use of their extrapolation formula in terms of resistance, frequency and inductance, which necessitates the use of standard inductances or capacities; (3) an increase in the size of the electrode to at least 25 mm., preferably to 50 mm., at the same time with a construction of the cell and a method of using such *that the resistance of the solutions measured in that cell is above a certain minimum.*

The first two methods call for inconvenient experimental procedures and calculations; the third method possesses the advantage that any necessary alterations in the design of the cell or any restrictions, which must be placed on the resistance of the solutions measured in the cell, can be made once and for all at the beginning of the research. The subsequent determinations involve no more labor than when platinized electrodes can be used. Furthermore, if by simply fixing the minimum resistance to be measured in a given cell, small electrodes can be used, the

TABLE I

THE VARIATION OF THE APPARENT RESISTANCE WITH A CHANGE IN FREQUENCY USING CELLS WITH DIFFERENT AREA OF ELECTRODE SURFACE AND SOLUTIONS OF DIFFERENT ELECTROLYTES IN DIFFERENT SOLVENTS

Resistance R		Diff. in R at 1000 and 500 in %	Resistance R		Diff. in R at 1000 and 500 in %
1000~	500~		1000~	500~	
CELL 6—BRIGHT ELECTRODES, 13 MM. IN DIAMETER					
KCl-water solutions					
274.22[a]	277.14[a]	1.055	8946.9	8954.5	0.085
584.02[a]	588.05[a]	0.690	9086.0	9093.5	.083
1455.05	1457.8	.189	10644.5	10653	.080
2264.0	2268.6	.203	13047	13059	.092
3419.4	3422.3	.085	13352	13365	.097
4909.6	4912.8	.065	18113	18138	.138
6309.4	6314.0	.073	26889	26938	.182
6640.6	6644.5	.059	30190	30250	.198
6853.3	6857.0	.054	39882	39992	.276
7260.8	7267.5	.092	42277	42397	.284
8529.0	8535.5	.076	65701	65971	.411
KCl-alcohol-water solutions					
12095	12105	0.083	43490	43620	0.299
16680	16700	.120	82910	83305	.476
24515	24550	.143	...	...	...

LiBr-acetophenone solutions

17270	17290	0.116	92100	92500	0.424
32950	33010	.182	203496	205645	1.056

CELL 4—ROUGHENED ELECTRODES, 13 MM. IN DIAMETER

KCl-water solutions

183.46[a]	185.50[a]	1.112	1255.8	1259.4	0.287
360.68[a]	363.10[a]	0.671	9433.0	9440.0	.074
857.1	859.92[a]	0.329	...	...	...

KCl-alcohol-water solutions

190.82[a]	192.42[a]	0.838	6783	6787.1	0.060
440.35	441.47[a]	.254	17388	17410	.127
984.94	985.79	.086	23679	23725	.194
2014.6	2016.0	.069	34954	35034	.229
3617.3	3619.3	.055	38242	38340	.256

LiBr-acetophenone solutions

2755.0	2758.0	0.109	15595	15615	0.128
14025	14040	.107	23111	23141	.130

CELL 2—ROUGHENED ELECTRODES, 13 MM. IN DIAMETER

KCl-water solutions

399.47[a]	404.55[a]	1.522	2486.5	2492.0	0.221
651.96[a]	656.21[a]	0.652	2516.0	2521.0	.199
914.77	917.74[a]	.297	3531.2	3535.0	.108
1114.2	1116.0	.162	9533.0	9540.0	.073
1957.9	1962.9	.255			

KCl-alcohol-water solutions

631.98	633.46[a]	0.234	16585	16599	0.084
1391.3	1392.8	.108	18435	18460	.136
2044.0	2046.0	.098	21018	21052	.162
3646.3	3648.3	.055	29919	29972	.174
6945.0	6949.2	.060	...	...	...

LiBr-acetophenone solutions

1440.7	1442.0	0.090	16395	16415	0.122
2782.0	2785.0	.108	23550	23580	.127

CELL 3—ROUGHENED ELECTRODES, 38 MM. IN DIAMETER

KCl-water solutions

112.23[a]	112.23[a]	0.000	973.1	973.1	0.000

KCl-alcohol-water solutions

140.54[a]	140.64[a]	0.071	701.23	701.23	0.000
206.73	206.81[a]	.039	1513.7	1513.7	.000
369.22	369.29	.019	9054.6	9057	.027

LiBr-acetophenone solutions

317.59	317.7[a]	0.035	5637.2	5638.5	0.023
1448.0	1448.0	.000	7466	7469	.040
3076.1	3076.9	.036	12210	12213	.025
4004.1	4005.3	.030	39355	39356	.002

[a] For this measurement a mica condenser was used.

economy of both platinum and solution possible would certainly justify any attempt to use such a method.

Therefore, since of all the cells on the market the Washburn Types A and B were the most carefully designed and capable of giving the range of conductance we needed with the minimum volume requirement and exposure of the solution to the air in transferring, an investigation was undertaken to determine for each cell a minimum resistance, above which the difference in the result due to frequency would be negligible. Taylor and Acree made no measurements above 534.4 ohms at 1000 cycles, but estimated that in general above 10,000 ohms the resistance measured at 1000 cycles would not differ from the true resistance by more than 0.01%. In Table I are values, each an average of a number of readings, for the resistance in ohms at 1000 and 500 cycles and the differences between these values, in percentage of the value of 1000 cycles. Cells 2, 4, and 6 are of Type B, Nos. 2 and 4 with a range at 10^{-4} to 10^{-6} reciprocal ohms, No. 6 with a range of 10^{-3} to 10^{-5} reciprocal ohms. Cell 3 is of Type A with a range of 10^{-5} to 10^{-7} reciprocal ohms.

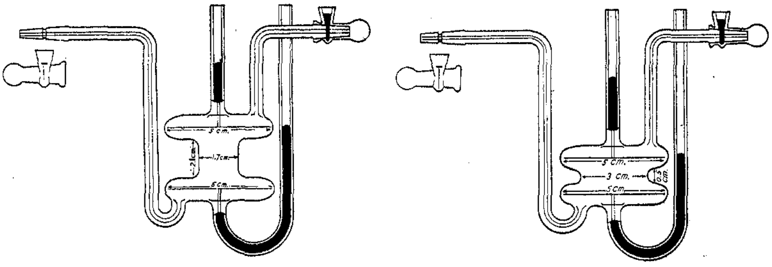
While these data show that for Cells 2, 4 and 6 the differences in resistances at the two frequencies are comparable to the values obtained by Taylor and Acree, *in the range covered by these investigators*, for their 13 mm. bright electrodes, these differences do not decrease continuously in the manner predicted, but pass through a minimum between 5000 and 10,000 ohms. That this phenomenon is not peculiar to any one cell or solution but to the size of the electrode is shown by the fact that when three different types of solutions are used in all 3 cells having the same size electrodes, the results are similar. That it is due to some cause inherent in the cell and not in the assembly is shown by the results obtained with Cell 3. In this case, with the larger electrodes, the differences are smaller throughout the entire range and do not increase above 10,000 ohms. The slight irregularities in these differences can readily be attributed to the difficulty in taking the readings at 500 cycles during the day, since the telephone was not tuned particularly to this frequency.

Apparently then, for cells having bare platinum electrodes, there is, for a maximum allowable error, no *mimimum* resistance above which a given cell may be used, but an *optimum* range of resistances throughout which the differences in resistance with differences in frequency may or may not, depending on the size of the electrode, be small enough to come within this limit of error. As the size of the electrode increases (at least up to 50 mm.) these differences in the resistances throughout this optimum range become smaller, and the range throughout which the cell may be used becomes larger. *In other words, to choose the cell so that the resistance of a solution in it is large does not give the same results experimentally as to increase the size of the electrode and reconstruct the cell.*

At very high resistances, 90,000 ohms or over, with Cell 3 in the water-bath, there was observed on some days a *decrease* in resistance at 500 cycles. When measured in an oil-bath this decrease disappeared and the usual slight increase was noted. At lower resistances, however, no differences in resistance of a cell in a water-bath or an oil-bath could be observed. Evidently this phenomenon is due to the capacity effects prevalent when a high resistance is measured in a water-bath. Since this effect was not always the same in the same laboratory and could conceivably be quite different in different laboratories, depending upon the grounding facilities, etc., Washburn's suggestion[1] that in the design of a conductivity cell a maximum resistance of 10^4 ohms should be imposed when possible seems especially pertinent.

Throughout the work the capacities were measured and found to be greater at 500 than at 1000 cycles, but as the difference in the resistance at the two cycles increased the difference in the capacity decreased. Inasmuch as the condensers were of the type used to balance out capacity in the cell and were not standardized, the actual values are qualitative and are therefore not given.

Cell Design.—Since the only conditions imposed upon the use of Washburn's simplified Equation 4 in place of Equation 3 are that the specific conductance L^{-} shall not be less than 10^{-7} reciprocal ohms, the maximum resistance R not greater than 10^5 ohms, the frequencies not greater than 1000 cycles and the dielectric constant of the liquid not greater than 80, there was no reason why, for the non-aqueous solutions to be measured, the Type B cells could not be used, except for the fact that, due to the small size of the electrodes, the resistance at 1000 cycles is not the true resistance of the solutions. From Taylor and Acree's values and from the results with Cell 3 with electrodes 38 mm. in diameter, which showed that although there was a decided decrease in the difference at two frequencies this difference was not entirely eliminated, it was assumed that this error would probably be negligible were the diameter of the elec-



DB Nº 1

DB Nº 2

Fig. 1

trodes increased to 50 mm. Accordingly, since the size of the electrodes was fixed, calculations were made by Washburn's Equations 24 and 25 to determine the dimensions of the construction between the electrodes.

The cells and their essential dimensions are shown in Fig. 1. The circular, sand-blasted electrodes were made of platinum 0.15 mm. thick with a rod 1.0–1.5 mm. in diameter securely welded to the center of the disc. The cells were of Jena glass. Since the solvents used were hygroscopic and volatile, the arms of the cells carried the mercury seals shown in the figure.[9] Cell DB No. 1 has a cell constant approximately 1.39 and can be used for 0.02 N potassium chloride solution with a resistance of approximately 500 ohms. With 400–500 ohms minimum resistance there can be no errors due to the measurement at any one frequency, and only air condensers are needed. Cell DB No. 2 overlaps the range of Washburn's Type A cell and Cell DB No. 1, although the resistance does not fall below 500 or rise much above 10^4 ohms. Unless extreme precision is desired, Washburn's Type A cell can be used with roughened or sand-blasted electrodes, although an increase in the diameter to 50 mm. would be an improvement.

Solutions having resistances ranging from 300 to 60,000 ohms were measured in both of the new cells. Since there was no difference in the resistance with the change in frequency to 500 cycles the resistance measured at 1000 cycles was assumed to be the true resistance of the solution.

The Methods of Cleansing and Drying Cells.—Little attention has been given by previous investigators to one factor which, in this Laboratory, has been found to be of the greatest importance, namely, the history and treatment of the electrodes previous to their use. Taylor and Acree[2] found that unless their cells were "scrupulously clean" the resistance of a filled cell varied with a change in voltage. This fact they used as a criterion of cleanliness, but suggested no method for either cleaning or drying. Possibly, since they used water solutions, they did not dry their cells before filling but rinsed them with successive portions of the solution to be measured. Such a procedure is almost impossible with hygroscopic solvents, however, and at best is wasteful of the liquids which are usually expensive and purified with difficulty. Kraus and Bishop[10] also reported some trouble in checking their values for amyl alcohol when they used a cell that was dried after being steamed, but they gave no practical method for obviating the difficulty. In our own experience, when the cells were cleaned with chromic acid mixture, steamed, or rinsed with hot conductivity water, and then dried with warm, purified air either directly or after rinsing with redistilled alcohol, the values for the resistance of a given solution varied so capriciously and the variations were of such magnitude that quite

[9] These cells were made by Mr. H. O. Morgan of Eimer and Amend.

[10] Kraus and Bishop, This Journal, **44,** 2206 (1922).

evidently the greatest source of error in the conductance method lies in the pre-treatment of non-platinized electrodes.

Since the discrepancy among results with any one solution was more apparent when the measurement was made in cells with electrodes near to one another, a series of determinations was made in which various methods of cleaning and drying Cells 3 and DB No. 2 were employed to discover if possible the cause of the error and, in any case, a method for the preparation of the cell that would give results consistent with those obtained when the cells were not dried but were rinsed with the solution. In the failure to develop such a method errors arising from the factors discussed in the foregoing sections of this paper are of little moment, as the error from this source alone frequently rises as high as 2 to 3%. The following is typical of the behavior of the 2 cells when the same solution is measured in both.

Cells cleaned with chromic acid-mixture, thoroughly rinsed with hot conductivity water and, without drying, finally rinsed with the solution to be measured, and allowed to stand for 1 hour after filling. Resistance: Cell DB No. 2, 11799 ohms; Cell 3, 801 ohms.

Cells cleaned with chromic acid, rinsed as before, and dried by passing purified air through them; the same solution was used and the cells were allowed to stand for 1 hour after filling. Resistance: Cell DB No. 2, 11940 ohms; Cell 3, 816 ohms.

After cleaning, etc., the cells were allowed to stand for 24 hours. Resistance: Cell DB No. 2, 12158 ohms; Cell 3, 815 ohms.

The same cells were allowed to stand for an additional 12 hours. The resistance of the cells decreased because of movement of cell or lead but finally became constant. Resistance: Cell DB No. 2, 12112 ohms; Cell 3, 815 ohms.

The cells were refilled without cleaning or drying them. Resistance: Cell DB No. 2, 11805 ohms; Cell 3, 801 ohms.

The cells were cleaned with chromic acid mixture, rinsed and dried as before and allowed to stand for 1 hour after filling. Resistance: Cell DB No. 2, 11860 ohms; Cell 3, 812 ohms.

The cells were refilled without cleaning or drying them $^1/_2$ hour after the previous measurement and allowed to stand for 1 hour after filling. Resistance: Cell DB No. 2, 11780 ohms; Cell 3, 797 ohms.

The cells were refilled 1 hour after the previous measurement, and allowed to stand for 1 hour after filling. Resistance: Cell DB No. 2, 11775 ohms; Cell 3, 799 ohms.

The same cells were again refilled, 2 hours after the previous measurement, and allowed to stand for 1 hour after filling. Resistance: Cell DB No. 2, 11774 ohms; Cell 3, 799.55 ohms.

The cells were thoroughly washed with hot conductivity water. Treatment with cleaning mixture was omitted. Resistance: Cell DB No. 2, 11843 ohms; Cell 3, 803 ohms.

These results and others, of which these are typical, show that without a doubt the treatment of the cells with cleaning mixture was responsible for a considerable part of the error. Kohlrausch[11] has discussed the difficulty in measuring the conductance of solutions of acids and bases

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[11] Ref. 7, p. 10.

with bare platinum electrodes due to the apparent absorption of the solute by the electrodes from stronger solutions, and the gradual liberation of the absorbed material to water and to the more dilute solutions. However, were this the only effect of the cleaning mixture in the case at hand the values for the resistances following such treatment should be lower, since the solution of material from the electrodes would increase the conductance of the solution between them. Furthermore, there should be no difference among values for wet or dry cells. Invariably in our work when a dry cell was used, the resistance of the solution was higher than the value in a wet cell, well rinsed. When the dried cell was immediately refilled without further cleaning or drying, the results were at first always too low, but on further refillings gradually rose to the normal value of the undried, rinsed cell. When the solution was left standing in the cell for 24 hours or more, the reading after the first refilling assumed its normal value. Were it not for the anomalously but uniformly high value obtained on the first filling of a dry cell, these data would seem to indicate the occurrence of phenomena similar to those observed by Kohlrausch.

The general theory underlying the measurement of an electrolytic cell by the Wheatstone bridge method is that when the cell, acting as a resistance and a capacity in series and shunted by a condenser in one arm, is balanced in the other arm by a pure resistance, shunted by an air condenser until no current flows through the telephone, the drop of potential along one half of the bridge is equal to the drop of potential along the other half, and therefore the resistances are equal. It is only, then, when there is a definite relationship between the resistances, the capacity and inductance, the drop of potential, and the current in one arm of the bridge to that in the other, that silence in the telephone can be obtained. A change in any one of these factors would cause a loss of balance in the bridge. In the present situation the only possible change is *in the conductance cell* itself, since the bridge assembly is identical for all the measurements.

In the cell the pure resistance is made up of the resistance of the solution and the small resistance of the electrodes both of which are constant for any one cell and solution. The capacity effects in a cell are assumed to be due to polarization and are dependent upon the area of the electrodes, the resistance of the solution between them and the frequency of the current. These also remain constant under the given conditions.

The only possibility remaining which would account for an unbalancing of the bridge network, otherwise in resonance, would seem to be that the cell filled with the solution in itself acts as a source of current. In this event the process of cleansing and drying the cells must in some way have so affected the electrodes that they are no longer similar pieces of the same metal dipping into the same solution but in effect two dissimilar electrodes giving a potential difference across the terminals of the cell. In reality, then, we seem to be measuring, instead of a resistance and a capacity, a voltaic cell, the potential difference of which depends upon the difference in effect on the two electrodes of the pre-treatment, which in turn depends upon the difference in the specimens of platinum comprising each electrode and in the time and methods of pre-treatment.

If this is, indeed, the correct explanation of the abnormal behavior of the dried cells, the problem becomes one of finding how to bring the electrodes to the same potential after they are immersed in the liquid, and at the same time keep the resistance of the solution the same, or how to clean and dry the electrodes so that the potential difference of each in contact with the liquid is the same in the first place.

Accordingly, to determine whether it was possible to bring the electrodes to equilibrium *after* they had been treated with chromic acid and dried, the cell was filled and the electrodes short-circuited overnight, but no change in the measured resistance was observed. Without breaking the connection between the electrodes, the cell was cleaned with cleaning mixture, rinsed, steamed for several hours, rinsed with hot conductivity water and allowed to stand filled with water for several days. The cell was then rinsed with redistilled alcohol and dried. With the electrodes still connected the cell was filled with some of the same solution and allowed to come to temperature equilibrium in the bath. The short circuit was then removed, the lead wires put in place and the following readings taken. Resistance: Cell DB No. 2, 11785 ohms; Cell 3, 801 ohms.

The cells were then allowed to stand with the electrodes on open circuit, when the resistance began to rise. Resistance: Cell DB No. 2, 11795 ohms; Cell 3, 803 ohms.

The connecting wire was then again replaced and the filled cells allowed to remain in the bath overnight. The next morning the readings were the same. The cells were then refilled without drying or rinsing. Resistance: Cell DB No. 2, 11760 ohms; Cell 3, 799 ohms.

Of a number of such determinations made by cleaning and drying the electrodes, connected or unconnected, only those gave results approaching the normal value that were made after the electrodes had been connected throughout the entire process of cleansing, drying, filling, and attainment of temperature equilibrium. As this method seemed a possible solution to our problem, a systematic series of determinations was made on another solution to see what variations in the method were possible and how often the cell could be used by simply rinsing with alcohol and drying between refillings. In the interests of economy of space the results are summarized in the following statement.

The variations in the results are greater with Cell 3 than with Cell DB No. 2, and greater with Cell DB No. 2 than with Cell DB No. 1. In fact, no difference could be observed when Cell DB No. 1 was used even when the chromic acid cleansing was followed only by the thorough rinsing with conductivity water before drying, while with Cells DB Nos. 2 and 3 variations of the same order of magnitude as in the typical data given above were observed. When the electrodes were short-circuited during the treatment with the cleaning mixture the discrepancies were reduced to about $^1/_4$ of those observed when the cell was cleaned with the electrodes on open circuit; similar differences were noted when the cells were steamed, large errors being obtained if the cells were dried after steaming with the electrodes on open circuit. When the cells with the electrodes on open circuit were rinsed with hot conductivity water, without previous treatment with chromic acid mixture, the results with Cell DB No. 2 were usually normal but those with Cell No. 3 showed variations of 0.2–0.5%. It was only when the *electrodes were short-circuited throughout the entire process of cleansing, drying and filling* that consistent values for the resistance of a given solution were obtained in all cells. Furthermore, as soon as the short circuit was broken the resistance began to rise; when the connection was replaced the reading became constant. Evidently the electrodes prepared in this way are under some sort of a strain which is relieved by their taking up some of the solute from the solution when the current is broken. On refilling the cell after such adsorption has taken place without rinsing or drying, the next result is invariably too low, just as in the first experiments given in this section after the treatment on open circuit of the electrodes with cleaning mixture. This would seem to indicate that the adsorbed material was given back to the next solution. When the circuit was left open too long in taking a series of readings consistent results for the next refilling were not given by the usual procedure of short-circuiting, rinsing with alcohol and drying. In such a case, filling the cell with hot conductivity water and allowing the electrodes on open circuit to soak overnight seemed to relieve them of the adsorbed material and the cell could then be employed as usual with success.

The number of continuous determinations possible with only a thorough rinsing with alcohol and drying between refillings seemed to be contingent on the length of time the electrodes were left unshorted during measurement. When great care was taken in this respect the cells could be used all day for several weeks, particularly when they were soaked overnight in conductivity water and kept free from atmospheric contamination. With a cell of the pipet type, which does not permit much movement of the contained liquid, our criterion for the equipotentiality of the electrodes was the constant value obtained on moving the leads or the cell sufficiently to change the position of the solution between the electrodes. With cells of the bottle type, however, there is a constant mixing of all parts of the solution possible; whether the final result is burdened with an error can be determined only by a previous rigid examination of the cell with a known solution to determine what treatment is necessary to make the cell usable.

All in all, then, the term "clean" applied to conductance cells made up with bare electrodes takes on a new meaning, involving the attainment of electrodes which will act as similar pieces of the same metal toward a solution, and the maintenance of such a state of equipotentiality throughout the time required for the measurement of the resistance of the solution. The following procedure is recommended for the "cleansing" of the cells. The electrodes, during the entire operation, are connected by a heavy copper wire dipping into the mercury cups. The cell is then filled with hot cleaning mixture and allowed to stand for a few minutes, rinsed thoroughly with distilled water and finally filled with hot conductivity water; it is then steamed by allowing the steam to pass up through the water; this permits enough steam to condense so that in time the water that has been in contact with the electrodes is automatically siphoned off. The steaming is continued for several hours, after which the cell is filled with hot conductivity water and the outlets closed. After it has been allowed to stand overnight, the cell is rinsed with alcohol, dried with a current of warm purified air, and filled at once with the solution to be measured. Only when the actual readings are being taken must the short circuit be broken; it should be replaced between check readings. Whenever the cell is not in use it should be filled with hot conductivity water and tightly closed to keep the water as free as possible from contamination. This method has been found infallible with the 3 cells used; nevertheless, there seems still to be present an element of caprice, for some determinations made on another Washburn cell of the same type as Cell 3, and purchased at the same time, gave very unreliable results. In the first place, it was difficult to check the readings even when the cell was not dried; in the second place, extreme precaution was needed to obtain any sort of consistent results with dried cells; and in the third place, only a few refillings could be made before it was necessary to subject the cell again to a most rigorous cleansing process. With the possible variations in any one piece of a metal and the still greater possible variations in pieces from different sources it is to be expected that such differences among cells will be found. To Taylor and Acree's experimental criterion[12] for good cells, namely, that whatever the solutions used, the ratios of the resistances of any solution in two such cells must be the same, must then be added the stipulation that *such cells can be cleaned and dried* successfully with comparative ease.

Especially interesting in this connection and confirmatory of our explanation of this phenomenon is the recent work of Willard and Fenwick[13] and of Beans and Hammett.[14] Willard and Fenwick found a great variation in the values for the potentials of supposedly similar platinum electrodes in a given solution, not only with different methods of pre-treatment but with repeated applications of the same method. Beans and Hammett found that a bare platinum electrode may differ in potential from a

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[12] Ref. 2, p. 2403.

[13] Willard and Fenwick, THIS JOURNAL, **44,** 2516 (1922).

[14] Hammett, *Dissertation,* Columbia University, **1922**.

similar platinized foil, both immersed in a 0.1 N hydrochloric acid saturated with hydrogen, by as much as 0.3 volt. In both of these researches the treatments which gave the greatest deviations in the values of the potentials for similar electrodes were of the same variety as those that gave for us the greatest increase in the resistance of the solution. There remains the possibility that even for the most persistently unreliable cells a method using polarizing currents, on treatment with alkaline cleansing solutions such as alcoholic potash, or of saturating the electrodes with some gas other than air can be developed; an attempt to find such a method is now being made in this Laboratory.

Variation of Resistance with Voltage.—Kraus and Parker[5] came to the conclusion that the only reason for the change in resistance with the change in voltage observed by them as well as by Taylor and Acree could not be the contamination of the solution from the cells, as suggested by Taylor and Acree, since with the greatest care they could not entirely eliminate this effect in some of their determinations. In the present research no *change in resistance with the change in the impressed voltage has been observed when the electrodes were properly cleaned.* With the great difference in the potential of the electrodes possible among different cells "cleansed" in the same or different ways, it is not surprising that such discrepancies should occur. In every case the method of cleansing and the criterion for clean cells should be given before any confidence can be placed in the experimental results.

Summary

A study has been made of the errors inherent in the design and use of conductance cells containing non-platinized electrodes, when employed for non-aqueous solutions, and the following general conclusions drawn.

1. In order to make accurate conductance measurements of dilute non-aqueous solutions, some comparison solution other than the very dilute aqueous solutions needed should be used, since the latter cannot be kept as free from contamination as the non-aqueous solutions which are to be measured. A solution of potassium chloride diluted with alcohol is suggested as the most convenient comparison solution.

2. The change in resistance with a change in frequency from 500 to 1000 cycles has been measured throughout a wide range of resistances, with a number of different cells and types of solutions. The results of Taylor and Acree have been confirmed in the range covered by them; however, the difference in resistance for small electrodes does not decrease continuously with an increase in resistance but passes through a minimum between 5000 and 10,000 ohms. There is *not*, as Taylor and Acree state, a minimum resistance above which a cell may be used with accuracy, but an optimum range which may or may not give results sufficiently accurate, depending upon the accuracy needed and the size of the electrodes;

as the size of the electrodes increases, the range and possible accuracy within the range increase. So choosing the cells that the resistance in them is large is not equivalent experimentally to increasing the size of the electrodes.

3. Cells have been designed, with the aid of Washburn's equations, which do not change in resistance with a change in frequency and which with the Washburn Type A Cell cover the range from 2×10^{-3} to 2×10^{-7} reciprocal ohms.

4. The method of cleansing and drying the electrodes has been found to be of far greater importance than any of the other factors involved, the errors from this source alone often being as high as 2 to 3%. The usual method of cleansing and drying seemed to make the cell, filled with its solution, not a resistance and a capacity but a voltaic cell, which gives the effect of an abnormally high resistance. A method is given for cleansing the cells which has for its underlying principle the production of 2 electrodes having as nearly as possible the same contact potential when immersed in the same solution; it involves thoroughly "scrubbing" the electrodes after any treatment with an acid cleaning mixture and keeping the electrodes short-circuited during all the processes of cleaning, drying and the bringing of the cell to temperature equilibrium.

5. It is believed that the difference in the potential developed by different electrodes when subjected to the same treatment accounts for the change in resistance with a change in the impressed voltage, and for the fact that some observers have not been able to eliminate the change by thorough cleansing while others have. The term "clean" applied to conductance cells should be more rigidly defined, if comparable values are to be obtained by different workers.

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THE OSMOTIC PRESSURES OF AQUEOUS SOLUTIONS OF PHENOL AT 30°

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Introductory

The only reference to be found in the literature of an attempt to determine experimentally the osmotic pressure of phenol solutions is that of Naccari,[1] whose results, being much lower than those theoretically expected and incapable of either duplication or accurate determination, were rejected by Naccari as unsatisfactory. Owing to the crudity of the method employed, which at its best could give but qualitative results, his data are of interest only from an historical standpoint.

[1] Naccari, *Atti. accad. Lincei.* **6**, 32 (1897).