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PREPARATION OF RESISTORS USING A LOW-TEMPERATURE-COEFFICIENT-OF-RESISTANCE ELECTROLYTE*

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ABSTRACT

An electrlytic solution containing acid, sugar, salt, and distilled water (boric acid, mannitol, and potassium chloride) was experimentally tested to determine its suitability for use in preparing "water resistors" which exhibit a low temperature coefficient of resistance throughout the range from 40°F to 160°F. The resistors use standard plastic containers provided with suitable end electrodes for containing the solutions. A scheme is presented for determining the amounts of the various electrolyte constituents to obtain any resistance value throughout the range from 10 K ohms to 100 K ohms. The resulting resistors exhibit excellent temperature characteristics from 60°F to 160°F, and acceptable characteristics down to a temperature of 40°F.

Considering 78°F as reference, a given resistance can be prepared to be within about 1% to 2% of a specified value at this temperature. A total change in resistance of about 2% is experienced throughout the temperature range from 60°F to 160°F. The short-term drift in resistance as the resistor is repeatedly cycled throughout the temperature range (40°F to 160°F) is less than 5%. The resistors are thus suitable for voltage-divider use in high-voltage pulse circuits and for providing loads for high-voltage pulse transformers. The results of a few tests indicate that the long-term stability of these resistors may be poor. Additional work should be done to evaluate the long-term stability characteristics.

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Special thanks go to John Sperry, who helped set up final experiments, and to Al Jenkins, who performed practically all of the final experiments, and without whose help the task could not have been completed.

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My special appreciation is expressed to my family for allowing me to work such abnormally long hours all summer to complete an almost endless task.

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INTRODUCTION

Resistors are frequently prepared using an electrolytic solution contained between two electrodes. Because the chemicals are usually dissolved in distilled water, these resistors are generally referred to as "water resistors," even though salts, acids, or combinations of chemicals may be employed to prepare the electrolyte. Resistors of this type are often employed in electrical circuits as load resistors for electrical devices (e.g., transformers) and thus may be also called "water loads." Salt-water solutions have found use as water loads for large, commercial power transformers, as well as loads for smaller pulse transformers used in electronic circuits. Salt-water solutions have also found extensive use as terminations or "loads" for high-power waveguides employing microwave frequencies. Water loads are used in the form of a water resistor in a voltage-divider network for measuring either the voltage or the current in a circuit, particularly a pulse circuit. In the latter application, it would be extremely desirable if the "water-resistor" were stable and constant, both as a function of time and of temperature.

Most electrolytic solutions exhibit a large negative temperature coefficient of resistance (or positive temperature coefficient of conductance). A graphical representation of the resistance as a function of temperature for electrolytic solutions exhibits a large negative slope. Conversely, a graphical plot of the conductivity as a function of temperature exhibits a positive slope. Frequently, it is more convenient to work with the conductivity-versus-temperature curve than with the resistance-versus-temperature curve because of the straight-line characteristics of the former. The conductivity-versus-temperature characteristics of various solutions are illustrated in Figure 1. It should be noted that the conductivity of the solutions differ, depending upon the electrolyte, and the slopes differ, depending not only upon the electrolyte, but also upon the concentration of the solution.

It would be desirable if an electrolytic solution with a low, or essentially a zero, temperature coefficient of resistance could be found for use in the above-mentioned applications, especially the voltage-divider circuit. A chemical solution which has some merit in this respect is Magnanini's Formula[1].

The formula is described by Lion[2] as follows:

> "A solution with an extremely small temperature coefficient of resistance is Magnanini's solution (121 grams of mannite, 41 grams boric acid, 0.04 grams potassium chloride, to one liter of solution; the temperature coefficient, at 18° C. is -0.1 per cent/° C; the resistivity is very high)."

Magnanini's scientific papers pertaining to the solution can be found in Gazzetta Chimica Italiana for the period 1889-1891.

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[1] Magnanini, Gaetano, Gazzetta Chimica Italiana, 44, pp. 396-398. C. A. (8:3017, 1914)

[2] Lion, Kurt S., Instrumentation in Scientific Research, p. 43, McGraw-Hill Book Co., Inc. (New York, 1959)

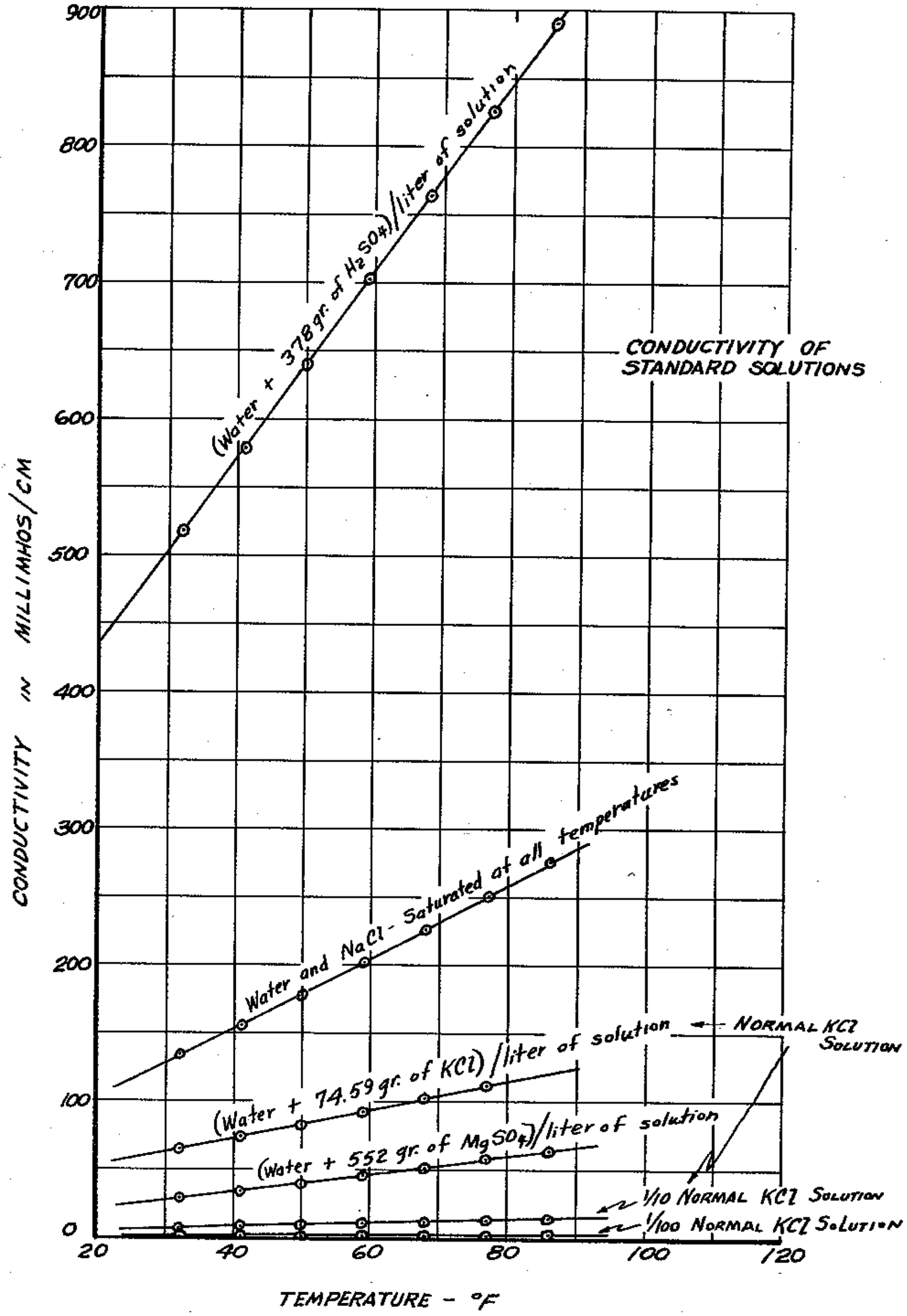

Figure 1. Conductivity of Standard Electrolytic Solutions

other investigators have tested a long series of compounds for their ability to raise the conductivity of a boric acid solution.[3]

Magnanini's formula consists of a sugar (mannite or mannitol, $C_6H_{14}O_6$, molecular weight of 182.172), a weak acid, (boric acid, H_3BO_3, molecular weight of 61.844), and a salt (potassium chloride, KCl, molecular weight of 74.557), in a ratio as given above by Lion of 121 grams of mannitol, plus 41 grams of boric acid, plus 0.04 grams of potassium chloride, per liter of solution. It should be noted that mannitol and boric acid are in the ratio of 1:1 based upon their molecular weights. These two constituents are known to enter into a complex* in the ratio of 1:1, forming an acid that is stronger than boric acid alone. This complex, mannitoboric acid, has a higher conductivity than a simple boric acid solution, but dissociates with elevated temperatures. This dissociation causes the resistance-temperature characteristic to have a positive slope over the range of temperature from about 50° F. to greater than 160° F; a characteristic quite unnatural for an electrolytic solution. This positive slope indicates that the mannitol-boric acid solution possesses a positive temperature coefficient of resistance over the temperature range specified. Once one has obtained such a solution as this,

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[3] Deutsch, A. and Osoling, S., Journal of the American Chemical Society, 71, pp. 1637-40, C.A. (43:6894, 1949)

*See Appendix A.

which exhibits a positive temperature coefficient of resistance, it is relatively simple to connect it in parallel or series with another resistance, which exhibits an equal but opposite temperature-coefficient-of-resistance characteristic, in order to obtain a composite resistance that has essentially a zero temperature coefficient of resistance. Magnanini's formula effectively connects two chemical solutions in parallel to bring about the "neutralization" of the two temperature coefficients of resistance.

Potassium chloride dissolved in distilled water exhibits a negative temperature coefficient of resistance (typical of most electrolytic solutions, but opposite to the mannitol-boric acid solution). Thus, one should be able to take two resistors, one made with the mannitol-boric acid solution and the other made with the potassium chloride solution, connect them in parallel, and adjust the concentration of each until a composite, parallel combination is obtained which exhibits essentially a zero temperature coefficient of resistance over a considerable temperature range. Fortunately, potassium chloride and the mannitol-boric acid combination can be placed in the same solution without the chemical characteristics of either one being appreciably affected. Thus, by controlling the concentration or ratio of the two groups of constituents, one is able to chemically obtain the parallel resistance effect described above. This is exactly what Magnanini's formula does in providing a solution whose temperature coefficient of resistance is so small over such a wide temperature range.

SCOPE OF THE PROJECT

On February 15, 1962, Sandia Corporation negotiated a contract (P.O. 14-6901) with the University of New Mexico for the purpose of determining the characteristics of Magnanini's formula in relation to its use as the electrolyte in a "water resistor." The contract states the purpose and the scope of the work as follows:

> "Development of a table of ratios of solutes and solvents for obtaining the optimum temperature coefficient for a standard-size water resistor throughout the resistance range of 1,000 ohms to 100,000 ohms."
>
> "The purpose of the work described in this proposal is to determine the effect upon the resistance when one alters the ratio of the constituents of Magnanini's formula, and to determine by experimental or theoretical methods, how to control the resistivity, and maintain a minimum temperature coefficient of resistance across the temperature range of 40° F. to 160° F."

The project was a joint effort between the Electrical Engineering and Chemical Engineering Departments at the University of New Mexico. Sandia Corporation supplied a temperature test chamber, an impedance bridge, and a number of plastic containers used in preparing the water resistors.

Although the limitations of Magnanini's solution made it impossible to obtain resistance values lower than 10,000 ohms, it was possible to satisfy the rest of the tasks specified in the contract. Basically, the problem was solved in a series of experimental steps. Because the plastic containers initially supplied were not provided with suitable thermal expansion chambers, the end-cap assembly had to be modified to provide for thermal expansion, as illustrated in Figure 2. Once the thermal expansion problem was solved, a plan was followed to determine how the various aspects of the contract could be satisfied.

Numerous experiments were performed to verify that each step in solving the problem was correct and repeatable. The approach was basically that used above in describing the action of Magnanini's formula. First, the basic characteristics of Magnanini's formula were studied to determine just what resistance values could be obtained using the standard plastic container illustrated in Figure 2. It was found that the basic constituents gave a resistance value of about 12 K ohms (12,000 ohms) and that the characteristics of the standard Magnanini formula were not nearly so good as described by Lion. Since 12 K ohms was the smallest resistance value obtainable with the standard Magnanini formula, it would not be possible to prepare resistance values in the 1,000 to 10,000 ohm range unless the formula were modified. The mannitol and boric acid are near saturation at the lower portion of the temperature range (40° F. to 60° F.) and an appreciable increase in concentration was not considered possible or desirable since some of the constituents might precipitate out of solution at the lower temperatures. Chemical tables[4] indicated that boric acid was closer to saturation than mannitol; therefore, an increase in mannitol content was

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[4] Olsen, John C., Van Nostrand's Chemical Annual, Student's Edition, 6th Issure, 1926, pp. 378-379, and pp. 436-437.

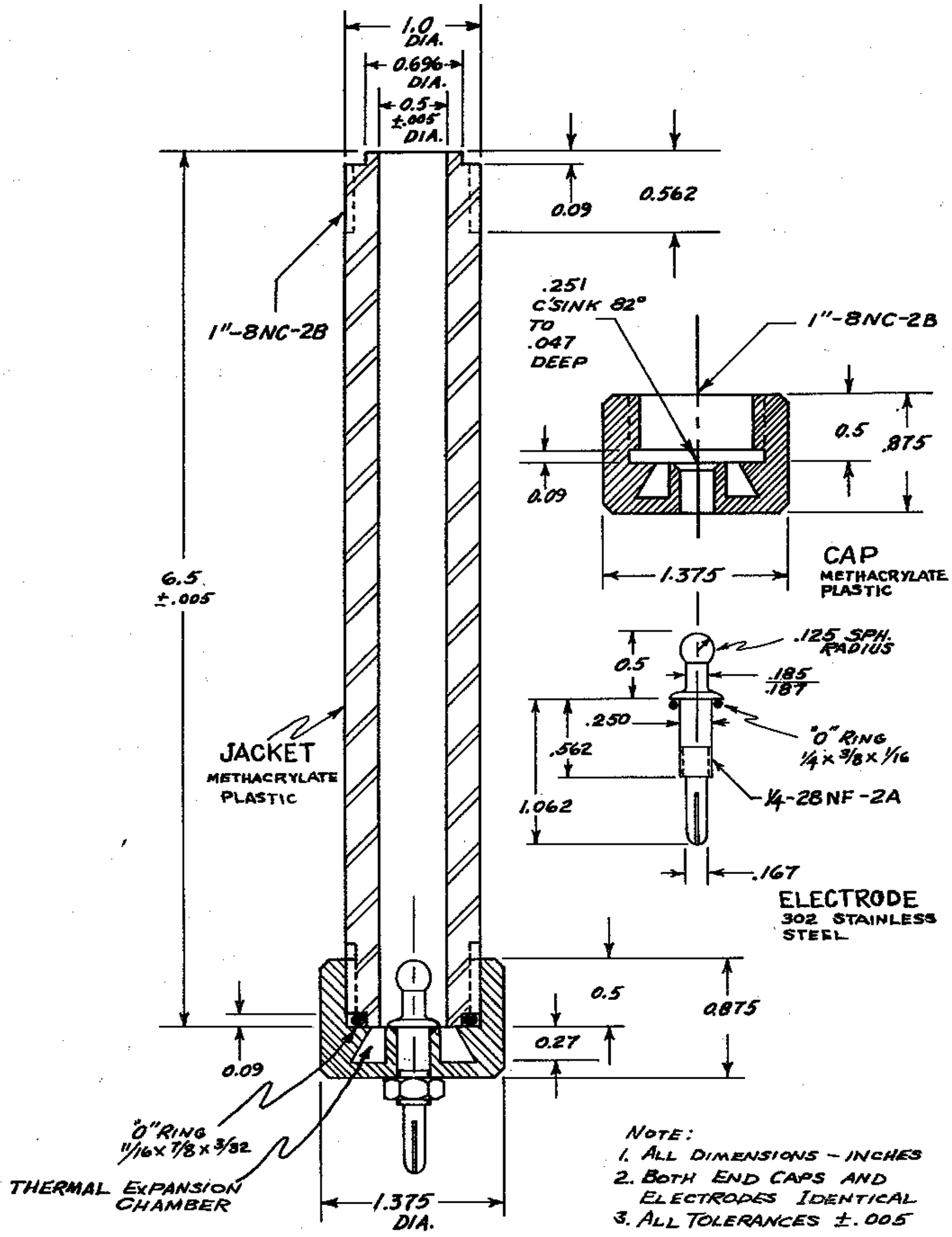

Figure 2. Standard Plastic Container for Preparing Water Resistors. Unit Consists of One Cylindrical Jacket, Two End Caps, Two Electrodes, and Four "O"-Rings.

possible. A modified version of Magnanini's formula was prepared in which the boric acid content was maintained at 41 grams per liter of solution, but the mannitol content was increased from 141 grams to 151 grams per liter. This change in the basic Magnanini's formula resulted in a higher conductivity solution, thus making it possible to prepare resistance values as low as 10,000 ohms. Of course, a new potassium chloride content was required to "neutralize" the temperature coefficient of resistance of the modified solution. The new "standard" solution became 151 grams of mannitol, plus 41 grams of boric acid, plus 0.122 grams of potassium chloride, per liter of solution.

When the standard solution is diluted with distilled water in order to lower its conductivity and obtain higher water resistor values, the temperature coefficient of resistance changes so much that the resistors are no longer satisfactorily neutralized. Therefore, in order to obtain higher resistance values which exhibit satisfactory resistance-temperature characteristics, it is necessary to modify the potassium chloride content relative to the mannitol-boric acid content. A series of experiments was performed to determine the "optimum" ratio of the potassium chloride content to mannitol-boric acid content for resistance values between 10 K ohms and 100 K ohms. A graphical presentation of this relationship was obtained from the experimental data, and an approximate equation was written which describes the relationship accurately. Subsequent experiments were performed to verify that the "optimized formulas" did produce repeatable and reliable results.

Using the equations to determine the optimized formula for any resistance value desired and the appropriate preparation techniques described in the Appendix*, one can prepare a given resistance to be within about 1% to 2% of the desired value. Use of the optimized formula insures that the resulting resistor will exhibit satisfactory resistance-temperature characteristics throughout the temperature range from 50° F. to 160° F. An inconclusive test indicates that there is some drift in characteristics with aging. The exact extent of the drift was not investigated, due to lack of time. The incomplete test indicated that the lower resistance values (10 K to 20 K ohms) were more stable than the higher resistance values (40 K to 80 K ohms). Additional experimental investigation is recommended in order to define the long-term stability characteristic of water resistors using these formulas.

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*See Appendix B.

CHAPTER II

PRELIMINARY INVESTIGATION OF THE WATER-RESISTOR CHARACTERISTICS EMPLOYING MAGNANINI's SOLUTION

Sixteen major experiments were performed in the course of establishing an optimized formula for use in preparing water resistors which employ a modified version of Magnanini's solution. The initial experiments concerned the study of the behavior of the basic Magnanini solution and the effect of using it in the standard plastic resistor containers. Subsequent intermediate experiments define the variations and limitations of Magnanini's solution, and the final experiments describe the optimized solutions that can be used to obtain any desired resistance value in the 10K-ohm to 100K ohm range.

The details of the initial and intermediate experiments will be partially omitted, and only the significant results will be presented, mostly in graphical form. Although one may desire to proceed immediately to the discussion of the final experiments (Experiments 11 through 16) for the purpose of more quickly applying the results of the experiments, it is considered helpful to read the initial results and secure a better over-all understaning of the nature of the problems encountered with these water resistors.

Experiment 1, entitled "Thermal Characteristics of the Resistor Units When Subjected to Abrupt Temperature Changes," was for the purpose of determining the necessary time interval between successive resistance-temperature measurements after setting a new temperature step in the automatic controller for the temperature test chamber. Although it was stated above that much of the detail would be omitted from the discussion of the initial experiments, some detail is necessary here in order to prepare for subsequent discussions. A complete equipment list is given in the appendix*.

In all of the experiments described, the general procedure was the same; a group of specially prepared water resistors was placed inside an environmental test chamber with each resistor provided with leads connecting it to a terminal board outside the test chamber where an a.c. impedance bridge was used to measure its resistance at specific values of temperature. A thermocouple bridge was used to measure the temperature inside the test chamber. The resistors were normally cycled in steps through the temperature range of 40°F to 160°F with a complete temperature cycling taking about one to thirty-nine hours, depending upon the magnitude of each temperature step. Usually each test would require several days, since readings were not usually taken between midnight and early morning.

In Experiment 1, the environmental test chamber was first provided with a flat aluminum plate, supported by four ceramic insulators, for holding, in a vertical position, twenty-five water resistor units in plastic containers of the type illustrated in Figure 2, Chapter 1. This metal plate

*See Appendix C

also acts as the common electrode for all the resistors during the testing of resistance-temperature characteristics. Each of the twenty-five resistors was provided with a suitable length of test-lead wire connecting its additional electrode to a terminal board located external to the test chamber. The test leads were numbered according to the 1-to-25 scheme used on both the terminal board and the common metal plate. A 26th wire was brought out of the test chamber to the terminal board and connected internally to the "common" metal plate. Thus, the 1000-cycle, a.c. resistance of each water resistor could be measured with the impedance bridge by merely connecting to the appropriate terminals on the terminal board. In order to be certain that the additional lead length did not affect the bridge measurements, known values of resistance (10K to 100K ohms) were measured first connected directly across the bridge terminals, and again connected at the end of the leads inside the test chamber. No noticeable difference between the two readings was experienced regardless of the resistance value within the above specified range.

Resistors under test were assigned numbers corresponding to their position on the metal plate inside the test chamber; e.g. R_1, R_2, etc. When two identical resistors were used, their average resistance was denoted as R_{1-2}, R_{3-4}, etc.

The temperature inside the test chamber was monitored with a thermocouple bridge. The thermocouple was inserted through the end cap of one of the filled resistors and located at about the center of the contained liquid. Thus, the temperature indicated was that of the electrolyte inside the water resistors.

With the test chamber loaded with a sufficient number of water resistors, the automatic temperature controller was set to provide a step change in the test-chamber temperature. The resulting transient effect in temperature was measured with the thermocouple bridge, and also by noting the time variation in resistance of a potassium chloride solution used in one of the resistor containers located inside the test chamber. Using temperature steps of various magnitudes, the effect of both positive and negative steps in temperature was noted.

The significiant results of the experiment are presented graphically in Figures 3, 4, and 5. In each figure is shown the temperature-time--and the resistance-time--variations of the solutions under test. Each curve indicates a thermal time constant of such a magnitude that one must allow at least a one-hour interval between a change-in-temperature setting and a set of resistance measurements, in order to let the resistor temperature stabilize. The curves indicate that this time constant prevails for both positive and negative temperature steps, regardless of the average temperature level, and for temperature steps in excess of 50°F. The results of this experiment pointed up the necessity for waiting,

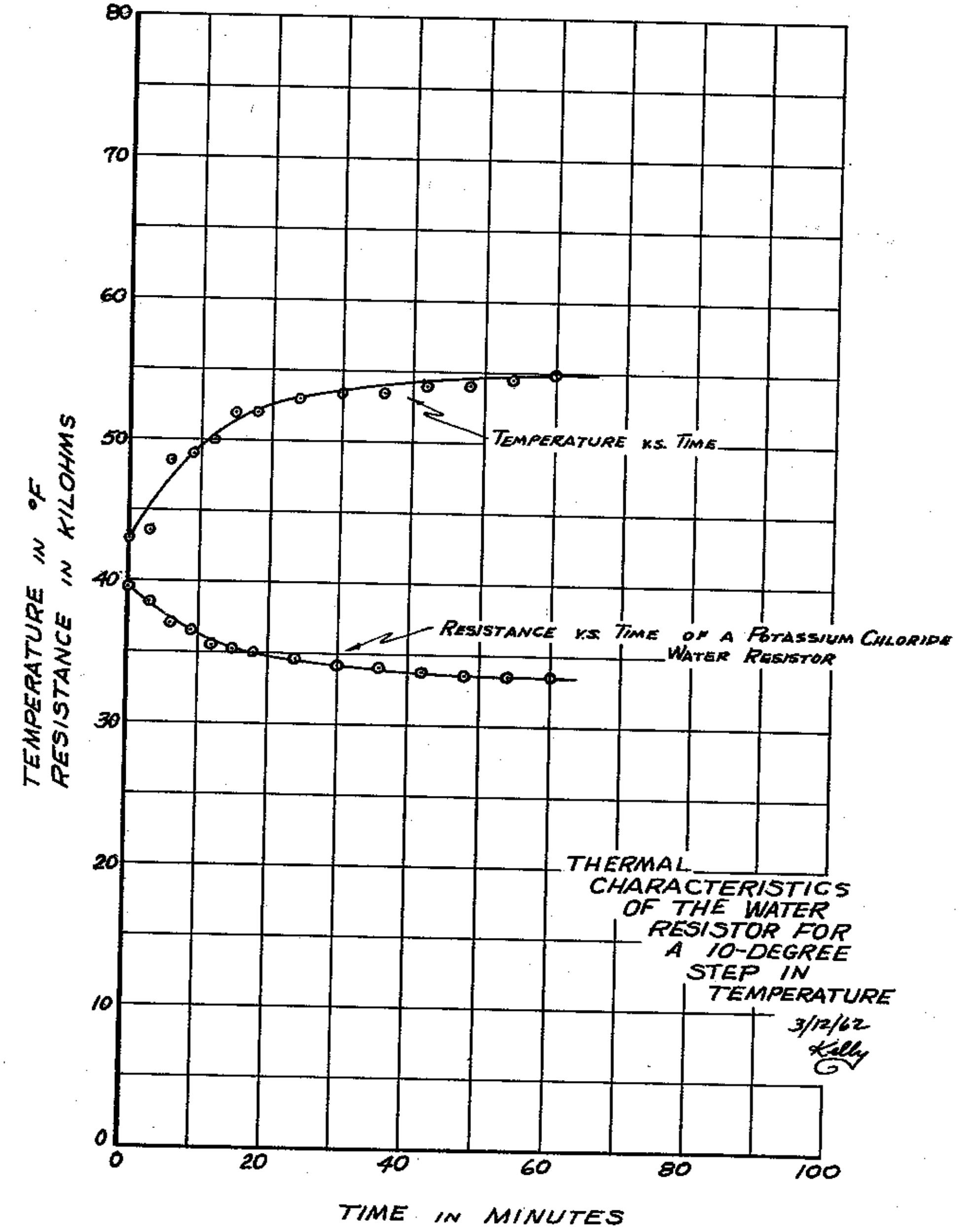


Figure 3. Thermal Characteristics of the Water Resistor Subjected to a 10^{o}F. -Step Increase in Temperature

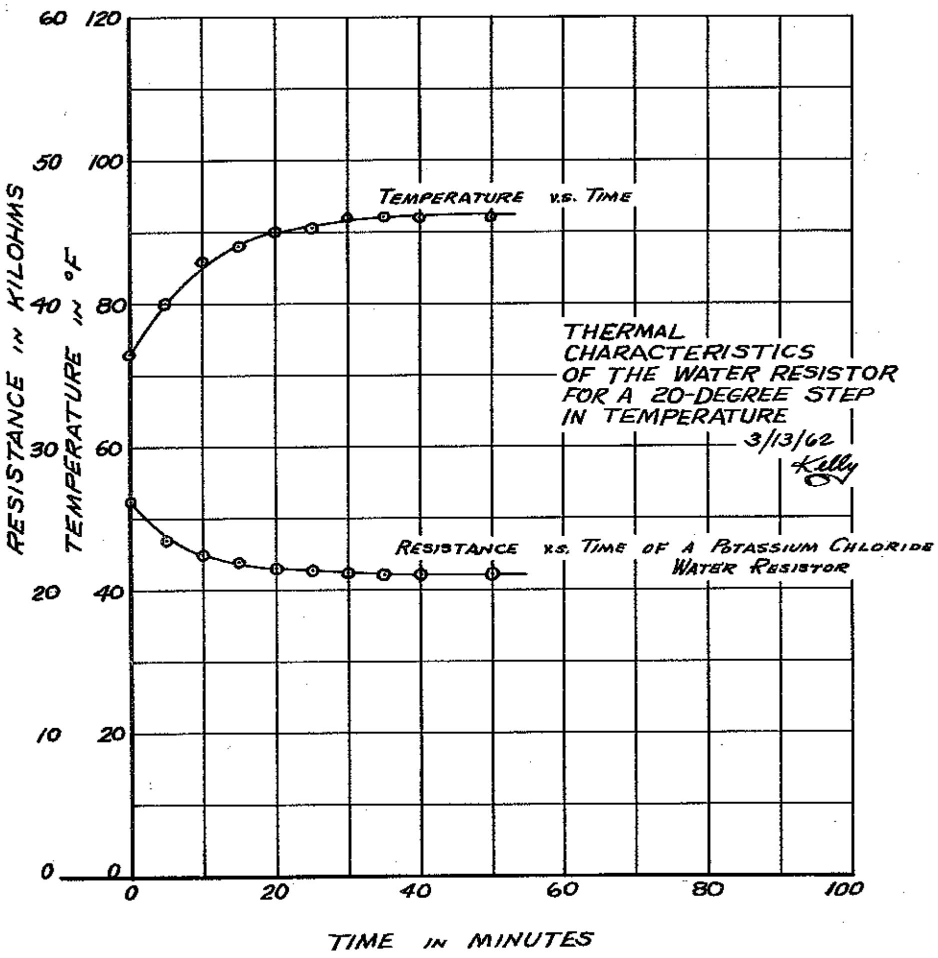


Figure 4. Thermal Characteristics of the Water Resistor Subjected to a 20°F. -Step Increase in Temperature

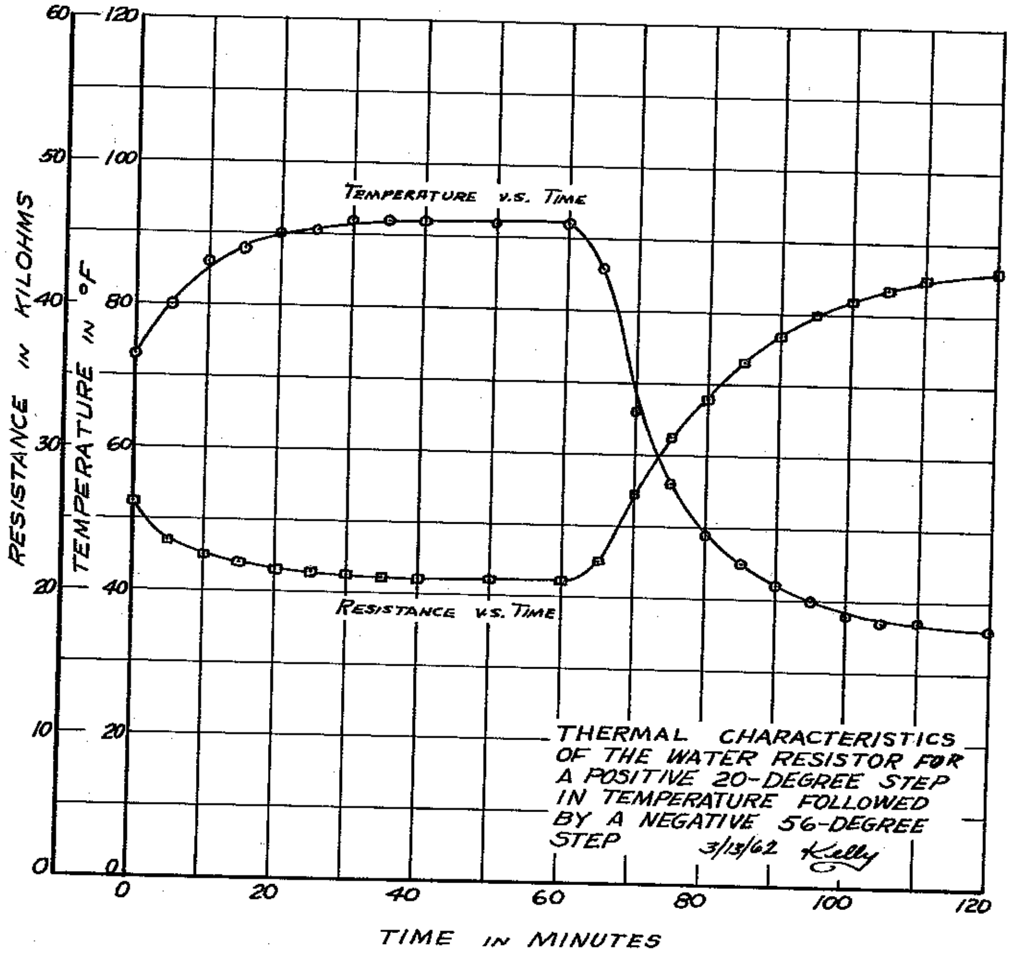


Figure 5. Thermal Characteristics of the Water Resistor Subjected to a 20°F. -Step Increase in Temperature, Followed by a 56°F. -Step Decrease in Temperature

after a temperature change had been made, for at least a one-hour period. In all subsequent experiments, no readings were taken in which the time between the readings and the previous temperature change was less than one hour.

Experiment 2, entitled "Characteristics of Magnanini's Solution--Variation of Potassium Chloride Content," was performed to determine how the potassium chloride content affects the resistance-temperature characteristics of a water resistor using the basic Magnanini solution. The basic Magnanini's solution consists of 121 grams of mannitol ($C_6H_{14}O_6$), plus 41 grams of boric acid (H_3BO_3), plus 0.04 grams of potassium chloride (KCl), per liter of solution.

The accurate control of the potassium chloride content poses a problem because the analytical balance used in the experiment cannot accurately measure the minute quantities of granular potassium chloride needed unless large volumes of Magnanini's solution are prepared. This is true not only because of the granular nature of the potassium chloride, but also because the analytical balance could not repeat measurements to within better than ± 1 milligram. Therefore, a scheme was devised whereby the smallest quantity of potassium chloride that it would be necessary to prepare would be in the order of 1/2 to 1 gram (500 to 1000 milligrams). This scheme requires that two large quantities of similar solutions be prepared; one solution containing the correct ratio of mannitol and boric acid, but not potassium chloride; and the second solution containing the correct ratio of mannitol and boric acid, but excessive potassium chloride. The first solution, Solution A, contains 121 grams of mannitol and 41 grams of boric acid per liter of solution. The second solution, Solution B, contains 242 grams of mannitol, 82 grams of boric acid, and 0.800 grams of potassium chloride dissolved in two liters of solution. It should be noted that both Solution A and Solution B contain the same ratios per liter of mannitol and boric acid. Thus, by combining various amounts of Solution A and Solution B, it is possible to obtain a composite solution which contains any desired potassium chloride content from 0.00 to 0.80 grams per liter.

Table I was compiled to facilitate in the preparation of the solutions containing various contents of potassium chloride. Although the preparation procedure outlined in Table I calls for a 100-ml volumetric flask, perhaps a better and more convenient method of preparation makes use of burettes. If burettes are used to measure the required portions of Solution A and Solution B, only two burettes will be necessary and the composite solutions can be mixed in ordinary beakers. In this manner, numerous solutions can be prepared with a minimum of effort.

Fourteen plastic containers of the type illustrated in Fig. 2, Ch. 1, were available for use in this experiment. (For final experiments, 34 containers were available.) Since each resistor requires approximately 20 milliliters of solution,

TABLE I

PREPARATIONS OF SOLUTIONS USING THE BASIC MAGNANINI'S FORMULA WITH VARIOUS VALUES OF POTASSIUM CHLORIDE CONTENT

	Mannitol Content Per 100 ml	Boric Acid Content Per 100 ml
	12.10 grams	4.10 grams
Solution Number	**Potassium Chloride Content per 100 ml**	**Solution B Content per 100 ml**
00	0.000 grams	0.00 ml
01	0.001	2.50
02	0.002	5.00
03	0.003	7.50
04	0.004	10.00
05	0.005	12.50
06	0.006	15.00
07	0.007	17.50
08	0.008	20.00
09	0.009	22.50
10	0.010	25.00

Preparation of Solution A:

121.0 grams Mannitol

41.0 grams Boric Acid

Dilute with distrilled water to 1 liter(1000 ml)

Preparation of Solution B

0.800 grams Potassium Chloride

242.0 grams Mannitol

82.0 grams Boric Acid

Dilute with distilled water to 2 liters (2000 ml)

Preparation of Solutions 00 through 10:

In a 100 ml volumetric flask, add the prescribed amount of Solution B measured accurately with a microburette. Dilute this with Solution A to 100 milliliters.

four resistors can be easily prepared from the 100 ml amounts prescribed in Table I. Because of the limited number of resistor containers, only three different solutions were tested in the temperature test chamber at a time. On the first run of the experiment, three of the solutions given in Table I were used; one with Magnanini's basic formula (solution 04), one with twice the KCl content as Magnanini's basic formula (solution 08), and another with zero KCl-content (solution 00). Since these three solutions required the use of twelve plastic containers in order to have four resistors of each of the three solutions, the remaining two containers were used respectively for temperature measurements and for obtaining data on a solution containing only potassium chloride and distilled water. The units thus prepared were placed in the temperature chamber and carried through the temperature range from about 150°F down to about 40°F. In a second experimental run, other solutions with different KCl concentrations (solutions 01, 06 and 10) were evaluated as a function of temperature in a similar manner with one notable exception; in this second case, the resistors were cycled in approximately 10° steps from about 150°F down to 40°F then back up to 140°F.

The data for the above two experimental runs are presented graphically in Figures 6 and 7, respectively. Note that the basic Magnanini formula (solution 04) shown in Figure 6 gives a resistance value of approximately 12K ohms and is not, as a function of temperature, the most constant resistance tested. Of the six solutions tested, Solution 10 with 0.10 grams of potassium chloride per liter appears to possess the most desirable resistance-temperature characteristics.

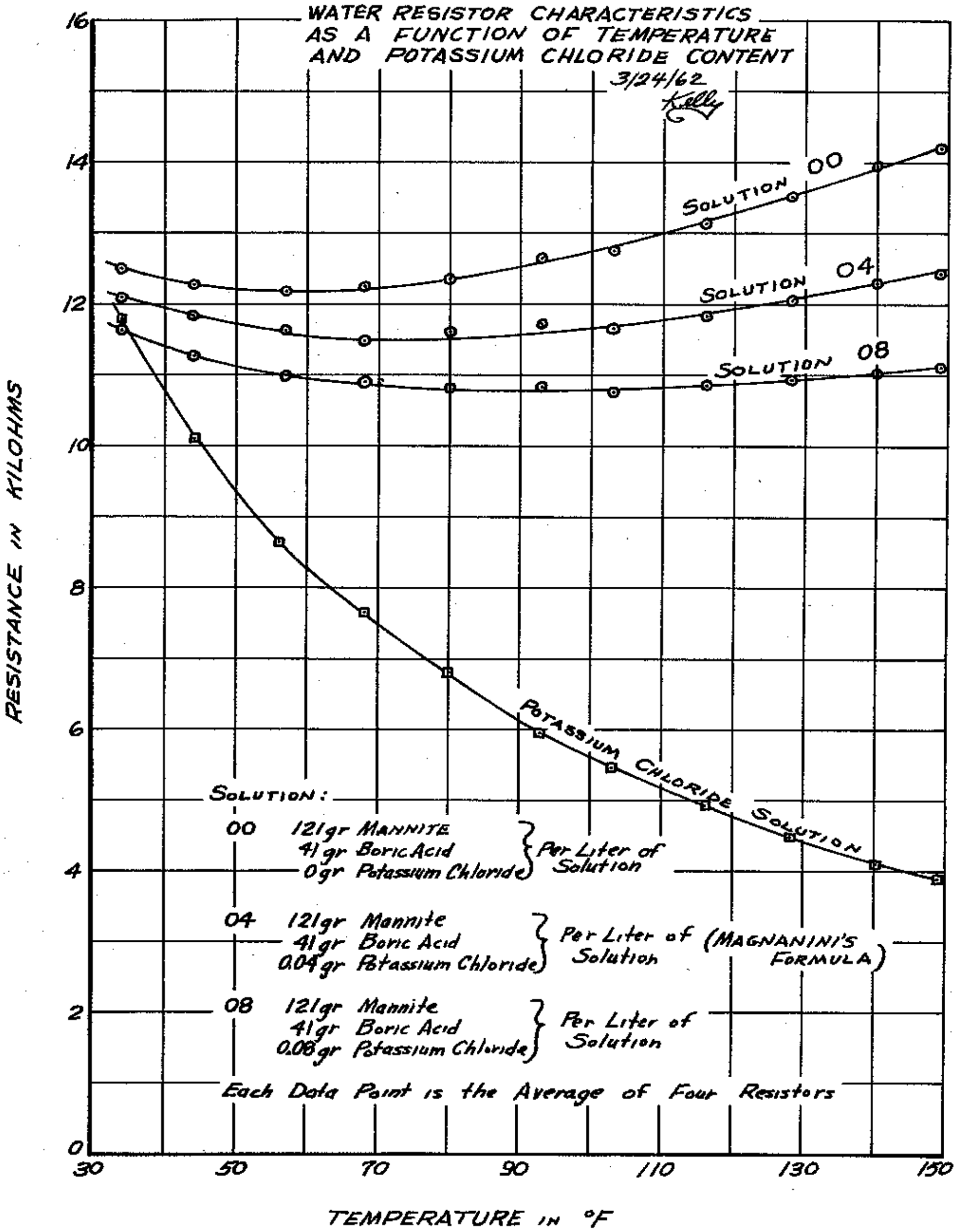
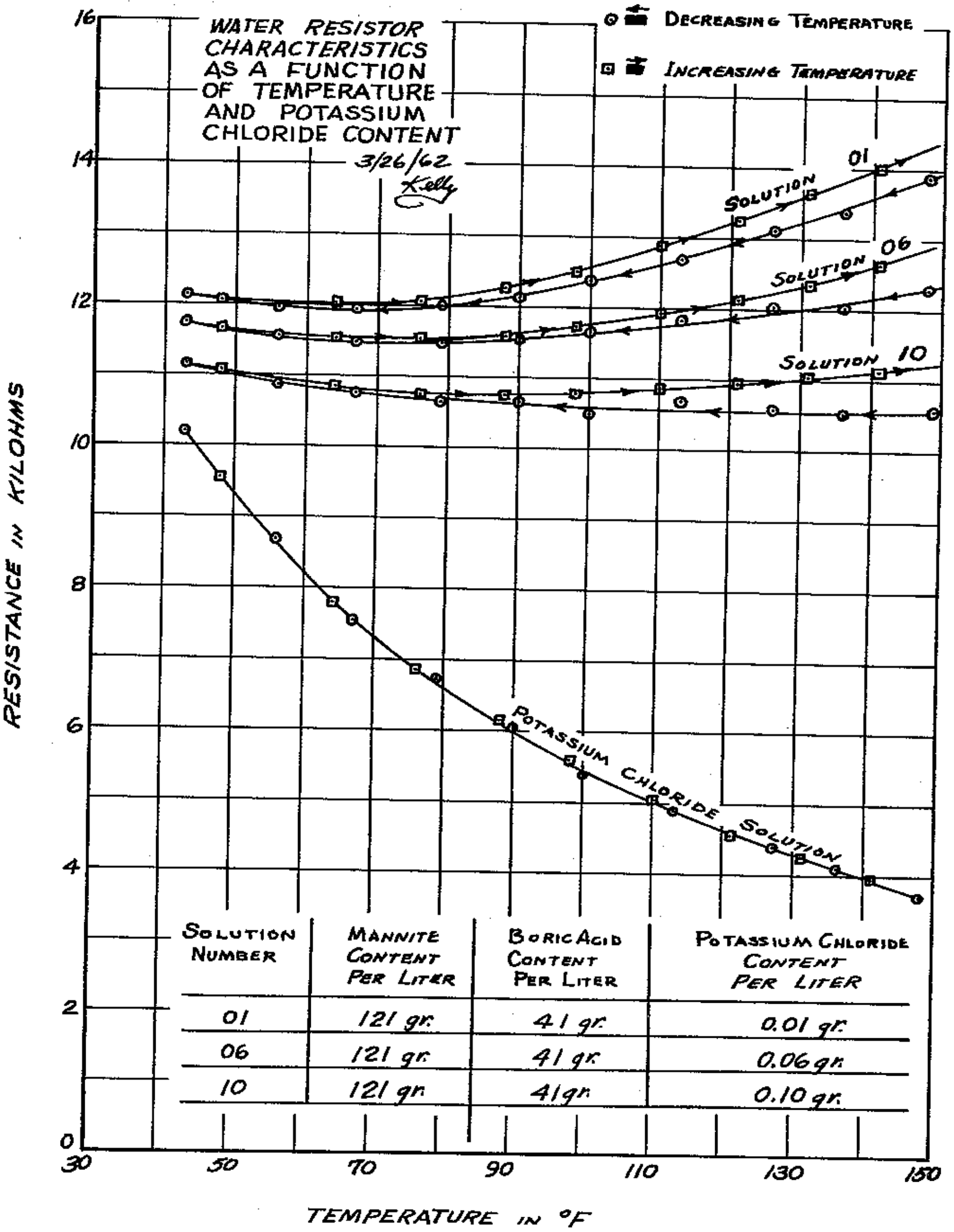


Figure 6. The Effect of Potassium Chloride Content Upon the Resistance-Temperature Characteristics of Water Resistors Which Use Magnanini's Solution.



SOLUTION NUMBER	MANNITE CONTENT PER LITER	BORIC ACID CONTENT PER LITER	POTASSIUM CHLORIDE CONTENT PER LITER
01	121 gr.	41 gr.	0.01 gr.
06	121 gr.	41 gr.	0.06 gr.
10	121 gr.	41 gr.	0.10 gr.

Figure 7. The Effect of Potassium Chloride Content for Both Increasing and Decreasing Temperature Cycles, Upon the Resistance-Temperature Characteristics of Water Resistors Which Use Magnanini's Solution.

Each of the resistance-temperature characteristics exhibit a minimum resistance in the 60°F-to-90°F range with higher resistance being experienced at both the lower temperatures (about 40°F) and at the higher temperatures (about 150°F). Also of interest is the relative characteristic of a potassium chloride solution shown in each figure. The superior resistance-temperature characteristics of Magnanini's solution is noticeably demonstrated in comparison to the potassium chloride solution.

It should be pointed out that at the time Experiment 2 was performed, the end caps of the plastic resistor containers were not provided with the thermal expansion chambers as illustrated in Figure 2, Chapter 1, but rather were completely solid with no provision whatever for thermal expansion of the electrolyte. In fact, after the resistor units had been cycled to elevated temperatures in this experiment, crystals of the various chemicals were found encrusted around the top end cap, indicating that some of the electrolyte had been forced out around the O-ring seals, due to the pressure of thermal expansion. Much of the cause for the non-repeatibility of the resistance-temperature curves illustrated in Figure 7 is a result of the thermal expansion problem. However, not all of the non-repeatibility of the characteristics can be attributed to thermal expansion since the potassium chloride solution shows good repeatibility and yet it was subjected to the same temperature cycle (but perhaps not to the same thermal expansion).

Although the resistance-temperature characteristics obtained in Experiment 2 is representative of the relative effect upon resistance that is obtained as the potassium chloride content is varied, the results cannot be considered repeatable because of the thermal expansion problem existing when this experiment was performed. Although additional experiments were performed before the thermal expansion problem was solved, the results of these experiments are considered only relative, or qualitative, and no quantitative conclusion should be drawn from them.

Experiment 3, entitled, "Water Resistor Characteristics as a Function of Dilution," was performed to determine if a simple procedure, such as diluting Magnanini's standard solution with distilled water, would allow one to obtain higher resistance values which were still neutralized with regard to temperature coefficient of resistance. Also, investigated in this experiment was the possibility of eliminating some of the non-repeatability of the resistance-temperature characteristics by removing most of the gases entrapped in the electrolyte. This latter investigation was prompted by the appearance of many small bubbles clinging to the inside walls of the plastic container after the resistor had been subjected to a temperature cycle. The entrapped gases were eliminated by first temperature cycling the electrolytic solutions in an open container before the solution was poured into the plastic resistor containers. This precaution did eliminate the bubbles which formed on the resistor walls; however, it did not solve the problem of the large bubble that forms at the top of the resistor around the electrode. This large bubble was largely a result of the thermal expansion forcing some of the electrolyte out of the container at elevated temperatures.

Using solution 10, Table I, as the standard solution, because it possessed the smallest temperature coefficient of resistance of the samples evaluated in Experiment 2, various amounts of distilled water were added in order to obtain diluted versions of this standard solution which had higher resistance values.

Four different concentrations of Solution 10 were tested; 100%, 50%, 33-1/3%, and 25%. The results of the resistance-temperature data for these solutions are presented graphically in Figure 8. The significant aspects of these curves are their change in slope with concentration. The more dilute solutions have a noticeable change in resistance with temperature. The 25% solution has a total change in resistance of 8.4K ohms over the temperature range of 40°F to 150°F, a 16.6% change compared to its 90°F value. It is evident from these curves (Fig. 8) ~~that~~ high resistance values cannot be obtained by merely diluting the standard solution with distilled water, especially if the temperature coefficient of resistance must be maintained low. Results of subsequent experiments (Experiments 11 through 16) show that the

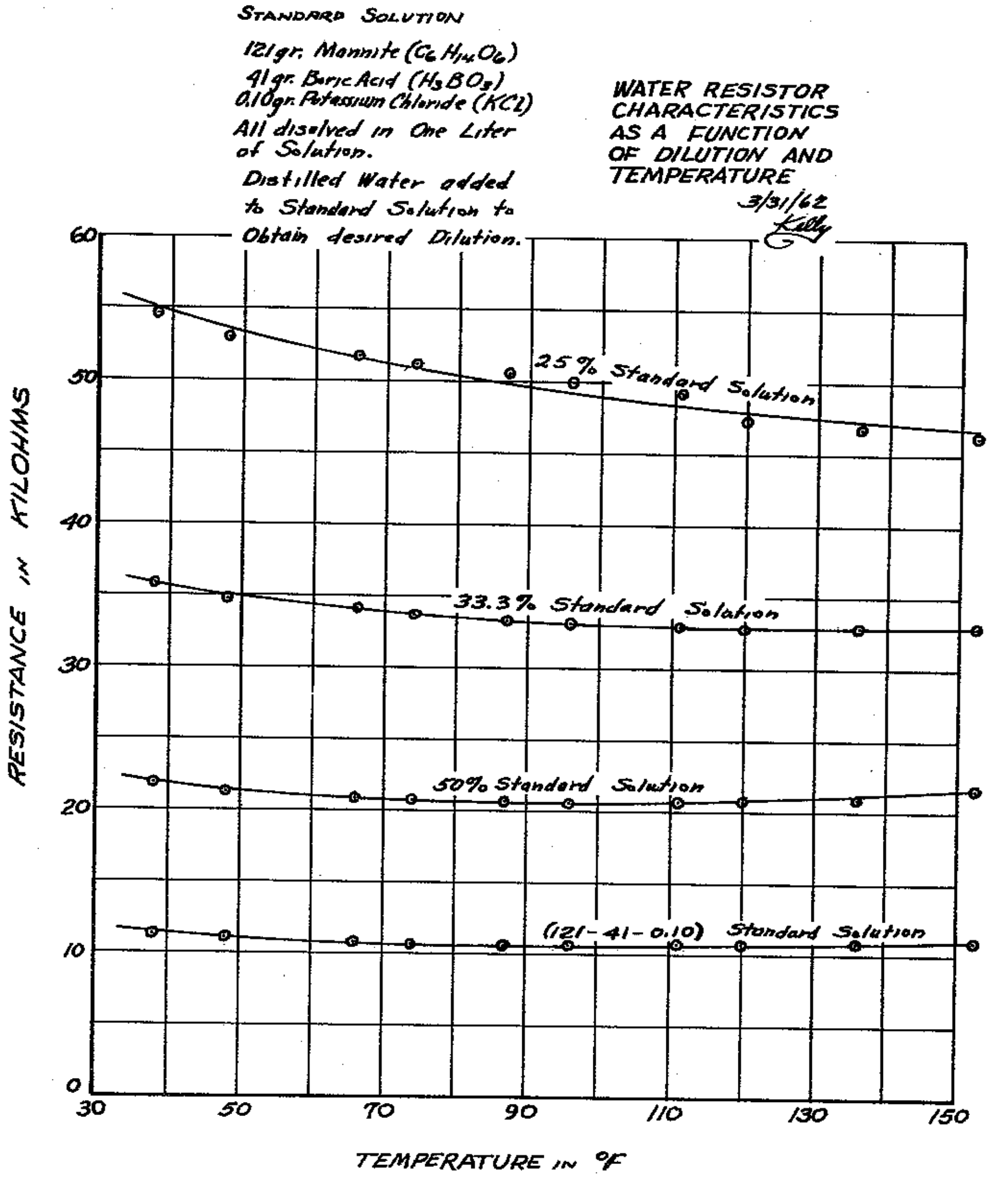


Figure 8. The Effect that Dilution with Distilled Water has Upon the Resistance-Temperature Characteristics of Water Resistors Which use a Modified Version of Magnanini's Solution.

potassium chloride content must be reduced more than the mannitol-boric acid content is reduced in order to obtain high resistance values which possess a low temperature coefficient of resistance.

The curves shown in Figure 9 illustrate the results obtained in Experiment 3 when the electrolyte is pre-heated before preparing the resistor units. The pre-heating cycle consists of placing an open beaker containing the solution inside the temperature chamber and raising the temperature to 140°F for a one-hour period. After cooling the solution to room temperature, the resistor units are prepared. This pre-heating technique eliminates the formation of bubbles on the inside walls of the water resistor, but as the curves in Figure 9 indicate, there is negligible difference between the preheated and non-preheated resistance characteristics. Although not shown on the curves of Figure 9, all three resistor units were cycled completely through the temperature range from 150°F down to 40°F (illustrated) and back up again (not illustrated). The portion of the cycle from 40°F back up to 150°F on the second half of the temperature cycle is not shown because the points were so nearly identical that including this data would have unnecessarily complicated the graph. This test, therefore, did not indicate that preheating of the electrolyte improved the characteristics of the resulting resistor in any appreciable way. Consequently, heating of the electrolyte was discontinued in later experiments after the thermal expansion problem was solved.

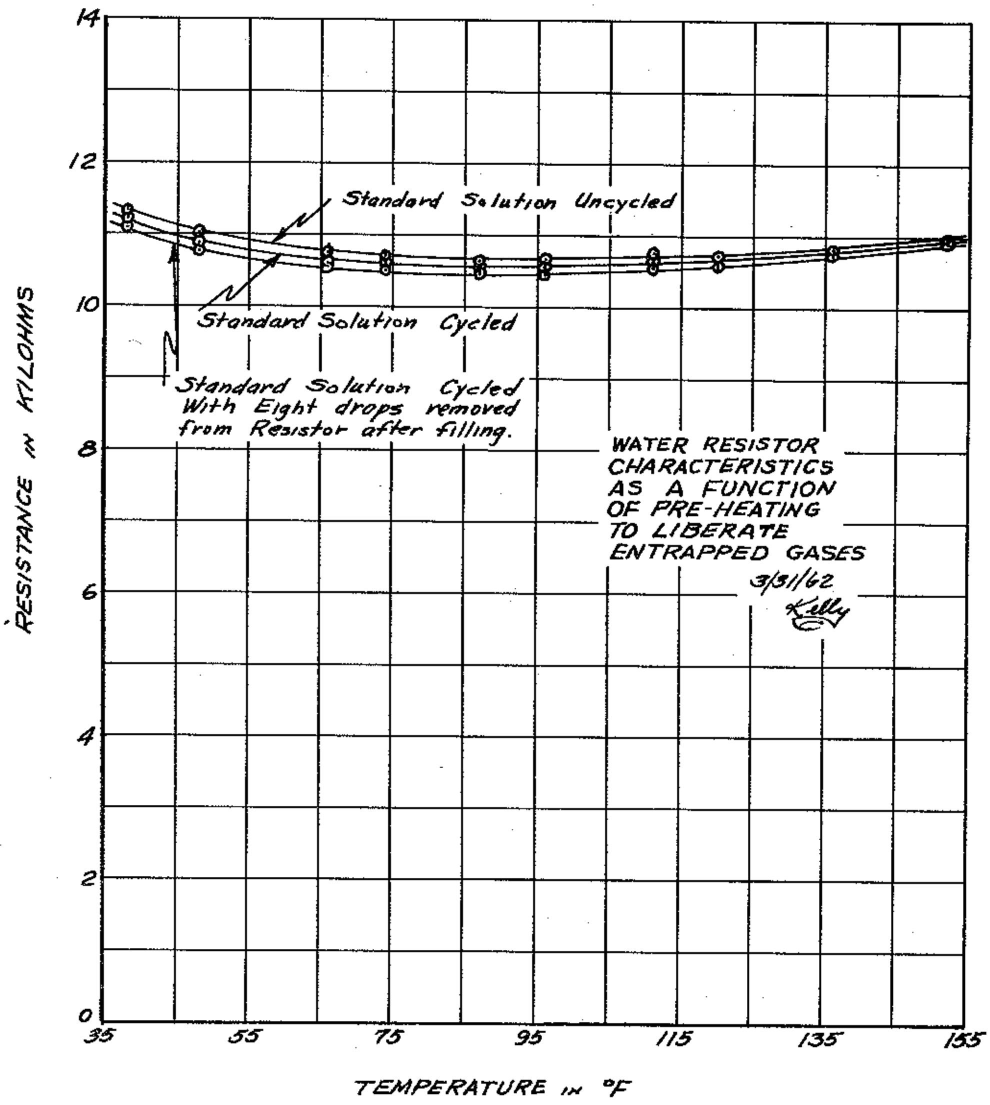


Figure 9. The Effect that Pre-heating of the Electrolyte to Liberate Entrapped Gases has Upon the Resistance-Temperature Characteristic of Water Resistors Which Use a Modified Version of Magnanini's Solution.

Experiment 4, entitled "Evaluation of Thermal Expansion Chamber," was performed to prove that the thermal expansion problem had been solved by channeling the end caps of the resistor containers as illustrated in Fig. 2, Chapter 1. The end cap was originally constructed without the thermal expansion chamber. As initially constructed, the end cap seated firmly against the end of the jacket and the large O-ring. An additional O-ring fits between the electrode and the end cap to prevent electrolyte leakage there. The thermal expansion chamber was added in the form of an annular chamber around the electrode assembly. The chamber is 0.27 inches deep and is cut in such a manner that a large volume is provided for expansion, and yet sufficient plastic is left to insure proper seating of the end cap against the end of the jacket and large O-ring. An expansion chamber is provided in each end cap so that the resistor may be operated in the vertical position with either end at the top. This design of a thermal expansion chamber requires that the resistor be operated in a vertical position. Perhaps a better end-cap design would be desirable which would provide more mechanical strength than the make-shift design used in modifying the end caps for this experiment and allow for operation in some position other than vertical.

In order to compare the characteristics of a set of resistors provided with thermal expansion chambers with another set without such provisions, two sets of four resistors each were prepared using identical electrolyte--one set with expansion chambers as described above, and the other set without expansion chambers. The results of the experiment were rather unexpected. The characteristic curves of each set, shown respectively in Figures 10 and 11, seem to be practically identical, even though each set was cycled together twice through the temperature range of about 40°F to 150°F. Both sets of resistors show a spread of less than 5% at any given temperature (3.1% at 90°F for the channeled cap set and 2.78% at 90°F for the unchanneled set). Yet, there is a difference between the two sets which doesn't appear in the graphical presentation: it is the formation of a crust around the top cap of the un-channeled set. Such an unpredictable situation, with the amount of electrolyte being forced out past the O-rings at elevated temperatures, cannot be tolerated. Thus, all subsequent experiments were performed using resistors provided with thermal expansion chambers in the end caps, even though the single experiment, which was designed to prove the superiority of resistors provided with the thermal expansion chambers, was inconclusive. Even when the channeled-cap units were operated at 160°F, a visual inspection proved that the expansion chamber was not completely filled with electrolyte, but could tolerate operation at an even higher temperature without forcing electrolyte out past the O-ring seals. This, and the fact that no crust formed about the top end-cap of the channeled resistors,

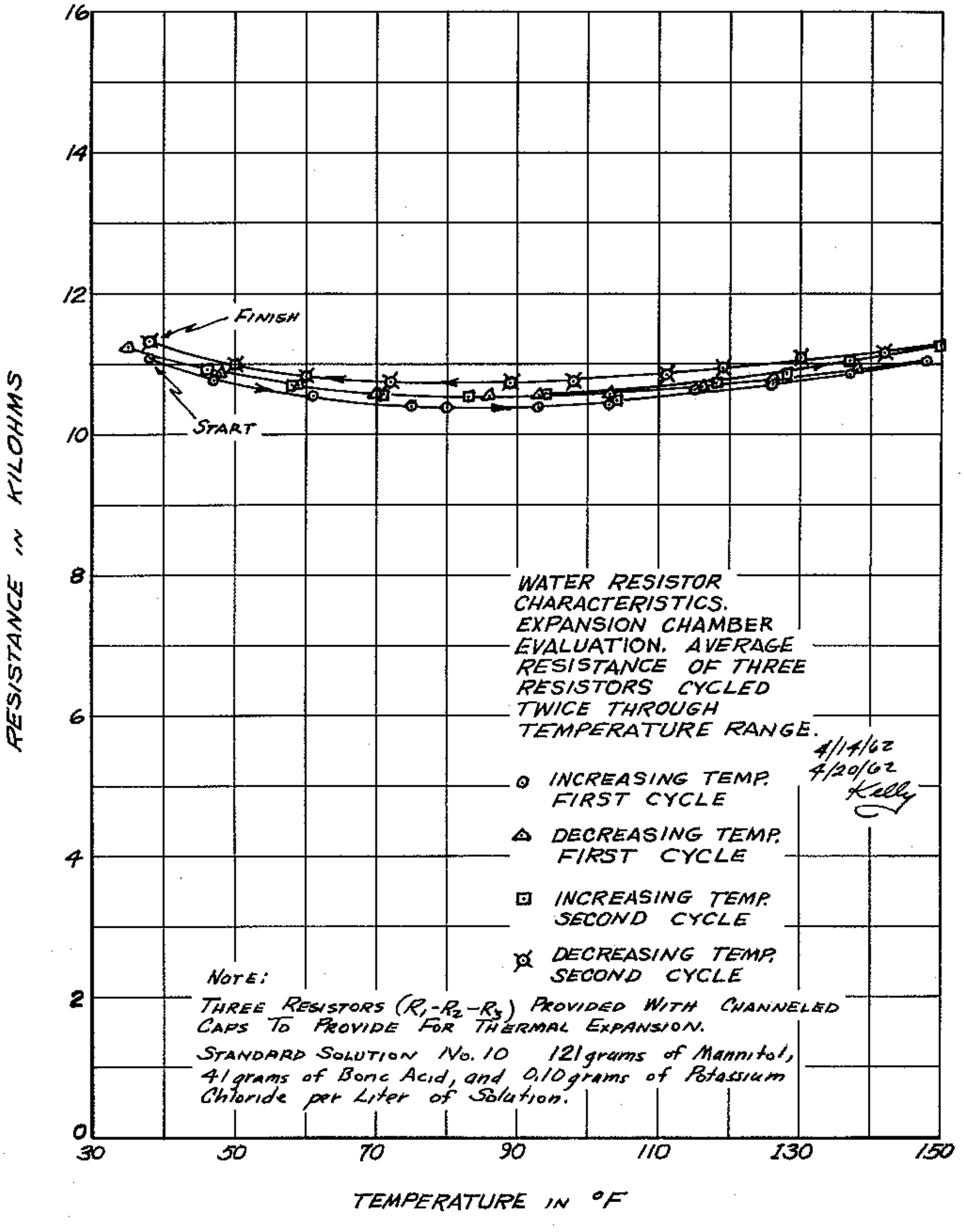
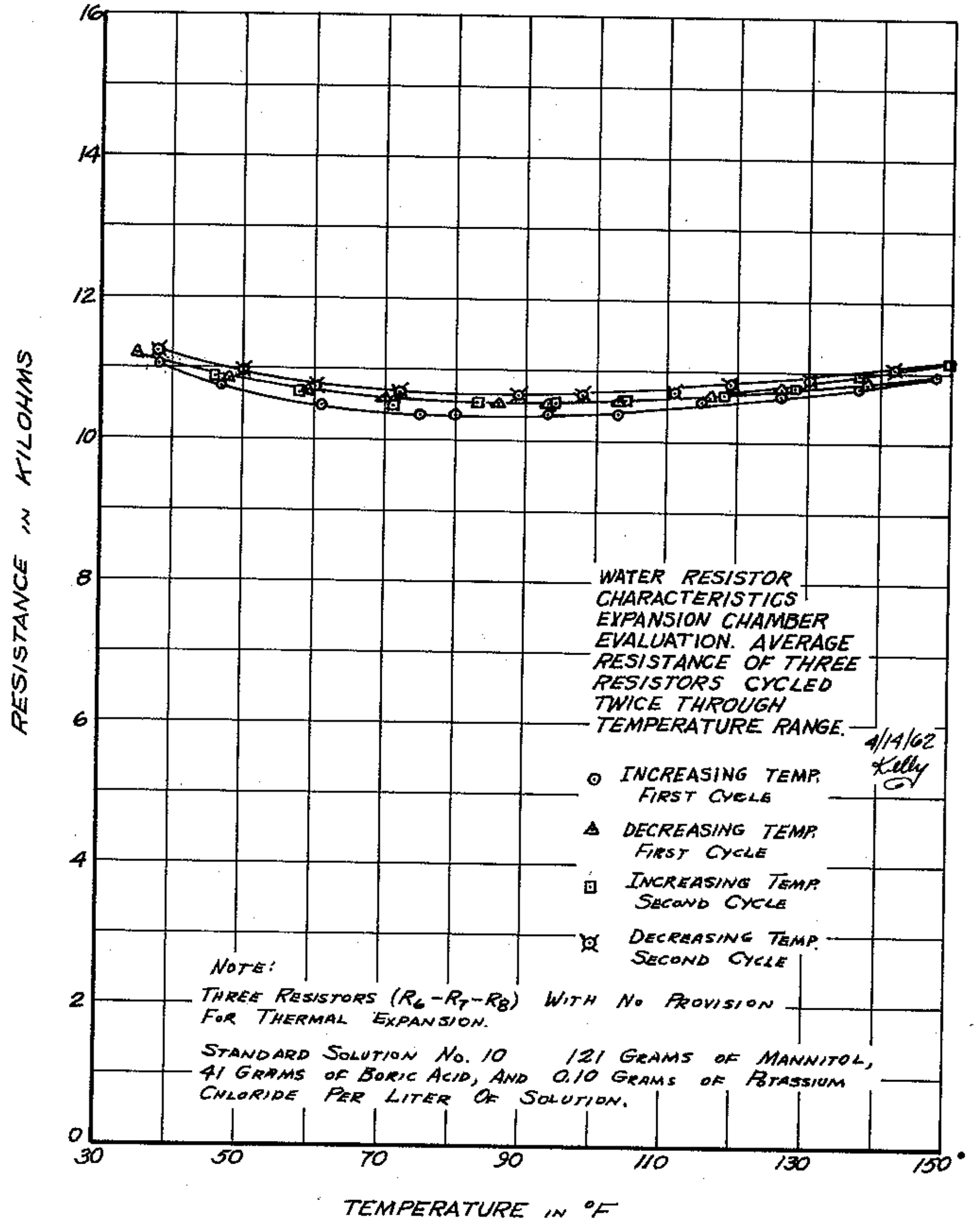


Figure 10. Average Resistance-Temperature Characteristics of Three Resistors Provided with Expansion Chambers, Cycled Twice Through 40°F. to 150°F. Temperature Range.



WATER RESISTOR CHARACTERISTICS EXPANSION CHAMBER EVALUATION. AVERAGE RESISTANCE OF THREE RESISTORS CYCLED TWICE THROUGH TEMPERATURE RANGE.

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NOTE:
THREE RESISTORS ($R_6 - R_7 - R_8$) WITH NO PROVISION FOR THERMAL EXPANSION.

STANDARD SOLUTION No. 10 121 GRAMS OF MANNITOL, 41 GRAMS OF BORIC ACID, AND 0.10 GRAMS OF POTASSIUM CHLORIDE PER LITER OF SOLUTION.

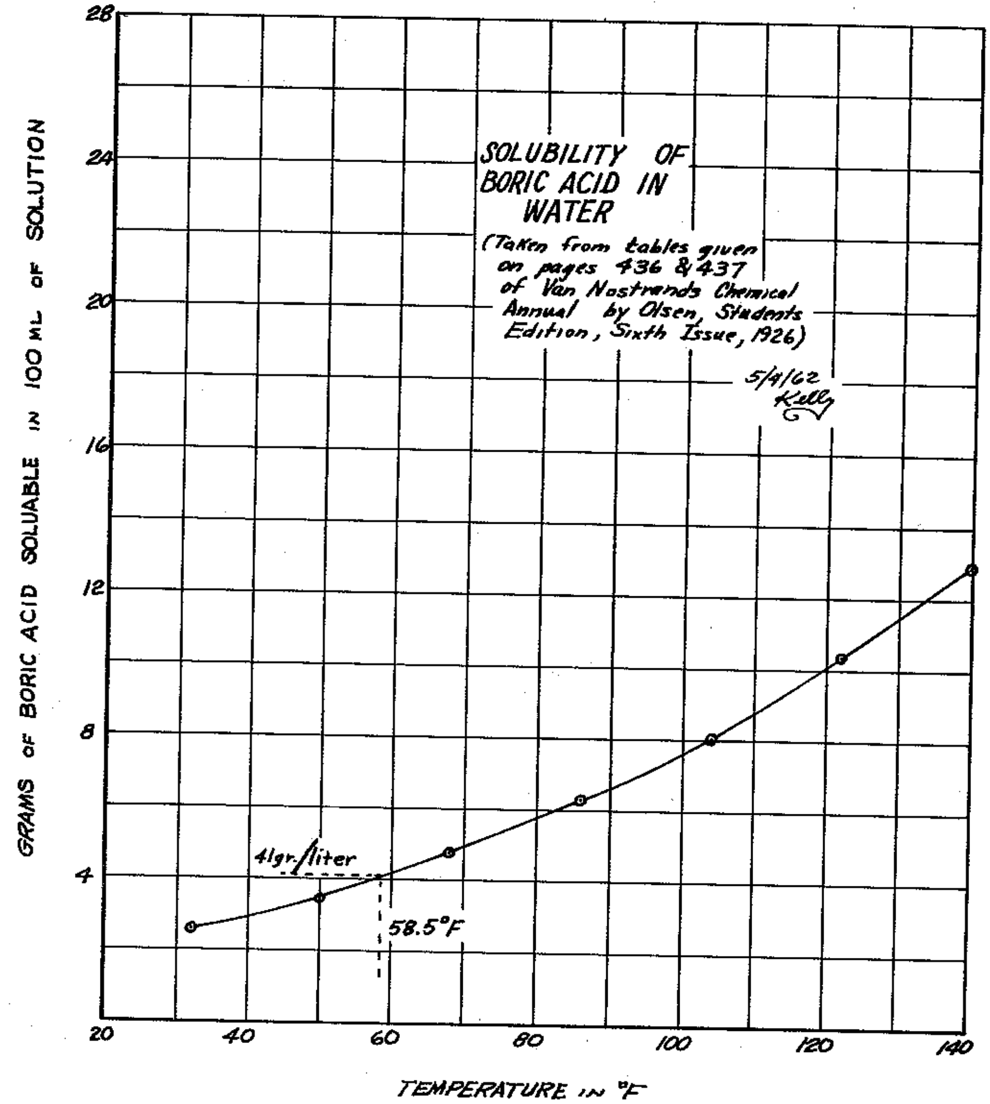
Figure 11. Average Resistance-Temperature Characteristics of Three Resistors, not Provided with Expansion Chambers, Cycled Twice Through 40°F. to 150°F. Temperature Range.

was proof enough that the modification to the caps was justified. After the thermal expansion problem was successfully solved, the data obtained in subsequent experiments could be accepted with confidence.

Experiment 5, entitled "Search for a Mannitol-Boric Acid Content that Allows Resistance Values of 10K ohms or less," was performed to determine if a more conductive solution could be obtained by increasing the mannitol content above the value called for in Magnanini's formula. The basic Magnanini's formula provides a resistance value, which at its lowest point, is in excess of 10K ohms. Since it was evident that resistance values much less than 10K ohms would not be possible with Magnanini's solution, it was decided to at least modify the basic formula to such an extent that resistance values from 10K ohms to 100K ohms would be possible.

A search of the chemical handbook[5] provided information concerning the solubility of boric acid in distilled water. Figure 12 presents a curve relating the solubility of boric acid in water to temperature. The 41 grams per liter of boric acid called for in Magnanini's formula is indicated as being saturated at about 58.5°F. Whether additional boric acid could be dissolved in the solution, because of some effect brought about by the presence of mannitol in the solution, was not investigated. However, the same chemical handbook indicated that 206.6 grams of mannitol was soluble in one liter of water at 24° C. Based upon this information, it was

[5] Olsen, John C., Van Nostrands Chemical Annual, Student's Edition, Sixth Issue, 1926, pp 436, 437.



SOLUBILITY OF BORIC ACID IN WATER

(Taken from tables given on pages 436 & 437 of Van Nostrands Chemical Annual by Olsen, Students Edition, Sixth Issue, 1926)

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Figure 12. Solubility of Boric Acid in Distilled Water

decided that Experiment 5 would be performed to determine how much additional mannitol could be added to the basic Magnanini's Solution and whether an increased mannitol content would increase the conductivity sufficiently to allow resistors of less than 10K ohms to be prepared.

By taking the ratio of mannitol to boric acid in the standard Magnanini's formula, one obtains a value of 121/41 = 2.951. Other values of this ratio from 50% to 125% of the standard value were calculated for use in Experiment 5. If the boric acid content is maintained constant, the 50%, 75%, 100%, and 125% ratios of mannitol to boric acid become, respectively, 60.5/41, 90.6/41, 121/41, and 151.2/41. An additional ratio of 180/41 was later added to the experiments. Solutions were mixed according to the above ratios of mannitol to boric acid; no potassium chloride was used in this experiment. Three resistors of each ratio were prepared, except for the 180/41-ratio which was added later. After the first group of resistors were prepared, they were cycled from approximately 150°F down to about 40°F in 10° steps. In order to have resistor containers in which to prepare the 180/41 solution, the 60.5/41 ratio was eliminated from the experiment, and the new group of resistors and the remaining old group of resistors were cycled back up in temperature from 40°F to 150°F. The results of these tests are presented graphically in Figures 13 and 14 which show the resistance-temperature characteristics and the conductance-temperature characteristics,

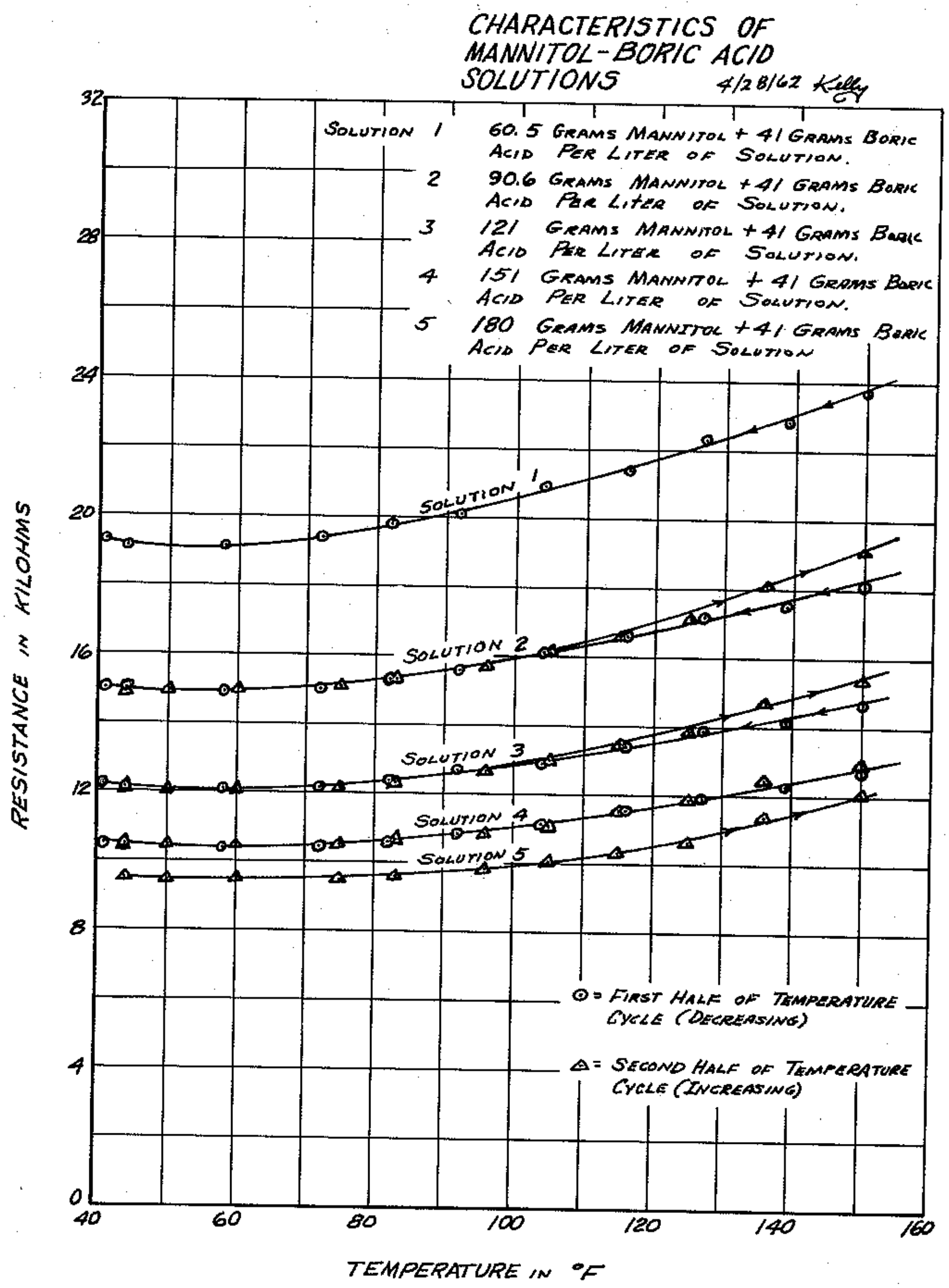


Figure 13. The Effect of Mannitol Content Upon the Resistance-Temperature Characteristics of Mannitol-Boric Acid Solutions

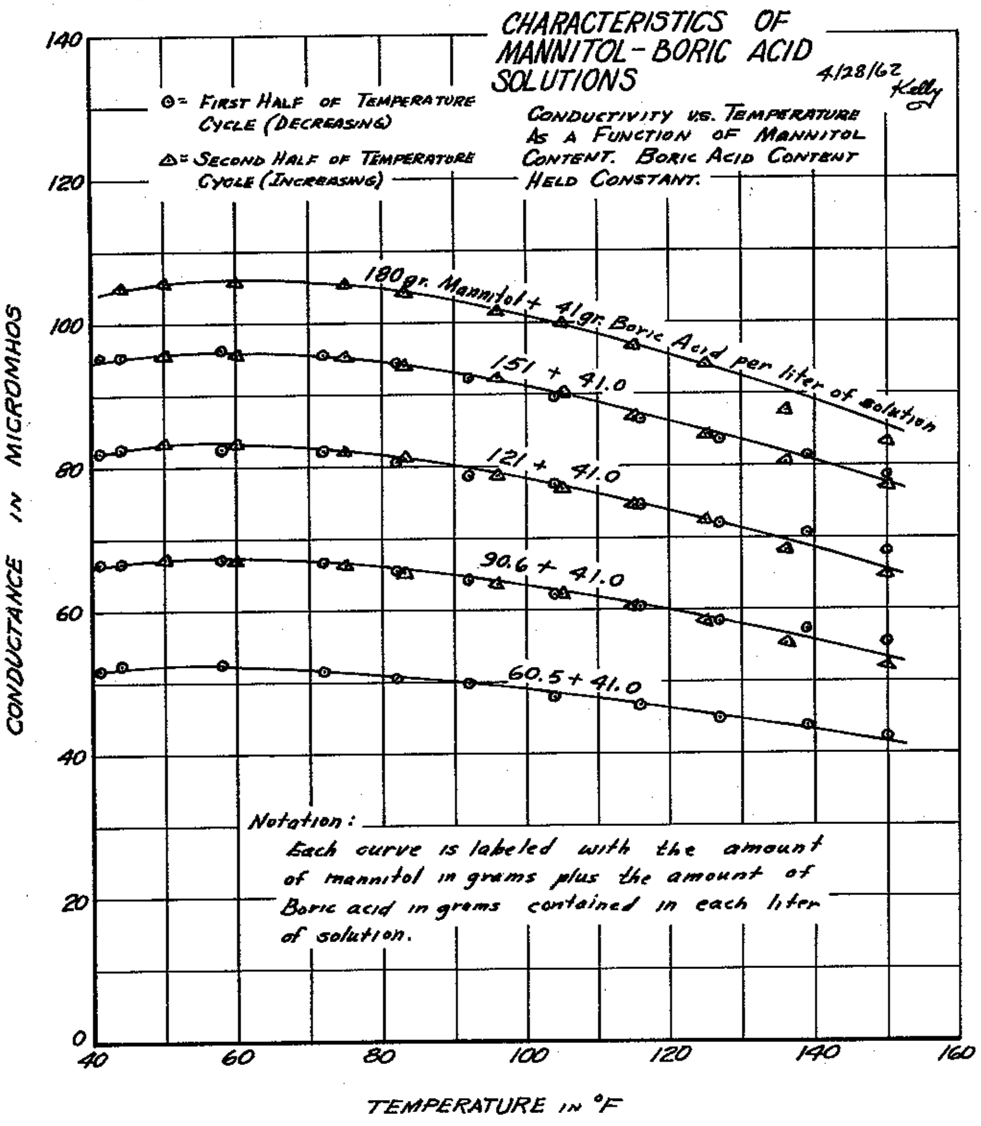


Figure 14. The Effect of Mannitol Content Upon the Conductance-Temperature Characteristics of Mannitol-Boric Acid Solutions

respectively. Although resistance-temperature characteristics have been used exclusively to demonstrate the results of all previous experiments, it now becomes necessary to bring the conductance-temperature characteristics into the discussion, since subsequent experiments employ a prediction scheme based upon the latter characteristics.

The curves shown in Fig. 13 indicate that increasing the mannitol content brings about an increase in conductivity and a resulting decrease in resistance as predicted. Solution No. 4, consisting of 151 grams of mannitol and 41 grams of boric acid per liter of solution, has a characteristic curve close enough to the 10K ohm value that, when the correct amount of potassium chloride is added, resistance values of 10K ohms can be achieved. Solution No. 4 also indicates that is has a repeatable characteristic curve since data for both halves of the temperature cycle seem to coincide. This concentration of mannitol and boric acid was chosen for use throughout the remaining experiments.

The same data used in Figure 13 is converted into conductance-temperature form and presented graphically in Figure 14. The shape of the conductance-temperature characteristic suggests that a straight line could be used to approximate any one of the curves from about 60-70°F. out to about 160°F.

When the conductance-temperature characteristics of two resistors are known, the conductance-temperature characteristic of the parallel combination can be found by adding the conductance values of the individual characteristic curves point by point. It was hypothesized that since the mannitol-boric acid solutions and the potassium chloride solutions are both characterized by approximate straight-line conductance-temperature characteristics, it would be simple to predict graphically the conductance-temperature characteristics of a parallel arrangement of the two water resistors. Furthermore, since the two solutions exhibit oppositely sloped characteristics, it should be possible to determine the appropriate potassium chloride characteristics necessary to produce a combined conductance-temperature characteristic that has essentially a zero slope. The two solutions could certainly be placed in individual plastic resistor containers and be electrically connected externally to obtain the composite resistor described. The next step is to determine if the two solutions can be paralleled chemically to produce the same effect, and if the results can be predicted graphically.

The experiments described in the following section determine that it is possible to chemically combine the mannitol-boric acid solution with an appropriate amount of potassium chloride solution to obtain a composite solution which has an effectively "neutralized" temperature coefficient of resistance and whose characteristics are predictable.

A number of other intermediate experiments were performed (Experiments 6 through 10) to verify that it was possible to predict with some degree of accuracy what type of composite solution would be obtained when various mannitol-boric acid and potassium chloride concentrations were employed in its preparation. Most of these experiments employed a laboratory-constructed conductivity cell which would allow rapid determination of the conductance-temperature characteristics of a particular solution. The conductivity cell could be immersed in a beaker containing an amount of a given solution. The solution contained in the beaker was heated with a gas burner to change its temperature. For various temperatures, as indicated by a standard thermometer, the resistance of the conductivity cell was measured with a General Radio impedance bridge. In this manner a number of solutions could be rapidly evaluated. Once the "neutralization" technique described above was demonstrated by means of the conductivity-cell experiments, a full-scale experiment was performed using the plastic resistor containers and the environmental test chamber. These intermediate experiments will not be discussed here, since they would only duplicate the final, full-scale experiments described in the next section (Chapter III).

CHAPTER III

The final experiments described in this chapter (Experiments 11 through 16) relate to the development of optimized formulas for use in preparing water resistors which exhibit a low temperature coefficient of resistance throughout the temperature range of 40°F to 160°F and whose nominal resistance can be any value between 10K and 100K ohms. The first experiment (Experiment 11) is divided into two parts. Part I, entitled "Using Characterisitcs of Mannitol-Boric Acid Solutions and Potassium Chloride Solutions to Predict by Graphical Methods the Proper Potassium Chloride Content of Water Resistors," was an attempt at using a first-order approximation to predict the formula and the resistance-temperature behavior of water resistors. Part II of Experiment 11 concerns the experimental verification of the results of Part I.

The first step in Experiment 11 was the preparation of three solutions; Solution A, Solution B, and Solution C. The three solutions were prepared in the following manner:

(a) Solution A = 302 grams of mannitol, plus 82 grams of boric acid, per 2 liters of solution (diluted to 2 liters at 25.3°C with singly-distilled water)

(b) Solution B = 302 grams of mannitol, plus 82 grams of boric acid, plus 1.000 grams of potassium chloride, per 2 liters of solution (diluted to 2 liters at 25.1°C with singly-distilled water)

(c) Solution C = 1.000 grams of potassium chloride per 2 liters of solution (diluted to 2 liters at 27°C with singly-distilled water)

These solutions were developed at standard constituents for use in the remaining experiments and are the ones adopted for use in preparing the optimized water resistor formulas. It should be noted that the temperature is given at which the solutions were prepared since volumetric measurements are employed and these solutions have large thermal expansion coefficients. The temperature at preparation should be identical for all three solutions. The temperature at which the water resistors are prepared should also closely correspond to these same values of temperature since volumetric measurements are used in specifying the amounts of each solution to be used in the optimized formula.

In part I of Experiment 11, Solutions A and C are evaluated independently for the purpose of determining the basic characteristics of each solution. Solution B was not used in Part I of the experiment. Additional distilled water was added to various amounts of Solution A in order to obtain ten different concentrations of this solution. A similar procedure was followed in preparing four different concentrations of this Solution C. In Table II are presented the amounts of Solution A, Solution C, and water used in the preparation of each solution.

TABLE II

Amounts of Each Chemical Constituent Used in Preparing the Resistors Tested in Experiment 11, Part I.

Solution No.	Resistor No.	Solution A ml	H_2O ml	Solution C ml
1	1 - 2	100 ml	0 ml	0 ml
2	3 - 4	47.5	52.5	0
3	5 - 6	35.0	65.0	0
4	7 - 8	28.0	72.0	0
5	9 -10	23.5	76.5	0
6	11 -12	20.5	79.5	0
7	13 -14	18.0	82.0	0
8	15 -16	17.0	83.0	0
9	17 -18	16.0	84.0	0
10	19 -20	15.0	85.0	0
11	21	0	88.0	12.0
12	22	0	93.0	7.0
13	23	0	97.0	3.0
14	24	0	99.0	1.0

The twenty-four resistors were placed in the environmental test chamber and cycled through the temperature range of 40°F to 140°F in steps of about 20°F. In order to insure that the resistors had stabilized at the new temperature setting, a period of at least one hour was allowed between the time at which a change in settings of the automatic temperature controller was made, and the time at which a set of resistance readings were taken. The resistance-temperature characteristics of the two groups of solutions are presented graphically in Figures 15 and 16, respectively. Normally, in a group of

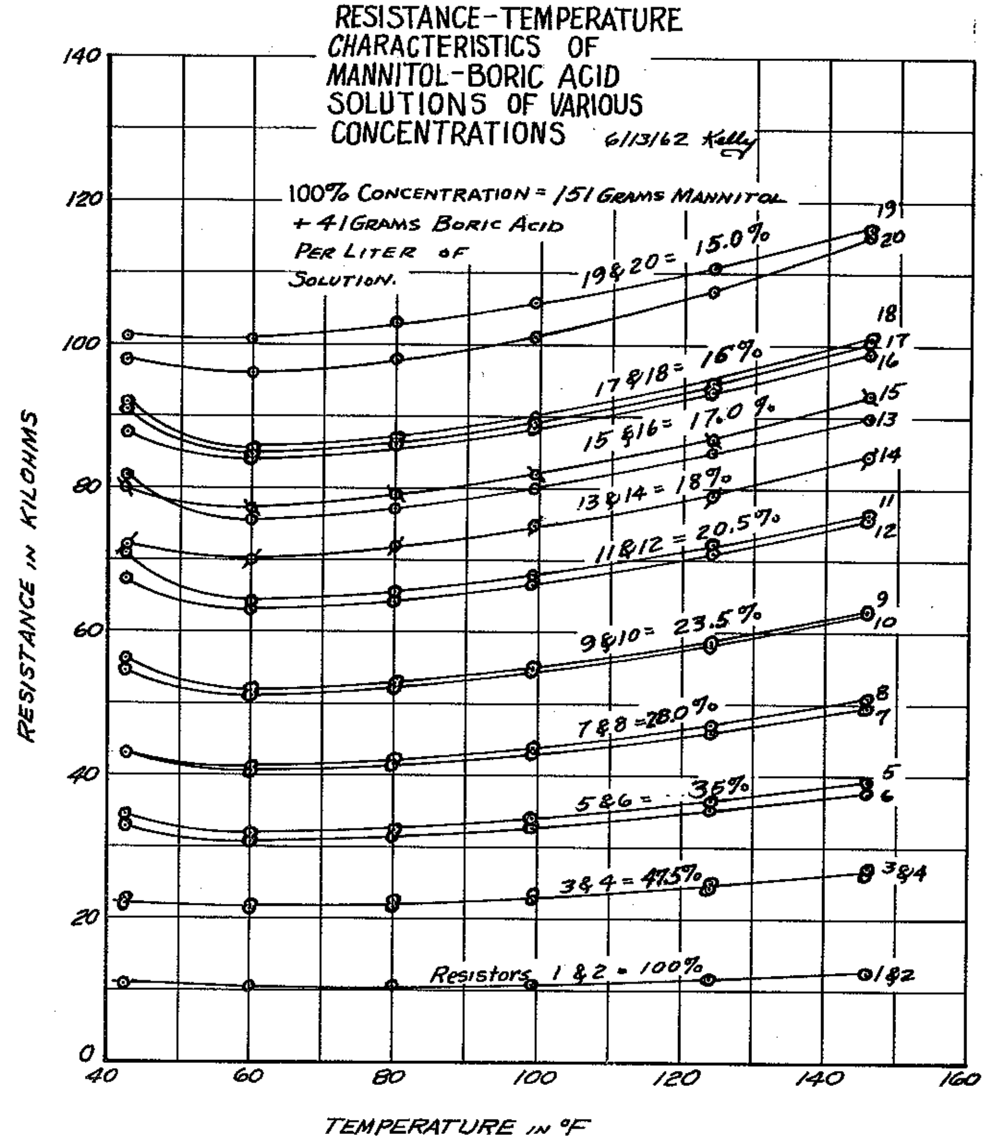


Figure 15. The Effect that Dilution with Distilled Water has Upon the Resistance-Temperature Characteristics of a Mannitol-Boric Acid Solution.

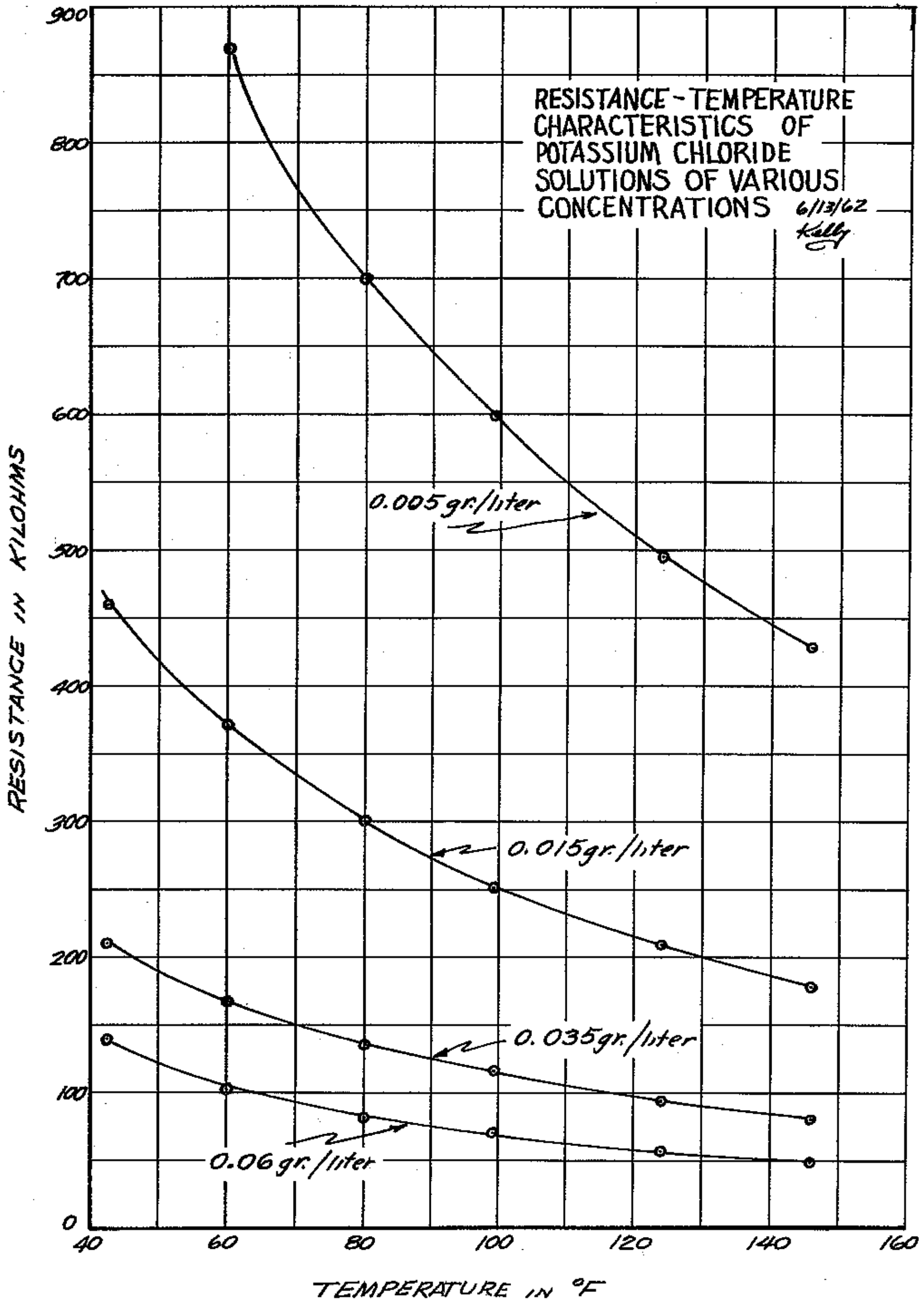


Figure 16. The Resistance-Temperature Characteristic of Potassium Chloride Solutions of Various Concentrations.

curves such as those shown in Figure 15, the average of the two resistors containing the same solution would be presented; however, in this particular experiment, individual characteristic curves are shown because there is considerable difference in some cases. This difference is attributed to the fact that the electrode and end-cap assembly was not dismantled when cleaning. It is believed that this caused the higher resistance values to deviate with temperature probably as a result of contamination from the improperly cleaned end-cap assembly (In subsequent experiments, the electrode-end cap assembly was dismantled for cleaning and this discrepancy never occurred again).

The same data used for presenting the resistance-temperature characteristics shown in Figures 15 and 16 are presented in a differenct manner (conductance-temperature characteristics) in Figures 17, 18, and 19. In these three figures, straight-line approximations are made of the characteristics over the range in temperature from about 70°F to 160°F. Also shown on each curve is the slope of the straight-line approximation in milli-micrombhos per degree Farenheit. Although not stated on the Figures, it is rather obvious, that all the conductance-temperature curves for the mannitol-boric acid solutions (Figures 17 and 18) have a negative slope, while those of the potassium chloride solutions (Figure 19) have a positive slope.

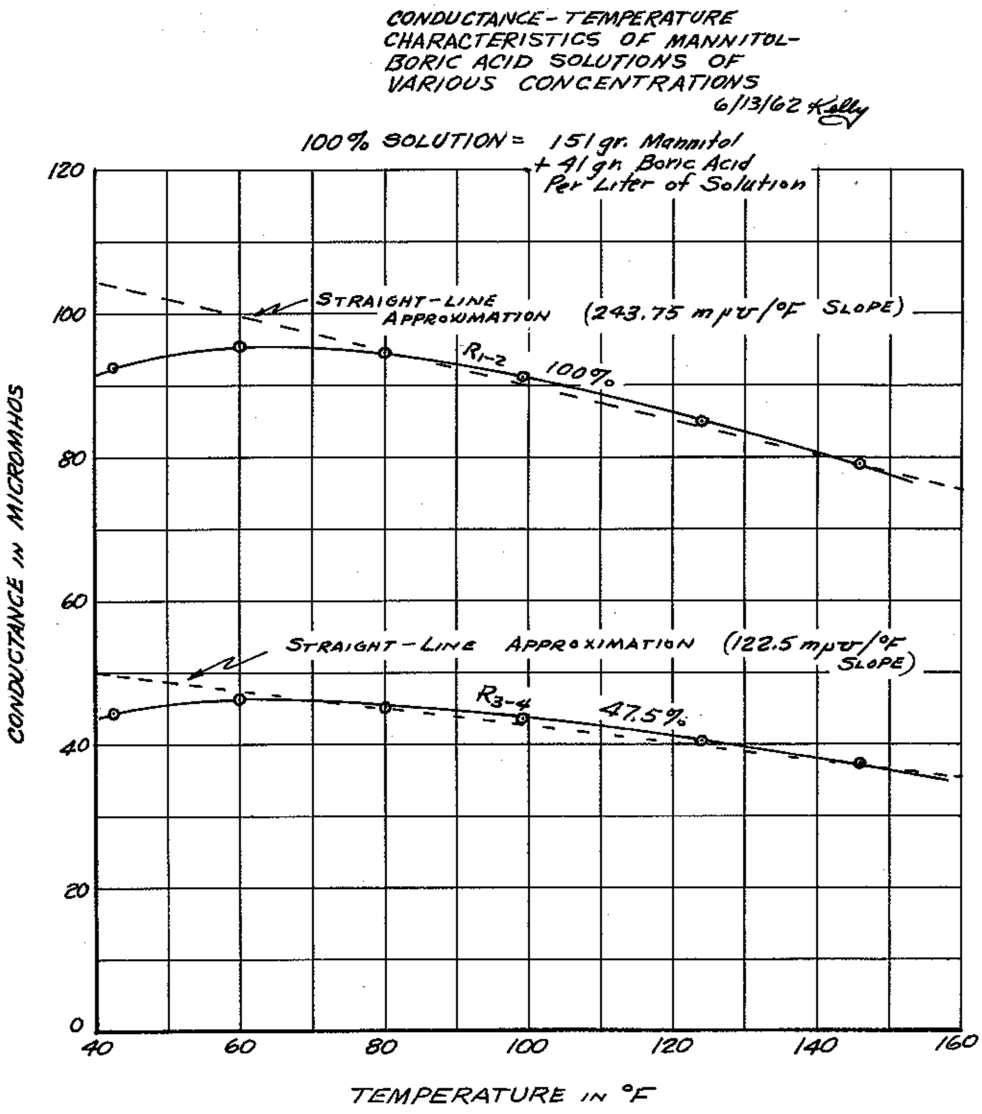


Figure 17. Conductance-Temperature Characteristics of Mannitol-Boric Acid Solutions of Various Concentrations (40 to 100 micromhos)

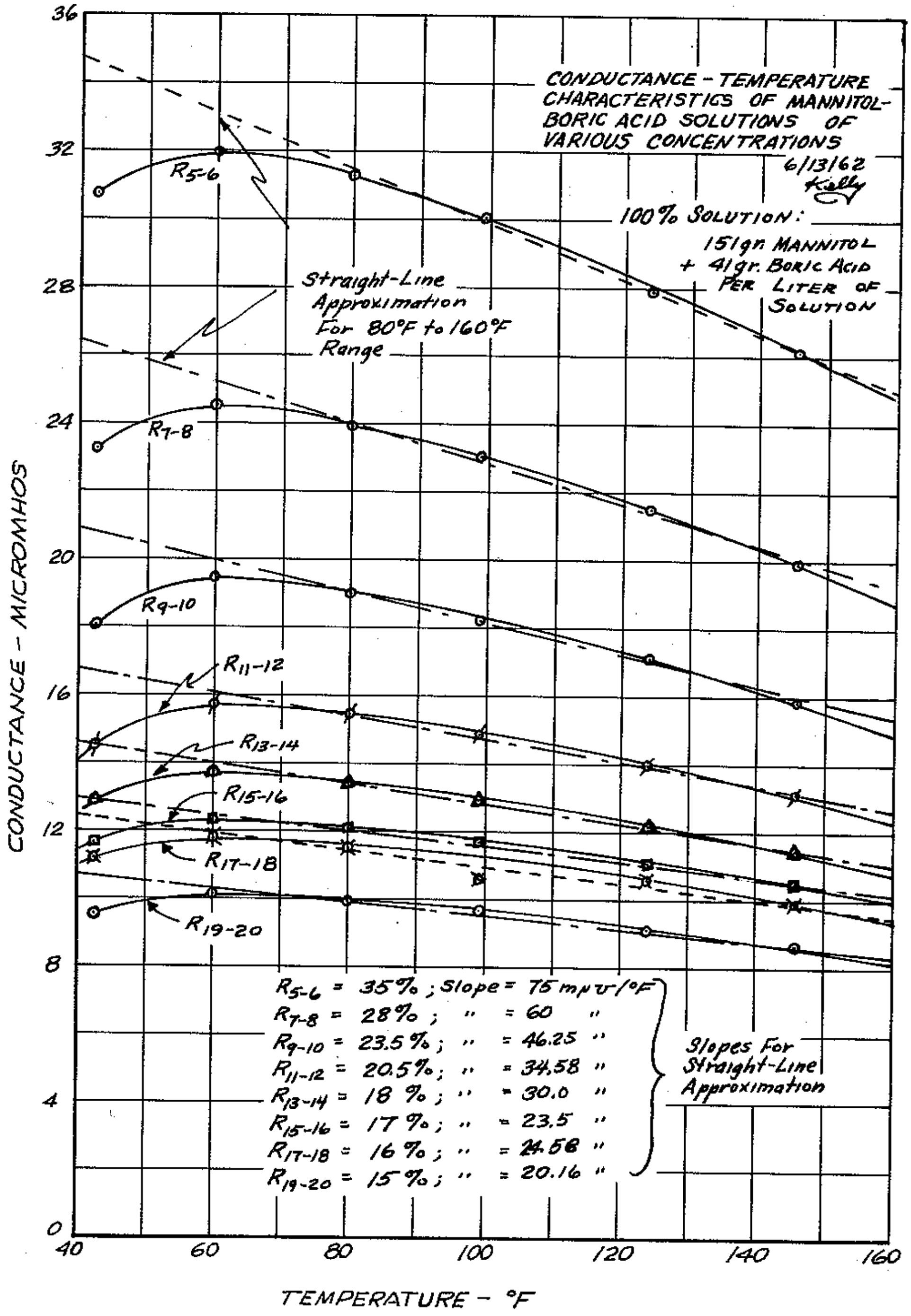


Figure 18. Conductance-Temperature Characteristics of Mannitol-Boric Acid Solutions of Various Concentrations (0 to 40 micromhos)

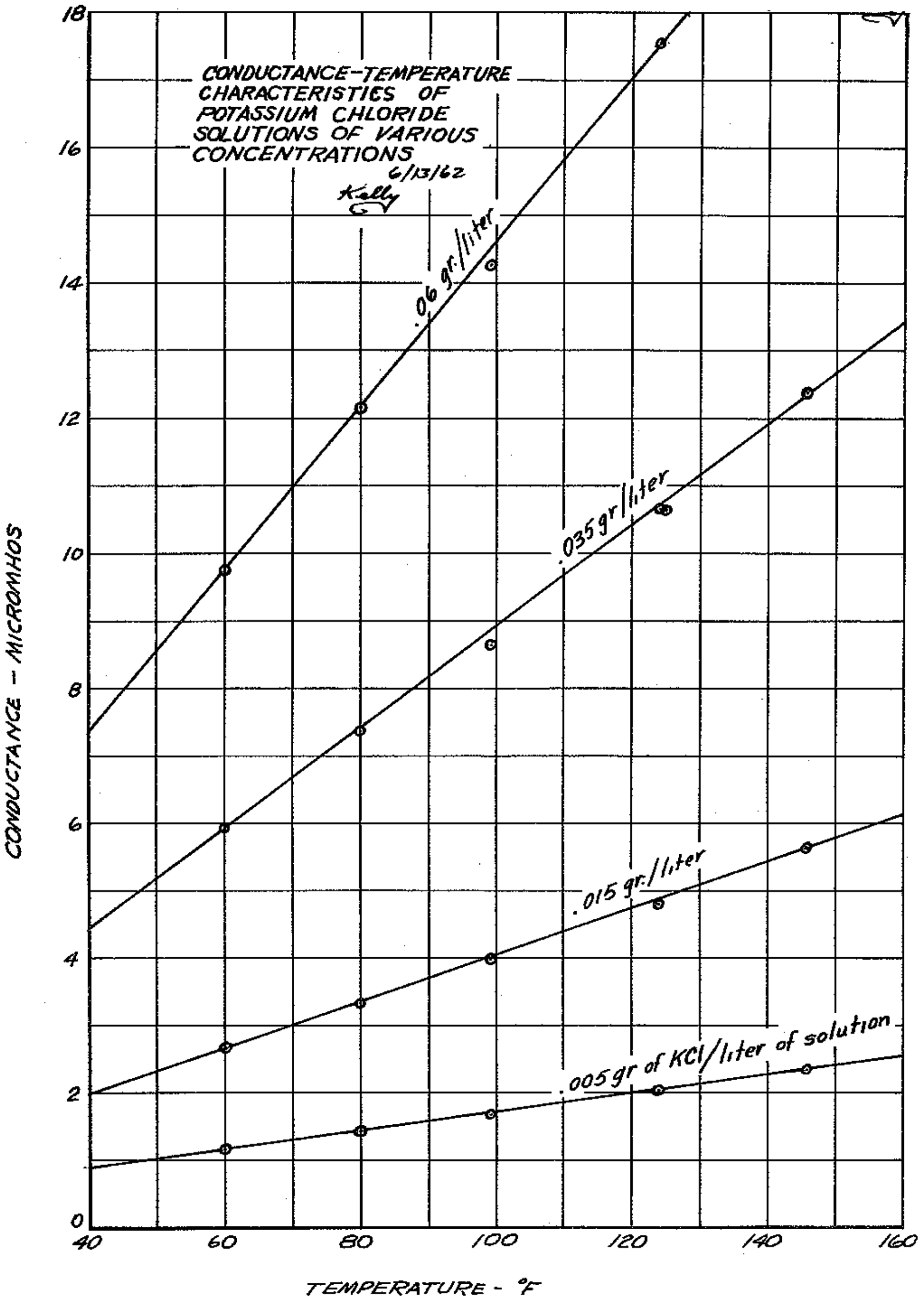


Figure 19. Conductance-Temperature Characteristics of Potassium Chloride Solutions of Various Concentrations (0 to 18 micromhos)

It was hypothesized that it is possible to combine a mannitol-boric acid solution with a potassium chloride solution (based upon the respective concentrations in a single amount of distilled water) and predict the conductance-temperature characteristic of the composite solution by adding together, point by point, the conductance-temperature curves of the individual solutions. Furthermore, if the average slopes of the conductance-temperature curves of the individual solutions are equal in magnitude, the resulting composite conductance characterisitc will be constant with respect to temperature because the slopes of the different solutions are opposite in sign and effectively "neutralize" one another.

In order to use the hypothesis described above, several additional graphical presentations are employed; these include:

1. Figure 20 - Slope of the conductance-temperature characteristics curves of various potassium chloride solutions versus potassium chloride concentration.
2. Figure 21 - Slope of the conductance-temperature characteristic curves of various mannitol-boric acid solutions versus mannitol-boric acid concentration.
3. Figure 22 - 90°F conductance values of mannitol-boric acid solution versus mannitol-boric acid concentration.
4. Figure 23 - 90°F conductance values of potassium chloride solutions versus potassium chloride concentration.

The data required to obtain the curves shown in Figures 20, 21, 22, and 23, was obtained from the curves shown in Figures 17, 18, and 19, and is presented in Table III and Table IV.

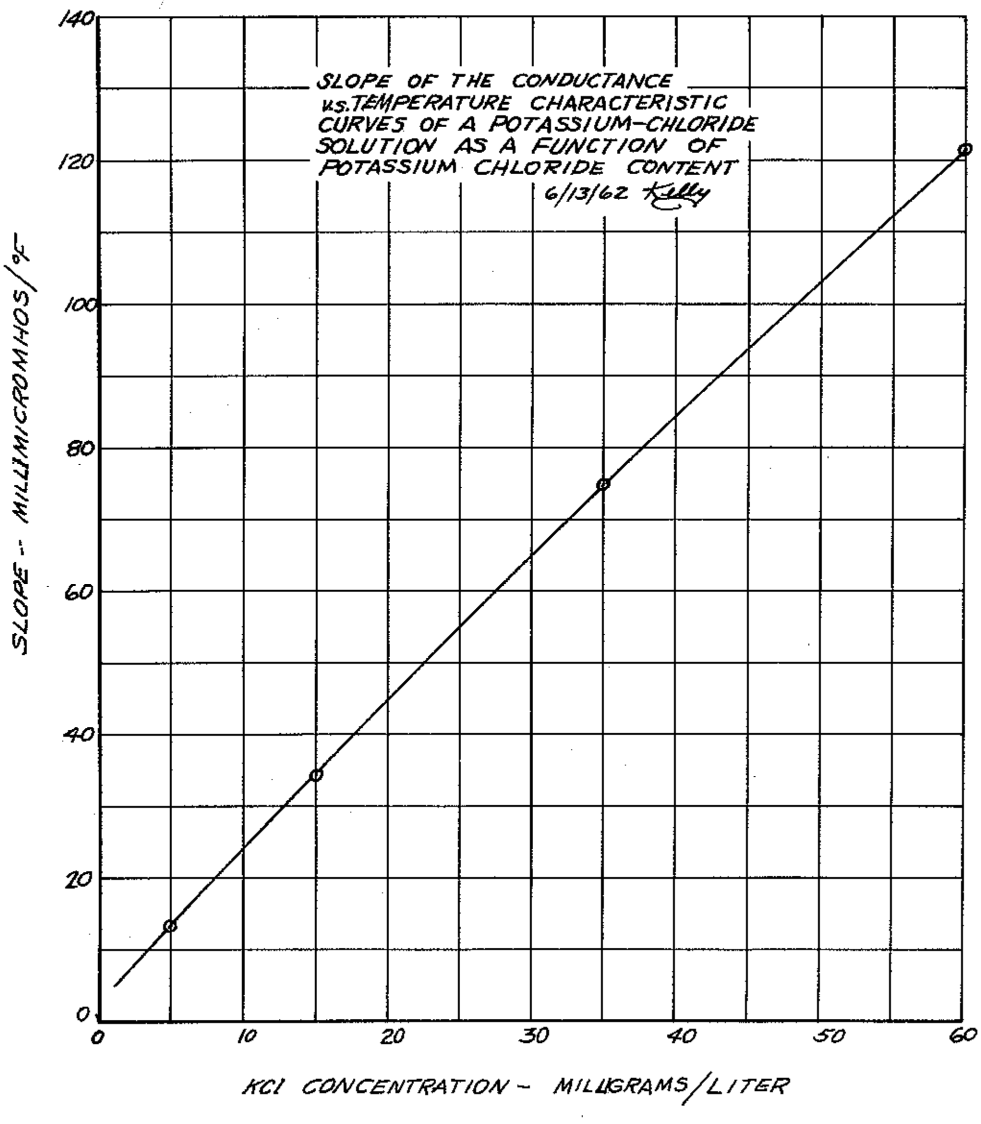


Figure 20. Slope of the Conductance-Temperature Characteristic Curves of Potassium Chloride Solutions as a Function of Potassium Chloride Content

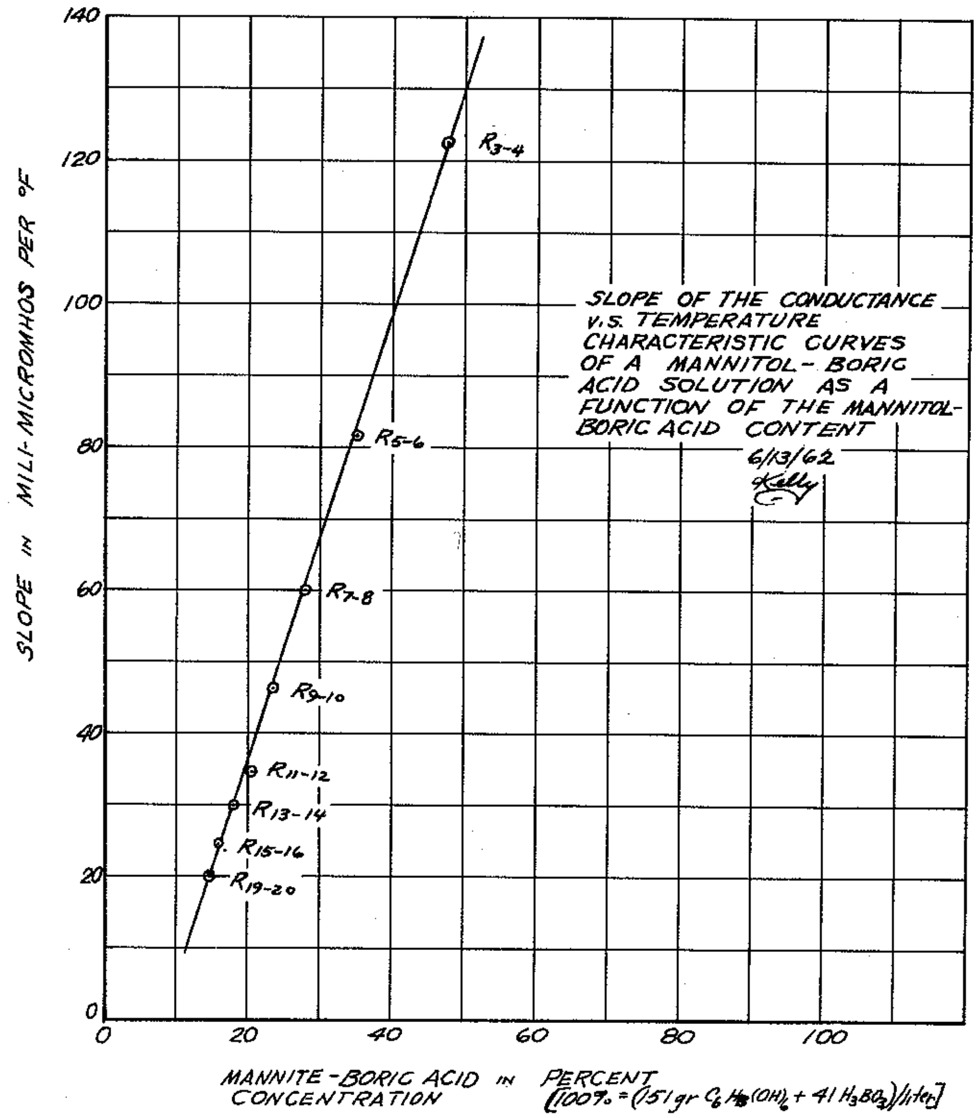


Figure 21. Slope of the Conductance-Temperature Characteristic Curves of Mannitol-Boric Acid Solutions as a Function of Mannitol-Boric Acid Content

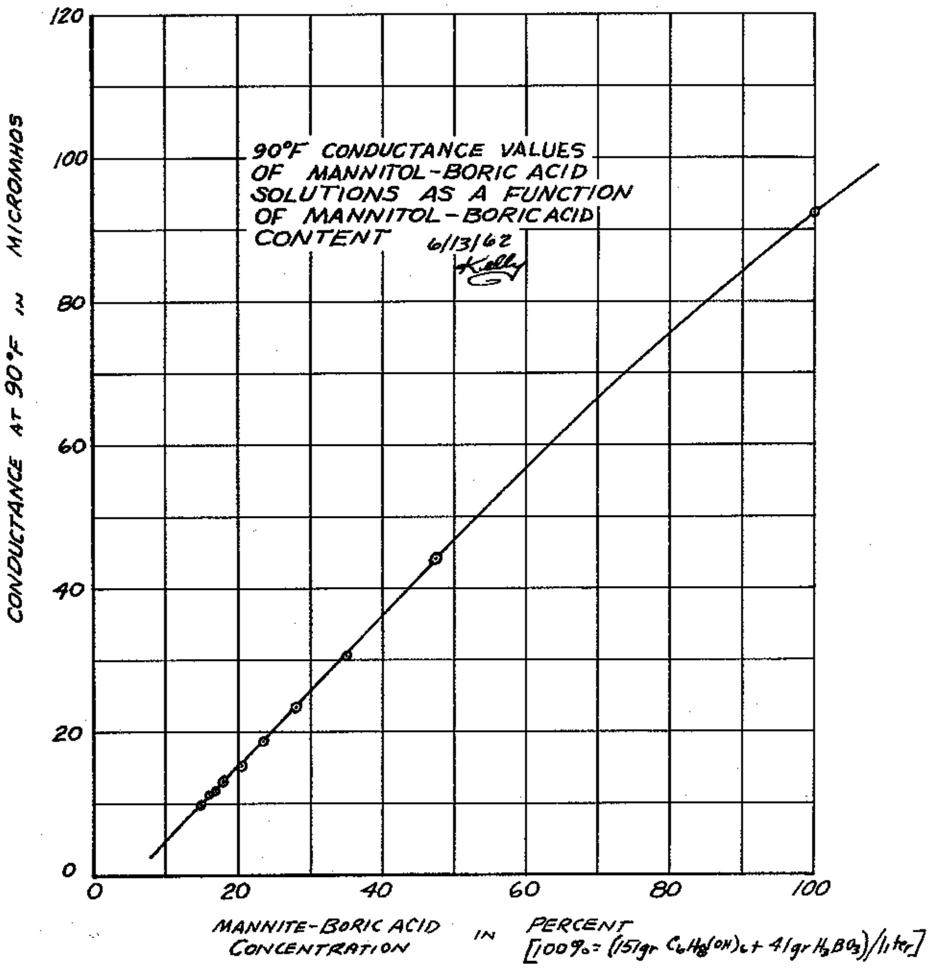


Figure 22. Conductance of Mannitol-Boric Acid Solutions at 90°F. as a Function of Mannitol-Boric Acid Content

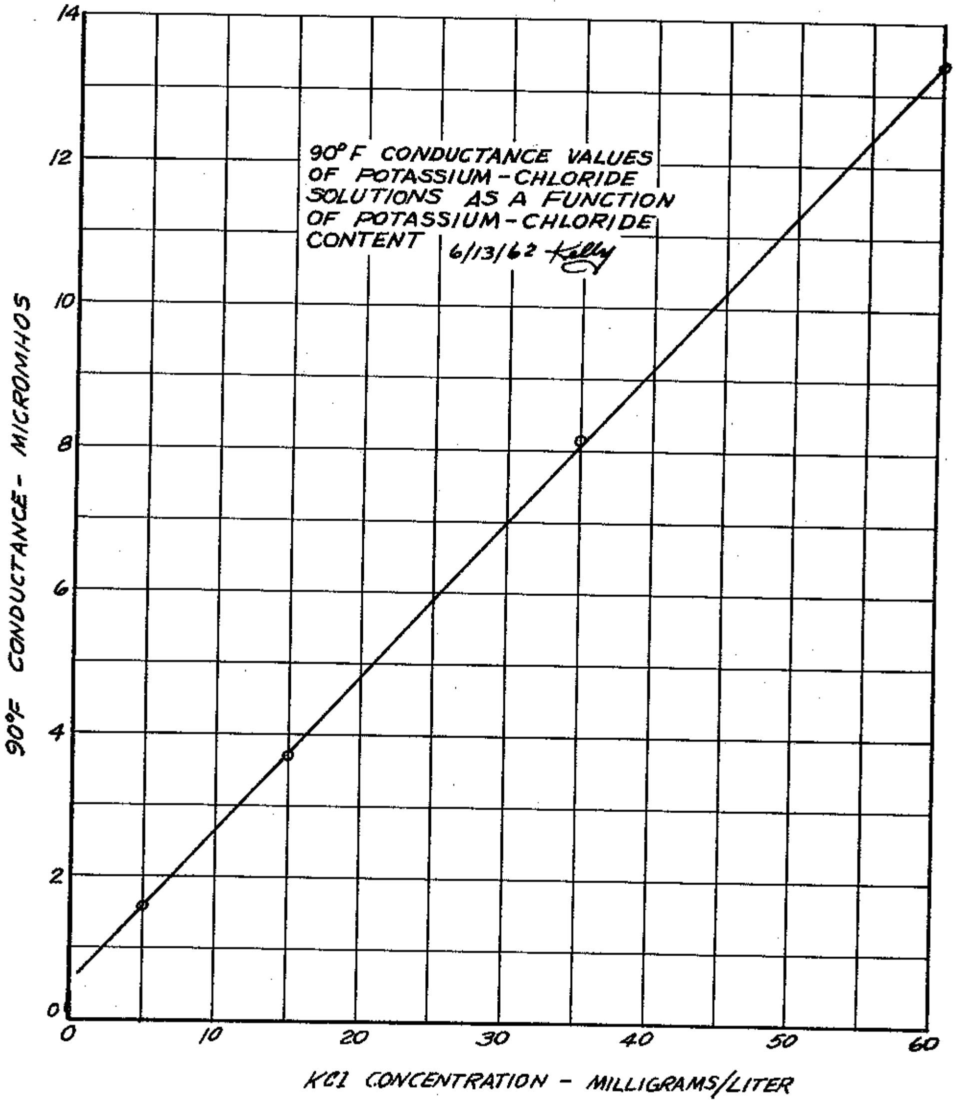


Figure 23. Conductance of Potassium Chloride Solutions at 90°F. as a Function of Potassium Chloride Content

TABLE III (Compiled 6-14-62)

Slope of (Conductance-vs-Temperature Curves) for Mannitol-Boric Acid Solutions of Various Concentrations

Solution No.	Resistors No.	Concentration of Boric-Acid-Mannitol % or ml of A per 100 ml	Intercepts in micromhos		Slope in	90°F Conductance in micromhos
			40°F	160°F		
1	1 - 2	100%	104.5	75.25	243.75	92.4
2	3 - 4	47.5	50.2	35.5	122.5	44.1
3	5 - 6	35.0(curveB)	34.8	25.0	81.7	30.7
4	7 - 8	28.0	26.4	19.2	60.0	23.4
5	9 -10	23.5	20.9	15.35	46.25	18.6
6	11-12	20.5	16.75	12.6	34.58	15.05
7	13-14	18.0	14.6	11.0	30.0	13.1
8	15-16	17.0	12.95	10.13	23.5	11.8
9	17-18	16.0	12.45	9.5	24.58	11.2
10	19-20	15.0	10.72	8.3	20.16	9.75

TABLE IV (Compiled 6-15-62)

Slope of Conductance-vs-Temperature Curve for Potassium Chloride Solutions of Various Concentrations

Solution No.	Resistor No.	Concentration in mg/liter	Intercepts in micromhos		Slope /°F	90°F Conductance in micromhos
			40°F	140°F		
11	R_{21}	5 mg/l	0.9	2.24	13.4	1.6
12	R_{22}	15 mg/l	1.97	5.4	34.3	3.7
13	R_{23}	35 mg/l	4.41	11.9	74.9	8.15
14	R_{24}	60 mg/l	7.33	17.54*	121.5	13.4

*at 124°F

Using the graphical representations of Figures 20, 21, 22, and 23, data is obtained for the conductance of a composite solution (one which is neutralized) as a function of the mannitol-boric acid content (with the appropriate potassium chloride content) in the following manner:

(a) From Figures 20 and 21, obtain the mannitol-boric acid concentration and the potassium chloride concentration for identical values of slope.

(b) Using the mannitol-boric acid and potassium chloride concentrations found in (a), find the 90°F conductance value for each concentration from Figures 22 and 23.

(c) Add the two 90°F conductance values found in (b) to obtain the corresponding 90°F conductance value of the composite solution.

(d) After obtaining a sufficient number of different 90°F conductance values for the composite solution by repeating steps (a), (b), and (c), a curve may by plotted of these values as a function of either the mannitol-boric acid concentrations or the potassium chloride concentration.

The curves shown in Figure 24 are merely expanded and extended versions of the curves shown in Figures 22 and 23, and were prepared in order to obtain interpolated and extrapolated values of the slope for the higher values of concentration. The curves illustreated in Figure 24 were used to predict the potassium chloride concentration necessary to neutralize 80% and 100% concentrations of mannitol-boric acid solutions.

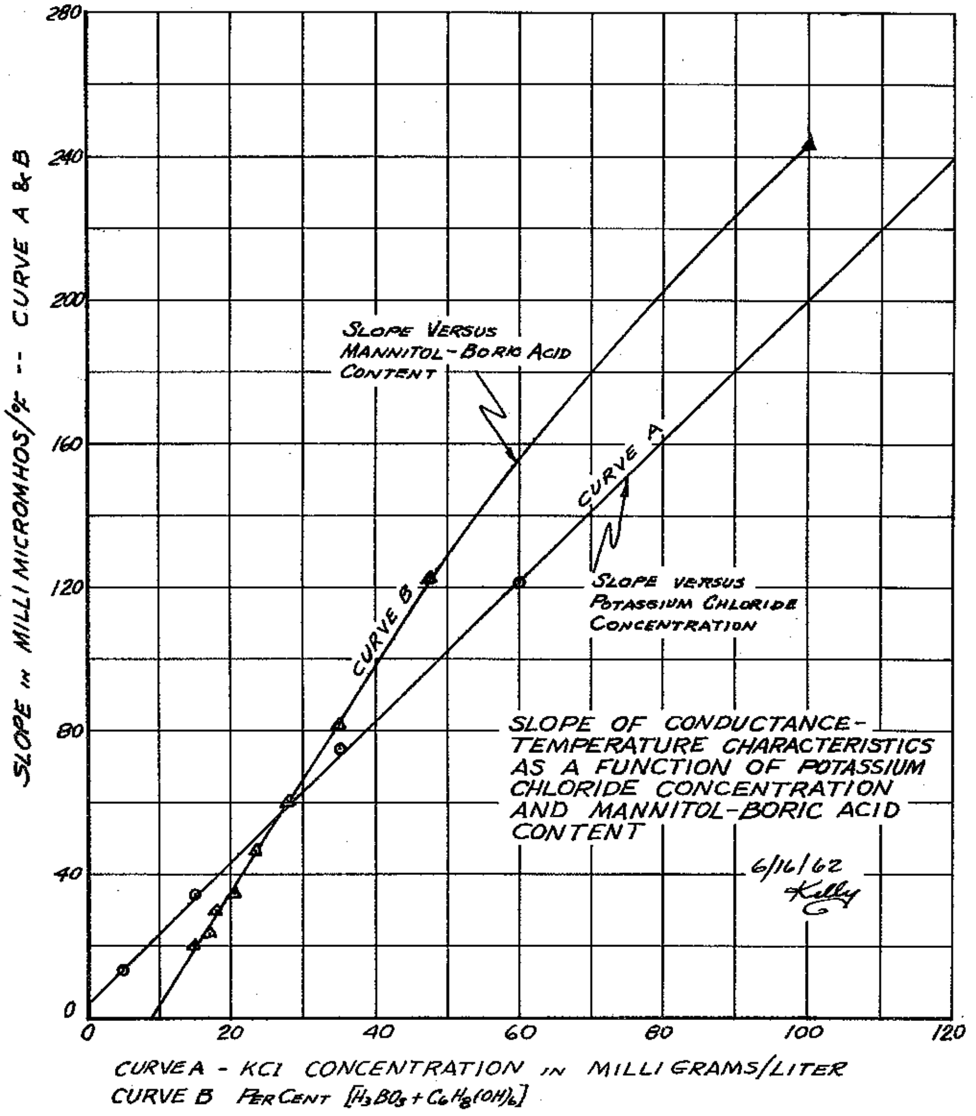


Figure 24. Slope of the Conductance-Temperature Characteristic Curves of Potassium Chloride and Mannitol-Boric Acid Solutions

The results obtained by using the above procedure to determine the 90°F conductance for various mannitol-boric acid concentrations are presented in Table V.

The data given in Table V is presented graphically in Figure 25. In Figure 25, the circled data points up to a mannitol-boric acid concentration of 47.0% represents the data given as readings 1 through 11 in Table V; the two data points designated by crosses at 80% and 100% were also predicted by the same technique, but after Part II of Experiment 11 was performed. Although Part II of Experiment 11 has not been discussed, it should be pointed out that its purpose was to verify the predictions given in Table V and that its results were superimposed (small triangles) upon Figure 25 to illustrate how well the experimental results agreed with the predictions. In Figure 25 is shown the straight-line prediction made initially based upon the graphical extrapolation of the first eleven readings shown in Table V. The linear extrapolation was hastily made and was not checked by the methods outlined in steps (a) through (d). The initial straight-line prediction implied that the 80% and 100% concentrations would give composite conductance values of 100 micromhos and 135 micromhos, respectively; however, as illustrated in Figure 25, the experimental values differed considerably from the predicted values in these two cases. All other experimental results checked closely with predicted values. Upon re-investigating the two points in question, it was discovered that, by proper use of the

TABLE V

Predicted Mannitol-Boric Acid to Potassium Chloride Ratios and Resulting Composite Conductance Values for Temperature-Corrected Water Resistors (6-15-62)

Reading No.	Slope /°F.	% Mannitol-Boric Acid in (ml of sol. A)/(100 ml of sol.)	Potassium Chloride Concentration in mg per liter of sol.	90°F Conductance M-BA micro-mhos	KCL micro-mhos	Composite micro mhos
1	20	15.0	8.2	10.0	2.25	12.25
2	30	17.0	12.8	12.0	3.25	15.25
3	40	21.3	17.7	16.3	4.31	20.61
4	50	24.5	22.6	20.0	5.37	25.37
5	60	28.0	27.5	23.5	6.43	29.93
6	70	31.0	32.6	26.7	7.54	34.24
7	80	34.2	37.8	30.0	8.66	38.66
8	90	37.4	43.0	33.5	9.79	43.29
9	100	40.5	48.3	37.0	10.9	47.9
10	110	43.8	53.7	40.2	12.05	52.25
11	120	47.0	59.25	43.5	13.25	56.75
12	212.5	80.0	101.00	75.5	18.85	94.35
13	243.0	100.0	122.00	92.4	22.34	114.74

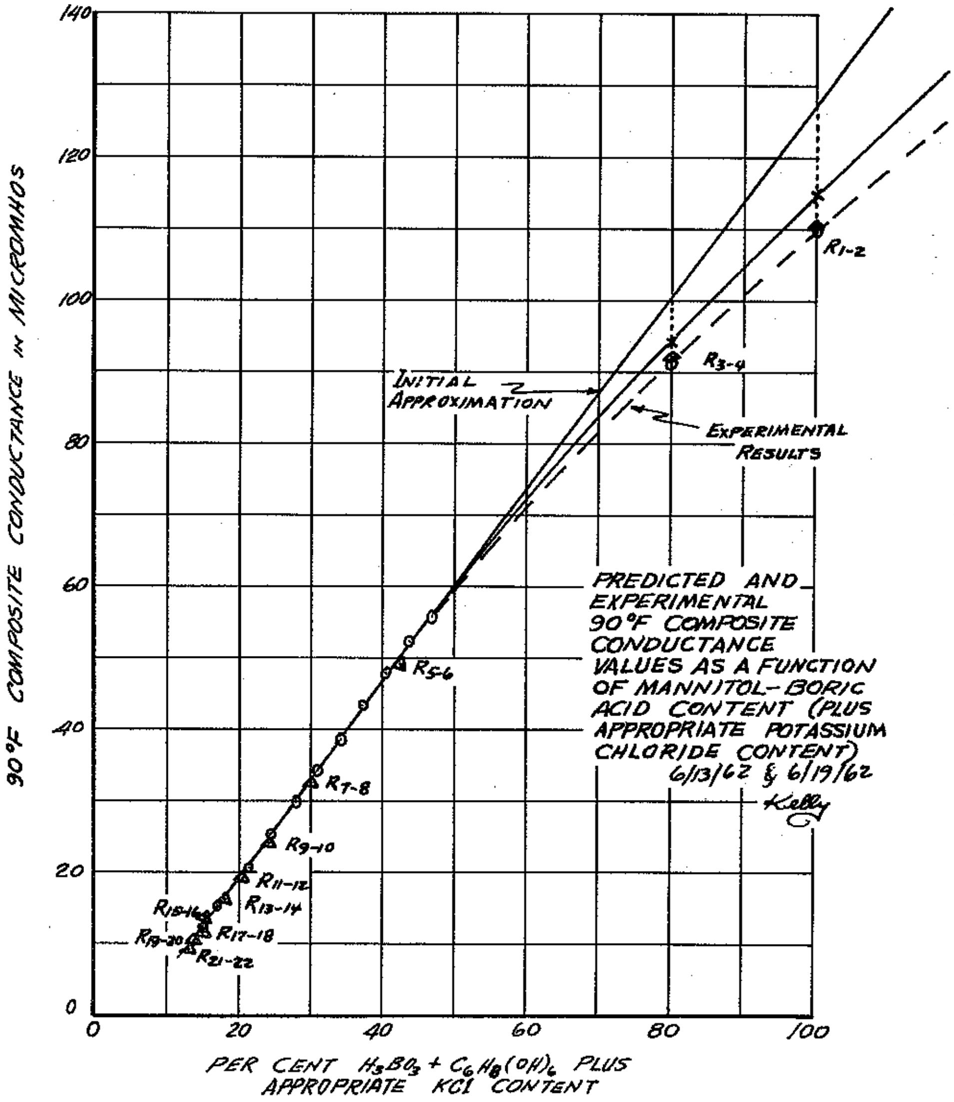


Figure 25. Predicted and Experimental 90°F. Conductance Values of Mannitol-Boric Acid-Potassium Chloride Solutions as a Function of Mannitol-Boric Acid Content

predicting techniques outlined above, the two conductance data points designated by crosses (x) at 80% and 100% concentrations gave theoretical conductance values which are within 2.3% and 4.24%, respectively, of the corresponding experimental results. A more detailed explanation of Part II of Experiment 11 follows.

As mentioned above, Part II of Experiment 11 was for the purpose of experimentally determining how close an agreement exists between the theoretical predictions of Part I and the Experimental results of Part II. Curves shown in Figures 20 through 25 were used to predict the proper amounts of Solutions A, B, C, and distilled water required to produce resistance values at 10K ohm intervals from 10K ohms to 100K ohms. The results of the predictions are shown in Table VI along with the measured values of the two resistors prepared using each solution. The initial values shown, measured at room temperature, proved to be rather close to the predicted values. It should be pointed out that Solution B must be employed to obtain the proper potassium chloride content on the more concentrated mannitol-boric acid solutions, but that only Solution A, Solution C, and distilled water are required for the more dilute mannitol-boric acid solutions.

TABLE VI

Res No.	Predicted Values of Res. Ohms	Predicted Values of Cond. Micromhos	Measured Values of Two Resistors (Made at Room Temp. 27.1°C)		Volume % M-BA ml Sol A/ 100 ml	Slope milli/°F micro/ mhos/	Proper KCl Concentration mg/ Liter	ml Sol A	ml Sol B	ml Sol C	ml Distilled H_2O
1-2	Ro(8.72*)	(114.74)*	9.05	9.15	100%	244	122	75.6	24.4	0	0
3-4	10K(10.6K*)	100(94.35*)	10.85	10.73	80	202	101	59.8	20.2	0	0
5-6	20K	50	20.6	20.2	42.5	106	52	42.5	0	10.4	47.1
7-8	30K	33.3	31.0	30.8	30	66	32	30.0	0	6.4	63.6
9-10	40K	25.0	41.24	41.5	24.2	44	21.5	24.2	0	4.3	71.5
11-12	50K	20	51.7	51.5	20.5	36.5	16.5	20.5	0	3.3	76.2
13-14	60K	16.66	62.0	61.3	18.0	28.5	12.5	18.0	0	2.5	79.5
15-16	70K	14.3	72.7	72.4	16.33	23.0	9.5	16.33	0	1.9	81.77
17-18	80K	12.5	83.4	83.0	15.0	19.0	7.7	15.0	0	1.54	83.46
19-20	90K	11.11	93.1	93.1	13.9	16.0	6.2	13.9	0	1.24	84.86
21-22	100K	10.0	102.0	103.0	13.0	13.0	5.0	13.0	0	1.0	86.0

* Values re-calculated after experiment using proper technique for making predictions.

The twenty-two resistors described in Table VI were placed in the environmental chamber and cycled through the temperature range from 150°F to 40°F in approximately 20° steps. The resistance-temperature characteristics for this experiment are presented graphically in Figure 26. All of the curves seem to be effectively "neutralized" with respect to the temperature coefficient of resistance as evidenced by their almost constant resistance as a function of temperature. All of the curves in Figure 26 have some small variation with temperature, and each of the 90°F values differed a small percentage from the predicted value. In Table VII are tabulated the results of the curves shown in Figure 26. Using the readings at 86.5°F and at 152.5°F to determine the average slope of each curve, the change in resistance between these two temperatures is compared to the total resistance values at 86.5°F, and the result is expressed as a slope in percent.

Also shown in Table VII is the percentage difference between the predicted value of resistance and the experimental value of resistance. It should be noted that the predicted resistance values are within 2.5% to 10.1% of the experimental values with an average disagreement of only 5.47%, a fairly close agreement for a first-order approximation. The 90°F results of this part of the experiment have been superimposed upon the initial prediction curves of Figure 25 (small triangles). The agreement between the predicted values and the experimental values is evident.

RESISTANCE-TEMPERATURE CHARACTERISTICS OF RESISTOR UNITS EMPLOYING INITIALLY PREDICTED FORMULA AND SINGLY-DISTILLED WATER

6/19/62
Kelly

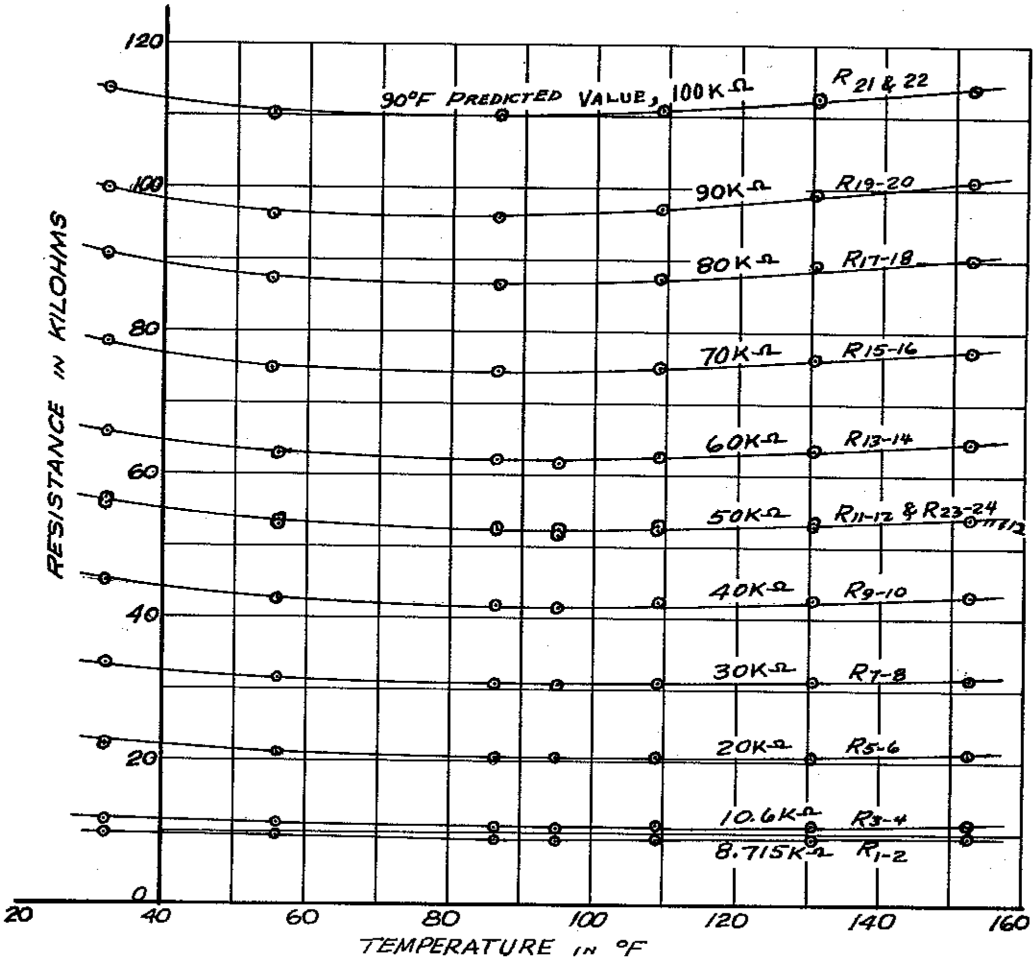


Figure 26. Resistance-Temperature Characteristics of Water Resistors Employing Initially-Predicted, Modified-Versions of Magnanini's Solution and Singly-Distilled Water

TABLE VII (from p 124 Master Data Book)

Resistance No. Average of Two Resistors	$90^{\circ}F$ Predicted Value K	Ra, Exp. Value of Resistance at $86.5^{\circ}F$ K	Rb, Exp. Value of Resistance at $152.5^{\circ}F$ K	Slope $\frac{R_b-R_a}{R_a}$ x 100%	% Error in Prediction $\frac{\text{exp.-nom.}}{\text{nom.}}$ x 100%
R_{1-2}	8.72	9.11	9.43	+3.51%	+4.53%
R_{3-4}	10.6	10.95	11.375	+3.88	+3.30
R_{5-6}	20	20.50	21.05	+2.685	+2.5
R_{7-8}	30	30.95	31.70	+1.925	+3.17
R_{9-10}	40	41.95	43.15	+2.865	+4.88
R_{11-12}	50	52.80	54.15	+2.555	+5.6
R_{13-14}	60	62.15	64.7	+4.11	+3.58
R_{15-16}	70	74.5	77.65	+4.23	+6.43
R_{17-18}	80	86.55	90.30	+4.34	+8.19
R_{19-20}	90	95.95	101.1	+5.37	+7.89
R_{21-22}	100	110.1	114.1	+3.64	+10.1

Table VII - Comparison of Graphically Predicted Values of Resistors With the Experimental Results of Experiment 11, Part II, and the Slope of the Resulting Resistance-Temperature Characteristics.

The slope as a function of temperature is also of interest. The maximum percent change in resistance as the temperature changes from 86.5°F to 152.5°F is 5.37% for the 90K ohm resistor. The change in resistance with temperature ranges from 1.925% to 5.37% with an average of 3.55%. This is also a remarkable result considering the technique used to predict the needed potassium chloride content to bring about neutralization of the temperature coefficient of resistance. In general for each curve, the resistance drops as the temperature decreases below 86.5°F, reaches a minimum between 60°F and 80°F, and rises drastically in the 30°F to 40°F region. For the 32°F reading, the resistance increases about 6 to 9% above the 86.5°F value. However, if one is aware of the consequences of operating in this low temperature region, measures can be taken to avoid this area of operation. There is a range of temperature from about 50°F to 150°F, throughout which the resistance doesn't very over 5% from its mid-range value. Knowledge of this desirable temperature range should allow one to design his application of these resistors to take advantage of this desirable range.

Before proceeding to the next experiment it would perhaps be informative to point out a few more things which pertain to Experiment 11. The curve in Figure 27 shows that the graphically-predicted potassium chloride content required to neutralize the temperature coefficient of resistance is not a linear function of the mannitol-boric acid content. Also, since this curve does not pass through the origin, it is evident that a simple diluting of Magnanini's formula will not produce high resistance values which possess low temperature coefficients of resistance. The curves shown in Figure 28, resulting partly from graphical predictions and partly from the data of Part II of Experiment 11, illustrate the relationship between the various constituents of the water resistors and the corresponding conductance values. It is evident that a simple relationship exists only for the conductance as a function of the potassium chloride content, a linear dependence for all practical purposes.

Experiment 12 was planned for determining how close one could predict the resistance value obtained from a given water resistor formula with predictions based upon the results of Experiment 11. Based upon the 86.5°F readings obtained in Part II of Experiment 11, the content of mannitol, boric acid, and potassium chloride in new solutions for producting certain resistance values would be predicted. The results obtained in Part II of Experiment 11 are tabulated in Table VIII as follows on page 75.

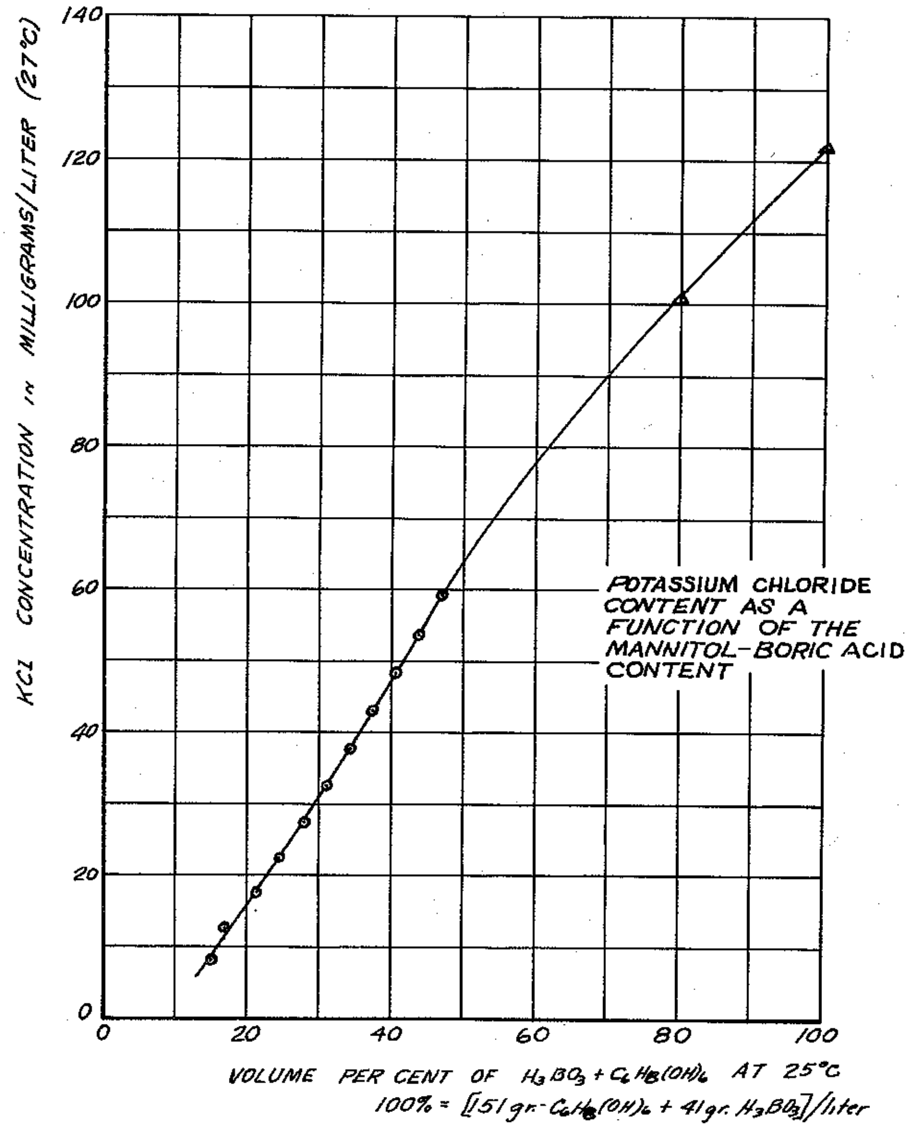


Figure 27. Potassium Chloride Content Versus Mannitol-Boric Acid Content Predicted by Graphical Methods

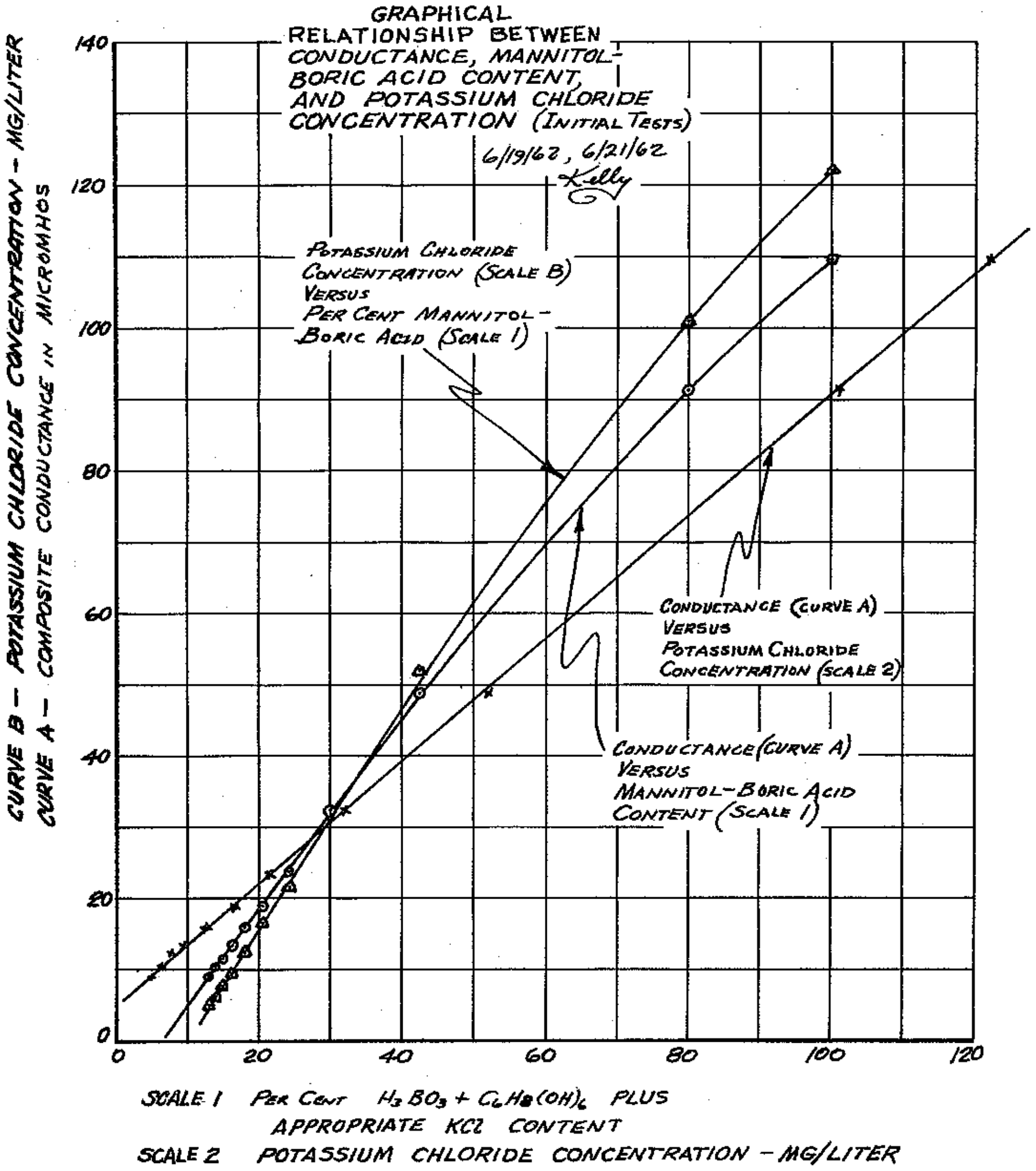


Figure 28. Graphical Relationship Between Conductance, Mannitol-Boric Acid Content, and Potassium Chloride Content for Water Resistors that Possess Neutralized Temperature Coefficient of Resistance Characteristics

TABLE VIII

Tablulated Results of Experiment 11, Part II

Experimental Values

Resistance Number R1-2	Orig.Nominal Value	86.5°F Resistance	Conductance	%M-BA Std. Sol. by Volume	KCl Content mg/liter
1-2	8.72*	9.11 K	109.77	100%	122
3-4	10.6 *	10.95 K	91.324	80	101
5-6	20 K	20.50 K	48.780	42.5	52
7-8	30 K	30.95	32.310	30	32
9-10	40 K	41.95	23.838	24.2	21.5
11-12	50 K	52.80	18.939	20.5	16.5
13-14	60 K	62.15	16.090	18.0	12.5
15-16	70 K	74.5	13.423	16.33	9.5
17-18	80 K	86.55	11.554	15.0	7.7
19-20	90 K	95.95	10.422	13.9	6.2
21-22	100 K	110.1	9.083	13.0	5.0

* Values re-calculated after Exp. 11 using proper technique for making predictions.

The data on Table VIII for the conductance and the mannitol-cobric acid and potassium chloride content was plotted in Curve 25 (small triangles) and from this corrected curve solution contents to produce a new set of desired resistance values were determined. The new set of predicted resistance and conductance values and the corresponding chemical contents are tabulated in Table IX.

The solutions indicated in Table IX were prepared in 100-milliliter batches, and from each of these solutions, two resistors were prepared and the remainder of the solution kept in capped containers. The experimental values were extremely close to the predicted values, differing from zero to about 2.5% with an average difference of about 1.0% As shown in Figure 29, the entire group of resistors varied with temperature the same as the initial group did in Experiment 11. There was one notable exception, and that was that the 80 K and 100 K resistance values behaved badly compared to the rest of the resistors, especially at the higher temperatures. Both the 80 K and the 100 K resistance values increased about 7% at 140°F, whereas the average of the other resistors was about as in Experiment 11 -- only 2 to 3%. It was thus apparent from this experiment that it would not be satisfactory to continue to base the potassium chloride content upon the original first-order approximation neutralization technique, and that a correction factor would need to be introducted.

TABLE IX (6-22-62)

Res.No.	Predicted Values		%-BA-M* by Vol[1]	K Content	To Prepare 100 ml batches use the following amounts of each solution			
	Conductance	Resistance			Sol A(ml)	Sol B(ml)	Sol C(ml)	H20 (ml)
R 1-2	100 micro-mhos	10 K ohms	89%	111 mg/	66.8	22.2	0	11
R 3-4	80	12.5 K	69%	87	69.0	0	17.4	13.6
R 5-6	69	14.5 K	59.5	74.7	59.5	0	14.94	25.56
R 7-8	60	16.6 K	51.8	64.0	51.8	0	12.80	35.4
R 9-10	50	20 K	43.5	52.0	43.5	0	10.4	46.1
R 11-12	30	33.3 K	28.4	28.5	28.4	0	5.7	65.9
R 13-14	20	50 K	21.0	17.2	21.0	0	3.44	75.56
R 15-16	16.66	60 K	18.5	13.3	18.5	0	2.66	78.84
R 17-18	12.5	80 K	15.5	8.5	15.5	0	1.7	82.8
R 19-20	10	100 K	13.5	5.5	13.5	0	1.1	85.4

* Equivalent precent of Solution A

1 Read from Figure 25.

Table IX - Resistance and Conductance Values and Corresponding Chemeical Contents Used in Experiment 12.

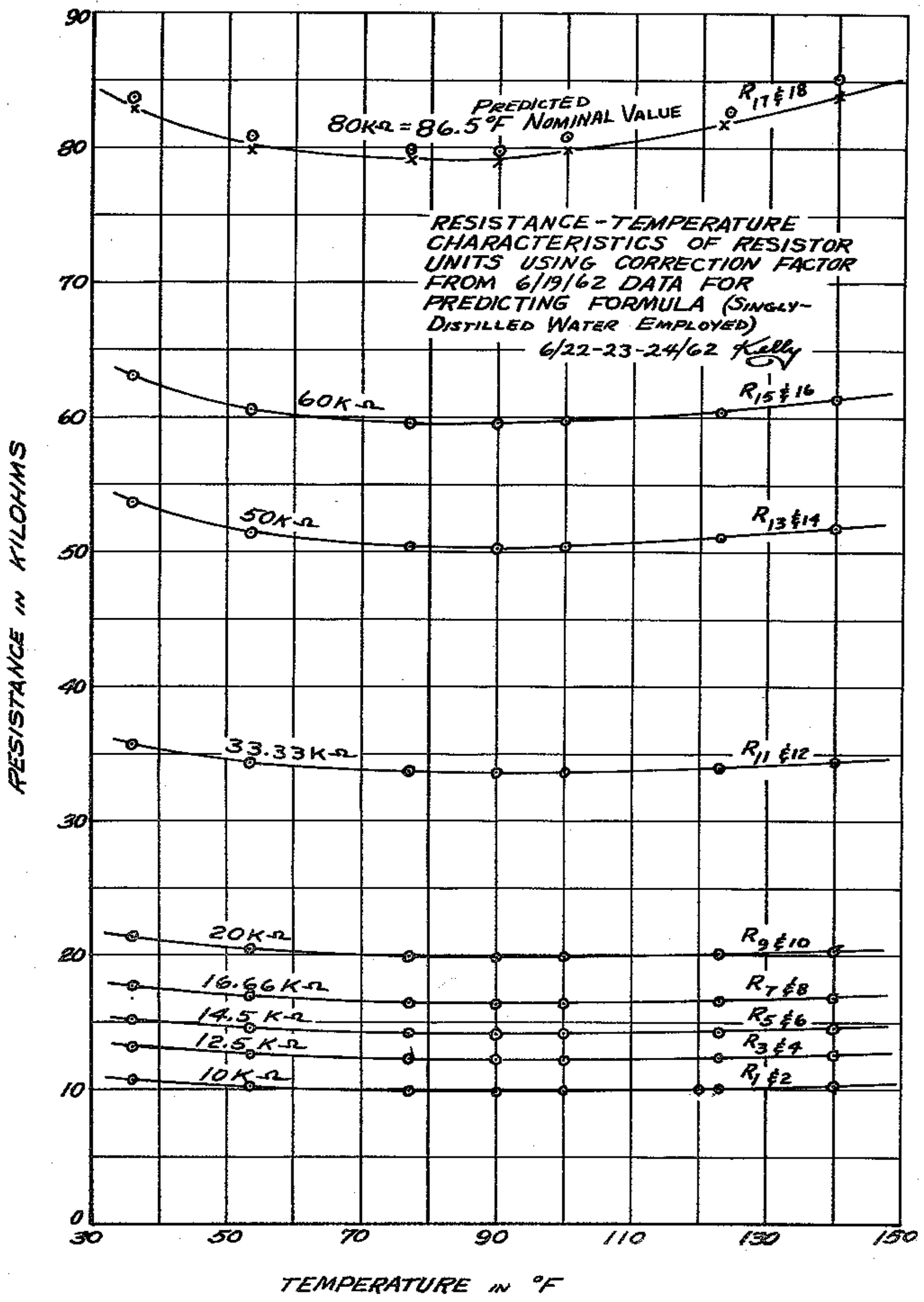


Figure 29. Resistance-Temperature Characteristics of Water Resistors Employing a Correction Factor Applied to Initially-Predicted Modified-Versions of Magnanini's Solution and Singly-Distilled Water

It was thought that experimental work could be terminated with Experiment 12 unitl the results of the resistance-temperature characteristics of the higher resistance values were observed. Another experiment (Experiment 13) was formulated simultaneously with Experiment 12 for the purpose of determining the spread of resistance values when a large number of resistors are prepared. In Experiment 13, nominal values of resistance of 10K-ohm, 20K-ohm, and 100K-ohm were chosen, and eight of each value were prepared and tested throughout the 40°F to 160°F temperature range. The results of this test are presented in tabular form in Table X. The data in Table X are normalized with respect to the nominal values in each case. Based upon the average of the 88°F readings, one may expect to prepare a resistor to be within about 1% to 2% of the desired value. Although more desirable resistance-temperature characteristics are exhibited by the resistors developed in subsequent experiments, the results of Experiment 13 indicate what sort of spread in resistance values one should expect.

A new experiment (Experiment 14) was formulated to determine the optimum potassium chloride content to more nearly neutralize the temperature coefficient of resistance. In this experiment six carefully-chosen nominal values of conductance were selected which would best define a new curve of conductance versus potassium chloride-mannitol boric acid content. At each level of conductance, the mannitol-boric acid content was held constant, and the potassium chloride content varied

TABLE X

Normalized Results of Experiment 13
Resistors 1-8

	Nominal 10K ohm								
Temp °F	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8	Avg.
88	.980	.988	.978	.990	.984	.988	.976	.986	.9838
139	1.004	1.018	1.000	1.020	1.018	1.020	1.000	1.016	1.0120
118	.990	1.004	.984	1.004	1.000	1.004	.988	1.004	.9973
100	.984	.996	.978	1.000	.992	.996	.980	.996	.9903
79	.984	1.000	.982	1.000	.994	.998	.982	.988	.9910
56	1.004	1.016	1.000	1.024	1.018	1.018	1.004	1.018	1.0128
42	1.038	1.052	1.036	1.056	1.044	1.050	1.038	1.052	1.0458
60	1.000	1.016	.996	1.020	1.010	1.014	1.000	1.016	1.0090
78	.984	1.000	.980	1.006	.994	.998	.984	1.000	.9933
100	.984	1.000	.980	1.012	.996	.996	.984	1.000	.9940
121	.998	1.012	.992	1.024	1.006	1.006	1.000	1.012	1.0063
138	1.016	1.030	1.008	1.040	1.022	1.020	1.018	1.026	1.0225
160	1.036	1.054	1.030	1.072	1.046	1.044	1.040	1.054	1.0470

TABLE X (con't)

Normalized Results of Experiment 13
Resistors 9-16
Nominal 20K

Temp °F	R_9	R_{10}	R_{11}	R_{12}	R_{13}	R_{14}	R_{15}	R_{16}	AVG.
88	1.00	1.005	1.00	.990	.990	.982	.982	.996	.9932
139	1.02	1.035	1.02	1.015	1.02	1.00	1.01	1.02	1.0175
118	1.01	1.025	1.01	1.01	1.005	.995	1.00	1.005	1.0075
100	1.005	1.0125	1.00	1.005	1.00	.988	.990	1.00	1.0000
79	1.005	1.01	1.005	1.005	1.00	.992	.988	1.005	1.0015
56	1.025	1.025	1.02	1.025	1.02	1.01	1.005	1.02	1.0190
42	1.06	1.055	1.055	1.055	1.055	1.04	1.035	1.055	1.0513
60	1.02	1.02	1.02	1.02	1.015	1.01	1.00	1.02	1.0157
78	1.01	1.01	1.01	1.005	1.005	.995	.9875	1.00	1.0028
100	1.005	1.01	1.005	1.01	1.005	.995	.9875	1.00	1.0022
121	1.02	1.025	1.015	1.015	1.0125	1.005	1.00	1.0125	1.0132
138	1.03	-	1.02	1.03	1.025	1.015	1.015	1.02	1.0222
160	1.045	-	1.04	1.05	1.05	1.035	1.145	1.04	1.0579

TABLE X (con't)

Normalized Results of Experiment 13
Resistors 17-24

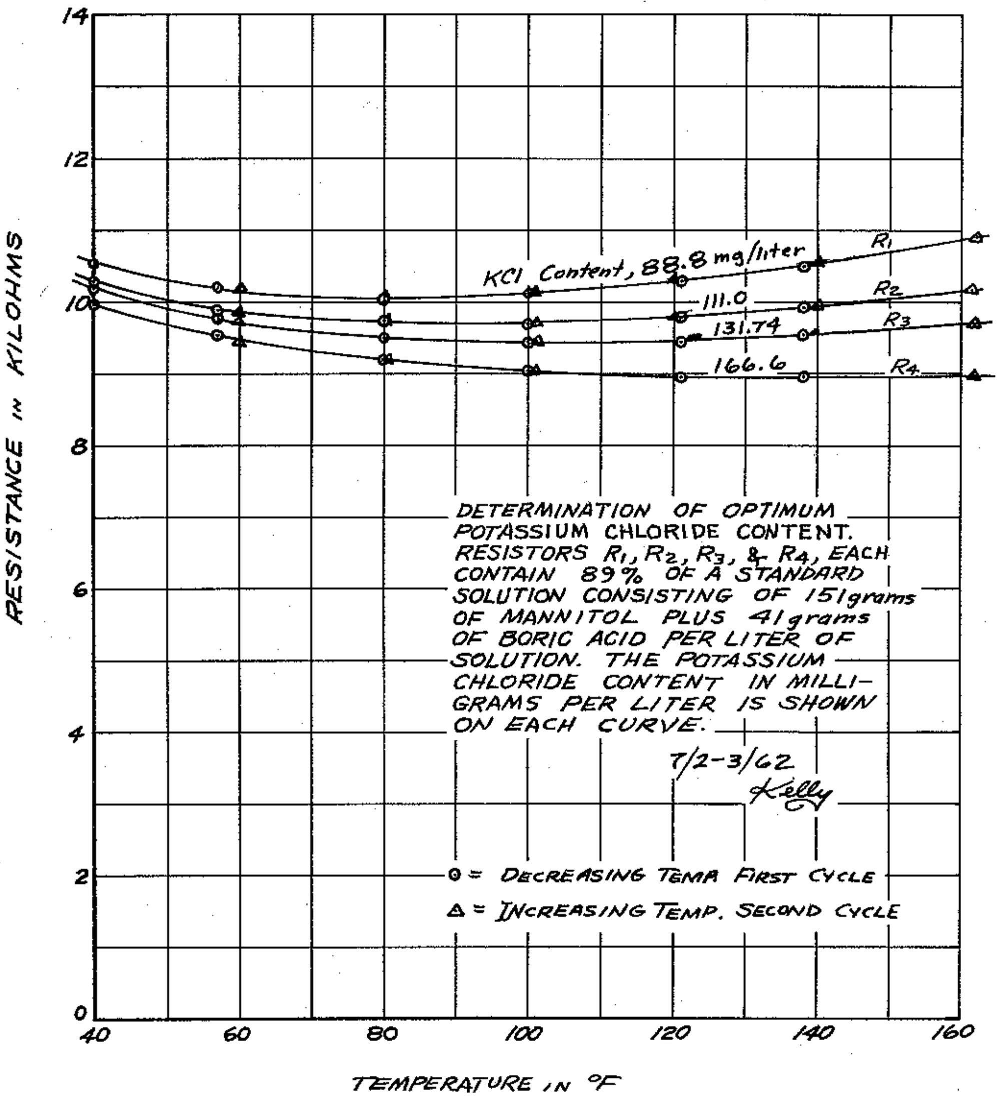
	Nominal 100 K								
Temp °F	R_{17}	R_{18}	R_{19}	R_{20}	R_{21}	R_{22}	R_{23}	R_{24}	Avg.
88	.956	.980	.984	.972	.984	.980	.990	.972	.9773
139	1.012	1.036	1.056	1.024	1.040	1.056	1.060	1.040	1.0405
118	.988	1.016	1.038	1.000	1.016	1.038	1.036	1.020	1.0190
100	.970	1.000	1.024	.984	.996	1.028	1.028	1.002	1.0040
79	.960	.990	1.020	.980	.984	1.026	1.020	.998	.9973
56	.964	.992	1.020	.986	.986	1.032	1.024	1.000	1.0005
42	.980	1.014	1.036	1.002	1.008	1.046	1.040	1.020	1.0183
60	.964	.994	1.020	.984	.988	1.034	1.030	1.002	1.0020
78	.964	.992	1.024	.984	.990	1.040	1.038	1.010	1.0053
100	.976	1.004	1.036	1.000	1.000	1.058	1.058	1.024	1.0195
121	.996	1.030	1.060	1.024	1.024	1.070	1.078	1.042	1.0405
138	1.020	1.052	1.080	1.050	1.048	1.086	1.092	1.062	1.0613
160	1.044	1.080	1.086	1.080	1.080	1.070	1.100	1.068	1.0760

from about 50% to 150% of the previously used values. The group of twenty-four resistors was cycled in 20°F temperature steps through the range from 40°F to 160°F. The results of this test are presented graphically in Figures 30 through 34. From this family of curves, a new ratio of mannitol, boric-acid, potassium chloride, and distilled water was chosen for each group of solutions used. The third resistor in each group, representing about 125% of the previously used amount of potassium chloride, was chosen as the most desirable of the group. A new curve relating conductance to the potassium chloride and mannitol-boric acid content was prepared and used for subsequent testing. (See Figure 35, optimized curve)

Since the conductance versus potassium chloride content curve in Figure 35 is a straight line, its equation was written, and subsequent potassium chloride content was determined from this equation. The equation is

$$G = 0.76\ C + 4 \qquad (1)$$

where G is the conductance of the desired resistor in micromhos and C is the potassium chloride concentration in milligrams per liter. The correct mannitol-boric acid concentration was graphically determined from Figure 35. Using the value of C determined from Equation (1) for the potassium chloride content and the concentration of the mannitol-boric acid solution as read from Figure 35, a new group of resistors were prepared using a set of nominal conductance values which would provide data so that the curves in Figure 35 could be better defined. The new solution constituents are given in Table XI.



DETERMINATION OF OPTIMUM POTASSIUM CHLORIDE CONTENT. RESISTORS R_1, R_2, R_3, & R_4, EACH CONTAIN 89% OF A STANDARD SOLUTION CONSISTING OF 151 grams OF MANNITOL PLUS 41 grams OF BORIC ACID PER LITER OF SOLUTION. THE POTASSIUM CHLORIDE CONTENT IN MILLIGRAMS PER LITER IS SHOWN ON EACH CURVE.

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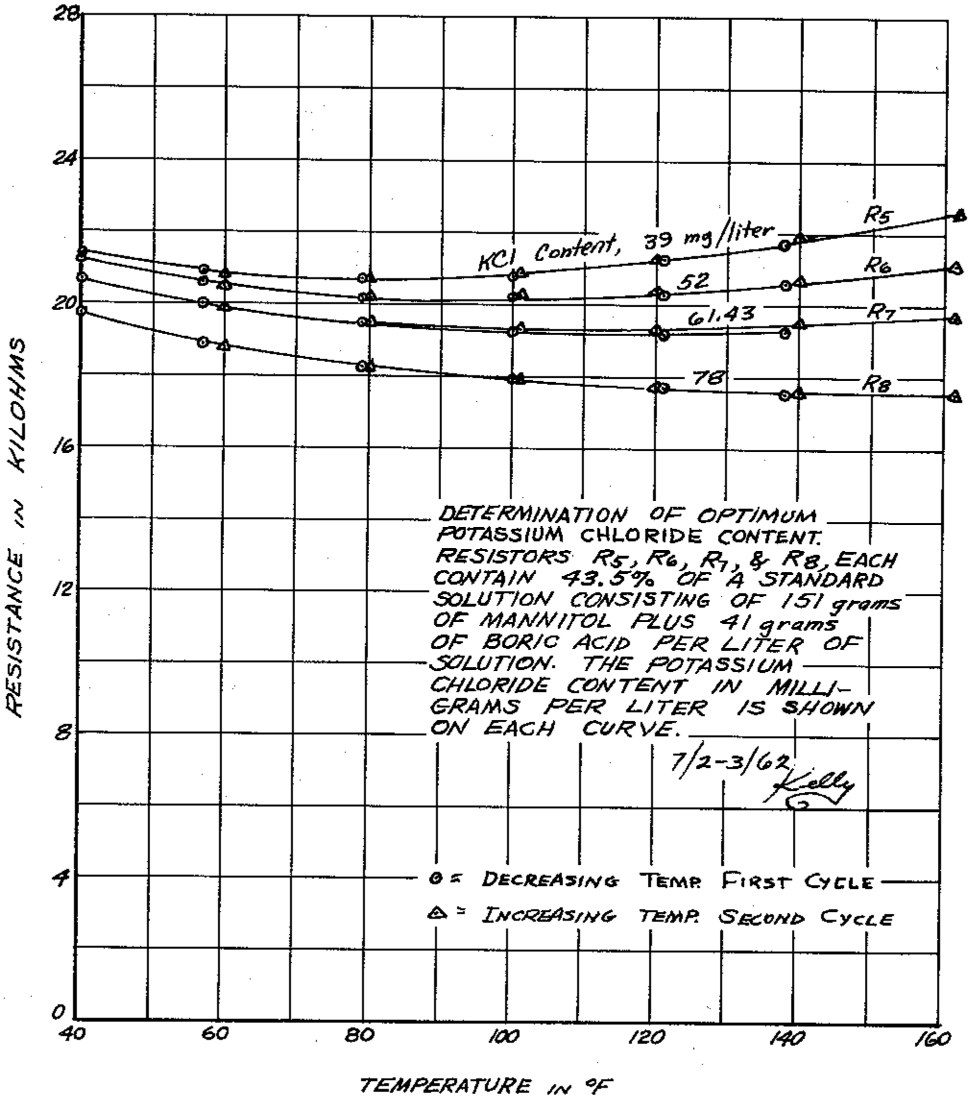
Figure 30. Determination of the Optimum Potassium Chloride Content for an 89% Mannitol-Boric Acid Solution



DETERMINATION OF OPTIMUM POTASSIUM CHLORIDE CONTENT. RESISTORS R_5, R_6, R_7, & R_8, EACH CONTAIN 43.5% OF A STANDARD SOLUTION CONSISTING OF 151 grams OF MANNITOL PLUS 41 grams OF BORIC ACID PER LITER OF SOLUTION. THE POTASSIUM CHLORIDE CONTENT IN MILLIGRAMS PER LITER IS SHOWN ON EACH CURVE.

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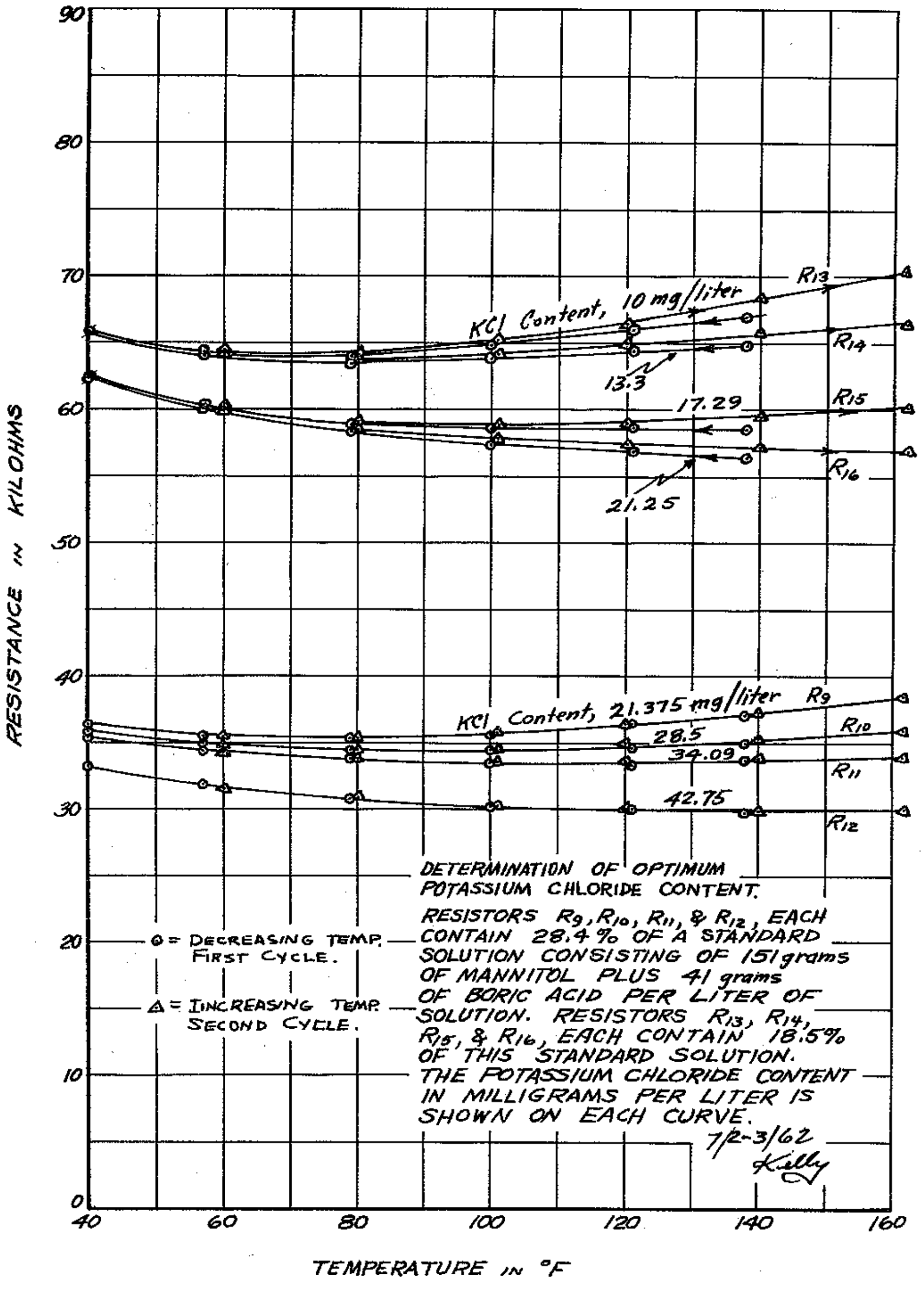
Figure 31. Determination of the Optimum Potassium Chloride Content for a 43.5% Mannitol-Boric Acid Solution



DETERMINATION OF OPTIMUM POTASSIUM CHLORIDE CONTENT.

RESISTORS R_9, R_{10}, R_{11}, & R_{12}, EACH CONTAIN 28.4% OF A STANDARD SOLUTION CONSISTING OF 151 grams OF MANNITOL PLUS 41 grams OF BORIC ACID PER LITER OF SOLUTION. RESISTORS R_{13}, R_{14}, R_{15}, & R_{16}, EACH CONTAIN 18.5% OF THIS STANDARD SOLUTION. THE POTASSIUM CHLORIDE CONTENT IN MILLIGRAMS PER LITER IS SHOWN ON EACH CURVE.

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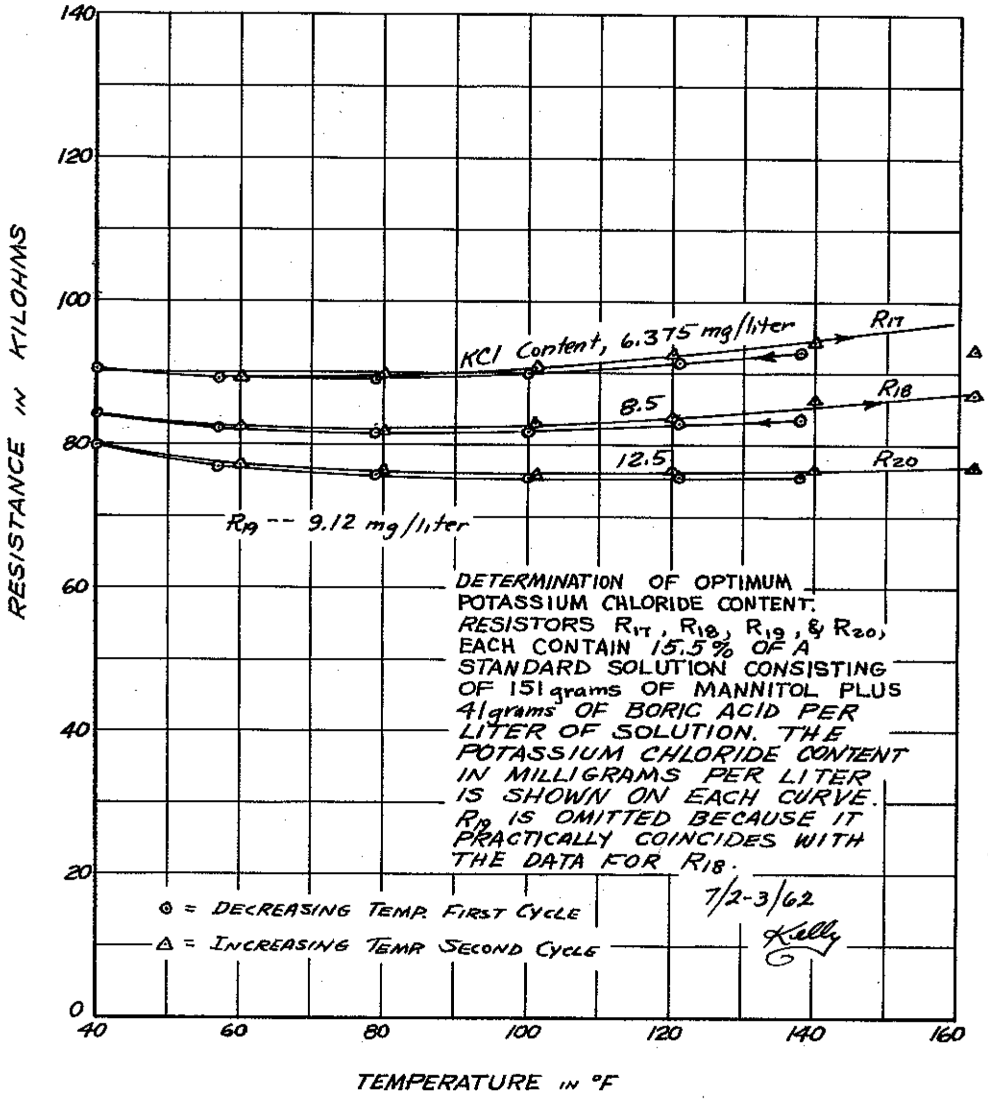
Figure 32. Determination of the Optimum Potassium Chloride Content for 28.4%, and 18.5% Mannitol-Boric Acid Solutions



DETERMINATION OF OPTIMUM POTASSIUM CHLORIDE CONTENT. RESISTORS R_{17}, R_{18}, R_{19}, & R_{20}, EACH CONTAIN 15.5% OF A STANDARD SOLUTION CONSISTING OF 151 grams OF MANNITOL PLUS 41 grams OF BORIC ACID PER LITER OF SOLUTION. THE POTASSIUM CHLORIDE CONTENT IN MILLIGRAMS PER LITER IS SHOWN ON EACH CURVE. R_{19} IS OMITTED BECAUSE IT PRACTICALLY COINCIDES WITH THE DATA FOR R_{18}.

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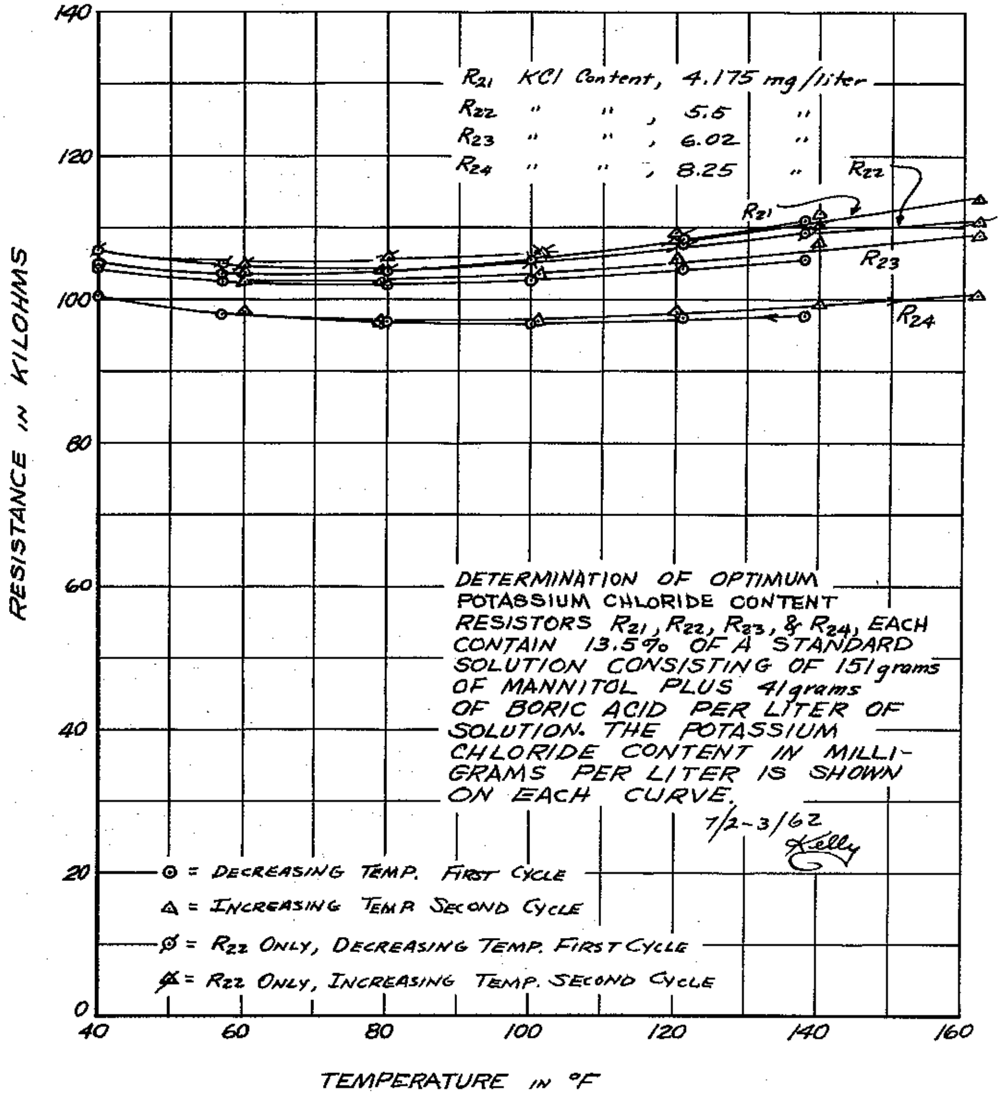
Figure 33. Determination of the Optimum Potassium Chloride Content for a 15.5%, Mannitol-Boric Acid Solution



DETERMINATION OF OPTIMUM POTASSIUM CHLORIDE CONTENT RESISTORS R21, R22, R23, & R24, EACH CONTAIN 13.5% OF A STANDARD SOLUTION CONSISTING OF 151 grams OF MANNITOL PLUS 41 grams OF BORIC ACID PER LITER OF SOLUTION. THE POTASSIUM CHLORIDE CONTENT IN MILLIGRAMS PER LITER IS SHOWN ON EACH CURVE.

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Figure 34. Determination of the Optimum Potassium Chloride Content for a 13.5%, Mannitol-Boric Acid Solution

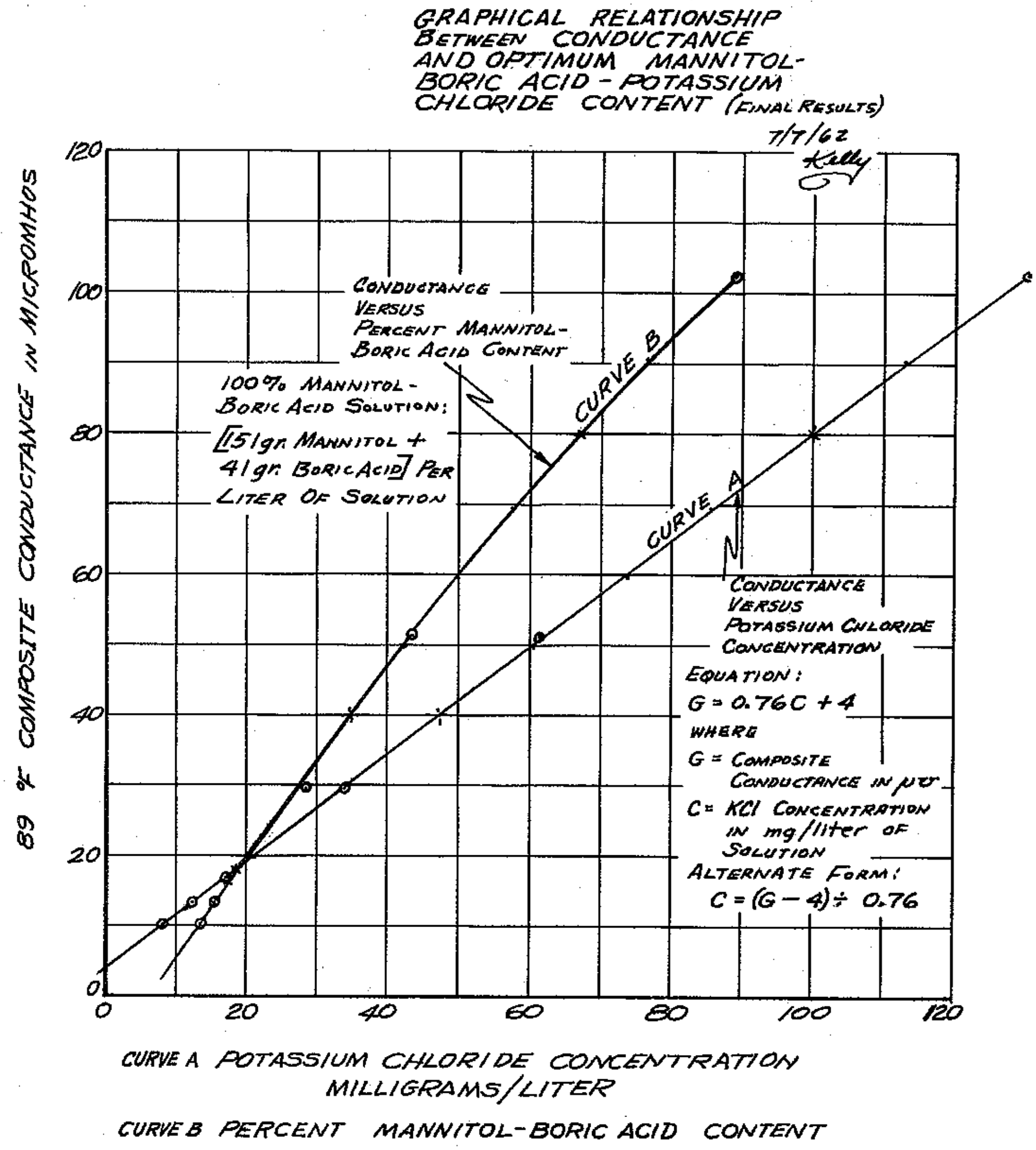


Figure 35. Conductance at 89°F. versus Mannitol-Boric Acid Content and Potassium Chloride Content of Water Resistors Employing an Optimized Version of Magnanini's Formula.

TABLE XI

Chemical Constituents Used in Evaluating Optimized Formulas

Res.No.	Predicted 80°F Value		From Curve 35 Vol. % of Mannitol-Boric Acid Solution	$C=\frac{G-4}{0.76}$ Potassium Chloride Content mg/liter	To prepare 100-ml batches, use the following amounts of ea.sol.			
	Conductance micromhos	Resistance K ohms			Sol. A ml	Sol. B ml	Sol. C ml	H_2O ml
1-2	100	10	86.7	126.4	61.42	25.28	0	13.3
3-4	90	11.1	76.4	113.2	53.76	22.64	0	23.6
5-6	80	12.5	67.0	100.0	47.0	20.0	0	33.0
7-8	69	14.5	57.5	85.5	57.5	0	17.10	25.4
9-10	60	16.66	50.0	73.7	50.0	0	14.74	35.26
11-12	50	20	42.3	60.5	42.3	0	12.10	45.60
13-14	40	25	34.9	47.36	34.9	0	9.472	55.628
15-16	30	33.3	27.7	34.2	27.7	0	6.84	65.46
17-18	20	50	20.5	21.05	20.5	0	4.21	75.29
19-20	16.66	60	18.0	16.65	18.0	0	3.33	78.67
21-22	12.5	80	15.0	11.19	15.0	0	2.238	82.762
23-24	10	100	13.3	7.9	13.3	0	1.58	85.12

Resistors Mixed at 81°F

Although the quantities specified for Solutions A, B, C and water are given for preparing a 100 milliliter batch of a given solution, R 1-2 through R 11-12 were prepared in 50 milliliter batches, and one-half of each of the constituents listed for these resistors was used. When preparing the resistors, it is important to maintain the temperature at approximately the same value at which the original Solutions A, B, and C were mixed, since volumetric measurements are being used and these solutions have a relatively large coefficient of thermal expansion.

The results of resistance versus temperature and of conductance versus temperature for the above resistors is presented graphically in Figures 36 through 38. Since approximately equal conductance steps of 10 micromhos each are taken in Table XI, the results presented in Figure 36 are crowded in the 10K to 20K region; however, the trend of the curves is evident, and it is apparent that the temperature coefficient os resistance is effectively neutralized over a considerable range of temperature.

The conductance-versus-temperature plot shown in Figure 37 presents a better graphical distribution of the family of curves than does Figure 36. This curve represents the variations in conductance with temperature as the temperature of the resistors was reduced from 141°F down to 40°F in approximately twenty-degree steps. The same information is plotted in Figure 38, in addition to the conductance variations as the temperature is cycled back up in about twenty

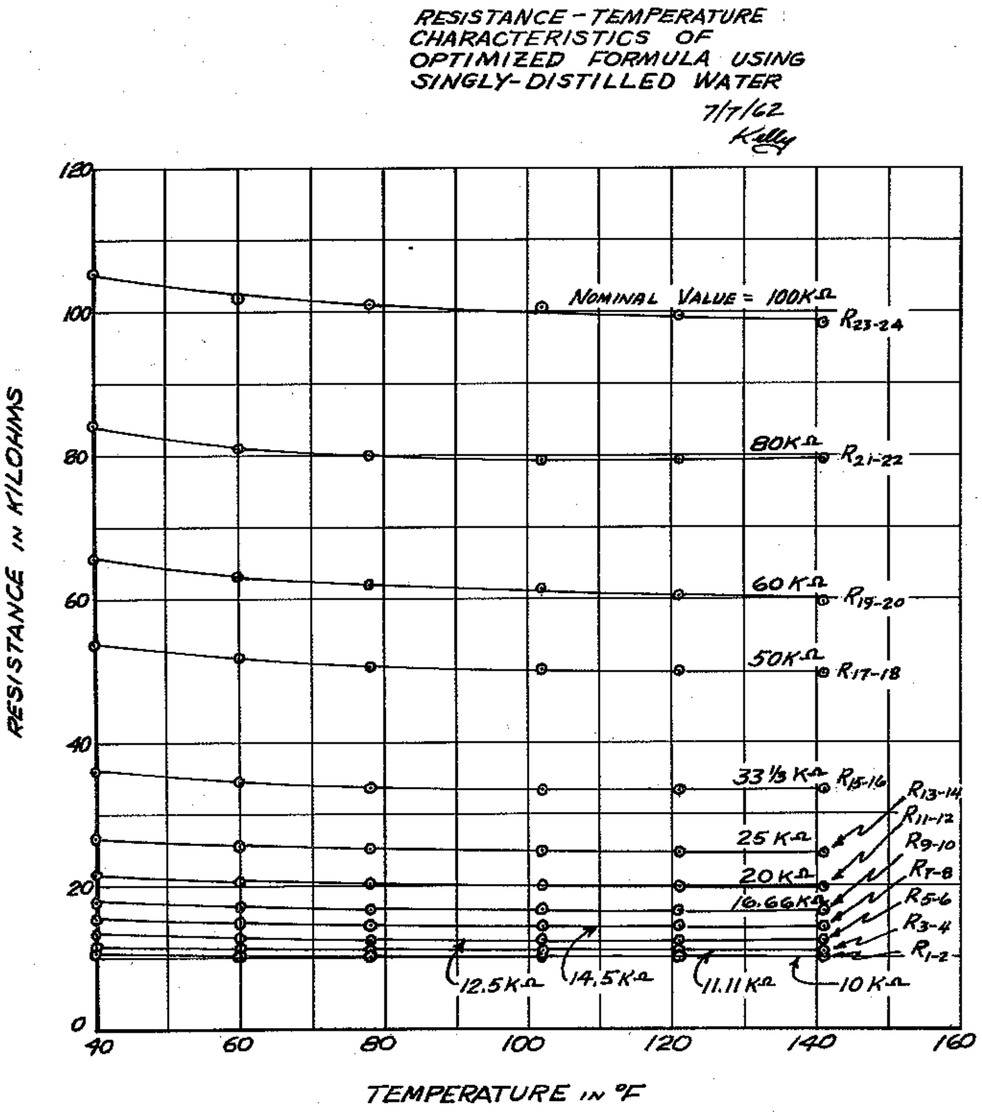


Figure 36. Resistance-Temperature Characteristics of Water Resistors Using an Optimized Version of Magnanini's Formula and Singly-Distilled Water.

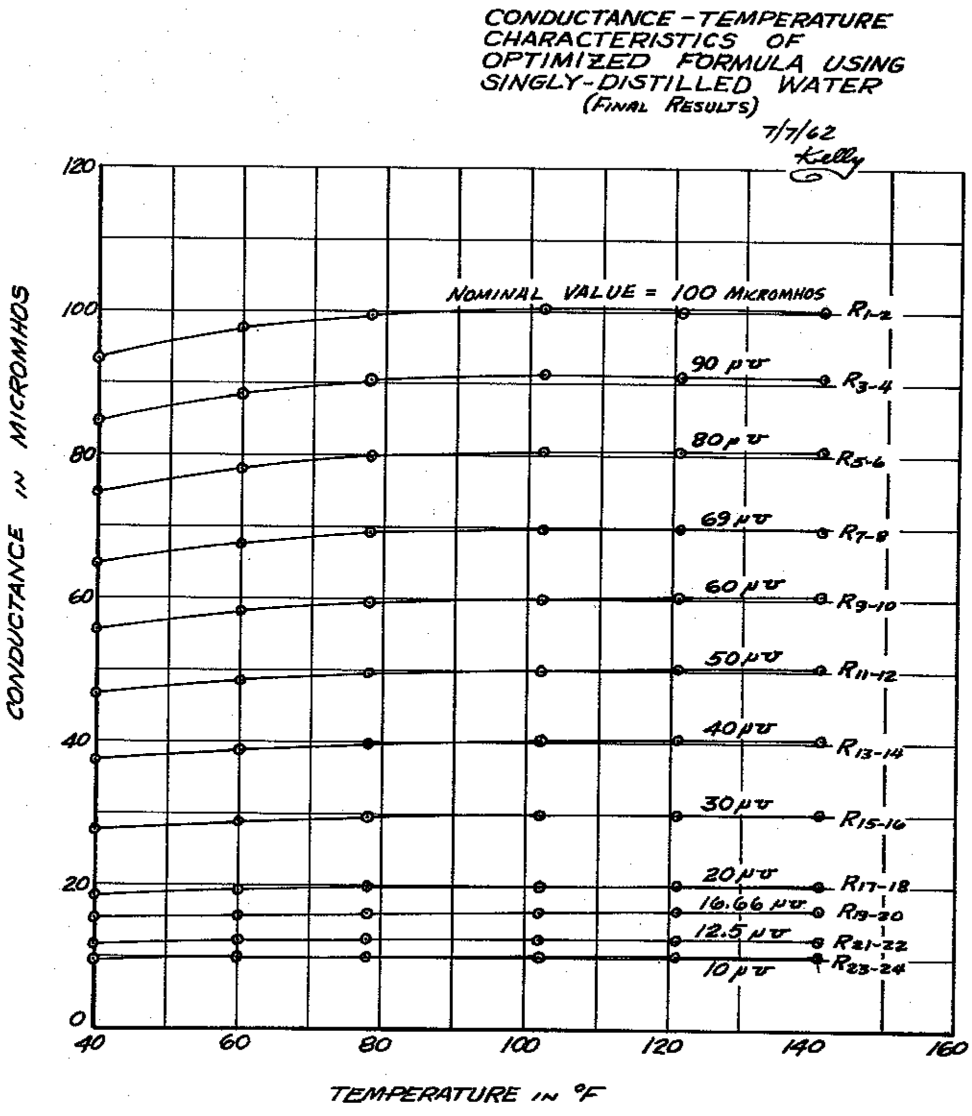


Figure 37. Conductance-Temperature Characteristic of Water Resistors Using an Optimized Version of Magnanini's Formula and Singly-Distilled Water.

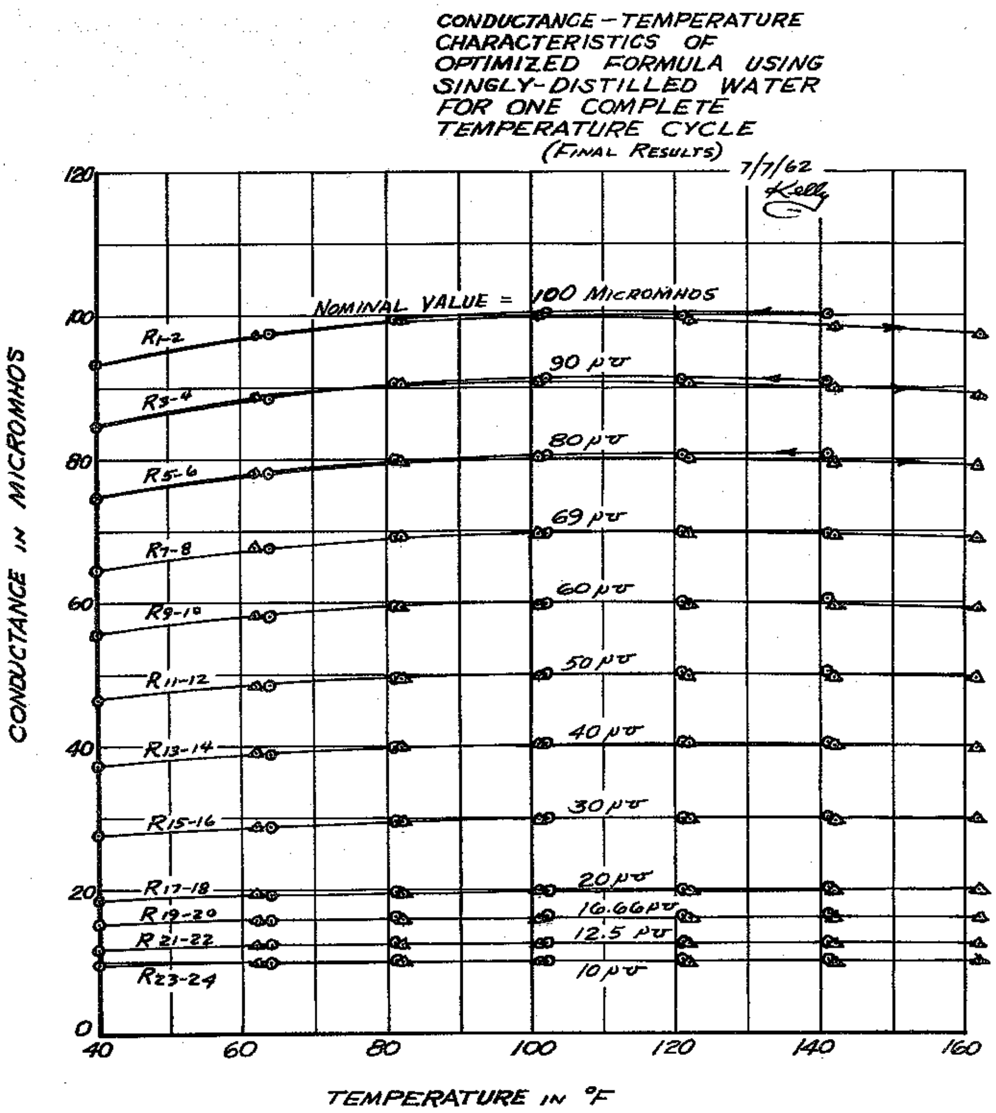


Figure 38. Conductance-Temperature Characteristics of Water Resistors Using an Optimized Version of Magnanini's Formula and Singly-Distilled Water (Increasing and Decreasing Temperature Cycles Shown).

degree steps to a maximum value of 162°F. The closeness of the two curves is an indication of the repeatability of the cycle. In order to better show how closely these resistors maintain their value as the temperature is varied, another form of graphical representation is employed. All of the resistance measurements are normalized relative to the 78°F value in each of the respective groups; e.g., the nominal 20K-ohm resistor (R 11-12) had a value of 20.175K ohms at 78°F, and all of the readings for this resistor group were normalized with respect to 20.175K ohms.

The normalized values of resistance are averaged at each temperature, and these results are plotted in Figure 39. The average of all twelve nominal resistance values is shown as well as the maximum and minimum values experienced. The trend shows the resistors to be above nominal at the higher temperature values (about 2% at 160°F) to swing below nominal at about 100°F (about 1%), and to rise up considerably above nominal value at 40°F (about 6%). The results indicates that from about 60°F up to 160°F the curve has a total deviation of only about 2%, while most of the curve is within 1%. The trend of the curve indicates that there is a slight shift in characteristics with temperature cycling, and other tests bear this out.

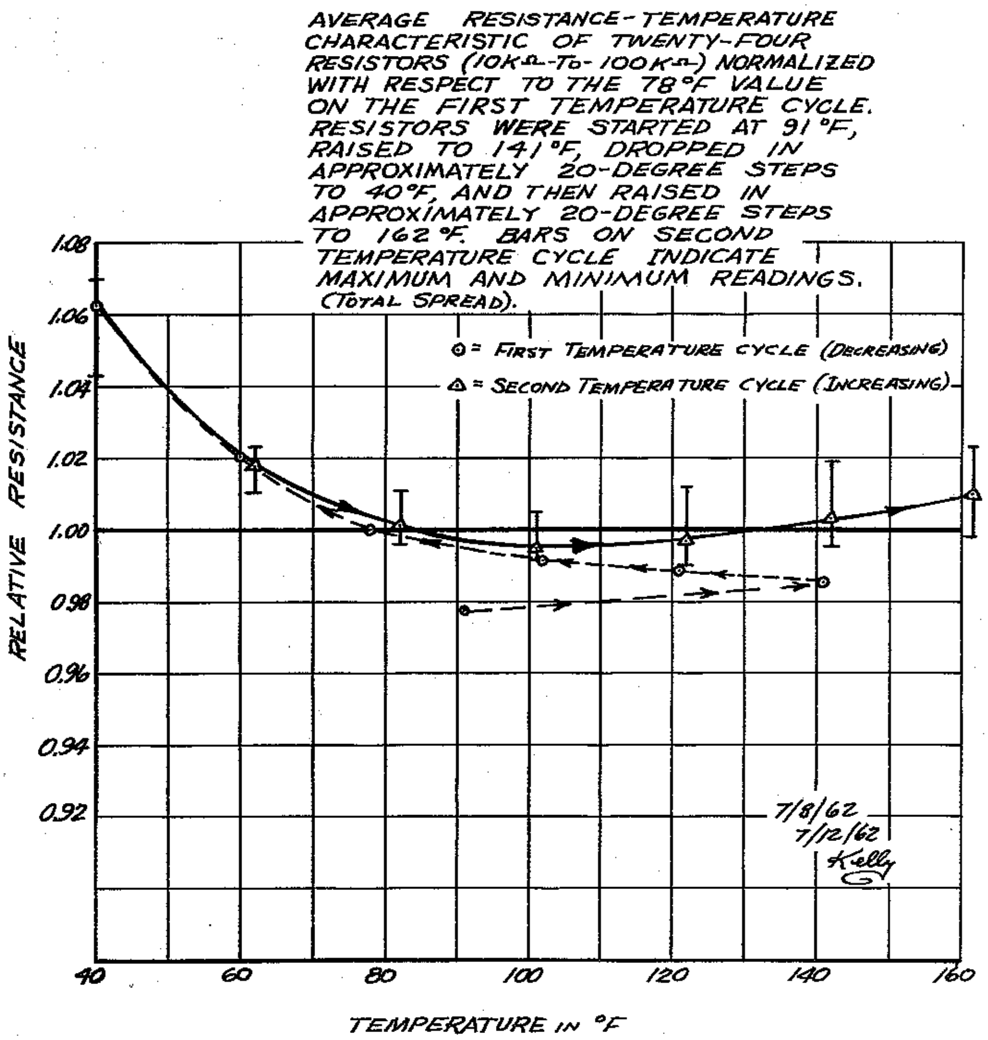


Figure 39. Average, Normalized, Resistance-Temperature Characteristics of Twenty-Four Water Resistors Employing an Optimized Version of Magnanini's Formula and Singly-Distilled Water

Experiment 16 was performed to demonstrate that both the singly-distilled water available at the University of New Mexico Chemical Engineering Department and the triply-distilled water obtained from Org. 1413 at Sandia Corporation are equally suitable for use in preparing the "water resistors" as specified by the optimum formulas developed in Experiment 14. Although the optimum formulas developed in Experiment 14 employed the singly-distilled water, the same results were obtained, for all practical purposes, when the identical experiment was performed using triply-distilled water.

Experiment 16 provided the answer to two important questions: First, it proved that one may use triply-distilled water in the same ratio as the formula states that singly-distilled water is to be used; secondly, by remixing another set of solutions using singly-distilled water, it is demonstrated that the resistance values may be quite accurately repeated from experiment to experiment.

In this experiment, two identical groups of resistance values were tested, one group using singly-distilled water the same as was used in Experiment 15, and the other group using triply-distilled water and exactly the same formula for their preparation as used for the singly-distilled case. The results of this experiment are illustrated graphically in Figures 40 through 46. In this group of Figures, resistance values throughout the range of 10 K ohms to 100 K ohms are illustrated to show that the use of triply-distilled water

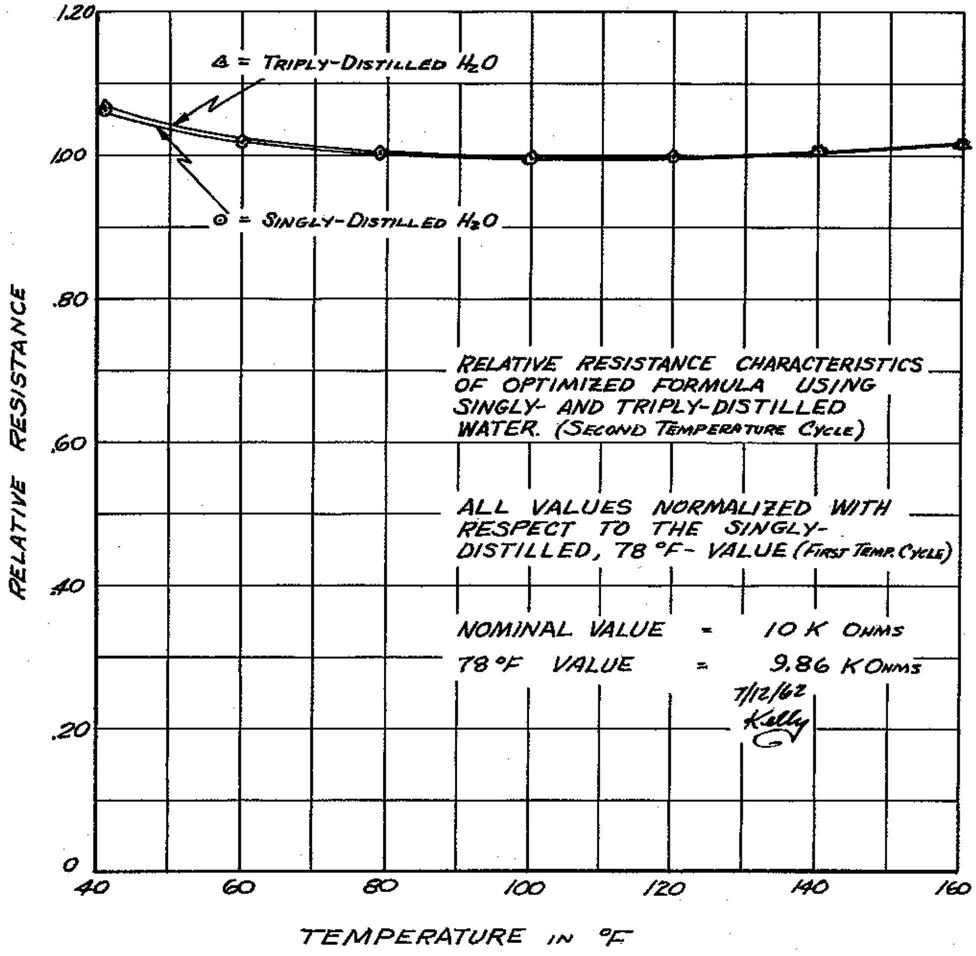


Figure 40. Relative Resistance-Versus-Temperature Characteristics of Water Resistors Using an Optimized Version of Magnanini's Formula for Both Singly- and Triply-Distilled Water (10 K ohms).

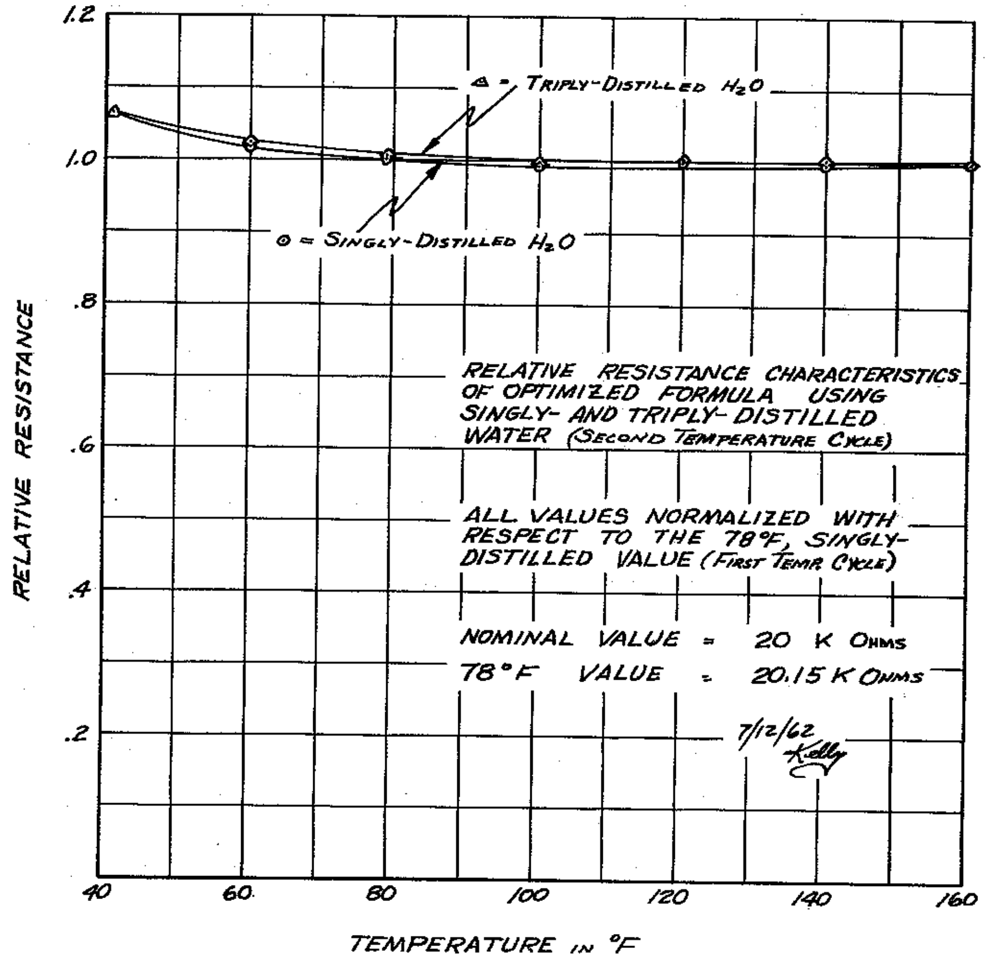
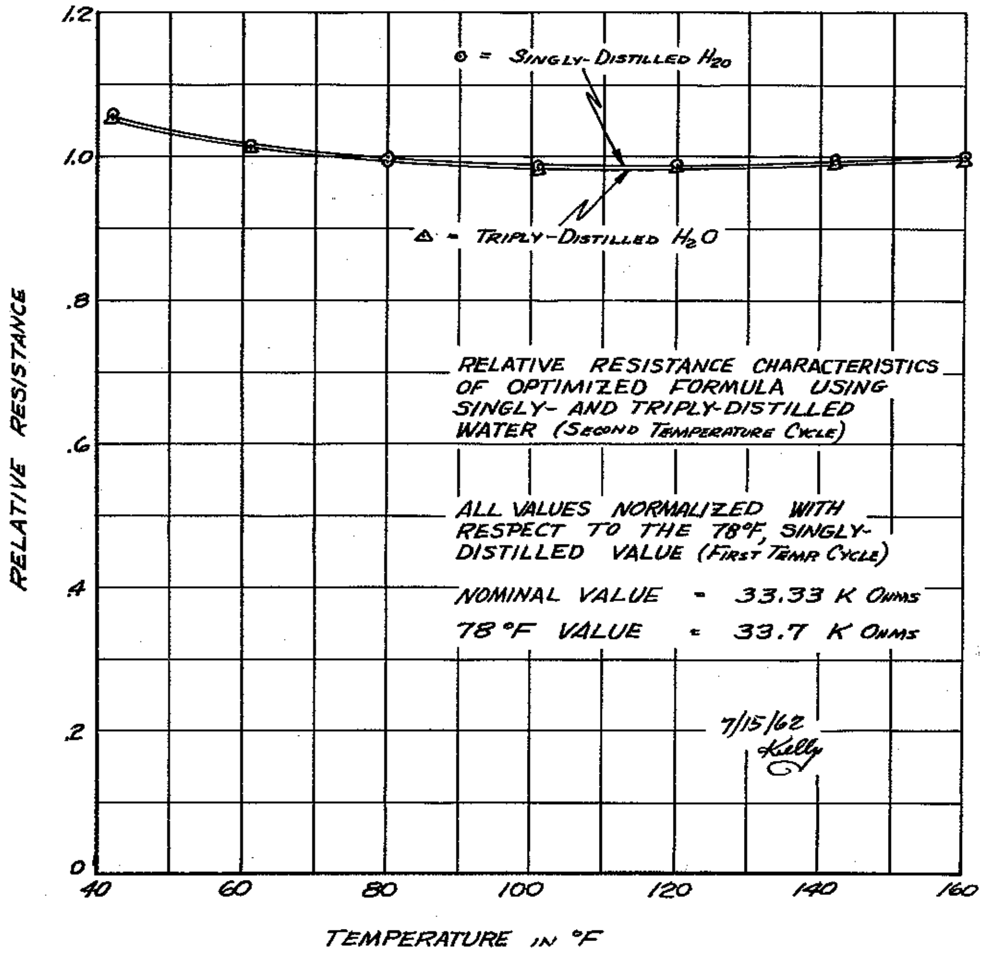


Figure 41. Relative Resistance-Versus-Temperature Characteristics of Water Resistors Using an Optimized Version of Magnanini's Formula for Both Singly- and Triply-Distilled Water (20 K ohms).



RELATIVE RESISTANCE CHARACTERISTICS OF OPTIMIZED FORMULA USING SINGLY- AND TRIPLY-DISTILLED WATER (SECOND TEMPERATURE CYCLE)

ALL VALUES NORMALIZED WITH RESPECT TO THE 78°F, SINGLY-DISTILLED VALUE (FIRST TEMP CYCLE)

NOMINAL VALUE = 33.33 K OHMS

78 °F VALUE = 33.7 K OHMS

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Figure 42. Relative Resistance-Versus-Temperature Characteristics of Water Resistors Using an Optimized Version of Magnanini's Formula for Both Singly- and Triply-Distilled Water (33.33 K ohms).

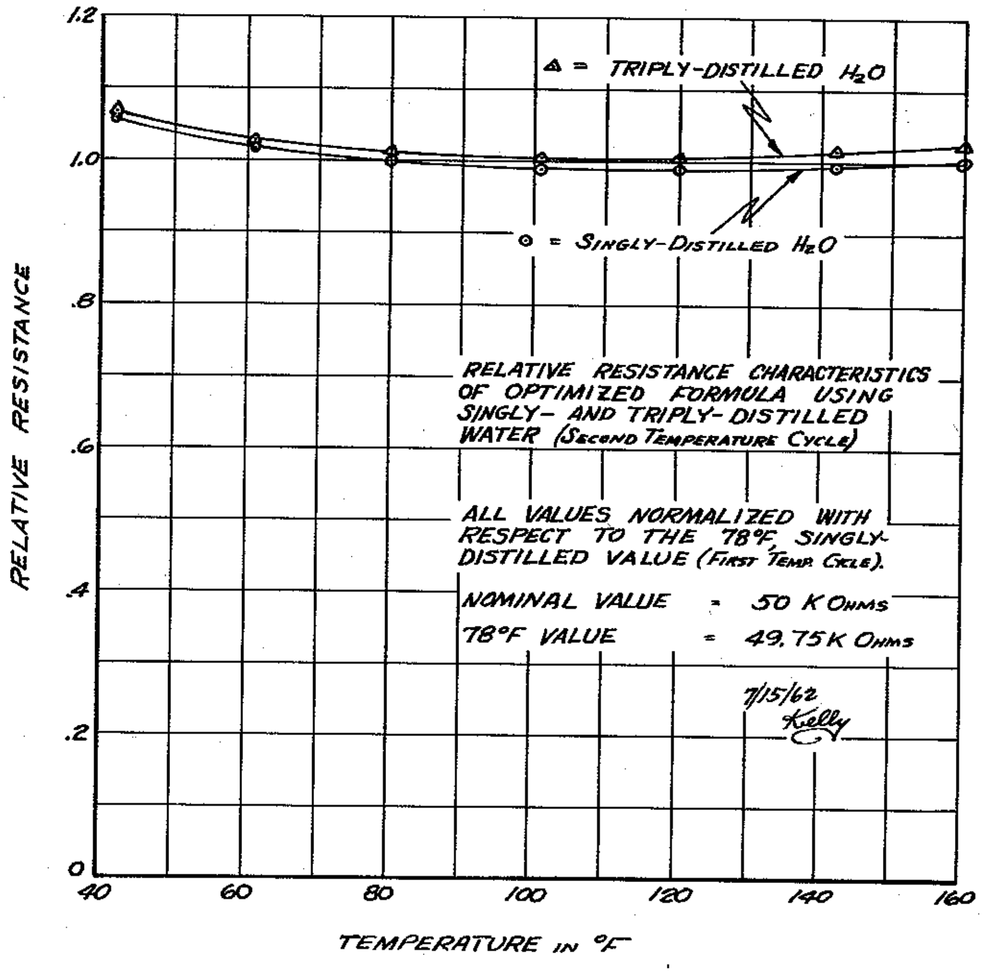
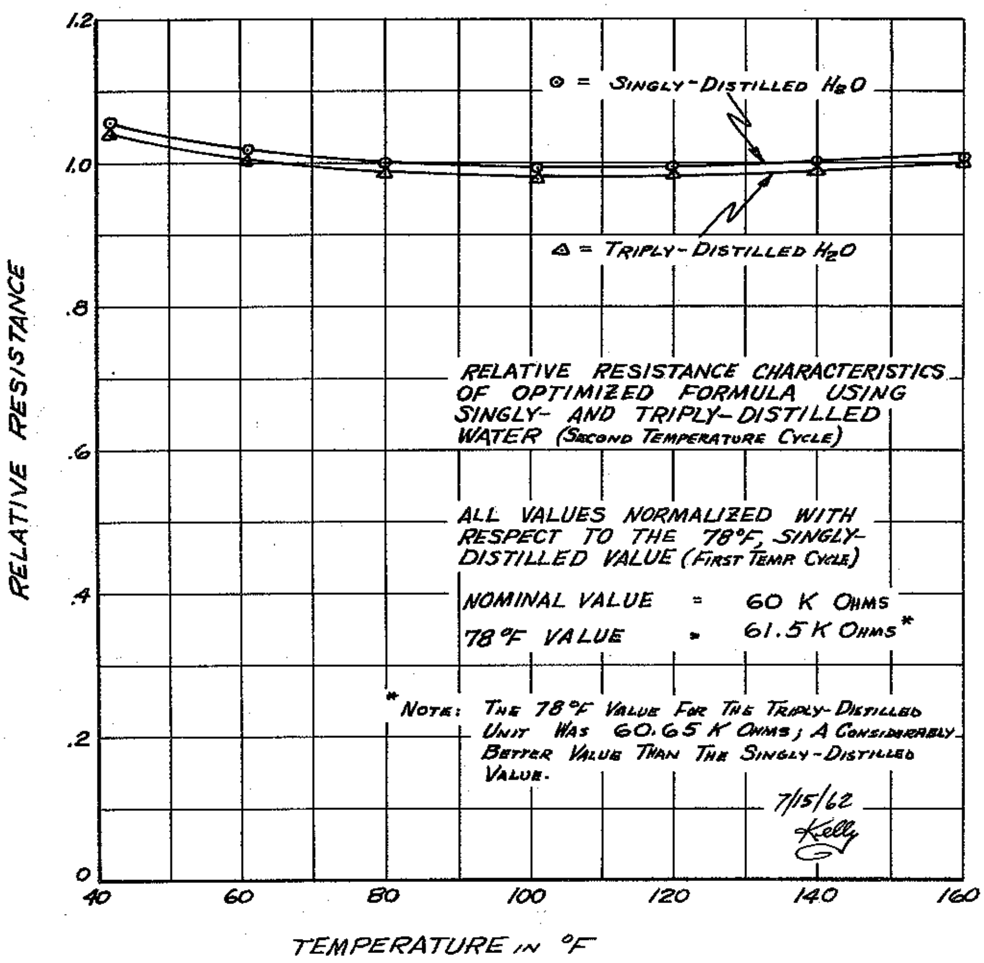


Figure 43. Relative Resistance-Versus-Temperature Characteristics of Water Resistors Using an Optimized Version of Magnanini's Formula for Both Singly- and Triply-Distilled Water (50 K ohms).



RELATIVE RESISTANCE CHARACTERISTICS OF OPTIMIZED FORMULA USING SINGLY- AND TRIPLY-DISTILLED WATER (Second Temperature Cycle)

ALL VALUES NORMALIZED WITH RESPECT TO THE 78°F, SINGLY-DISTILLED VALUE (First Temp Cycle)

NOMINAL VALUE = 60 K Ohms

78°F VALUE = 61.5 K Ohms*

*Note: The 78°F Value For The Triply-Distilled Unit Was 60.65 K Ohms; A Considerably Better Value Than The Singly-Distilled Value.

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Figure 44. Relative Resistance-Versus Temperature Characteristics of Water Resistors Using an Optimized Version of Magnanini's Formula for Both Singly- and Triply-Distilled Water (60 K ohms).

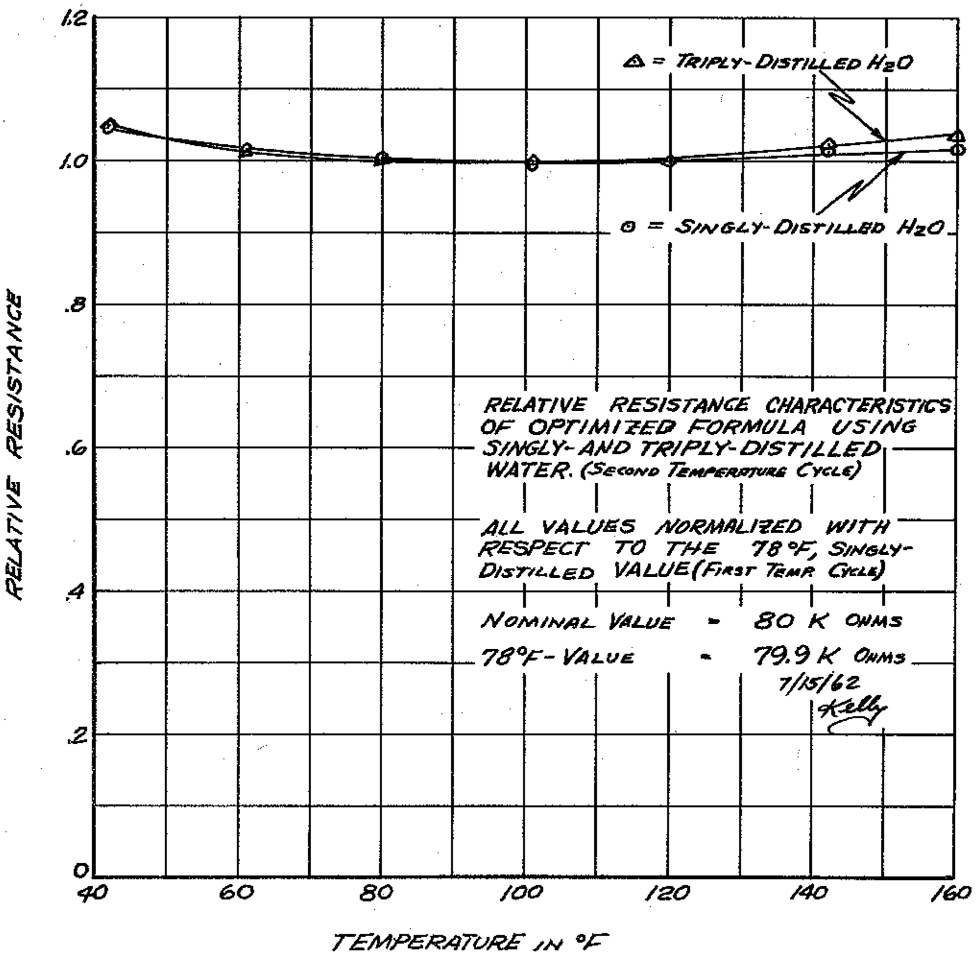

Figure 45. Relative Resistance-Versus Temperature Characteristics of Water Resistors Using an Optimized Version of Magnanini's Formula for Both Singly- and Triply-Distilled Water (80 K ohms).

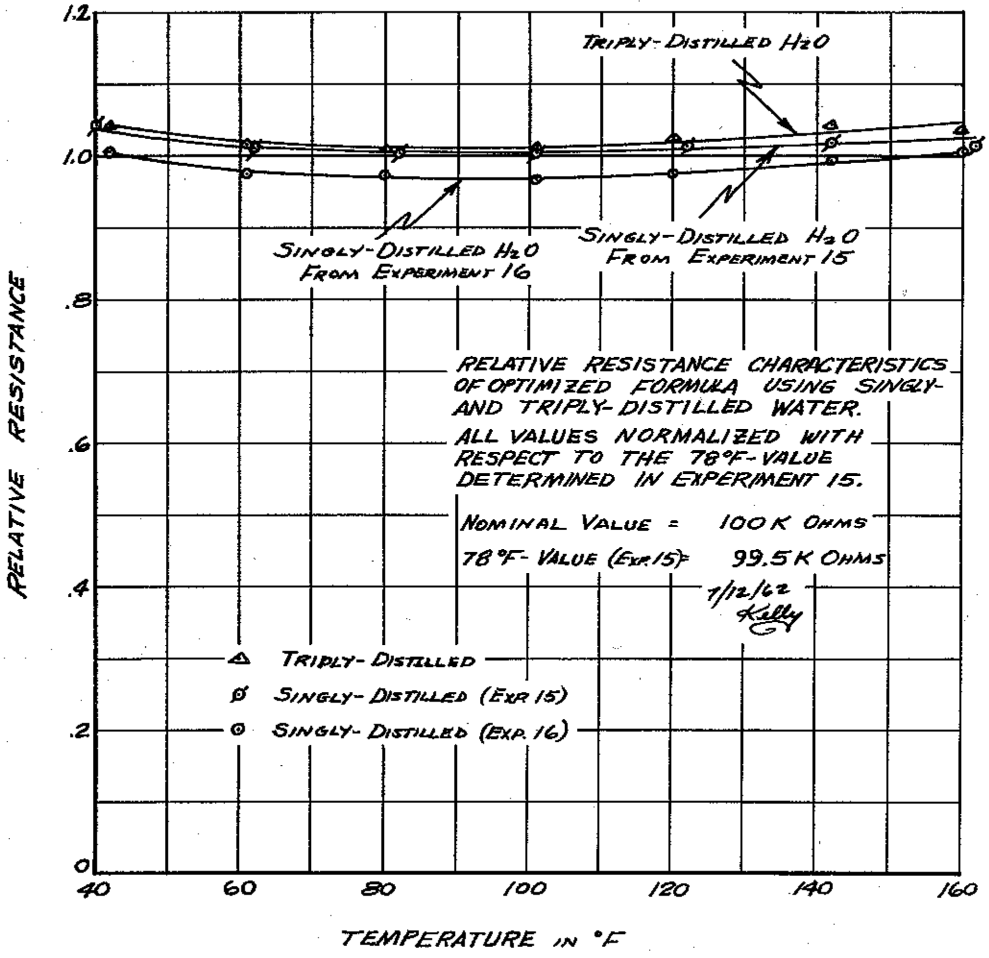

Figure 46. Relative Resistance-Versus-Temperature Characteristics of Water Resistors Using an Optimized Version of Magnanini's Formula for Both Singly- and Triply-Distilled Water (100 K ohms).

does not have a significant effect upon the experimental results. This fact is quite evident if one notes the insignificant difference between the two curves presented in each figure. Each resistance value is presented in a separate figure in order to emphasize, and more clearly illustrate, the effect that the water had on the resistance values.

In each Figure, the relative difference between the singly-distilled cases and the triply-distilled cases is demonstrated by normalizing the data with respect to the 78°F value that the singly-distilled resistor exhibited on its first temperature cycle. The second temperature cycle is illustrated in each case, and the repeatibility with cycling is demonstrated by the closeness of each curve to the normalized value of 1.00.

One would expect the impurities in the distilled water to affect the resistance value more at higher temperature since the impurities behave like any other electrolytic solution; their resistance decreases with temperature, and, acting as a paralleling resistance with the normal resistance, causes the most effect when its resistance is the smallest at the highest temperature. That there is no definite trend in this direction is demonstrated by the fact that in some cases the singly-distilled resistor is higher than the triply-distilled resistor (just the reverse to what should be expected); e.g., see Figure 44. And in other cases the two curves run essentially parallel, with the triply-distilled resistor possessing the greater resistance value as seen in Figure 42. One would not expect the amount of distillation of affect the lower resistance values as much as it does the higher resistance values, that is if the impurities are expected to act as though they form a temperature-sensitive, high-resistance in parallel with the normal resistor. Figures 40-46 definitely show that the 80K ohm and 100K ohm values are affected the most, and more at the higher temperatures than at the lower temperature, but still by a negligible amount. Also, these Figures illustrate that the lower resistance values are insignificantly affected by the type of distilled water employed.

A note of explanation is required for the 100K ohm resistors illustrated in Figure 46. The original singly-distilled resistors used in Experiment 15 had resistance values very close to the 100K ohm nominal value when the optimized formula was used, and the triply-distilled water units also had values very close to 100K ohms; however, in Experiment 16, the singly-distilled units were about 3.6% low compared to their predicted values. For this reason, the data from Experiment 15 for the 100K ohm units was used to normalize the results of the triply-distilled 100K ohm units.

The curves shown in Figure 46 show that the singly-distilled 100K ohm units of Experiment 15 and the triply-distilled 100K ohm units of Experiment 16 are quite close to the nominal values, but that the singly-distilled, 100 K ohm units of Experiment 16 are about 3% too low. The normalized data used to plot the curves shown in Figures 40 through 46 is given in Table XII.

Preparation of Resistors

From the discussion of the preceding experiments, is is evident that one can readily prepare resistance values throughout the range from 10 K ohms to 100 K ohms by using the optimized formulas developed in Experiment 14. The procedure to be followed for future preparation should be based upon these findings; however, there should be a more precise method of determining the constituents of the formulas than the reading of values from a curve. In order to prevent personal judgment in reading values from a curve from affecting the outcome of any future experiment, equations have been developed which will allow one to accurately calculate the portions of the various constituents to be used in preparing any resistance value. The curves relating the conductance of any desired resistance value to the mannitol-boric acid and potassium chloride contents are presented in Figure 35, and a number of points which lie on the curves are tabulated in Table XIII.

TABLE XII

NORMALIZED RESISTANCE VALUES OBTAINED IN EXPERIMENT 16

Normalized with respect to the 78°F - first temperature cycle- values of the singly-distilled samples.

Nominal Values =	33.33 K		50 K		60 K		80 K		100 K*		100 K**	
Temp. °F.	A 3-4	B 15-16	A 5-6	B 17-18	A 7-8	B 19-20	A 9-10	B 21-22	A 11-12	B 23-24	A 11-12	B 23-24
90	.9941	.9955	.9920	.9950	.9675	.9759	1.1097	1.1085	.9886	.9938	.9578	.9628
137	.9807	.9777	.9829	.9990	.9780	.9764	.9994	1.0025	1.0124	1.0322	.9809	1.0000
118	.9859	.9792	.9849	1.0020	.9854	.9797	.9994	1.0019	1.0021	1.0384	.9709	1.0060
100	.9881	.9807	.9869	1.0030	.9894	.9821	.9969	.9981	.9959	1.0363	.9648	1.0040
78	1.0000	.9941	1.0000	1.0111	1.0000	.9862	1.0000	1.0019	1.0000	1.0363	.9688	1.0040
59	1.0208	1.0163	1.0201	1.0342	1.0203	1.0057	1.0219	1.0182	1.0145	1.0488	.9829	1.0161
42	1.0593	1.0519	1.0583	1.0683	1.0561	1.0398	1.0470	1.0495	1.0394	1.0747	1.0070	1.0412
61	1.0171	1.0126	1.0171	1.0291	1.0195	1.0016	1.0157	1.0144	1.0073	1.0498	.9759	1.0171
80	.9985	.9926	.9999	1.0121	.9992	.9862	1.0031	1.0019	1.0041	1.0415	.9729	1.0090
101	.9866	.9822	.9899	1.0051	.9919	.9789	.9965	.9994	1.0010	1.0446	.9698	1.0120
120	.9896	.9837	.9899	1.0060	.9951	.9821	1.0006	1.0094	1.0083	1.0591	.9769	1.0261
142	.9948	.9896	.9950	1.0161	1.0016	.9886	1.0119	1.0232	1.0249	1.0757	.9930	1.0422
160	1.0015	.9955	1.0010	1.0251	1.0081	.9992	1.0169	1.0357	1.0373	1.0716	1.0050	1.0381

A = Singly distilled units

B = Triply distilled units

* normalized with respect to the 78°F value of the singly-distilled water resistor of Experiment 16.

** normalized with respect to the 78°F value of the singly-distilled water resistor of Experiment 15.

TABLE XII (continued)

NORMALIZED RESISTANCE VALUES OBTAINED IN EXPERIMENT 16
Normalized with respect to the 78^{o}F. - first temperature cycle - values of the singly-distilled samples.

Nominal Values =	10 K		20 K		Nominal Values =	100 K*
Temp ^{o}F	A 1-2	B 13-14	A 11-12	B 23-24	Temp. ^{o}F	A 23-24
90	.9919	.9959	.9876	.9926	40	1.0432
139	1.0010	1.0061	.9861	.9950	62	1.01005
119	.9949	.9990	.9901	.9926	82	1.00302
101	.9919	.9980	.9901	.9950	101	1.00503
78	1.0000	1.0041	1.0000	1.0050	122	1.01206
60	1.0193	1.0233	1.0199	1.0199	142	1.01909
41	1.0629	1.0700	1.0645	1.0645	162	1.01106
60	1.0193	1.0223	1.0199	1.0248		
79	1.0010	1.0030	1.0012	1.0062		
100	.9940	.9959	.0993	.9999		
120	.9970	.9999	.0010	1.0025		
140	1.0071	1.0071	.9975	.0020		
160	1.0172	1.0193	1.0012	1.0099		

A = Singly Distilled Units

B = Triply Distilled Units

* Data from Experiment 15, normalized with respect to the 78^{o}F resistance value in that experiment.

TABLE XIII

Conductance Values and the Corresponding Chemical Constituents Used to Prepare Resistors Exhibiting These Values of Conductance.

Nominal Values at 89°F Conductance Micro mhos	Resistance Kilohms	Solution A Content Milliliter	Potassium-Chloride mg/liter	Content ml of Sol. C Equivalent
100	10	86.7	126.4	25.28
90	11.11	76.4	113.2	22.64
80	12.5	67.0	100	20.00
69	14.5	67.5	85.5	17.10
60	16.66	50.0	73.7	14.74
50	20.0	42.3	60.5	12.10
40	25.0	34.9	47.36	9.47
30	33.33	27.7	34.2	6.84
20	50.0	20.5	21.05	4.21
16.66	60.0	18.0	16.65	3.33
12.5	80.0	15.0	11.19	2.24
10.0	100.0	13.3	7.9	1.58

Curve A in Figure 35 is a straight line passing through the points (4.0 micromhos, 0 KCl content) and (80 micromhos, 80 mg/liter of KCl). Thus, the equation for this curve relating the conductance value ($G=\frac{1}{R}$) of the desired resistance is

$$G = 0.76C + 4 \qquad (1)$$

where G is the desired conductance in micromhos, and C is the potassium chloride content in milligrams per liter of solution. This equation can be re-arranged to represent C as a function of desired conductance as

$$C = \frac{G - 4}{0.76} \qquad (2)$$

Although this form of the quation was used in all the experiments described above using the optimized formula, a more convenient form might be the milliliter equivalent of Solution C desired. Since Solution C consists of 0.5 grams of potassium chloride dissolved in one liter of distilled water, one can easily specify the number of milliliters of Solution C required to prepare a given formula. The quation relating the desired amount of Solution C to the desired conductance value is:

$$C_C = \begin{array}{l}\text{No. of ml of solution}\\ \text{C per 100 ml of formula}\end{array} = \frac{G - 4}{0.76} \times 2 \times 10^{-1} \qquad (3)$$

The relationship between the desired conductance and mannitol-boric acid content is not so easily expressed in an equation form. However, in order to prevent determining this content by graphical means, an expression was obtained by assuming that curve B, Figure 35, could be expressed by an equation of the form

$$C_{M-BA} = a\,G^3 + b\,G^2 + d\,G + e \qquad (4)$$

and solving for the coefficients a, b, d, and e, using known values of C_{M-BA} (mannitol-boric acid content in milliliters per 100 ml of solution) and G (the desired value of conductance in micromhos). The coefficient of the desired equation was obtained by using the points $(G_n, C_n) = (100, 86.7)$, (80, 67.0), (50, 42.3), and (10, 13.3). The resulting equation is

$$C_{M-BA} = (+2.031746 \times 10^{-5})G^3 - (1.43968 \times 10^{-3})G^2 + (7.483968 \times 10^{-1})G + (5.939682) \qquad (5)$$

where C_{M-BA} is the number of milliliters of Solution A per 100 ml of formula, and G is the conductance of the desired resistor in micromhos. The accuracy of the C_{M-BA} value is better than 1% when obtained by this equation; however, the equation may be rounded off to

$$C_{M-BA} = (2.0317 \times 10^{-5})G^3 - (1.44 \times 10^{-3})G^2 + (0.748G) + 5.94 \qquad (6)$$

and an accuracy of better than 1% can still be maintained. The accuracy of duplicating each of the values given in Table XIII by employing Equation (6) is presented in Table XIV.

One should carry about three significant figures to the right of the decimal on all terms of Equation (6) and should round off the C_{M-BA} answer only after the calculations are complete; for example, C_{M-BA} calculated as 86.657 in the first case cited in Table XIV may be rounded off to 86.7 which corresponds exactly to the experimentally used value (Refer to

TABLE XIV

VALUES OF C_{M-BA} RESULTING FROM THE USE OF EQUATION (6)

Value of C_{M-BA} Used in Exp.15 &16 ml/100 ml of Formula	Conductance, G in Micromhos	$(+2.0317\times10^{-5}G^3)-(1.44\times10^{-3}G^2)+(0.748G)$			+ 5.94	=	C_{M-BA}	% Error Calculated Relative to Experimental
86.7	100	+ 20.317	- 14.40	+ 74.8	+ 5.94	=	86.657	+ .0658
76.4	90	+ 14.811	- 11.66	+ 67.32	+ 5.94	=	76.411	+ .0144
67.0	80	+ 10.404	- 9.22	+ 59.84	+ 5.94	=	66.964	- .0537
57.5	69	+ 6.674	- 6.86	+ 51.61	+ 5.94	=	57.364	- .2365
50.0	60	+ 4.388	- 5.18	+ 44.88	+ 5.94	=	50.028	+ .056
42.3	50	+ 2.540	- 3.60	+ 37.40	+ 5.94	=	42.280	- .0473
34.9	40	+ 1.300	- 2.30	+ 29.92	+ 5.94	=	34.860	- .1146
27.7	30	+ 0.549	- 1.296	+ 22.44	+ 5.94	=	27.633	- .2563
20.5	20	+ 0.163	- .576	+ 14.96	+ 5.94	=	20.487	- .063
18.0	16.66	+ 0.094	- .400	+ 12.46	+ 5.94	=	18.094	+ .522
15.0	12.5	+ 0.040	- .225	+ 9.35	+ 5.94	=	15.105	+ .70
13.33	10.0	+ 0.020	- .144	+ 7.48	+ 5.94	=	13.296	- .03

Appendix B for detailed instructions that are to be followed in the actual preparation of the solutions and the resistors).

Note on the Long-Term Stability of Resistors Prepared Using the Optimized Formula

Because of the expiration of contract time and funding, it was not possible to obtain detailed information on the long-term stability of water resistors using the optimized chemical formulas developed. However, some indication of long-term stability was obtained from a set of four resistors which were tested over a one-month period. It must be pointed out that these four resistors did not use exactly the optimized formula, and they represent only single resistance values. In the normal testing procedure, never were less than two resistors used to predict the final outcome of the optimized formula. Therefore, although there seems to be a trend indicated by this four-resistor group, I would hesitate to draw any final conclusions from these results. A well-planned experiment conducted over a period of several months and dealing with a quantity of resistors would be necessary to definitely establish the long-term stability characteristics of "water resistors" prepared using the optimized formulas.

Four resistors, R_4 - R_5 - R_9 - R_{17}, were saved from the group of twenty-four tested in Experiment 11, Part II, dated 6/19/62 and 6/20/62. Subsequent resistance-temperature data were obtained on these resistors on 6/22/62, 6/23/62, 6/24/62, 7/15/62, and 7/16/62. The complete resistance-temperature data obtained during this one-month period has been normalized and is presented graphically in Figures 47-50. Since each resistor behaved differently, a separate graph is presented to simplify discussing the characteristic of each.

The measurements performed on resistance R_4, a nominal 10.4 K ohm resistor, during the period 6/19/62 to 6/25/62, indicate that the resistance-temperature characteristic was initially neutralized, and (at any one temperature) had a total spread of only about 5%. No measurements were made during the interval from 6/25/62 to 7/15/62; however, the data dated 7/16/62 shows that the average characteristic curve has shifted to a level about 10% higher than the earlier-dated characteristic curve. In fact, the characteristic curve seems to be better neutralized with respect to the temperature coefficient of resistance than it was initially. These initial non-optimized resistors had a deficiency of potassium chloride; therefore, the new curve has effectively had an increase in the ratio of potassium chloride to the mannitol-boric acid content.

Since the chemical action which allows the neutralization of the temperature coefficient of resistance to be possible in the first place depends upon the chemical complex of mannitol-boric acid dissociating with elevated temperatures, the results obtained above seem to imply that the complex is not stable, is breaking up with age, and is not reforming. This is particularly suggested by the fact that the flatness

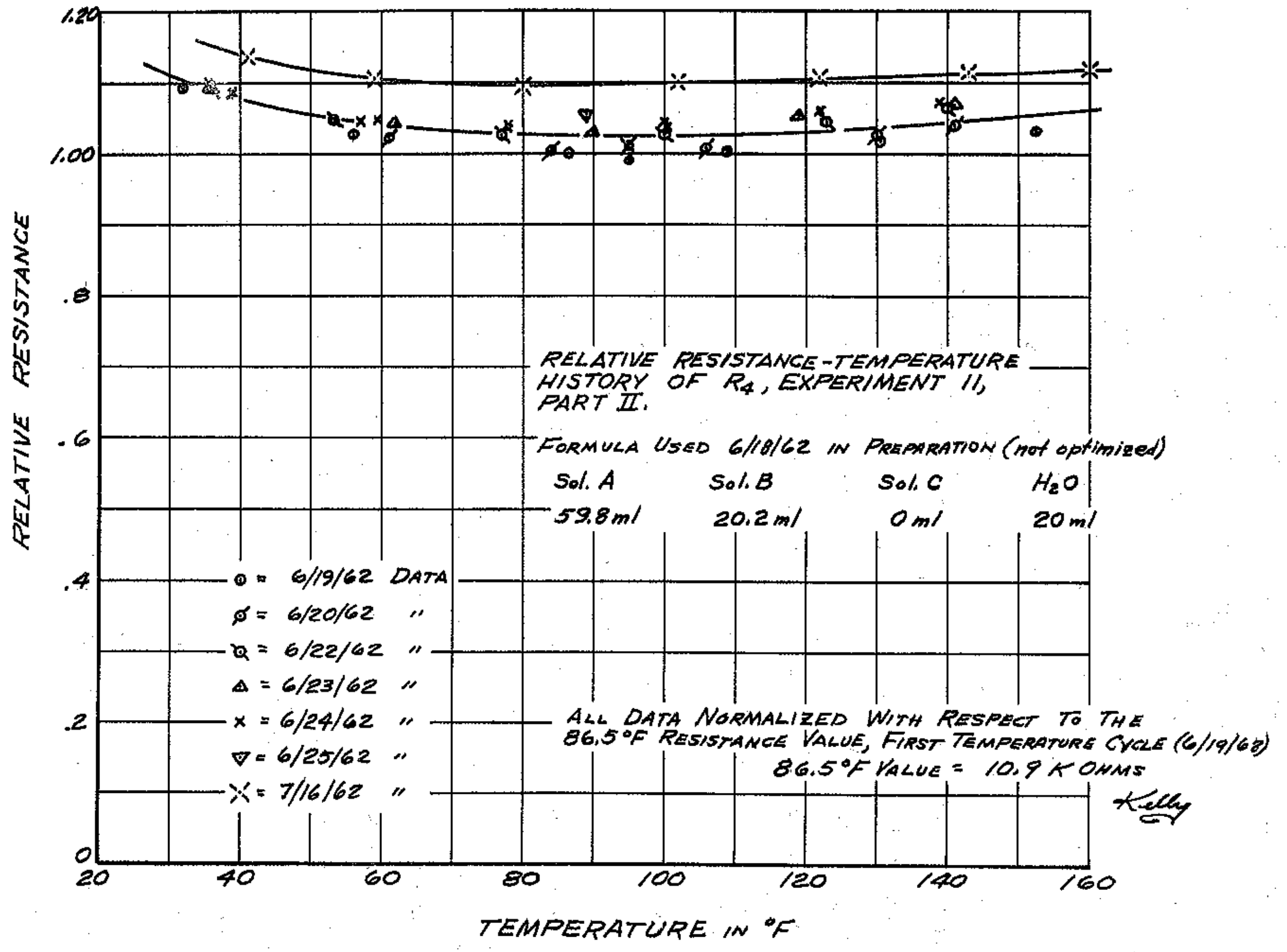

Figure 47. Relative Resistance-Temperature History of Resistor R_4 Prepared for Part II of Experiment 11 (10.9 K ohms)

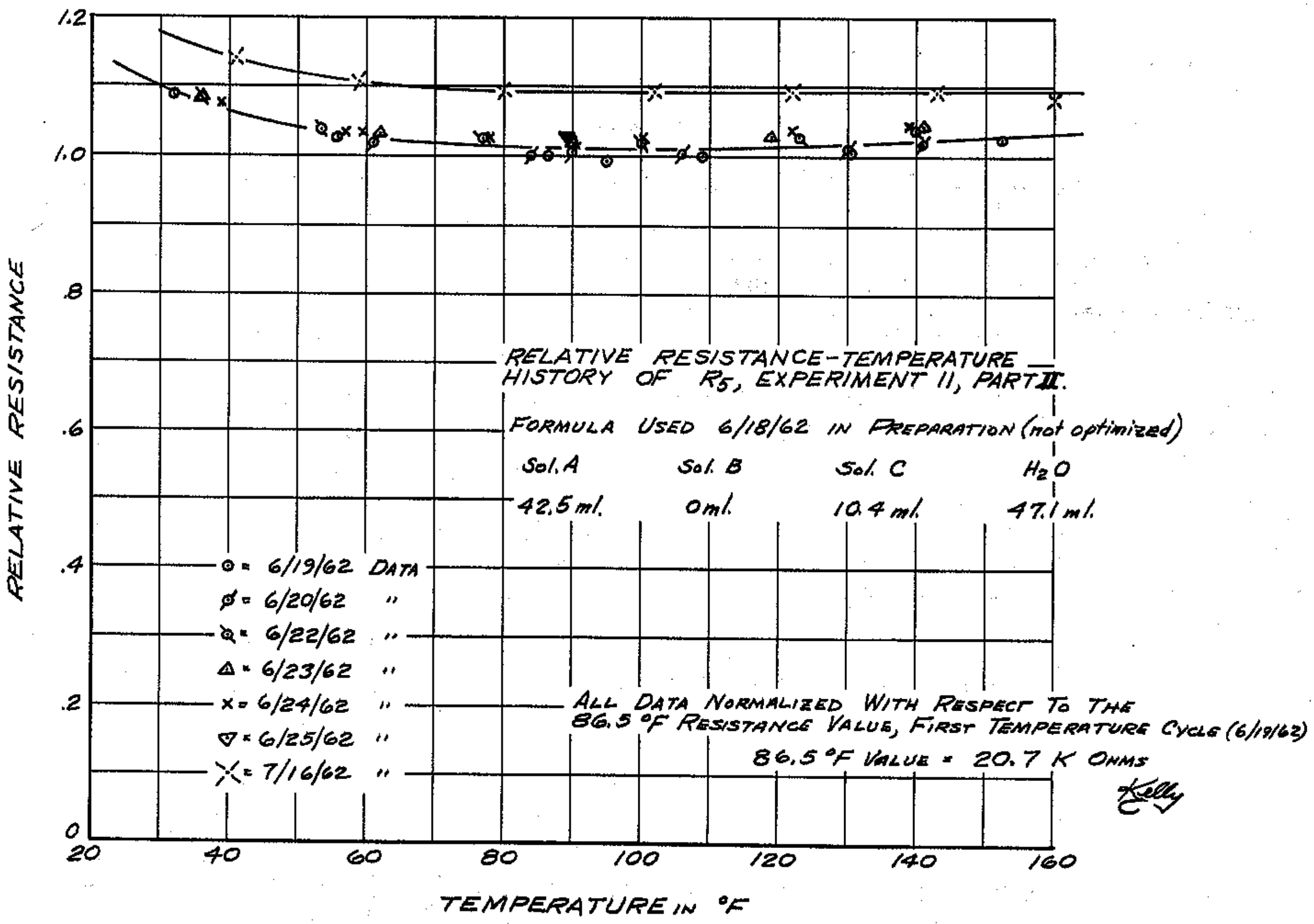

Figure 48. Relative Resistance-Temperature History of Resistor R_5 Prepared for Part II of Experiment 11 (20.7 K ohms)

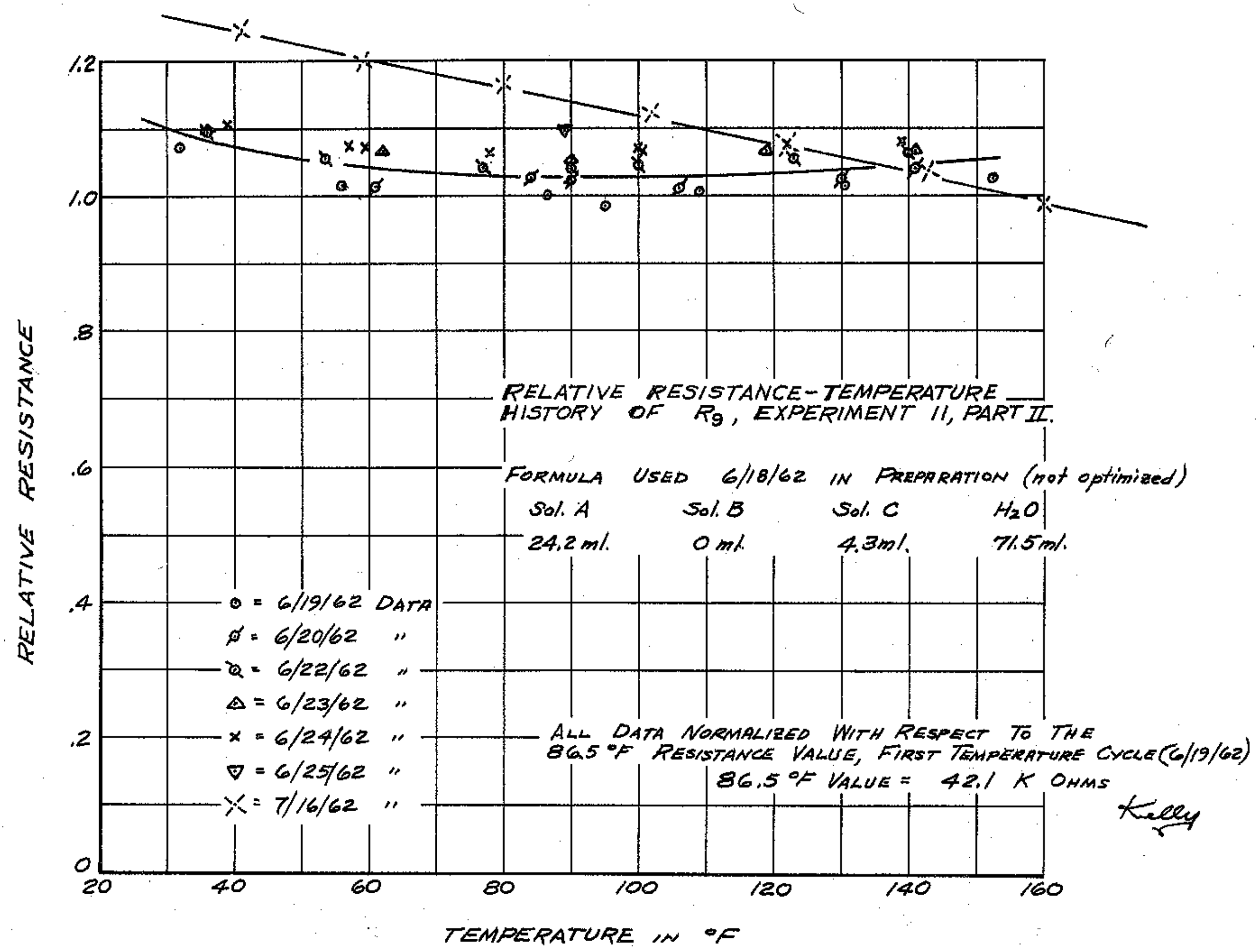

Figure 49. Relative Resistance-Temperature History of Resistor R_9 Prepared for Part II of Experiment 11 (42.1 K ohms)

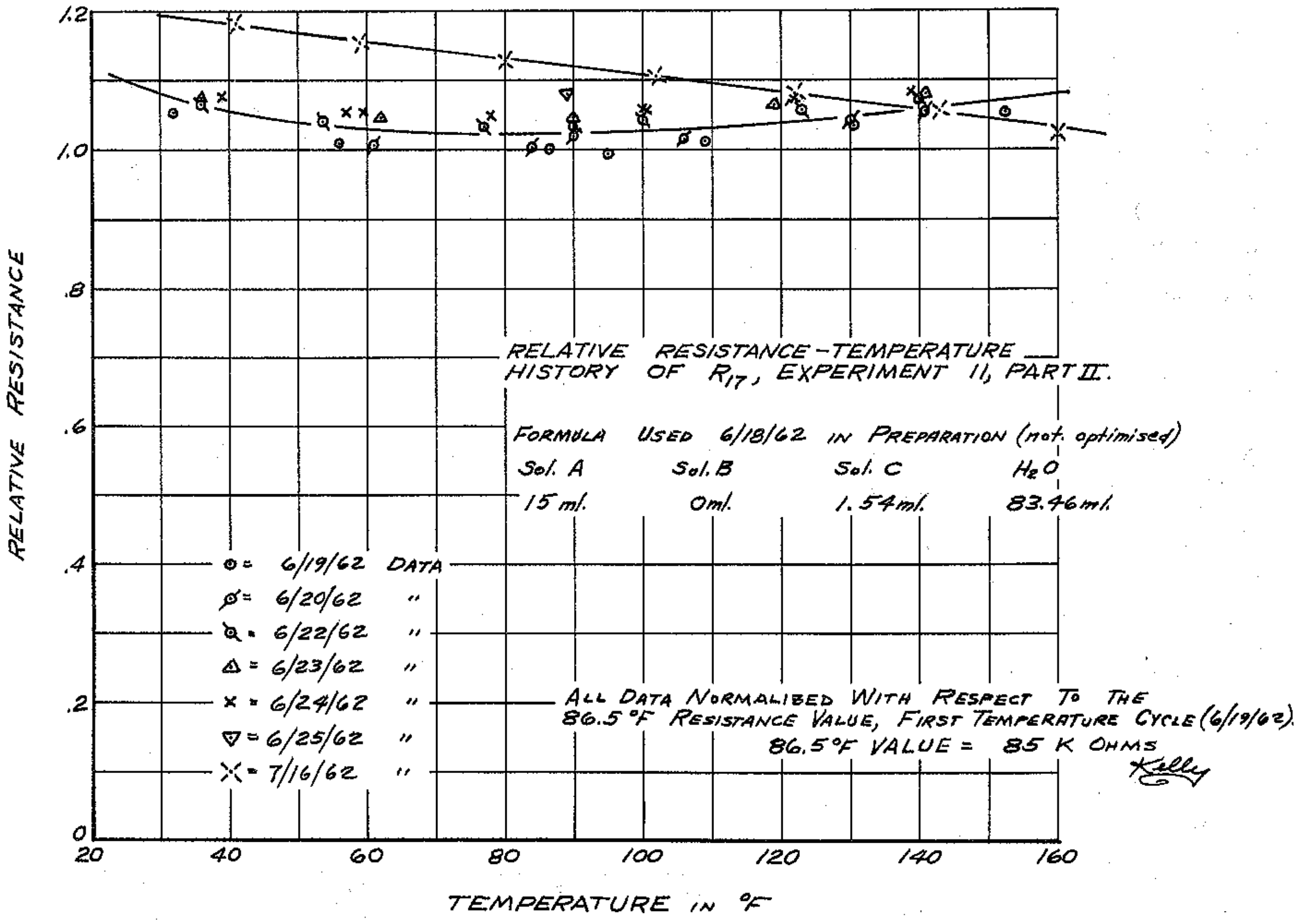

Figure 50. Relative Resistance-Temperature History of Resistor R_{17} Prepared for Part II of Experiment 11 (85 K ohms)

of the characteristic curve is improved with aging. The reasoning behind this last statement is based upon the fact that a relative increase in the potassium chloride content compared to the mannitol-boric acid content causes a depression of the resistance-temperature characteristic, especially at the higher temperature. In Figure 47, one should note that although the over-all characteristic curve of the month-old resistor has risen, the characteristic is more depressed at the higher temperatures (100°F to 160°F) than is the curve for the earlier experimental tests. In fact, if the mannitol-boric acid content continues to diminish with age, the characteristic curve will eventually attain a negative slope, a condition that evidently has taken place in the higher resistance values represented by Figures 49 and 50.

The data for resistance R_5, a nominal 20.7 K ohm resistor, is presented graphically in Figure 48. It is not necessary to enter a detailed discussion of this curve since it it almost identical to that of resistance R_4 above.

The data for resistances R_9, a nominal 42.1 K ohm resistor, and R_{17}, a nominal 85 K ohm resistor, are presented respectively in Figures 49 and 50 and deserve some additional discussion. The resistance-temperature history of these two units are very similar, since each initially appeared to have essentially a neutralized characteristic, but both, with aging, appear to have an excess potassium chloride content. As stated above, in the discussion of R_4, it is postulated that this change in characteristics is brought about by the dissociation of the mannitol-boric acid complex, mannitoboric acid. Evidently, the dissociation is more pronounced in the higher resistance, more dilute solutions (R_9,R_{17}) than it is in the lower resistance, more concentrated solutions (R_4, R_5), so much so that the negative slope potassium chloride characteristic becomes predominant and causes the resistance-temperature characteristic to exhibit a very negative slope with aging. If these four resistors are typical of the general behavior of the formula, there is need for concern when using the mannitol-boric acid potassium chloride combination to prepare water resistors. However, a more thorough experimental investigation is deemed necessary in order to establish if these four resistors are typical of the group. It has been suggested* that a more stable constituent than mannitol be used in conjunction with boric acid to produce the complex; for example, glycerol. The possibility of using glycerol instead of mannitol has not been investigated.

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* Private conversation with Professor Yamouchi, University of New Mexico Chemistry Dept.

CONCLUSIONS

It has been demonstrated that mannitol, boric acid, potassium chloride, and distilled water can be combined in a specified manner to obtain a "water resistor" which will exhibit a low value of temperature coefficient of resistance. These solutions can be prepared for use in standard, plastic, cylindrical containers fitted with suitable end electrodes, to produce resistance values within the range of 10K ohms to 100K ohms. A set of equations, (3) and (6) may be employed to determine the correct amount of each chemical for producing any particular resistance value within the above range with an accuracy of about 1% or 2%. The resulting resistance will exhibit a resistance-temperature characterisitc that is essentially flat throughout the temperature range from 60°F to 160°F, deviating from the nominal resistance value by only 2% (Fig. 39). The resistor is usable down to a temperature of about 40°F, exhibiting an increase in resistance of about 6% at this temperature.

An incomplete, stability study (made on only 4 resistors) indicates that the resistance value increases with age (Figures 47-50), and that the resistance temperature characteristic stays flat for the lower resistance values (at least up to 20K ohms), but that this characteristic develops a noticeable negative slope for the higher resistance values (40K and 80K ohms). Further study will be necessary in order to establish the exact long-term stability to be expected from a typical water resistor using this formula. These findings do throw some doubt upon the long-term stability characteristics of these water resistors; however, it must be pointed out that the four resistors did not contain the optimized formulas developed for present use, and the plastic containers and end electrodes did not have the scrupulous cleaning that was used when developing the final optimized formulas. Although this stability test might indicate that a further study should be made, using the final cleaning techniques and optimized formula, one should not overlook the fact that the present techniques and formulas gave much more repeatable data than was achieved when the above four resistors were prepared. Although the stability results of these four resistors should not be used to draw final conclusions, their existence must be pointed out. Based upon the excellent results obtained after the optimized formula was developed and the scrupulous cleaning techniques employed, one should have a great deal of confidence in these resistors and feel that their long-term stability might be better than indicated by the four resistors tested.

In order to obtain resistance values in the range from 1K to 10K ohms, it will be necessary to re-design the standard plastic container. If the inside diameter is increased from 0.5 inches (the present inside diameter) to 1.58 inches, the resistance values obtainable will be 1/10 those that are obtainable using the present container. However, if any re-design is done, the end cap-electrode assembly should also be changed to allow for greater thermal expansion. A possible end-cap design could follows the pattern illustrated in Figure 51.

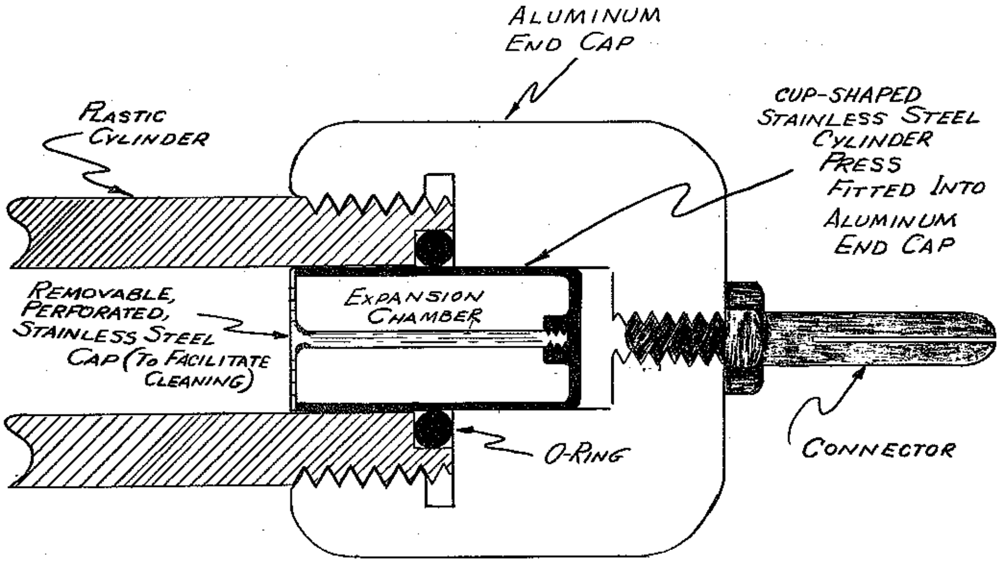

Fig. 51. Proposed Pattern for New End Cap-Electrode Assembly with Provision for Thermal Expansion

APPENDIX A*

Different individuals have tested a long series of compounds in relation to their ability to raise the conductivity of a boric acid solution.[1] The formation of a complex was indicated by an increase in mutual solubility, an increase in acidity, and a change in optical rotation. Solutions of boric acid became acidic to litmus with the addition of sugars.

Ageno and Valla[2] studied the molecular proportions in which mannitol and boric acid unite in the formation of the acid, mannitoboric. The strength of the acid was determined by conductivity measurements, and it was found that the two compounds unite in the ratio of one to one.

Deutsch and Osoling[3] by measuring the conductivity and pH of solutions of mannitol and boric acid found that two complexes were formed according to the following regulations:

M = mannitol $\qquad$ $B^- = H_2BO_3^-$

(1) $HB = H^+ + B^-$

(2) $B^- + M = BM^-$

(3) $B^- + 2M = BM_2^-$

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[1] Deutsch, A. and Osoling, S., Journal of the American Chemical Society; 71, 1637-40, C. A. (43: 6894, 1949)

[2] Ageno, F. and Valla, E., Gazzetta Chimica Italiana; 43, 163-174, C. A. (8:340, 1914).

[3] Deutsch (loc. cit.)

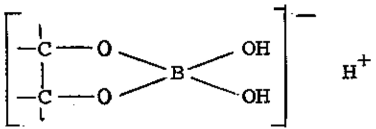
*The material in this Appendix is part of the EE-172 Senior Seminar Report prepared by Messrs. Mike Bolduc, Ray Baca, and Mike Luke, Semester II, 1961-62.

They also found out that the complexes were not destroyed in basic solution.

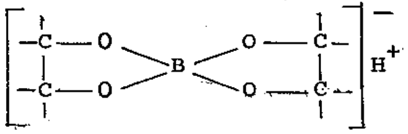
Souchay and Lourijsen[4] found that boric acid forms complexes containing one or two moles of polyalcohol per mole of borate. With mannitol, the two mole complex is formed easily, while the one complex undergoes a condensation reaction.

Two possible structures[5] for the formation of the mannitoboric acid are the following:

(1)



(2)



Structure (1) is a di-ester formed by splitting out two molecules of water between one hydrated borate ion and one molecule of a glycol (di-alcohol grouping). Structure (2) is formed by splitting out four molecules of water between one hydrated borate ion and two molecules of a glycol. The second complex is often of great acidic strength.

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[4] Souchay, P., and Lourijsen, M., Bull. Soc. Chim. France, 893-8; C. A. (50:16511, 1956).

[5] Deutsch, etc. (loc. cit.).

APPENDIX B

PROCEDURE FOR PREPARING WATER RESISTORS USING OPTIMIZED FORMULAS

Cleaning and Preparation of Resistor Containers, Electrodes, O-rings, Solution Containers, Beakers, Burets, Stirring Rods, Thermometers, etc.

It cannot be stressed too strongly the need for cleanliness in the preparation of water resistors. All the containers, etc., required in the preparation of water resistors should be scrupulously cleaned if one expects to have repeatable results. The cleaning technique outlined below for cleaning the water resistor containers was followed religiously during the development of the optimized formulas, and it may be applied to the cleaning of any item which might come in contact with the chemicals or chemical solutions.

1. If the water resistor containers are filled with electrolyte from previous use, the units may be soaked in warm water for about a half hour in order to loosen up the threads of the end caps. If the containers have been in contact with oil, a rinse in toluene followed by a rinse in grain alcohol (pure ethanol) would be in order.
2. The entire resistor-container assembly should be disassembled and rinsed in the warm water used above after the electrolyte has been emptied. (The O-rings should be placed on a wire loop to prevent their loss in the bath.)

3. A Chemical cleaning agent should be used to prepare a bath for cleaning all the resistor-container assembly (e.g., Alconox). In this cleaning bath, the end caps, electrodes, O-rings, threads and inside of the cylinder should all be scrubbed with a brush to remove any crystals of the chemicals which might have formed.
4. All the resistor-container assembly should next be rinsed in tap water and placed in a bath of distilled water. They should then be rinsed again in distilled water before being rinsed in alcohol.
5. After the second rinse in distilled water, the resistor-container assembly is rinsed in absolute ethanol. If a quantity of resistors are being prepared, the ethanol used to rinse the assembly parts is saved and used in the first rinse of succeeding assemblies.
6. A second and final rinse, in new, clean ethanol is made by pouring the new ethanol over the assembly parts. This ethanol should be caught and saved for use in the first ethanol rinse when preparing subsequent groups of resistor containers.
7. After the second and final rinse of the assembly parts in ethanol, the entire group is placed to dry (about a half hour) in a clean, sheltered area.
8. After the parts are completely dry, the electrodes, small O-rings, and end caps are assembled, being careful not to touch the part of the electrode which will contact the electrolyte.

9. After all the electrode-end cap parts have been assembled, one electrode-end cap assembly is securely screwed onto one end of the cylinder assembly using a large O-ring to insure a proper seal.
10. The other electrode-end cap assembly should be loosely screwed on the cylinder assembly to keep out dust, etc., until the water resistor is to be prepared. The other large O-rings should be stored in a clean container until ready for final assembly.

Preparation of Solutions A, B, and C

1. Prepare three large containers capable of holding more than two liters of solution, using the same washing, rinsing and drying technique outlined above.
2. Measure the chemicals to be used in the following amounts:

Solution A

(a) For Solution A, measure out 302 grams of Mannitol, using an accurate balance. It may be measured on an analytical balance if measured in several parts so as not to overload the balance. Mannitol is a light, fluffy substance and will fill a large beaker (2 liters). Make sure the beaker has previously been cleaned using the technique outlined above. To get the mannitol contained in the beaker into a two-liter volumetric flask which is also clean, one may add distilled water to the mannitol in the beaker to first make a slurry that can be poured into the volumetric flask. Additional distilled water can be used to wash the remaining contents from the beaker and this rinse also poured into the volumetric flask. This process may be repeated several times until all of the mannitol is in the flask.

(b) Using the analytic balance, measure 82 grams of boric acid into a clean beaker. The 82 grams of boric acid can be rinsed from this beaker and emptied into the two-liter volumetric flask using the same procedure outlined in (a) above for mannitol.

(c) There is some heat of formation when boric acid and mannitol are mixed, thus, the two-liter flask should not be topped off until the temperature is back to normal. Also, some difficulty may be experienced in dissolving the mannitol and boric acid in the distilled water. This difficulty can be overcome by filling the volumetric flask until the level is within an inch or so of the full mark, and waiting overnight for the chemicals to go into solution. Shaking the flask with a swirling motion helps, but it is not recommended that the contents be heated to accelerate dissolving of the chemicals. After the flask has been left overnight, the chemicals should be completely dissolved and the temperature back down to normal. Measure and record the temperature of the solution in the flask (it should be approximately 78° F.). Add sufficient distilled water to top off the two-liter flask at this temperature. This completes the preparation of Solution A. The contents of the flask may be emptied into one of the large containers mentioned in Step 1 above. The solution may be more thoroughly mixed by shaking, or it may be left for a long enough period for the chemicals to diffuse uniformly throughout the solution.

Solution B

(d) To prepare Solution B, the same procedure may be followed as used in preparing Solution A with the exception that 1.000 grams of potassium chloride is measured into a clean beaker and also added to the solution. Solution B thus contains 302 grams of mannitol, 82 grams of boric acid, and 1.000 grams of potassium chloride per two liters of solution. The gram of potassium chloride should be accurately measured on an analytical balance (the balance used in the experiments of this report was capable of measuring this quantity of potassium chloride to within a few tenths of a milligram). Since it may require that Solution B be left overnight in the two-liter volumetric flask to insure that all of the chemicals are dissolved, it is convenient to have two or even three volumetric flasks with a two-liter capacity available for use in preparing all the required solutions. The temperature of Solution B should be noted and recorded when the two-liter flask is finally topped off with distilled water, and this temperature should be very close to the temperature at which Solution A was topped off. Since volumetric measurements are employed in preparing all solutions, it is important to note and maintain approximately the same temperature when preparing all solutions. If an air-conditioned building is available, there should be no difficulty in satisfying the temperature requirements. Solution B may be stored in one of the large containers mentioned in Step 1 above.

Solution C

(e) Solution C contains one gram of potassium chloride dissolved in two liters of distilled water, and is the easiest of the solutions to prepare. However, extreme care must be exercised to insure that exactly 1.000 gram of potassium chloride is used. The 1.000 gram of potassium chloride should be measured into a clean beaker and the contents rinsed with distilled water into a two-liter volumetric flask. The flask may be topped off to two liters with distilled water, but the temperature must be maintained close to the temperature used in preparing Solutions A and B above. Solution C may be stored in one of the large containers mentioned in Step 1 above. Since solutions A and B must be left overnight to insure the chemicals are properly dissolved, it might be advantageous to let Solution C also sit overnight to insure that the potassium chloride has diffused throughout the solution.

Preparation of Resistors

The methods used for measuring out the required amounts of Solutions A, B, C, and distilled water must be precise, otherwise repeatable results cannot be expected. The procedure outlined below employs the techniques used in developing the optimized formulas.

One should decide which resistance values between 10 K ohms and 100 K ohms are to be prepared, since the solutions required will depend upon the resistance value. The more concentrated solutions which produce resistance values near 10 K ohms (10 K to 15 K) require Solutions A, B, and distilled water, while more dilute solutions which produce higher resistance values employ Solutions A, C, and distilled water. The reason for this is quite simple: When preparing a 100 milliliter batch of formula, if the sum of the amount of Solution A required to give the correct mannitol-boric acid content, and the amount of Solution C required to give the correct potassium chloride content exceeds 100 milliliters, then Solutions A and B must be employed. Otherwise, Solutions A and C may be used. Two examples will be cited to illustrate the two situations.

Assume that it is desired to prepare a 10 K ohm and a 100 K ohm resistor. First, convert each resistance value into its equivalent conductance value.

Let $R_1 = 10$ K ohms, then $G_1 = \frac{1}{10\ K}$ mhos = 100 micromhos

and

$R_2 = 100$ K ohms; $G_2 = \frac{1}{100\ K} = 10$ micromhos

The required potassium-chloride content required (in terms of Solution C) can be determined by employing Equation (3).

$$C_c = \frac{\text{No. of milliliters of Solution C}}{\text{per 100 milliliters of formula}} = \frac{G-4}{0.76} \times 2 \times 10^{-1} \qquad (3)$$

where G is the conductance of the desired resistor in micromhos. For the two cases under consideration,

$$G_1 = 100 \text{ micromhos and } C_{c1} = \left(\frac{100-4}{0.76}\right) 2 \times 10^{-1} \text{ ml.}$$
$$= 25.28 \text{ milliliters of Sol. C.}$$

and

$$G_2 = 10 \text{ micromhos; } C_{c2} = \left(\frac{10-4}{0.76}\right) 2 \times 10^{-1} \text{ ml.}$$
$$= 1.58 \text{ milliliters of Sol. C.}$$

In order to determine the amount of mannitol-boric acid required (in terms of Solution A), Equation (6) may be employed.

$$C_{M-BA} = (2.0317 \times 10^{-5})\ G^3 - (1.44 \times 10^{-3})\ G^2 + (0.748)\ G + 5.94 \qquad (6)$$

where C_{M-BA} is the mannitol-boric acid content in milliliters of Solution A per 100 milliliters of formula, and G is the desired conductance of the water resistor in micromhos.

For our two examples (see Table XIV),

C_{M-BA1} = 86.7 milliliters, and C_{M-BA2} = 13.33 milliliters. Summarizing the above results in tabular form:

Res. No.	Resistance	Conductance	C_c	C_{M-BA}
R_1	10 K ohms	100 micromhos	25.28ml.	86.7 ml.
R_2	100 K ohms	10 micromhos	1.58ml.	13.33 ml.

It is obvious that for R_1, the 10 K-ohm resistor, that $C_c + C_{M-BA} > 100$ ml; therefore, it is necessary in this case to use Solutions A, B, and distilled water in order to obtain the desired resistor value. Thus, if 25.28 milliliters of Solution B are used, the potassium chloride content will be provided, but this will also simultaneously supply an amount of mannitol-boric acid that is equivalent to 25.28 milliliters of Solution A, since Solution B contains mannitol and boric acid in addition to potassium chloride. Consequently, the amount of Solution A specified by C_{M-BA} determined from Equation (6) will be diminished by 25.28 milliliters. The amount of Solution A required to provide the necessary mannitol-boric acid content is

$$86.7 - 25.28 = 61.42 \text{ milliliters}$$

Since the sum of the amounts of Solution A and Solution B required is only 86.7 milliliters, a 13.3 milliliter amount of distilled water will be required to produce the 100-milliliter batch of formula. Therefore, the final amounts of the various constituents required to prepare a 100 milliliter batch of electrolyte for resistor R_1 (10 K ohms) are

61.42 milliliters of Solution A
25.28 milliliters of Solution B
00.00 milliliters of Solution C
13.30 milliliters of Distilled water
100.00 milliliters of electrolyte.

The amounts of the various constituents required for preparing resistor R_2 (100 K ohms) can be determined in a similar manner. For R_2, $C_c = 1.58$ ml. and $C_{M-BA} = 13.33$ ml., therefore, Solutions A, C, and distilled water may be used in preparing the electrolyte for this resistor. The amounts of these constituents required to produce a 100-milliliter batch of electrolyte for resistor R_2 (100 K ohms) are

13.33 milliliters of Solution A
00.00 milliliters of Solution B
1.58 milliliters of Solution C
85.12 milliliters of distilled water
100.00 milliliters of electrolyte

Now that we have arrived at the constituents required for obtaining the two different electrolytes, it is necessary that techniques be used in measuring out these quantities which will allow precise measurements to be made. The techniques described below were used throughout the development of the optimized formulas.

1. Prepare three Mohr burets (or equivalent) with 50 milliliter capacity and 0.10 milliliter graduations, and one microburet with a 10 milliliter capacity and 0.02 milliliter graduations, using the cleaning techniques outlined at the outset.
2. Fill the three Mohr burets, respectively, with Solutions A, B, and distilled water, and fill the microburet with

Solution C. The microburet, capable of more precise measurements than the other burets, is used for Solution C because smaller amounts of Solution C are required than of any other solution. The temperature of the various solutions should be checked with a clean thermometer to make sure they do not differ greatly from the temperature at which they were initially prepared.

3. Use a large beaker for waste and drain and dispose of the contents of each buret. This action will insure that the burets are working satisfactorily and will help wet and clean the walls of the burets. (This action is particularly important if the burets have just been rinsed out with distilled water and were not yet dry when filled. If the burets were completely dry initially, this step may be omitted.) Refill each buret with the appropriate solution.
4. A difference-in-reading technique may be employed when using the burets to measure out the appropriate amount of a given solution, but it is suggested that the level in the buret be set on a particular graduation by drainsome of its contents into the waste beaker. Be certain to touch the wall of the waste beaker to the tip of the buret in order to let the last partial drop hanging there fall into the waste beaker. This will insure that the starting point for each measurement is consistent. When the proper amount of a given solution has been

removed from the buret into a beaker when preparing a formula, use the same technique of touching the wall of this beaker to the tip of the buret in order to obtain the last partial drop in the formula.

5. Take a clean beaker, capable of containing at least 100 milliliters of electrolyte, and measure into this beaker the prescribed amounts of the various constituents as calculated from Equations (3) and (6). Be very careful to measure the precise amounts. With a clean stirring rod, mix the constituents until the solution appears uniform when held up to the light (swirls will be seen in the electrolyte when first mixed, but these will disappear when mixing is complete). It would be advisable to allow about one-half hour for the chemicals to diffuse more uniformly throughout the electrolyte. The temperature may be checked with a clean thermometer to see if it is approximately the same value that existed when the original solutions were prepared. If the temperature differs drastically from 78° F., the batch should be discarded and the solutions brought to this temperature before preparing the electrolyte again.

6. From the 100 milliliter batch of electrolyte prepared in Step 5, it is possible to obtain four identical resistors. Into a clean resistor container which has one end-cap assembly securely tightened, pour enough solution to half fill the resistor. Then, swing the resistor

container around in an arc at arm's length in order to cause the centrifugal force to push electrolyte into every part of the thermal expansion chamber. Inspect the partially filled water resistor to see that all bubbles are removed from the thermal expansion chamber, and if they are, continue filling the resistor container with electrolyte until the meniscus is above the open end of the container. Take the other electrode-end cap assembly and large O-ring and screw it on the resistor container. Some electrolyte will spill out as the electrode is moved into position; however, with proper care, the resistor will be completely filled, and electrolyte will extend somewhat up into the upper thermal expansion chamber. If care is not exercised, a bubble may appear around the upper electrode. If this is the case, the upper end cap should be removed and the last filling operation repeated until the resistor container is properly filled. Once the resistor container is properly filled with electrolyte, the water resistor is finished. However, one additional precaution should be pointed out. In all of the experiments performed in developing the optimum formulas, the resistors were placed in the environmental test chamber and raised to 160° F. and brought back down to 87° F. before they were expected to achieve their desired resistance value. After about 12 hours at room temperatures, however, the resistor should be essentially stabilized at the desired value. Check the resistance value on an a.c. impedance bridge at 1000 cycles to see that it possesses the proper value. The resistance should be within a few percent of the desired value.

APPENDIX C

Equipment List:

1. Tenny Environmental Test Chamber, Model No. TMUF-1.5-100240, Ser. No. 3300, S-43581.
2. General Radio Impedance Bridge, Type 1650A, Ser. No. 2749 S-115683.
3. Minneapolis Honeywell Thermocouple (Bridge) Thermometer, Ser. No. S-113657.
4. Cristian Becker, Analytical Balance, Ser. No. B-45093 (Approx. 100 gram capacity ± .001 gr. accuracy).
5. Thirty plastic water-resistor containers of the type shown in Figure 2, approx. 20 ml. capacity.
6. General Radio Impedance Bridge, Type 650A, Ser. No. 6850 (used in conductance cell measurements only).
7. Modern Electronic Co. Oscillograph (oscilloscope) Model 830B, Ser. No. 374 (used as a balance indicator for item No. 6).
8. Exax micro buret, 10 milliliter capacity with 0.02 ml. graduations, 123 sec, 20° C.
9. Three Exax Mohr burets, 50 milliliter capacity with 0.10 ml. graduations, 20° C.
10. Various liter, two-liter, and 100-ml graduated flasks; various liter, 500-ml, 100-ml and 50-ml beakers; and various bottles for containing two-liter batches of solutions.
11. OHAUL Scale Corp. Balance, 5 kilogram capacity.
12. TAG thermometer, 18° C. to 28° C. with 0.01-degree graduations; No. 893-182, and SSS Corp. -10° C. to + 110° C. with 1.0 degree graduations.
13. Precision Scientific Co. Water Still, 1 gal. per hour capacity, Ser. No. 1105-16.

Chemical List

1. Mallinckrodt Boric Acid, No. 2549 (H_3BO_3) 1-pound units.
2. J. T. Baker Co., Mannitol Powder, No. 2554, $C_6H_{14}O_6$, 1 pound units.
3. Braun Chemical Co., Mannite, Neutral-boron free, Lot No. 0453, 5-pound unit.
4. Mallinckrodt Potassium Chloride, No. 6858, 1-pound unit.
5. Braun Chemical Co., Toluene.
6. Absolute Ethanol, obtained from the Chemistry Dept., University of New Mexico.

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