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FREEZING TEMPERATURE OF BENZOIC ACID AS A FIXED POINT IN THERMOMETRY

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ABSTRACT

The freezing temperature of benzoic acid is found to be reproducible with a precision comparable to that of the ice point and somewhat superior to that of the steam point as usually observed in standardizing laboratories. For use in the calibration of thermometric instruments the acid is contained in a partially evacuated glass cell provided with a thermometer well. When thus confined, and if not heated excessively, the substance maintains a constant composition for long periods of time. When properly manipulated, the acid in a given cell exhibits a freezing temperature reproducible from day to day within 1 millidegree.

The triple point of pure benzoic acid is $122.362^{\circ} \pm 0.002^{\circ} \text{C}$. Under a pressure of 1 atmosphere of dry air the freezing temperature is 0.013 degree higher. Corresponding elevations for oxygen and nitrogen are 0.001 and 0.015 degree, respectively. The pressure coefficient of the freezing temperature is 0.039 degree/atm. The change in volume of the acid on freezing is $-0.138 \text{ cm}^3/\text{g}$. The corresponding calculated value for the density of the solid at the freezing temperature is 1.27 g/cm^3 . The solubility of oxygen in the liquid at its freezing temperature, under a pressure of 1 atm., is 0.132 g/1,000 g of acid; that of nitrogen is 0.073 g .

An appendix deals with a method of calculating temperatures, in the ranges -190° to 0°C and 0° to 660°C , from observations with a platinum thermometer. For this purpose power-series equations are used instead of the Callendar and Callendar-Van Dusen equations. Tables are included to facilitate the computation of temperature.

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I. INTRODUCTION

Temperatures in the range 0° to 660° C, on the International Temperature Scale, are defined in terms of platinum resistance thermometers, of specified characteristics, by means of the equation

$$R_t = R_0 (1 + At + Bt^2).$$

R_0 is the resistance at the temperature of equilibrium between ice and air-saturated water at normal atmospheric pressure, and A and B are constants determined by calibration at the temperatures of condensing water vapor and sulfur vapor, respectively, each under a pressure of 1 atm. The temperature of melting ice is relatively insensitive to variations of atmospheric pressure (0.0076 degree C/atm.), but the accuracy of calibration at the steam and sulfur points is limited by the accuracy which can be attained in making barometric measurements. The boiling temperature of water changes by 0.001 degree C with a change in pressure of 0.027 mm of mercury. Since barometric pressure measurements commonly are not made to an accuracy greater than about 0.1 mm of mercury in standardizing laboratories, the accuracy of calibration of platinum thermometers is limited to 0.003 to 0.004 degree C, except in a very few laboratories that are equipped for fundamental work in thermometry. The sulfur point, used with the steam and ice points to determine the constant in the second-power term in the equation, need not be fixed as accurately as the steam point unless temperatures are measured near the sulfur point or in the range beyond it.

A readily reproducible fixed temperature in the vicinity of 100° C, insensitive to variations in barometric pressure, would be useful for the calibration of thermometers, even if it could not be reproduced more exactly than the steam point, because the calibration procedure would be greatly simplified if barometric measurements did not need to be made. The present paper deals with the use for this purpose of the freezing temperature of benzoic acid. The term "freezing temperature" is here used in preference to "freezing point" because, as will be explained later, it is proposed to establish arbitrary conditions of observation, which may cause the freezing temperature to be fixed anywhere between the triple point (122.362° C) and the freezing point (freezing temperature under 1 atm. of dry air, 122.375° C).

Experience with benzoic acid in another project¹ indicated that this substance possesses the properties required of a thermometric standard, of which the more important are as follows: (1) Availa-

¹ Frank W. Schwab and Edward Wichers, *Preparation of benzoic acid of high purity*, J. Research NBS **25**, 747 (1940) RP1351.

bility in an adequate degree of purity; (2) sufficiently large latent heat at the change of phase; (3) adequate velocity of crystallization; (4) existence in only one crystalline form at temperatures near the freezing point; and (5) stability under the conditions of use. Benzoic acid can be obtained commercially in a degree of purity better than 99.95 mole percent, and the purity can be increased to 99.998 mole percent or better by relatively simple laboratory procedures, most readily by a method of fractional freezing described in a previous paper.² The cryoscopic behavior of the substance is such that 0.001 mole percent of impurity dissolved in the liquid acid (but insoluble in the solid) depresses the freezing temperature 0.00075 degree C. Hence the attainable purity will permit reproducing the freezing temperature to within 0.001 to 0.002 degree C. The same amount of impurity causes the freezing temperature of the acid to change 0.00075 degree C between 0- and 50-percent frozen. As will be shown later, variations in the proportion frozen can be held within a small part of this range.

The heat of fusion of benzoic acid is reported to be about 140 j/g, or 150 j/ml, which is a little less than half that of water. Many observations made during earlier work show that the heat of fusion, combined with a high velocity of crystallization, is sufficient to maintain satisfactory thermal equilibrium between the solid and liquid when the system loses heat at any reasonably slow rate. During these observations no evidence was ever obtained of the transformation of the liquid to more than one crystalline form.

II. MATERIALS, APPARATUS, AND PROCEDURES

1. MATERIAL AND PROCEDURE FOR FILLING THE CELLS

The benzoic acid used for the experimental work reported in this paper was prepared by fractionally freezing a quantity of commercial benzoic acid as described by the authors in an earlier publication.³ Measurements of the freezing range,⁴ when the acid was freed of water in a manner which did not cause the formation of a significant amount of benzoic anhydride, indicated that the acid used to determine the reproducibility of the freezing temperature was 99.998 mole percent pure. That used to study some of the properties of the acid was of somewhat lower purity.

To avoid variations in freezing temperature which would have resulted from changes in the moisture content of air had the acid been frozen in open vessels, the acid was kept in sealed cells for all observations of the constancy and reproducibility of the freezing temperature. These cells, shown in figure 1, were cylindrical in shape, 5 cm in diameter, and about 25 cm long. A thermometer well 8 mm in diameter extended nearly the length of the cylinder, and an extension of the well about 12 cm long served as a handle. The capacity of each cell was about 425 ml.

² Frank W. Schwab and Edward Wichers, *Purification of substances by slow fractional freezing*, J. Research NBS **32**, 253 (1944) RP1588.

³ See footnote 2.

⁴ Frank W. Schwab and Edward Wichers, *Precise Measurement of the Freezing Range as a Means of Determining the Purity of a Substance, Temperature—Its Measurement and Control in Science and Industry*, p. 256-264 (Reinhold Publishing Corporation, New York, N. Y., 1941).

Before the cell was sealed to the apparatus shown in figure 2, about 380 g of the acid (365 ml), carefully fused in a beaker or other suitable vessel and containing a small amount of water, was transferred to the cell through a side tube. The volume of liquid acid was adjusted so as to leave a free space of 50 to 60 ml in the cell. The acid was allowed to freeze completely and the cell was sealed in place as shown

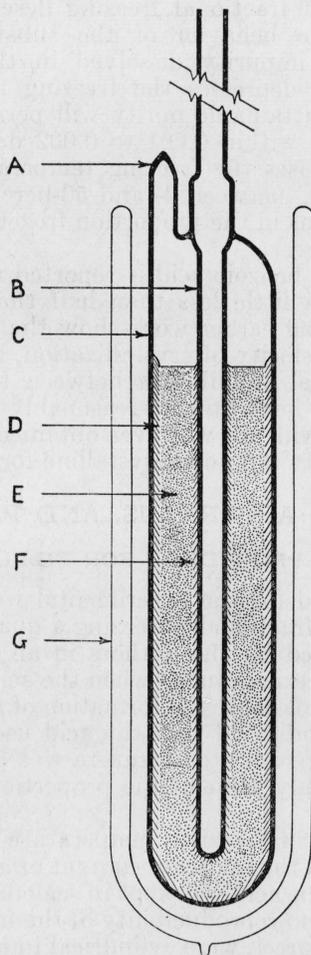


FIGURE 1.—Benzoic acid fixed-point cell.

A, Side-tube; B, thermometer well; C, cell proper; D, solid benzoic acid; E, mixture of crystals and liquid; F, solid benzoic acid; G, Dewar flask.]

in figure 2, with the aeration-tube, *B*, completely withdrawn. The acid was melted again and tube *B* was inserted, through the sidearm extended, into the liquid and adjusted with its end near the bottom of the cell. The opening at *K* between *B* and the side arm extended was closed by forcing a short piece of rubber tubing over the outside tube and was finally sealed with pycene. With stopcock 9 open,

and stopcock 2 open to outlet 1, the liquid was saturated with air, which was dried over phosphorus pentoxide and free of carbon dioxide, forced under the necessary pressure into the system at *H*.

The next steps in the procedure were designed to remove the water which is always present when benzoic acid is fused in contact with ordinary air. Liquid benzoic acid saturated, at temperatures near its freezing point, with air having a partial pressure of 5 mm of water vapor, contains about 0.06 mole percent of dissolved water. This amount of water depresses the freezing temperature between 0.04 and 0.05 degree C. In addition to moisture gained from the air there was

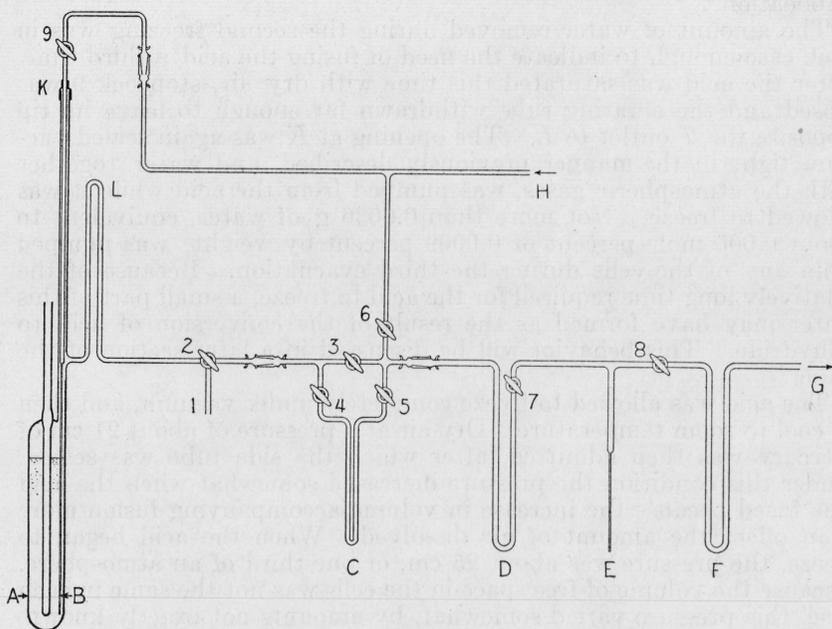


FIGURE 2.—Apparatus for filling the benzoic acid fixed-point cell and for determining water in benzoic acid.

A, Benzoic acid fixed-point cell; *B*, aeration-tube; *C*, manometer; *D*, trap of known volume; *E*, capillary trap; *F*, trap; *G*, vacuum connection; *H*, dry air source; *K*, rubber-tubing-connection sealed with pycene; *L*, air condenser for benzoic acid; 1, outlet for dry air; 2, 3, 4, etc. 2-mm stopcocks.

usually some that had been added intentionally to convert to benzoic acid small amounts of benzoic anhydride which might have been formed during the operations of purification. It was therefore necessary to dry the acid in the cells quite thoroughly to avoid excessive differences among the freezing temperatures in the several cells. This was done by pumping off the gases evolved while the acid slowly froze in the cell. The evolution of dissolved oxygen and nitrogen helped materially to sweep out the water vapor. The acid was allowed to freeze completely. To keep it from freezing so rapidly as to entrap much of the evolved gases, it was warmed at intervals with the soft flame of a hand torch. The acid was again fused and saturated with dry air. During this operation much of the acid that had sublimed while it was previously freezing and had condensed in the cell side of the inverted U-tube, *L*, melted and flowed back into the cell. The

acid was allowed to freeze a second time. This time the discharged gases were pumped off through stopcock 2, which was open to the manometer, *C*, and trap *D* with stopcock 6 closed. During the pumping the trap was cooled with liquid air. When the pumping was completed, the trap was isolated from the rest of the apparatus, by closing stopcocks 3 and 7, and allowed to warm to room temperature. The known volume of the trap and the pressure indicated by the manometer gave a measure of the amount of water removed from the acid. *E* is a capillary receiver not used in this work and *F* is a guard trap. This apparatus and its use are described in greater detail in another publication.⁵

The amount of water removed during the second freezing was in each case enough to indicate the need of fusing the acid a third time. After the acid was saturated this time with dry air, stopcock 9 was closed and the aerating tube withdrawn far enough to leave its tip opposite the *T* outlet to *L*. The opening at *K* was again sealed vacuum tight in the manner previously described, and water, together with the atmospheric gases, was pumped from the acid while it was allowed to freeze. Not more than 0.0036 g of water, equivalent to about 0.006 mole percent or 0.0009 percent by weight, was pumped from any of the cells during the third evacuation. Because of the relatively long time required for the acid to freeze, a small part of this water may have formed as the result of the conversion of acid to anhydride. This behavior will be discussed in a later section of the paper.

The acid was allowed to freeze completely under vacuum, and then to cool to room temperature. Dry air at a pressure of about 21 cm of mercury was then admitted, after which the side tube was sealed. Under this condition the pressure increased somewhat when the acid was fused because the increase in volume accompanying fusion more than offset the amount of air dissolved. When the acid began to freeze, the pressure was about 25 cm, or one-third of an atmosphere. Because the volume of free space in the cells was not the same in each case, this pressure varied somewhat, by amounts not exactly known, in the group of cells prepared for observations of the freezing temperature.

Several other cells, filled in the manner described, were used for observations on the stability of the acid. Still another cell (fig. 4), to be described later, was provided with a side arm assembly consisting of a stopcock and a ball-joint connection so that various gases could be admitted at known pressures for observations on the effect of pressure and of dissolved atmospheric gases. The triple point of the acid was also measured in this same apparatus.

⁵ Frank W. Schwab and Edward Wichers, *A physical method for determining residual water and other volatile materials in pure substances*, J. Research NBS **33**, 121 (1944) RP1600.

2. APPARATUS FOR MEASURING TEMPERATURES

The temperature measurements were made with platinum resistance thermometers of the coiled-filament type described by Meyers,⁶ with a resistance at 0° C of about 25 ohms. The outside diameter of the thermometers was about 7 mm and the length of the coiled filament was 3 to 3.5 cm. The resistances were measured with a precision Mueller⁷ bridge of the type G-2, No. 8069, made by the Leeds & Northrup Co. The apparatus was equipped with a switch that reversed the galvanometer current and thereby doubled the scale deflection caused by a given unbalance in the bridge. For convenience the bridge was connected to a four-place selector switch. The galvanometer had a sensitivity of 10 mm/microvolt, a period of not over 6 seconds, a critical external damping resistance of not less than 50 ohms and a coil resistance of 23.5 ohms. The optical arm of the galvanometer was 5.5 m long. With a reversing switch on the bridge, it provided a scale deflection of 32 mm for an unbalance of the bridge of 0.0001 ohm. It was thus readily possible to estimate changes in resistance to a few millionths of an ohm. All corrections were made to a millionth of an ohm in order to obtain an adequate measure of the reproducibility.

Before the series of measurements reported in this paper were made, the resistance bridge was calibrated by the Resistance Measurements Section of this Bureau. Two of the thermometers, 535 and 618, together with the bridge, were calibrated at the steam point to 0.0001 degree C by C. S. Cragoe and H. F. Stimson of the Heat Measurements Section, with a precision manometer by means of which the height of the mercury column was fixed with an accuracy within 1 micron. The sulfur point was determined in the regular way by the Thermometry Section, also of this Bureau. A much less accurate calibration was required at the sulfur point than at the steam point, since all of the temperatures measured were close to 122.4° C. At this temperature, errors arising from an error of calibration at the sulfur point are only about one-fiftieth of the error at the sulfur point itself. The bridge and each of the thermometers, 535 and 618, were calibrated in the same way after the measurements were completed, to disclose, if possible, any changes in the resistance-measuring equipment. The other thermometers, 515 and 587, were calibrated in the regular way by the Thermometry Section, before the measurements were begun. At the completion of the observations, thermometer 587 was also calibrated with the same accuracy as 535 and 618. The characteristics of the four thermometers, as determined by these calibrations, are given in table 1.

⁶ C. H. Meyers, *Coiled-filament resistance thermometers*, BS J. Research **9**, 807 (1932) RP508.

⁷ E. F. Mueller, *Precision Resistance Thermometry, Temperature—Its Measurement and Control In Science and Industry*, p. 162 to 179 (Reinhold Publishing Corporation, New York, N. Y., 1941).

TABLE 1.—Characteristics of thermometers

Calibration by N B S—	Date calibrated	c^a	δ^a
THERMOMETER 535			
Thermometry Section	Nov. 17, 1938	0.0039243	1.493
Heat Measurements Section	July 30, 1941	.00392454	1.4947
	Dec. 3 and 4, 1941	.00392453	1.4946
	Jan. 22, 1942	.00392452	1.4945
THERMOMETER 618			
Thermometry Section	Aug. 4, 1941	0.0039241	1.493
Heat Measurements Section	Dec. 3 and 4, 1941	.00392409	1.492 ₉
	Jan. 22, 1942	.00392409	1.492 ₉
THERMOMETER 587 ^b			
Thermometry Section	Sept. 27, 1940	0.0039244	1.494
Heat Measurements Section	July 30, 1941	.00392438	1.493 ₉
	Dec. 3 and 4, 1941	.00392441	1.494 ₀
	Jan. 22, 1942	.00392438	1.493 ₉
THERMOMETER 515			
Thermometry Section	Mar. 15, 1938	0.0039226	1.499
Heat Measurements Section	(^c)	(^c)	(^c)

^a c is the fundamental coefficient of the resistance coil of the thermometer and may be expressed as

$$\frac{R_{100} - R_0}{100R_0}$$

in which R_{100} and R_0 are the resistances of the coil at 100° and 0° C, respectively. δ is also a constant which is characteristic of the individual thermometer. It is determined by calibration at the ice, steam and sulfur points. Both constants are for the Callendar equation, which is given in the appendix to this paper.

The values for c and δ given in line 1 under each thermometer were determined in the regular way by the Thermometry Section of the National Bureau of Standards. The values given for δ in lines 2 and 3, under thermometer 618 and in lines 2, 3, and 4, under thermometers 535 and 587, were not determined but were computed from the new values of c , reported by the Heat Measurements Section and from the values of δ given in line 1.

^b The constants reported for Sept. 27, 1940, and July 30, 1941, were obtained before the thermometer was broken; the other constants were obtained after it was repaired.

^c No calibration.

3. PROCEDURES FOR MEASURING TEMPERATURES

(a) AT THE BENZOIC ACID POINT

The procedure usually followed in observing the freezing temperatures in the cells was as follows: The cell was heated in an electric oven kept several degrees above the freezing point of the acid, usually at about 130° C. When the acid was completely fused and had reached the temperature of the oven, the cell was removed and rather vigorously shaken so that the acid cooled uniformly. More rapid cooling at one point was caused by placing a cap of wet paper on the end of the side-tube (*A* in fig. 1). This caused a small amount of acid to crystallize and thus prevented excessive undercooling of the bulk of the liquid. If the crystals were not present, the acid sometimes undercooled as much as 15 degrees C, and the amount of solid suddenly formed was excessive. Normally, as the cell cooled, a mush of fine needle-like crystals appeared quite suddenly throughout the liquid. Although only a small fraction of the acid was frozen, the crystals were so well interlaced that they did not tend to settle out on subsequent standing. The cell was then rolled up in a piece of soft cloth

and placed in a close-fitting Dewar flask. The open end of the Dewar flask was packed with cotton to provide further insulation. Before the cell was put into it, the Dewar flask was warmed approximately to the freezing point of the acid by placing in it for 15 to 20 minutes a companion cell also containing freezing benzoic acid. This was done to prevent the rapid freezing of acid in the cell to be measured, which otherwise would have been caused by the loss of a considerable amount of heat to the cold flask. When the cell which was to be observed was in place in the Dewar flask, the resistance thermometer was inserted in the thermometer well. After about 10 minutes, measurements of resistance were begun. They were continued at least until the resistance reached its maximum (usually within 30 minutes) and nearly always for a considerably longer period. In a number of instances two sets of resistance measurements were made, one in which the thermometer current was 1.00 ma; the other, 1.41 ma. With the latter current the power input was twice that of the former. The difference in resistance between the two sets of measurements, when subtracted from the resistance observed with a current of 1 ma, provided the correction necessary to give resistances corresponding to zero thermometer current.

Usually, observations were made on several cells in close sequence by connecting the several thermometers to the bridge in rotation by means of the selector switch.

Temperatures corresponding to observed resistances were computed by the method described in the appendix to this paper. For observations of small differences in temperature, with a given thermometer, it was not always necessary to compute actual temperatures. For these relative measurements it was often sufficient to observe changes in the interval between the ice point and the benzoic acid point, since the change of resistance as a function of temperature in the vicinity of the benzoic acid point was accurately known. The approximate coefficient was 0.0001 ohm/millidegree.

(b) AT THE ICE POINT

The fundamental calibrations of the measuring instruments were made before and after the series of observations that gave the precision of the benzoic acid fixed-point cell. In addition, observations at the benzoic acid point were bracketed between observations at the ice point, made the same day, in order to disclose and, if possible, to correct for any variation in the resistance-measuring equipment. Two benzoic acid points and three ice points were usually measured with a thermometer during a day.

Measurements at the ice point were made as follows:⁸ Shaved ice obtained from clear cakes was washed with distilled water. The mush was thoroughly mixed in an open porcelain enamel pan to approach saturation with air, and then transferred to a precooled Dewar flask. The coil of the thermometer was immersed 20 to 25 cm, the mush was pressed lightly around the thermometer and measurements

⁸ The "ice point," or temperature of equilibrium between ice and air-saturated water at normal atmospheric pressure, has been a basic fixed point in nearly all measurements of temperature. It was reported in the Technical News Bulletin of the National Bureau of Standards, No. 305, p. 71 (1942), that for work of the highest precision it is desirable to avoid the small variations in the ice point resulting from contact of the melting ice with the atmosphere. For this purpose the triple point of water has advantages. A direct comparison between the ice point and the triple point for the same sample of water shows a difference of 0.00997 degree C.

of the resistances were recorded when they became constant. As with the measurements at the benzoic acid point, observations were made with thermometer currents of 1.00 and 1.41 ma, to permit extrapolation to zero current. A correction for impurities in the ice was obtained from conductivity measurements of the ice water at the time of calibration and on other occasions when it was desirable to report temperatures to the highest accuracy. Clear ice was of high purity and the correction was usually not more than 0.00001 to 0.00002 ohm.

In table 5 are given the resistances of thermometers 587, 535, 618, and 515 as measured at the ice points during the time most of the measurements reported in this paper were made. These measurements show the maximum variation observed during a period of about 1 month.

III. STABILITY OF BENZOIC ACID

In the course of this work, benzoic acid was not found to undergo any measurable irreversible decomposition when heated at temperatures below 150° C. Evidence of this will be presented later. However, the acid does undergo a reversible decomposition to benzoic anhydride and water. Since this reaction must be controlled if the acid is not to suffer a variable or progressive change in purity, and hence in freezing temperature, extensive observations concerning it were made. Some of these observations have been reported in an earlier publication.⁹ When the acid is enclosed in a sealed container the water produced simultaneously with the anhydride cannot escape, and the reaction therefore can proceed only until an equilibrium is reached. At the outset it was thought that the acid would have to be brought to some state of equilibrium with the products of its own dissociation if reproducible freezing temperatures were to be obtained. Accordingly, four cells were kept above freezing temperature, except during the short periods when observations of the freezing temperature were being made, until they reached equilibrium, as evidenced by constancy of the freezing temperature. This was done by keeping the cells in an electrically heated oven, in which mechanical circulation of air kept the temperature constant within 1 degree. The temperature of the oven was intended to be about 10 degrees C above the freezing temperature of the acid. An actual measurement made after the observations were begun showed the temperature of the oven to be 131.6° C. The observed freezing temperatures of the cells are given in table 2. It will be noted that 10 days or longer were required for the acid to reach equilibrium with benzoic anhydride and water. The slight variability in the observed temperatures over longer periods, up to 8 weeks, is attributable to a lack of reproducibility caused by the presence of about 0.015 mole percent each of dissolved anhydride and water. The small differences in the total depressions observed in the several cells were probably caused by differences in the initial content of water or of anhydride resulting from uncontrolled variations in the drying of the acid when the cells were filled.

⁹ Frank W. Schwab and Edward Wichers, *Preparation of benzoic acid of high purity*, J. Research NBS 25, 747 (1940) RP 1351.

TABLE 2.—Stability^a of benzoic acid at 131.6° C *

Cell 11		Cell 12		Cell 13		Cell 14	
Time at 131.6° C	T_F						
hr	° C						
0	122.3577	0	122.3558	0	122.3565	0	122.3598
21	122.351	123	122.344	-----	-----	20	122.356
38	122.347	161	122.343	432	122.343	58	122.346
105	122.341	265	122.342	560	122.342	97	122.343
124	122.340	301	122.342	671	122.338	223	122.339
143	122.341	383	122.342	693	122.338	558	122.338
161	122.340	419	122.339	730	122.339	964	122.337
180	122.341	530	122.341	-----	-----	1,075	122.337
247	122.338	548	122.336	-----	-----	-----	-----
265	122.339	566	122.338	-----	-----	-----	-----
284	122.339	602	122.340	-----	-----	-----	-----
302	122.339	671	122.338	-----	-----	-----	-----
337	122.340	707	122.338	-----	-----	-----	-----
405	122.339	726	122.338	-----	-----	-----	-----
422	122.339	1,073	122.336	-----	-----	-----	-----
525	122.337	1,325	122.337	-----	-----	-----	-----
579	122.339	1,391	122.337	-----	-----	-----	-----
682	122.338	-----	-----	-----	-----	-----	-----
977	122.337	-----	-----	-----	-----	-----	-----
995	122.337	-----	-----	-----	-----	-----	-----
1,061	122.337	-----	-----	-----	-----	-----	-----
1,281	122.336	-----	-----	-----	-----	-----	-----
1,300	122.337	-----	-----	-----	-----	-----	-----
1,318	122.338	-----	-----	-----	-----	-----	-----
1,361	122.337	-----	-----	-----	-----	-----	-----
After reversion.	122.3573	After reversion.	122.3549	After reversion.	122.3578	After reversion.	122.3600

* In column 1 under each cell is given the total time in hours that the cell was kept at 131.6° C. Proper allowance was made for each time the acid was frozen. The temperature of freezing (T_F °C) represents the maximum temperature observed.

A few observations of the equilibrium established at 150° C showed that at this temperature the final concentrations of anhydride and water are approximately double those at 131.6° C.

The last temperature recorded for each cell in table 2, designated "after reversion," indicates the freezing temperature after the completion of the other observations and after the original condition of the acid had been restored. It will be noted that in the long periods during which the cells were kept at 131.6° C, no measurable irreversible decrease in the purity of the acid occurred. The average deviation of the freezing temperatures at the end of the several periods from those at the beginning was 0.7 millidegree.

Further evidence of the absence of thermal decomposition was given by the behavior of one cell that was kept at 131.6° C for nearly a year. The total depression of the freezing temperature observed during this interval was 5 millidegrees. Since the thermometer used to measure the freezing temperature at the beginning of the period was subsequently found to be variable by more than 5 millidegrees, the change that may have occurred is not precisely known, but it obviously was not large. The same cell was later kept at 150° C for nearly a month. After the first few days required to establish the anhydride equilibrium, there was no further depression of the freezing temperature, which would have occurred had there been a measurable amount of thermal decomposition or of a chemical reaction with the glass of the containing vessel. From these results it may be concluded that benzoic acid is adequately stable for use in thermometry, provided it is not heated for long periods at temperatures much above

150° C, and provided account is taken of the reversible formation of benzoic anhydride and water.

During the observations made while the cells were kept at 131.6° C, it was noted that the freezing temperature tended to rise if the acid was kept near freezing for longer than the usual short periods required for measurements. If all the acid in a cell was allowed to freeze slowly and then remelted for a short time, there was a marked rise in the freezing temperature. When this was repeated several times, the freezing temperature returned to that of acid containing no anhydride, as shown in table 2. Obviously the acid in the cells was reverting to its original condition. This came about for two reasons. From the fact that the equilibrium concentrations of anhydride and water at 150° C were markedly greater than those at 131.6° C, it follows that the equilibrium concentrations near the freezing temperature (122.4° C) must be lower than those at 131.6° C. This alone is probably not enough to account for complete reversion to benzoic acid, although observations made at the freezing temperature indicate that the equilibrium concentrations of water and anhydride are lower than 0.003 mole percent each at this temperature. The probable explanation of complete reversion of the anhydride and water during slow freezing is as follows: As the acid freezes the anhydride and water remain almost completely in solution in the liquid phase. As freezing progresses, their concentrations in the liquid phase progressively increase. If the eutectic temperature of the system is as much as 10 degrees C below the freezing point of the acid, the initially minute concentration of the two "impurities" may be multiplied some thousands of times before the liquid phase completely disappears. This huge change in concentration causes the rate of recombination to increase enormously. It is doubtless true that the anhydride and water do not remain ideally in the liquid phase as freezing progresses, but this condition must be rather closely approached at the slow rate of freezing which occurs if the cell is kept in the Dewar flask.

From the data in table 2 it can be estimated that the initial rate of formation of anhydride and water at 131.6° C is not great enough to cause in 1 hour a lowering of the freezing temperature by as much as 1 millidegree. When a cell is prepared for an observation it takes only a short time, at most half an hour, to heat the acid, once it is completely fused, to a temperature a few degrees above its freezing point. As the rate of formation of the anhydride during the melting period, which is considerably longer, must be much lower than at 131.6° C, it may be concluded that the total amount of anhydride and water formed while the cell is being prepared for an observation is not enough to depress the freezing temperature by as much as 1 millidegree. Since even the minute amounts that are formed tend to revert to acid during the subsequent freezing, it is apparent that cells kept at room temperature during the periods between observations would not be unreliable because of the dissociation reaction. Because of the absence of appreciable amounts of anhydride and water as "impurities" in such cells, the observed freezing temperatures would also be more sharply reproducible than in cells maintained above the freezing temperature during the intervals between observations. Accordingly, all subsequent observations of the reproducibility of the freezing tempera-

ture were made on cells kept at room temperature when not in use. In occasional exceptions, for example, when the formation of crystals was faulty, the period required to reheat the cell was very short.¹⁰

IV. REPRODUCIBILITY OF THE FREEZING TEMPERATURE

After the acid in each of the five cells had been restored to the condition existing before the series of observations in which the cells were kept at 131.6° C, a large number of observations were made to determine the reproducibility of the freezing temperature.¹¹ Most of these observations were made during a period of 1 month. Four thermometers were used. Two of the thermometers, 535 and 618, were calibrated at the steam point with the high degree of accuracy previously mentioned. This made it possible to assign absolute values to the observed temperatures, although the emphasis in this series of observations was on the constancy and reproducibility of the temperature of a particular cell as measured with a particular thermometer. It should be noted that the observed temperatures have no significance either as the triple point of benzoic acid or as its freezing temperature under 1 atm of dry air, because the conditions in the cells were intermediate between these two defined conditions. The pressure in the cells was about one-third of an atmosphere, but there was some variation in the pressure from cell to cell, and also in the purity of the acid in the several cells, resulting from the way in which the cells were filled.

Figure 3¹² illustrates the course of measurements of a particular cell. The lower curve represents observations made with a thermometer current of 1.00 ma and the upper one with 1.41 ma. The average difference between the two sets of measurements, when subtracted from those represented by the lower curve, would give an extrapolated curve of resistances with zero thermometer current.¹³

In table 3 are given six sets of data, all for one cell, but obtained with three thermometers, similar to those used in figure 3 but extrapolated to zero thermometer current.

¹⁰ In connection with this discussion, it may be pointed out that the direction and magnitude of the shift in the equilibrium between the acid anhydride and water in the interval between 150° C and the freezing point suggest that no measurable amounts of anhydride and water are likely to exist under equilibrium conditions at room temperature.

¹¹ Thanks are expressed to J. L. Clark, of this Bureau, for his help during these observations.

¹² The observations in figure 3 were made by the Heat Measurements Section.

¹³ In accordance with a paper by Mueller (see footnote 7), it has been customary to assume that, in the range from 0° to 500° C, the temperature rise produced by a constant thermometer current is independent of the temperature and the medium in which the thermometer is placed. This is true only when the environments of the thermometer do not differ materially with respect to loss of heat at the temperatures being measured. In cases where there is doubt as to whether the heating is the same at all temperatures or in different media at one temperature, the observed resistances may be corrected to those corresponding to zero thermometer current by making observations with two different thermometer currents. For example, the environment of the thermometer in the measurements at the ice point reported in this paper, was shaved ice in water. At the benzoic acid point the thermometer, inserted in the well B of the cell (fig. 1) was separated from the freezing mixture of benzoic acid by the Pyrex thermometer well and a thin air space. Subtracting the difference between the resistances observed when 1.41 and 1.00 ma were used, from the resistance observed when 1.00 ma was used, gave the resistance for zero thermometer current. The difference between the resistances observed for each thermometer, 535, 618, 515 and 587, with thermometer currents of 1.41 and 1.00 ma, was 0.000209, 0.000184, 0.000167, and 0.000190 ohm at the benzoic acid point. The corresponding differences at the ice point were 0.000133, 0.000108, 0.000119, and 0.000120 ohms, respectively. The validity of these extrapolations is dependent on the assumption that the heat input and the temperature rise of the thermometers varies as the square of the current, which was verified by making measurements with thermometer currents of $\sqrt{0.50}$, 1.00, $\sqrt{2.00}$, and 2.00 ma. It is interesting to note that if the temperature at the benzoic acid point had been calculated from the resistances observed with 1.00 ma as the thermometer current, the benzoic acid point would have been in error by at least 0.5 millidegree (thermometer 515) and not more than 0.8 millidegree (thermometer 618). With a thermometer current of 2 ma, the error would have been 2.0 and 3.2 millidegrees, and larger for higher thermometer currents.

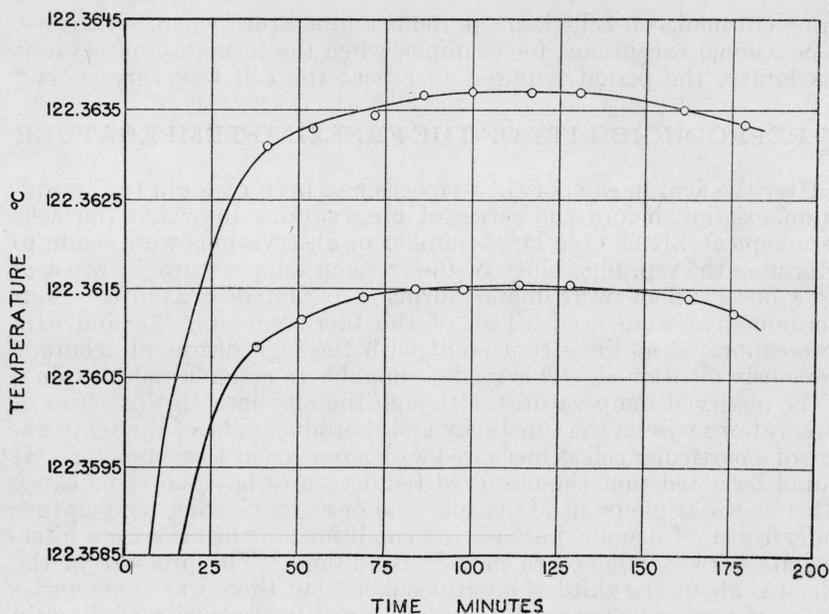


FIGURE 3.—Constancy of temperature in a benzoic acid fixed-point cell.
Lower curve, Thermometer current 1.00 ma; upper curve, thermometer current 1.41 ma.

TABLE 3.—Constancy of temperature in a benzoic acid fixed-point cell
[Cell 15]

Thermometer 587			Thermometer 535			Thermometer 618		
Date	Time	Temperature	Date	Time	Temperature	Date	Time	Temperature
	<i>min</i>	<i>°C</i>		<i>min</i>	<i>°C</i>		<i>min</i>	<i>°C</i>
Aug. 15, 1941	10	122.3577	Aug. 11, 1941	12	122.3602	Aug. 13, 1941	12	122.3606
	22	122.3596		24	122.3618		24	122.3622
	34	122.3600		36	122.3622		36	122.3632
	46	122.3601		46	122.3624		48	122.3634
	58	122.3601		60	122.3625		60	122.3634
	82	122.3600		72	122.3624		84	122.3634
	94	122.3599		84	122.3627	96	122.3634	
	108	122.3599		120	122.3629	108	122.3635	
	118	122.3599		132	122.3628	156	122.3638	
178	122.3599	180	122.3626					
			Aug. 12, 1941	11	122.3605	Aug. 22, 1941	11	122.3616
				23	122.3622		23	122.3633
				35	122.3626		35	122.3637
				47	122.3627		47	122.3638
				59	122.3628		107	122.3636
				83	122.3630			
			95	122.3630	Sept. 29, 1941	6	122.3625	
			119	122.3630		7	122.3627	
						8	122.3628	
						9	122.3629	
						15	122.3630	
						25	122.3633	
					38	122.3636		
					105	122.3636		
					148	122.3635		

• The thermometer was warmed to a temperature near the freezing temperature and then quickly placed in the cell.

TABLE 4.—Precision of benzoic acid fixed-point cells

Cell 11			Cell 12			Cell 13			Cell 14			Cell 15		
Date	Maximum temperature	Variation 60 to 120 minutes	Date	Maximum temperature	Variation 60 to 120 minutes	Date	Maximum temperature	Variation 60 to 120 minutes	Date	Maximum temperature	Variation 60 to 120 minutes	Date	Maximum temperature	Variation 60 to 120 minutes
THERMOMETER 535														
Aug. 22, 1941.....	122.3598	0.0005	Aug. 20, 1941.....	122.3594	0.0007	Aug. 13, 1941.....	122.3616	0.0001	Aug. 20, 1941.....	122.3635	0.0001	Aug. 11, 1941.....	122.3629	0.0004
Aug. 26, 1941.....	122.3604	.0005	Aug. 21, 1941.....	122.3592	.0003	Aug. 22, 1941.....	122.3611	.0005	Aug. 21, 1941.....	122.3635	.0005	Aug. 12, 1941.....	122.3630	.0002
Aug. 27, 1941.....	122.3608	.0007	Aug. 25, 1941.....	122.3593	.0005	Aug. 25, 1941.....	122.3611	.0003	Aug. 27, 1941.....	122.3635	.0002	Aug. 25, 1941.....	122.3637	.0006
Sept. 13, 1941.....	122.3608	.0002	Sept. 3, 1941.....	122.3592	.0003	Sept. 2, 1941.....	122.3606	.0003	Aug. 29, 1941.....	122.3632	.0003	Aug. 28, 1941.....	122.3633	.0001
Average.....	122.3604 ₅	0.0004 ₈	Average.....	122.3592 ₅	0.0004 ₅	Average.....	122.3611 ₀	0.0003 ₀	Average.....	122.3634 ₀	0.0002 ₅	Average.....	122.3632 ₅	0.0003 ₅
Average deviation....	0.0003 ₅	0.0001 ₄	Average deviation....	0.0000 ₅	0.0001 ₅	Average deviation....	0.0002 ₅	0.0001 ₀	Average deviation....	0.0001 ₂	0.0001 ₃	Average deviation....	0.0002 ₅	0.0001 ₅
Dec. 9, 1941.....	^a 122.3609	-----	Dec. 9, 1941.....	^a 122.3595	-----	Dec. 10, 1941.....	^a 122.3612	-----	Dec. 10, 1941.....	^a 122.3631	-----	Dec. 10, 1941.....	^a 122.3631	-----
THERMOMETER 618														
Aug. 28, 1941.....	122.3609	0.0002	Aug. 26, 1941.....	122.3589	0.0007	Aug. 20, 1941.....	122.3615	0.0003	Aug. 12, 1941.....	122.3637	0.0008	Aug. 13, 1941.....	122.3635	0.0001
Sept. 2, 1941.....	122.3611	.0003	Aug. 27, 1941.....	122.3600	.0007	Aug. 21, 1941.....	122.3617	.0001	Aug. 25, 1941.....	122.3634	.0005	Aug. 22, 1941.....	122.3638	.0002
Sept. 3, 1941.....	122.3610	.0001	Aug. 29, 1941.....	122.3594	.0003	Aug. 27, 1941.....	122.3618	.0005	Sept. 2, 1941.....	122.3627	.0003	Aug. 26, 1941.....	122.3636	.0000
Sept. 17, 1941.....	122.3612	.0001	Sept. 12, 1941.....	122.3593	.0001	Aug. 28, 1941.....	122.3611	.0001	Sept. 12, 1941.....	122.3634	.0000	Aug. 29, 1941.....	122.3634	.0002
Average.....	122.3610 ₅	0.0001 ₈	Average.....	122.3594 ₀	0.0004 ₅	Average.....	122.3615 ₂	0.0002 ₅	Average.....	122.3633 ₀	0.0004 ₀	Average.....	122.3635 ₈	0.0001 ₃
Average deviation....	0.0001 ₀	0.0000 ₈	Average deviation....	0.0003 ₀	0.0002 ₅	Average deviation....	0.0002 ₅	0.0001 ₅	Average deviation....	0.0003 ₀	0.0002 ₅	Average deviation....	0.0001 ₃	0.0000 ₈
Sept. 25, 1941.....	^a 122.3613	-----	Oct. 2, 1941.....	^a 122.3609	-----	Oct. 29, 1941.....	^a 122.3636	-----	Dec. 16, 1941.....	^a 122.3630	-----	Dec. 16, 1941.....	^a 122.3630	-----
THERMOMETER 515														
Aug. 29, 1941.....	122.3611	0.0004	Aug. 28, 1941.....	122.3601	0.0007	Aug. 29, 1941.....	122.3617	0.0007	Aug. 28, 1941.....	122.3640	0.0001	Aug. 27, 1941.....	122.3644	0.0004
Sept. 12, 1941.....	122.3617	.0001	Sept. 2, 1941.....	122.3610	.0002	Sept. 13, 1941.....	122.3633	.0004	Sept. 9, 1941.....	122.3638	.0000	Sept. 2, 1941.....	122.3637	.0002
Average.....	122.3614 ₀	0.0002 ₅	Average.....	122.3605 ₅	0.0004 ₅	Average.....	122.3625 ₀	0.0005 ₅	Average.....	122.3639 ₀	0.0000 ₅	Average.....	122.3640 ₅	0.0003 ₀
Average deviation....	0.0003 ₀	0.0001 ₅	Average deviation....	0.0004 ₅	0.0002 ₅	Average deviation....	0.0008 ₀	0.0001 ₅	Average deviation....	0.0001 ₀	0.0000 ₅	Average deviation....	0.0003 ₅	0.0001 ₀
Sept. 12, 1941.....	^a 122.3644	-----												
THERMOMETER 587														
Aug. 20, 1941.....	122.3572	0.0001	Aug. 22, 1941.....	122.3549	0.0005	Aug. 11, 1941.....	122.3577	0.0000	Aug. 13, 1941.....	122.3599	0.0000	Aug. 15, 1941.....	122.3601	0.0002
Aug. 21, 1941.....	122.3571	.0001				Aug. 12, 1941.....	122.3576	.0002	Aug. 22, 1941.....	122.3600	.0004	Aug. 18, 1941.....	122.3595	.0003
Aug. 25, 1941.....	122.3576	.0002				Aug. 25, 1941.....	122.3582	.0003				Aug. 20, 1941.....	122.3600	.0003
Average.....	122.3573 ₀	0.0001 ₃				Average.....	122.3578 ₃	0.0003 ₃	Average.....	122.3599 ₅	0.0002 ₀	Aug. 21, 1941.....	122.3600	.0004
Average deviation....	0.0002 ₀	0.0000 ₄				Average deviation....	0.0002 ₄	0.0003 ₀	Average deviation....	0.0000 ₅	0.0002 ₀	Average.....	122.3599 ₀	0.0003 ₀
												Average deviation....	0.0002 ₀	0.0000 ₄
												Dec. 18, 1941.....	^a 122.3634	-----

^a Values not included in the averages.

TABLE 5.—Measurements of the ice and benzoic acid points

Cell 11					Cell 12					Cell 13					Cell 14					Cell 15					
Date	Ice point	Average ice point	Benzoic acid point	ΔR	Date	Ice point	Average ice point	Benzoic acid point	ΔR	Date	Ice point	Average ice point	Benzoic acid point	ΔR	Date	Ice point	Average ice point	Benzoic acid point	ΔR	Date	Ice point	Average ice point	Benzoic acid point	ΔR	
THERMOMETER 535					THERMOMETER 535					THERMOMETER 535					THERMOMETER 535					THERMOMETER 535					
Aug. 22, 1941	<i>Ohms</i> {25.483892 25.483891}	<i>Ohms</i> 25.483891	<i>Ohms</i> 37.680482	<i>Ohms</i> 12.196591	Aug. 20, 1941	<i>Ohms</i> {25.483816 25.483878}	<i>Ohms</i> 25.483847	<i>Ohms</i> 37.680377	<i>Ohms</i> 12.196530	Aug. 13, 1941	<i>Ohms</i> {25.483897 25.483900}	<i>Ohms</i> 25.483899	<i>Ohms</i> 37.680662	<i>Ohms</i> 12.196763	Aug. 20, 1941	<i>Ohms</i> {25.483878 25.483892}	<i>Ohms</i> 25.483885	<i>Ohms</i> 37.680328	<i>Ohms</i> 12.196943	Aug. 11, 1941	<i>Ohms</i> {25.483890 25.483850}	<i>Ohms</i> 25.483875	<i>Ohms</i> 37.680761	<i>Ohms</i> 12.196886	
Aug. 26, 1941	<i>Ohms</i> {25.483779 25.483818}	<i>Ohms</i> 25.483799	<i>Ohms</i> 37.680400	<i>Ohms</i> 12.196601	Aug. 21, 1941	<i>Ohms</i> {25.483864 25.483891}	<i>Ohms</i> 25.483878	<i>Ohms</i> 37.680396	<i>Ohms</i> 12.196518	Aug. 22, 1941	<i>Ohms</i> {25.483891 25.483856}	<i>Ohms</i> 25.483874	<i>Ohms</i> 37.680581	<i>Ohms</i> 12.196707	Aug. 21, 1941	<i>Ohms</i> {25.483891 25.483899}	<i>Ohms</i> 25.483895	<i>Ohms</i> 37.680845	<i>Ohms</i> 12.196950	Aug. 12, 1941	<i>Ohms</i> {25.483834 25.483867}	<i>Ohms</i> 25.483851	<i>Ohms</i> 37.680735	<i>Ohms</i> 12.196884	
Aug. 27, 1941	<i>Ohms</i> {25.483885 25.483902}	<i>Ohms</i> 25.483894	<i>Ohms</i> 37.680581	<i>Ohms</i> 12.196687	Aug. 25, 1941	<i>Ohms</i> {25.483777 25.483675}	<i>Ohms</i> 25.483726	<i>Ohms</i> 37.680191	<i>Ohms</i> 12.196465	Aug. 26, 1941	<i>Ohms</i> {25.483818 25.483827}	<i>Ohms</i> 25.483823	<i>Ohms</i> 37.680502	<i>Ohms</i> 12.196679	Aug. 27, 1941	<i>Ohms</i> {25.483891 25.483892}	<i>Ohms</i> 25.483897	<i>Ohms</i> 37.680848	<i>Ohms</i> 12.196951	Aug. 25, 1941	<i>Ohms</i> {25.483975 25.483825}	<i>Ohms</i> 25.483750	<i>Ohms</i> 37.680657	<i>Ohms</i> 12.196907	
Sept. 13, 1941	<i>Ohms</i> {25.483935 25.483947}	<i>Ohms</i> 25.483941	<i>Ohms</i> 37.680646	<i>Ohms</i> 12.196705	Sept. 3, 1941	<i>Ohms</i> {25.483859 25.483885}	<i>Ohms</i> 25.483887	<i>Ohms</i> 37.680418	<i>Ohms</i> 12.196531	Sept. 2, 1941	<i>Ohms</i> {25.483903 25.483891}	<i>Ohms</i> 25.483897	<i>Ohms</i> 37.680570	<i>Ohms</i> 12.196672	Sept. 29, 1941	<i>Ohms</i> {25.483919 25.483892}	<i>Ohms</i> 25.483906	<i>Ohms</i> 37.680833	<i>Ohms</i> 12.196927	Aug. 28, 1941	<i>Ohms</i> {25.483937 25.483930}	<i>Ohms</i> 25.483934	<i>Ohms</i> 37.680889	<i>Ohms</i> 12.196955	
Average	25.483881	25.483881	37.680527	12.196646	Average	25.483835	25.483835	37.680346	12.196511	Average	25.483873	25.483873	37.680579	12.196706	Average	25.483896	25.483896	37.680839	12.196943	Average	25.483852	25.483852	37.680761	12.196908	
Range	0.000168	0.000142	0.000246	0.000114	Range	0.000216	0.000161	0.000227	0.000063	Range	0.000085	0.000076	0.000160	0.000091	Range	0.000041	0.000021	0.000020	0.000024	0.000024	Range	0.000262	0.000184	0.000232	0.000071
Average deviation.	0.000041	0.000036	0.000086	0.000050	Average deviation.	0.000059	0.000054	0.000077	0.000023	Average deviation.	0.000029	0.000025	0.000043	0.000030	Average deviation.	0.000009	0.000006	0.000008	0.000008	0.000008	Average deviation.	0.000056	0.000052	0.000040	0.000026
THERMOMETER 618					THERMOMETER 618					THERMOMETER 618					THERMOMETER 618					THERMOMETER 618					
Aug. 28, 1941	<i>Ohms</i> {25.578982 25.578998}	<i>Ohms</i> 25.578990	<i>Ohms</i> 37.819871	<i>Ohms</i> 12.240881	Aug. 26, 1941	<i>Ohms</i> {25.578852 25.578863}	<i>Ohms</i> 25.578858	<i>Ohms</i> 37.819437	<i>Ohms</i> 12.240629	Aug. 20, 1941	<i>Ohms</i> {25.578939 25.578947}	<i>Ohms</i> 25.578943	<i>Ohms</i> 37.819862	<i>Ohms</i> 12.240919	Aug. 12, 1941	<i>Ohms</i> {25.578870 25.578914}	<i>Ohms</i> 25.578892	<i>Ohms</i> 37.820009	<i>Ohms</i> 12.241117	Aug. 13, 1941	<i>Ohms</i> {25.579018 25.579015}	<i>Ohms</i> 25.579017	<i>Ohms</i> 37.820166	<i>Ohms</i> 12.241149	
Sept. 2, 1941	<i>Ohms</i> {25.578957 25.578960}	<i>Ohms</i> 25.578959	<i>Ohms</i> 37.819849	<i>Ohms</i> 12.240890	Aug. 27, 1941	<i>Ohms</i> {25.578888 25.578956}	<i>Ohms</i> 25.578922	<i>Ohms</i> 37.819682	<i>Ohms</i> 12.240760	Aug. 21, 1941	<i>Ohms</i> {25.578953 25.578969}	<i>Ohms</i> 25.578961	<i>Ohms</i> 37.819910	<i>Ohms</i> 12.240949	Aug. 25, 1941	<i>Ohms</i> {25.578803 25.578907}	<i>Ohms</i> 25.578858	<i>Ohms</i> 37.819922	<i>Ohms</i> 12.241064	Aug. 22, 1941	<i>Ohms</i> {25.578954 25.578911}	<i>Ohms</i> 25.578933	<i>Ohms</i> 37.820070	<i>Ohms</i> 12.241137	
Sept. 3, 1941	<i>Ohms</i> {25.578936 25.578883}	<i>Ohms</i> 25.578910	<i>Ohms</i> 37.819765	<i>Ohms</i> 12.240855	Aug. 29, 1941	<i>Ohms</i> {25.578954 25.578962}	<i>Ohms</i> 25.578958	<i>Ohms</i> 37.819675	<i>Ohms</i> 12.240717	Aug. 27, 1941	<i>Ohms</i> {25.578956 25.578960}	<i>Ohms</i> 25.578958	<i>Ohms</i> 37.819912	<i>Ohms</i> 12.240954	Sept. 2, 1941	<i>Ohms</i> {25.578930 25.578965}	<i>Ohms</i> 25.578963	<i>Ohms</i> 37.820009	<i>Ohms</i> 12.241046	Aug. 26, 1941	<i>Ohms</i> {25.578863 25.578894}	<i>Ohms</i> 25.578879	<i>Ohms</i> 37.819979	<i>Ohms</i> 12.241100	
Sept. 17, 1941	<i>Ohms</i> {25.578947 25.578969}	<i>Ohms</i> 25.578958	<i>Ohms</i> 37.819855	<i>Ohms</i> 12.240897	Sept. 12, 1941	<i>Ohms</i> {25.578974 25.578986}	<i>Ohms</i> 25.578980	<i>Ohms</i> 37.819699	<i>Ohms</i> 12.240719	Aug. 28, 1941	<i>Ohms</i> {25.578998 25.578978}	<i>Ohms</i> 25.578988	<i>Ohms</i> 37.819890	<i>Ohms</i> 12.240902	Sept. 12, 1941	<i>Ohms</i> {25.578936 25.578982}	<i>Ohms</i> 25.578984	<i>Ohms</i> 37.820110	<i>Ohms</i> 12.241126	Aug. 29, 1941	<i>Ohms</i> {25.578962 25.579023}	<i>Ohms</i> 25.578993	<i>Ohms</i> 37.820122	<i>Ohms</i> 12.241129	
Average	25.578954	25.578954	37.819835	12.240881	Average	25.578929	25.578930	37.819636	12.240706	Average	25.578963	25.578963	37.819894	12.240931	Average	25.578924	25.578924	37.820012	12.241088	Average	25.578956	25.578955	37.820084	12.241129	
Range	0.000115	0.000080	0.000106	0.000042	Range	0.000134	0.000122	0.000212	0.000131	Range	0.000059	0.000045	0.000050	0.000052	Range	0.000178	0.000126	0.000188	0.000080	0.000080	Range	0.000160	0.000138	0.000187	0.000049
Average deviation.	0.000024	0.000022	0.000025	0.000013	Average deviation.	0.000046	0.000040	0.000074	0.000039	Average deviation.	0.000015	0.000013	0.000018	0.000021	Average deviation.	0.000050	0.000049	0.000049	0.000033	0.000033	Average deviation.	0.000050	0.000050	0.000060	0.000014
THERMOMETER 515					THERMOMETER 515					THERMOMETER 515					THERMOMETER 515					THERMOMETER 515					
Aug. 29, 1941	<i>Ohms</i> {25.483294 25.483265}	<i>Ohms</i> 25.483280	<i>Ohms</i> 37.673587	<i>Ohms</i> 12.190307	Aug. 28, 1941	<i>Ohms</i> {25.483300 25.483277}	<i>Ohms</i> 25.483316	<i>Ohms</i> 37.673537	<i>Ohms</i> 12.190221	Aug. 29, 1941	<i>Ohms</i> {25.483265 25.483277}	<i>Ohms</i> 25.483271	<i>Ohms</i> 37.673629	<i>Ohms</i> 12.190358	Aug. 28, 1941	<i>Ohms</i> {25.483332 25.483292}	<i>Ohms</i> 25.483312	<i>Ohms</i> 37.673911	<i>Ohms</i> 12.190599	Aug. 27, 1941	<i>Ohms</i> {25.483278 25.483298}	<i>Ohms</i> 25.483288	<i>Ohms</i> 37.673923	<i>Ohms</i> 12.190635	
Sept. 12, 1941	<i>Ohms</i> {25.483326 25.483316}	<i>Ohms</i> 25.483321	<i>Ohms</i> 37.673701	<i>Ohms</i> 12.190380	Sept. 2, 1941	<i>Ohms</i> {25.483259 25.483216}	<i>Ohms</i> 25.483238	<i>Ohms</i> 37.673530	<i>Ohms</i> 12.190292	Sept. 13, 1941	<i>Ohms</i> {25.483235 25.483243}	<i>Ohms</i> 25.483239	<i>Ohms</i> 37.673739	<i>Ohms</i> 12.190500	Sept. 9, 1941	<i>Ohms</i> {25.483260 25.483267}	<i>Ohms</i> 25.483264	<i>Ohms</i> 37.673825	<i>Ohms</i> 12.190561	Sept. 2, 1941	<i>Ohms</i> {25.483261 25.483279}	<i>Ohms</i> 25.483270	<i>Ohms</i> 37.673825	<i>Ohms</i> 12.190555	
Average	25.483301	25.483301	37.673644	12.190344	Average	25.483277	25.483277	37.673534	12.190257	Average	25.483255	25.483255	37.673684	12.190429	Average	25.483288	25.483288	37.673868	12.190580	Average	25.483279	25.483279	37.673874	12.190595	
Range	0.000061	0.000041	0.000114	0.000073	Range	0.000116	0.000078	0.000007	0.000071	Range	0.000042	0.000032	0.000110	0.000142	Range	0.000072	0.000048	0.000086	0.000038	0.000038	Range	0.000037	0.000018	0.000098	0.000030
Average deviation.	0.000021	0.000021	0.000057	0.000036	Average deviation.	0.000039	0.000039	0.000004	0.000036	Average deviation.	0.000016	0.000016	0.000055	0.000071	Average deviation.	0.000024	0.000024	0.000043	0.000019	0.000019	Average deviation.	0.000010	0.000009	0.000049	0.000040
THERMOMETER 587					THERMOMETER 587					THERMOMETER 587					THERMOMETER 587					THERMOMETER 587					
Aug. 20, 1941	<i>Ohms</i> {25.567094 25.567147}	<i>Ohms</i> 25.567121	<i>Ohms</i> 37.803281	<i>Ohms</i> 12.236160	Aug. 22, 1941	<i>Ohms</i> {25.567151 25.567148}	<i>Ohms</i> 25.567150	<i>Ohms</i> 37.803100	<i>Ohms</i> 12.235950	Aug. 11, 1941	<i>Ohms</i> {25.567147 25.567151}	<i>Ohms</i> 25.567149	<i>Ohms</i> 37.803374	<i>Ohms</i> 12.236225	Aug. 13, 1941	<i>Ohms</i> {25.567168 25.567192}	<i>Ohms</i> 25.567180	<i>Ohms</i> 37.803630	<i>Ohms</i> 12.236450	Aug. 15, 1941	<i>Ohms</i> {25.567135 25.567132}	<i>Ohms</i> 25.567134	<i>Ohms</i> 37.803587	<i>Ohms</i> 12.236434	
Aug. 21, 1941	<i>Ohms</i> {25.567147 25.567163}	<i>Ohms</i> 25.567155	<i>Ohms</i> 37.803319	<i>Ohms</i> 12.236164	Aug. 25, 1941	<i>Ohms</i> {25.567134 25.567005}	<i>Ohms</i> 25.567134	<i>Ohms</i> 37.803274	<i>Ohms</i> 12.236226	Aug. 12, 1941	<i>Ohms</i> {25.567095 25.567134}	<i>Ohms</i> 25.567115	<i>Ohms</i> 37.803311	<i>Ohms</i> 12.236196	Aug. 22, 1941	<i>Ohms</i> {25.567148 25.567131}	<i>Ohms</i> 25.567140	<i>Ohms</i> 37.803578	<i>Ohms</i> 12.236438	Aug. 18, 1941	<i>Ohms</i> {25.567147 25.567191}	<i>Ohms</i> 25.567169	<i>Ohms</i> 37.803572	<i>Ohms</i> 12.236403	
Aug. 25, 1941	<i>Ohms</i> {25.567074 25.563988}	<i>Ohms</i> 25.567031	<i>Ohms</i> 37.803160	<i>Ohms</i> 12.236144	Average	25.567104	25.567104	37.803320	12.236216	Aug. 25, 1941	<i>Ohms</i> {25.567005 25.567091}	<i>Ohms</i> 25.567048	<i>Ohms</i> 37.803274	<i>Ohms</i> 12.236226	Average	25.567160	25.567160	37.803604	12.236444	Aug. 20, 1941	<i>Ohms</i> {25.567121 25.567175}	<i>Ohms</i> 25.567148	<i>Ohms</i> 37.803594	<i>Ohms</i> 12.236446	
Average	25.567102	25.567102	37.803253	12.236156	Range	0.000146	0.000101	0.000100	0.000030	Range	0.000061	0.000040	0.000100	0.000030	Range	0.000020	0.000020	0.000025	0.000006	0.000006	Range	0.000157			

In table 4 are recorded the systematic observations of five cells with the four thermometers. In addition to the date of each measurement, there are given the maximum observed temperature and the variation during the time interval 60 to 120 minutes. Also given are the averages of each set of measurements with a particular cell and thermometer and the average deviation of these measurements. Following these averages are single measurements of each of four cells with thermometer 535, and measurements of one cell (15) with each of the four thermometers, all made about 3 months after the others. At that time (Dec. 18, 1941, table 4) thermometer 587 had also been calibrated at the steam point with the same accuracy as 535 and 618, hence the measurements made with the three thermometers are directly comparable.

For a few days toward the end of the period during which the systematic observations were made, the humidity became so high that it had a significant effect on the behavior of the bridge and galvanometer. This was apparent from erratic observations of the ice point. Only those measurements that were unmistakably unreliable from this cause have been excluded from table 4.

1. RELATIVE REPRODUCIBILITY OF THE ICE POINT AND THE BENZOIC ACID POINT

In table 5 the resistances observed at the ice point and at the benzoic acid point have been listed to show the relative reproducibilities of these two fixed points. The average of the average deviations of the difference of resistances between the ice and benzoic acid points is 0.000025₇ ohm. The greatest difference between any two observations of the resistance, in a set of observations with one thermometer, was 0.000262 ohm at the ice point (cell 15, thermometer 535) and 0.000246 ohm at the benzoic acid point (cell 11, thermometer 535).

The average of the average deviations obtained from the respective averages of each set of observations is 0.000032₈ ohm at the ice point and 0.000043₉ ohm at the benzoic acid point. These two averages are in about the same ratio to each other as that of the respective total resistances, 25 to 37 ohms. This suggests that the main source of variability in the observations, both of the ice point and of the benzoic acid point, may have been in the bridge. If this was true, both fixed points were reproduced with about equal precision, and possibly with a greater actual precision than is shown by the recorded resistances.

2. COMPARISON OF THERMOMETERS

In table 6 the average maximum temperatures observed in each cell with each thermometer have been combined to show the differences between observations of a particular cell with all possible pairs of the four thermometers. It will be seen that the differences between thermometers 535 and 618 are the smallest. As previously noted, these thermometers had received the specially accurate calibration at the steam point. The other two were calibrated in accordance with the routine practice of the Thermometry Section. In view of the reproducibility of the freezing temperature of each cell, as shown by table 4, it may reasonably be concluded that the comparisons of all other

pairs of thermometers reflect uncertainties in the calibration of resistance thermometers as normally practiced. In view of the known reproducibility of the ice point, nearly all of the uncertainty must result from observations of the steam point. Assuming no error in calibration at the ice point, the interpolated error at the steam point is four-fifths the error at the benzoic acid point. These uncertainties are no larger than can be expected from the errors of barometric measurements. The largest difference, that between thermometers 515 and 587, corresponds to a difference of 0.09 mm in the respective barometric readings.

TABLE 6.—*Comparison of thermometers*^a

Cell	$T_{535}-T_{587}$	$T_{618}-T_{587}$	$T_{618}-T_{535}$	$T_{515}-T_{587}$	$T_{515}-T_{535}$	$T_{515}-T_{618}$
	°C	°C	°C	°C	°C	°C
11.....	0.0031 ₅	0.0037 ₅	0.0006 ₀	0.0041 ₀	0.0009 ₅	0.0003 ₅
12.....	.0043 ₈	.0045 ₀	.0001 ₂	.0056 ₅	.0012 ₇	.0011 ₂
13.....	.0032 ₇	.0036 ₉	.0004 ₂	.0046 ₇	.0014 ₀	.0009 ₈
14.....	.0034 ₅	.0033 ₅	.0001 ₀	.0039 ₅	.0005 ₀	.0006 ₀
15.....	.0033 ₅	.0030 ₈	.0003 ₃	.0041 ₅	.0008 ₀	.0004 ₇
Average.....	0.0035 ₂	0.0037 ₅	0.0002 ₇	0.0045 ₀	0.0009 ₈	0.0007 ₁
Average deviation.....	0.0003 ₄	0.0002 ₈	0.0002 ₁	0.0005 ₉	0.0003 ₅	0.0003 ₈

^a T is the average maximum temperature of a set of observations as given under each of the cells in table 4. The subscripts to T define the thermometers with which the measurements were made.

3. COMPARISON OF CELLS

In table 7 the data of table 4 are combined so as to show the differences between the maximum temperatures of all possible pairs of cells as measured with each of the four thermometers. The greatest difference between any pair (cells 12 and 15) is 4.2 millidegrees, and the smallest (between cells 14 and 15) is 0.05 millidegree. As previously noted, these differences are to be attributed partly to differences in the amount of benzoic anhydride or of water contained in the acid as the result of variations in the conditions under which the cells were filled. The differences may also result in part from differences in pressure of atmospheric gases in the cells when freezing begins. Although the pressures were nearly the same in all of the cells when they were sealed at room temperature, the pressures differed at the freezing point because the volume of free space (vapor space) was not closely controlled and the expansion which occurred as the cells were heated to the freezing temperature of the acid caused relative differences in the volumes of the free space. These differences between the freezing temperatures in different cells can undoubtedly be made smaller by more careful control of the indicated factors. The freezing temperatures can also be brought very close to a defined temperature, most readily to the triple point, by proper attention to the factors of purity and of pressure existing within the cell when freezing begins.

TABLE 7.—Comparison of cells ^a

Thermometer	$T_{12}-T_{11}$	$T_{13}-T_{11}$	$T_{14}-T_{11}$	$T_{15}-T_{11}$	$T_{13}-T_{12}$	$T_{14}-T_{12}$	$T_{15}-T_{12}$	$T_{14}-T_{13}$	$T_{15}-T_{13}$	$T_{15}-T_{14}$
	° C	° C	° C	° C	° C	° C	° C	° C	° C	° C
535	-0.0011 ₇	0.0006 ₃	0.0029 ₅	0.0028 ₀	0.0018 ₂	0.0041 ₂	0.0039 ₇	0.0023 ₀	0.0021 ₅	-0.0001 ₅
618	-0.0016 ₅	.0004 ₇	.0022 ₅	.0025 ₃	.0021 ₂	.0039 ₀	.0041 ₃	.0017 ₅	.0020 ₀	.0002 ₅
515	-.0008 ₅	.0011 ₀	.0025 ₀	.0026 ₅	.0019 ₅	.0033 ₅	.0035 ₀	.0014 ₀	.0015 ₅	.0001 ₅
587	-.0024 ₀	.0005 ₅	.0026 ₅	.0026 ₀	-----	-----	-----	.0021 ₂	.0020 ₇	-.0000 ₅
Average	-0.0012 ₂	0.0006 ₆	0.0025 ₇	0.0026 ₅	0.0019 ₆	0.0037 ₇	0.0038 ₈	0.0019 ₆	0.0019 ₆	0.0002 ₅
Average Deviation.	0.0002 ₈	0.0002 ₁	0.0002 ₁	0.0000 ₈	0.0001 ₀	0.0002 ₉	0.0002 ₆	0.0003 ₁	0.0002 ₀	0.0001 ₃

^a T is the average maximum temperature of a set of observations as given under each of the thermometers in table 4. The subscripts to T define the cells with which the measurements were made.

In connection with the foregoing discussion, it may be of interest to examine more closely the behavior of a cell as illustrated by figure 3 and table 3. It will be noted that some 35 or 40 minutes elapse before the temperature becomes constant within a few tenths of a millidegree in the normal course of observations. The lag of the thermometer can not account for more than a fraction of this interval, possibly 10 minutes. The remainder of the lag is believed to have the following explanation. Although the solid and liquid phases are brought very close to equilibrium by shaking the cell as the crystals form, a slight departure from equilibrium near the wall of the thermometer well occurs when the thermometer is placed in the well. Loss of heat to the thermometer causes a thin film of solid to form on the wall. Unless the acid is ideally pure this separation of crystals from the now unagitated liquid will lower the purity of the liquid in the region immediately adjacent to and in contact with this thin film of solid. By a process of diffusion, possibly aided by slow convection within the liquid, the composition of this liquid layer gradually approaches that of the bulk of the liquid. As this goes on, the freezing temperature rises until there is no further change in composition. A substantially constant temperature is then maintained for a while. This reasoning is supported by the observations made with thermometer 618 on Sept. 29, 1941 (see table 3), which were obtained under conditions different from normal. The thermometer was warmed at the freezing temperature in an auxiliary cell and then quickly transferred to cell 15. Under these conditions only a small quantity of acid froze around the thermometer well, with a correspondingly smaller change in concentration of impurity in the layer of liquid bounding this solid. It will be noted that in this instance the temperature rose to within a few tenths of a millidegree of the maximum in a much shorter time than usual.

Decline from the maximum temperature, as shown by the curves in figure 3, comes about from one or both of two causes. One is the increasing concentration of impurities in the liquid as freezing progresses from the outer wall of the cell toward the thermometer well. The other, and possibly the more significant one in this instance, is the lowering of pressure within the cell as freezing progresses. The contraction of the liquid on freezing is greater than the volume of atmospheric gases discharged by the liquid as it freezes. Hence there is a net decrease in pressure and, as will be shown in a later section of this paper, a lowering of the freezing temperature.

In cells to be prepared in the future it is proposed to use a much lower pressure of gas, so that the effects of a change of pressure during freezing will be minimized.¹⁴

V. FREEZING TEMPERATURES OF THE PURE ACID UNDER DEFINED CONDITIONS

In addition to the group of cells used for the study of the reproducibility of the freezing temperature, one cell was prepared for the measurement of the freezing temperature of the acid under known pressures of oxygen, nitrogen, and a mixture of these gases. The

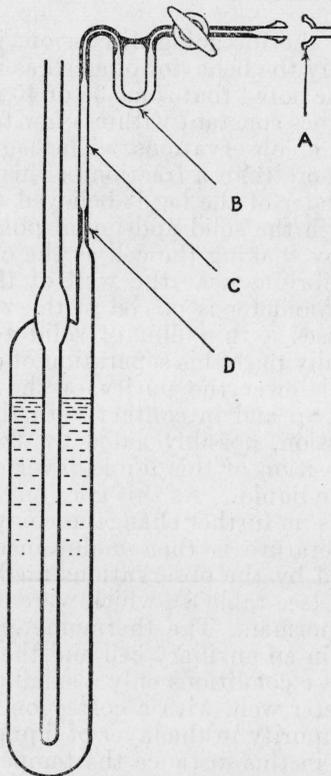


FIGURE 4.—Cell used for observations of the freezing temperature under defined conditions.

A, Movable ball-joint connection; B, trap; C, air condenser; D, capillary tube (2 mm).

triple point of the acid and the variation of the freezing temperature as a function of pressure were also measured in this cell. The cell, shown in figure 4, differed from the others in that it could be attached to a source of variable pressure of selected gases. The capillary

¹⁴ C. S. Cragoe and H. F. Stimson in unpublished observations at the triple point of water, made in a cell similar to that shown in figure 1, froze a thick layer of ice around the thermometer well and then, by warming the well, melted a thin layer next to it. This provided a surface at equilibrium temperature between ice and liquid water which had been purified by the process of freezing. This surface almost entirely surrounded the thermometer and hence controlled its temperature. This technic may prove advantageous with the benzoic acid cell but has not yet been tried. A similar technic was suggested by W. P. White, *J. Am. Chem. Soc.* **56**, 20 (1934).

portions of the connecting tube retarded the tendency for benzoic acid to sublime out of the cell when molten, and the larger portions served as condensers for the small amount of vapor that did pass the capillaries. The spherical joint, *A*, made it possible to rock the tube, if desired, while it was connected to the system for supplying gases and measuring the pressure.

When the acid in this cell was to be prepared for an observation, it was melted with a flame rather than in the oven. Care was taken to heat the acid slowly and uniformly so as to avoid overheating it. To get the desired mush of crystals in the liquid, the cell was manipulated in the manner previously described, with the additional detail that capillary *D* was kept cool, so that crystals of the acid would collect at this point and keep liquid from flowing into the trap or to the stopcock while the cell was being shaken. The cell was kept in a previously warmed Dewar flask during the temperature measurements. Further details of the manipulation required by special conditions of observation will be given in the appropriate paragraphs.

1. DETERMINATION OF THE TRIPLE POINT

To prepare for the determination of the triple point the acid was freed of water and atmospheric gases by evacuation of the cell while the acid was allowed to freeze slowly. The melting and freezing were repeated until no further change of pressure occurred when the cell was connected at *A* (fig. 4) to an evacuated system connected with a mercury manometer. Once the cell was freed of gases in the manner indicated, it did not require attachment to the gas-supply train during the observations of the triple point.

The triple point was measured on three consecutive days and twice more about a month later. The two later measurements were made between series of observations of the freezing temperatures under oxygen and nitrogen. They served as a check on the absence of any significant change in the composition of the acid which might have resulted from the repeated meltings.

The five observations of the triple point are given in table 8. It will be noted that the range of the five observations, including the two made after several measurements had been made under other conditions, is 0.9 millidegree, and that the changes during the series were not progressive. The small random variations possibly can be ascribed to differences in the fraction of acid frozen, that is, to the fact that observations were not made each time at exactly the same point in the freezing range of the slightly impure acid.

TABLE 8.—Triple point of benzoic acid

Date	Triple point
	°C
Sept. 23, 1941.....	122.361 ₃
Sept. 24, 1941.....	122.362 ₂
Sept. 25, 1941.....	122.362 ₁
Oct. 21, 1941.....	122.361 ₄
Oct. 24, 1941.....	122.362 ₂
Average.....	122.362 ₀

The acid used for these measurements was known to contain a small amount of impurity. To make the necessary correction of the triple point, the freezing temperature of the acid in this cell under 1 atm of dry air was compared with that of acid of known purity also under 1 atm of dry air and observed in another apparatus which will be described in a later section. The freezing temperature of the acid used for the triple-point measurements was 6 millidegrees below that of the pure acid. The amount of impurity, confirmed by a measurement of the freezing range, was found to be 0.0084 mole percent, which corresponds to a lowering of the freezing temperature of 6 millidegrees. This correction has been applied to the temperatures in table 8. By adding an uncertainty of 1 millidegree involved in the triple-point measurements to the uncertainty of 1 millidegree attached to the freezing temperature in dry air of the pure acid, the value of the triple point of pure benzoic acid can be given as $122.362^{\circ} \pm 0.002^{\circ} \text{C}$.

2. FREEZING TEMPERATURES UNDER DIFFERENT PRESSURES OF OXYGEN AND OF NITROGEN

To measure the freezing temperatures in equilibrium with selected pressures of oxygen or nitrogen, the acid in the cell was first freed of gases in the manner described in the preceding section. With the acid in the cell at room temperature, gas was admitted at a selected pressure; which, after a few trials, bore a known relation to the pressure which would exist in the cell after it was isolated from the train and the acid had been melted, shaken long enough to insure saturation with gas, brought to the standard conditions for observations of the freezing temperature, placed in a Dewar flask, and then shaken 15 minutes longer to insure equilibrium. When the freezing temperature reached its maximum value, the actual pressure in the cell was checked by setting the manometer to the predicted pressure and then opening the stopcock. The change in the manometer never exceeded a few centimeters. The pressure in the cell was computed from the manometer setting (predicted pressure), the observed pressure after the cell was opened to the manometer, and the known volumes of the gas space in the manometer and in the cell.¹⁵

The oxygen and nitrogen used for these measurements were, respectively, 99.87 and 99.74 percent pure, as determined from analyses made by Martin Shepherd and Shuford Schuhmann of the Gas Chemistry Section of this Bureau. Both gases contained some argon. Other impurities consisted primarily of oxygen in the nitrogen and of nitrogen in the oxygen. The gases were dried over phosphorus pentoxide but not otherwise purified. Each gas was introduced into the cell in three successive steps, up to a maximum pressure of about 2 atm. Between the two series of measurements, the triple point was redetermined to make sure that no change in the purity of the acid had occurred. The results of the measurements are given in the third column of table 9 and in curves B and D of figure 5. The

¹⁵ The ratios of the gas space of the system to the gas space of the cell v_s/v_c and of the gas space of the manometer to the gas space of the cell v_m/v_c were found to be 2.17 and 1.17, respectively. These ratios were constant over the range of pressures measured. The pressure in the cell was computed from the relation

$$p_c = 2.17P_s - 1.17p_m,$$

in which p_c = pressure in the cell, p_m = pressure in the manometer and P_s = pressure in the system, which consists of the cell and the manometer.

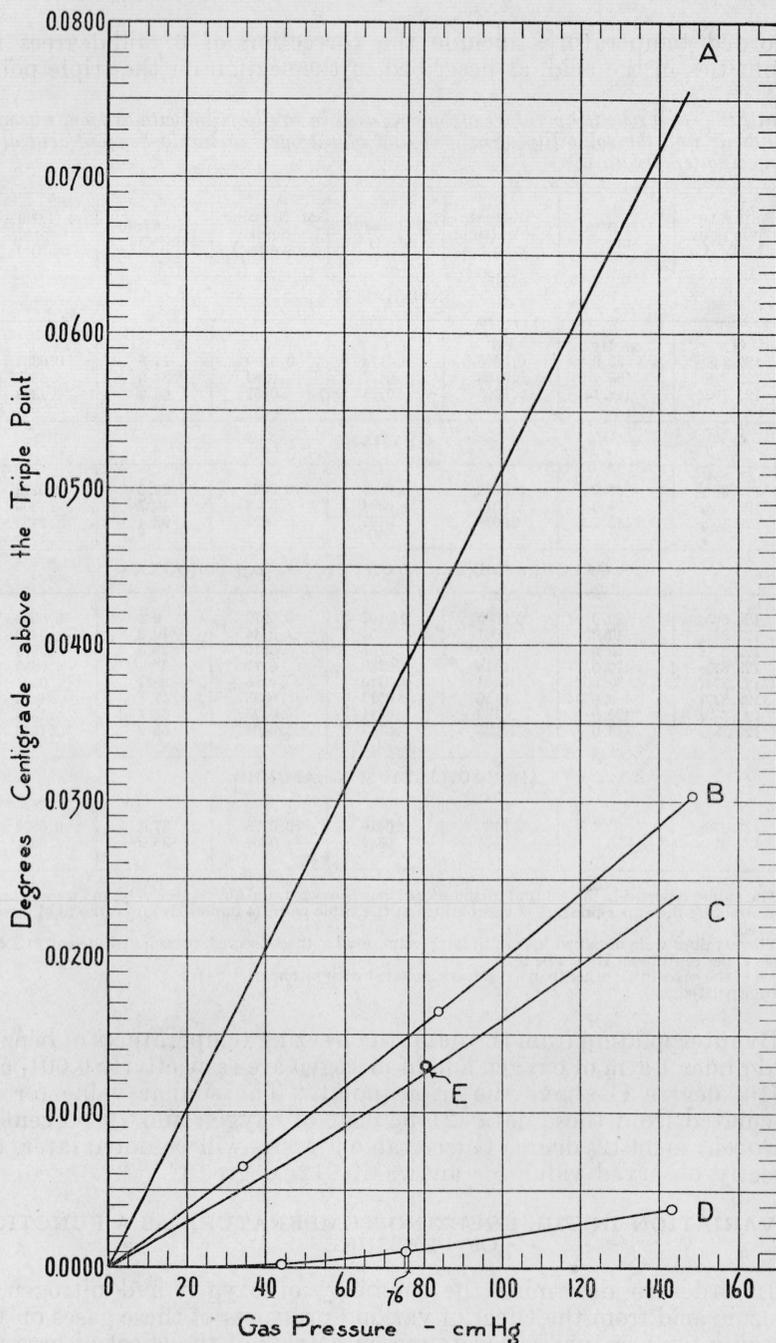


FIGURE 5.—Difference between the triple point and the freezing temperature of benzoic acid in equilibrium with variable pressures of nitrogen, of oxygen, and of air, and the effect of pressure on the freezing temperature.

A, Pressure effect; B, equilibrium with nitrogen; C, equilibrium with air (21 percent of oxygen and 79 percent nitrogen), computed from the observed values for oxygen and for nitrogen; D, equilibrium with oxygen; E, observed freezing temperature of benzoic acid (122.375°C) in equilibrium with air under a pressure of 80.1 cm of Hg (table 9).

recorded temperatures include the correction of 6 millidegrees for impurities in the acid, as described in the section on the triple point.

TABLE 9.—Freezing temperature of benzoic acid in equilibrium with oxygen, nitrogen, and air and the solubility of oxygen and of nitrogen in liquid benzoic acid at its freezing temperature

Temperature (triple point 122.362 ₀ ° C)	Gas pressure ^a	Degrees above triple point	Δt (pressure effect) ^b	Δt (freezing point lowering)	Mole fraction $\times 10^{-5}$	g (1,000 g benzoic acid) ⁻¹
NITROGEN						
°C	cm Hg	°C	°C	°C		
122.368 ₅	33.9	0.0065	0.0174	0.0109	14.5	0.0333
122.378 ₅	83.4	.0165	.0427	.0262	34.9	.0801
122.392 ₃	148.1	.0303	.0758	.0457	60.9	.1398
OXYGEN						
122.362 ₂	43.6	0.0002	0.0223	0.0221	29.5	0.0773
122.363 ₁	75.0	.0011	.0384	.0373	49.7	.1303
122.365 ₈	142.7	.0038	.0731	.0693	92.4	.2423
AIR CALCULATED FROM OXYGEN AND NITROGEN ^c						
122.365 ₀	20.0	0.0030	0.0102	0.0072	9.6	0.0226
122.368 ₁	40.0	.0061	.0205	.0144	19.2	.0452
122.371 ₂	60.0	.0092	.0307	.0215	28.7	.0678
122.373 ₈	76.0	.0118	.0389	.0271	36.1	.0853
122.374 ₄	80.0	.0124	.0410	.0286	38.1	.0901
122.377 ₆	100.0	.0156	.0512	.0356	47.5	.1122
122.380 ₀	120.0	.0189	.0614	.0425	56.7	.1340
122.384 ₃	140.0	.0223	.0717	.0494	65.9	.1558
AIR-EQUILIBRIUM MEASURED						
122.375 ₂	80.1	0.0132	0.0410	0.0278	37.1	0.0876
122.374 ₃	^d 76.0	.0125	.0389	.0264	35.2	.0832

^a The values reported in this column are those for nitrogen, oxygen, and air, respectively, and were obtained by subtracting the vapor pressure of benzoic acid at the triple point (4 mm of Hg) from the total pressure observed.

^b These values were obtained by multiplying column 2 by the observed pressure coefficient, 51.2×10^{-5} degree C per centimeter Hg (table 10).

^c All of the gases in air other than oxygen are included with nitrogen.

^d Interpolated.

By interpolation from the data, the freezing temperatures of benzoic acid under 1 atm of oxygen and of nitrogen are respectively 0.001₁ and 0.015₀ degree C above the triple point. The similar value for air calculated from these data (21 percent of oxygen and 79 percent of nitrogen) is 0.012₀ degree C (see table 9). As will be noted later, the directly observed value for air was 0.012₅ degree C.

3. VARIATION IN THE FREEZING TEMPERATURE AS A FUNCTION OF PRESSURE

In order to determine the solubility of oxygen and nitrogen in benzoic acid from the effect of varying pressures of these gases on the freezing temperature, separate measurements of the effect of pressure were necessary. These were made as follows: When certain of the observations of freezing temperature in equilibrium with measured pressures of a gas were completed, the pressure of the gas in the cell was suddenly changed to some higher value. This produced an instan-

taneous change in pressure but did not for some time alter the concentration of gas in the portion of the liquid around the thermometer well, especially in the region near the thermometer coil. This lag in the change of concentration of the gas was caused by the long path through which gases dissolving at the upper surface of the liquid would have to diffuse to reach the level of the thermometer coil. Care was taken not to agitate the cell during these observations. The change in temperature caused by the change in pressure usually was complete within 3 minutes and always within 5. The change was shown to be reversible by observations made when the sign of the pressure change was reversed. The observed effects of these changes in pressure are given in table 10. In the first column of table 10 is given the pressure in centimeters before and after the pressure was suddenly changed. The pressure interval is given in column 2 and the corresponding change in observed temperature in column 3. The changes in freezing temperatures for a change in pressure of 1 cm and of 1 atm, as calculated from the observed values, are given in columns 4 and 5, all of table 10. The pressure coefficient is 0.038_3 °C per atmosphere, as shown in curve *A* of figure 5.

TABLE 10.—Effect of pressure on the freezing temperature of benzoic acid

Pressure	Change of pressure ΔP	ΔT	$\Delta T/\Delta P \times 10^{-5}$	Change of temperature per atmosphere
cm Hg	cm Hg	°C	°C/cm Hg	°C/atm
59.9	56.8	0.028 ₈	50.4	0.038 ₃
116.7	30.3	.015 ₈	51.5	.039 ₁
147.0	—86.8	—0.044 ₈	+51.6	+0.039 ₂
60.2				
Average	-----	-----	51.2	.038 ₃

4. SOLUBILITIES OF OXYGEN AND OF NITROGEN IN BENZOIC ACID

In column 4 of table 9 are given the interpolated values of the effect of pressure corresponding to the pressures at which the system was observed in equilibrium with oxygen and nitrogen. By subtracting the "elevation of the triple point" (column 3) caused by a given pressure of gas at equilibrium from the corresponding elevation caused by pressure as such (column 4), the depression of the freezing temperature caused by the dissolved gas is obtained. These values are given in column 5. The corresponding mole fractions of dissolved gas given in column 6 were calculated on the basis of the equation ¹⁶

$$x = \frac{\Delta t L_{f_0}}{RT_{f_0}^2},$$

in which x is the mole fraction of the solute; T_{f_0} is the freezing point of the pure substance on the Kelvin scale; $\Delta t = T_{f_0} - T_f$, where T_f is the initial freezing temperature (the temperature at which an

¹⁶ Frank W. Schwab and Edward Wichers, Precise Measurement of the Freezing Range as a Means of Determining the Purity of a Substance, Temperature—Its Measurement and Control in Science and Industry, pp. 256-264 (Reinhold Publishing Corporation, New York, N. Y., 1941).

infinitely small quantity of solid is in equilibrium with the solution); L_{f_0} is the molal heat of fusion of the pure substance; and R is the gas constant. The solubility under a pressure of 1 atm, also shown in figure 6, is 0.132, and 0.073 g of oxygen and of nitrogen, respectively, per thousand grams of acid. From figure 5 it will be seen that the solubility of each gas appears to increase slightly less than in direct proportion to its increase in pressure. It is believed that the measurements were made with sufficient accuracy to justify this conclusion. In view of the slight bearing of these observations on the principal

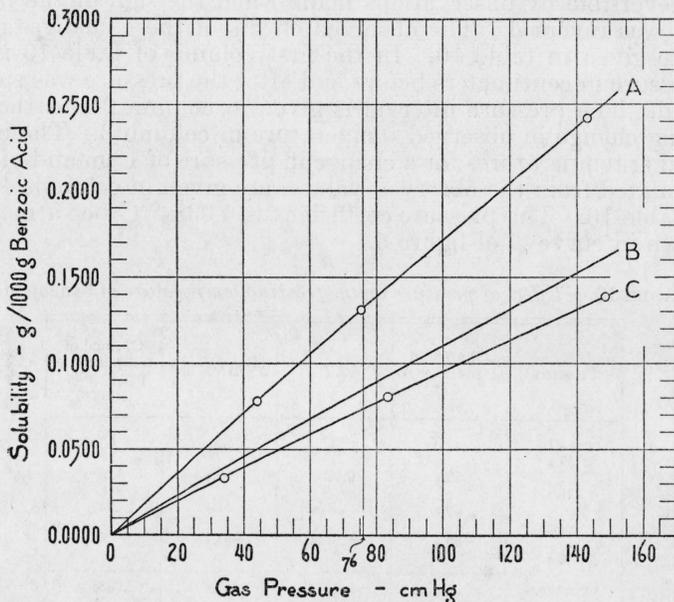


FIGURE 6.—Solubility of oxygen, nitrogen, and air in benzoic acid at the freezing temperature.

A, Solubility of oxygen, determined; B, solubility of air (21 percent oxygen and 79 percent nitrogen), computed from the determined solubility of oxygen and of nitrogen (table 9); C, solubility of nitrogen, determined.

object of this investigation, it did not appear justifiable to spend the time which would have been required to check the results by direct measurements of solubility.

5. FREEZING TEMPERATURE UNDER ONE ATMOSPHERE OF DRY AIR

The apparatus shown in figure 4 was used to determine the freezing temperature of the acid in equilibrium with air. The side arm of the cell was cut below D and a fritted-glass bubbler, which extended to the bottom of the cell, was inserted. It was attached with a ring seal arranged so that air could be forced into the liquid and out of the cell through a stopcock open to the atmosphere. Although liquid and solid acid were in the cell in about the same proportions as those existing during observations of the freezing temperature, dry air was passed through the cell long enough to insure a close approach to equilibrium

with dissolved oxygen and nitrogen under a combined pressure of 1 atm. The stopcock was then closed and the freezing temperature observed in the usual way. The freezing temperature was 122.375_2°C , and the simultaneously measured pressure in the cell was 80.5 cm of mercury (table 9 and fig. 5). During these observations the temperature of the upper end of the cell was probably slightly higher than it was while the air was being swept through the cell, hence the pressure rose slightly above 1 atm. The freezing temperature corrected to 1 atm was 122.374_5°C .

To determine the freezing temperature of benzoic acid in equilibrium with air in another manner, a different form of apparatus was used. This apparatus, which has been described in an earlier publication¹⁷ is shown in figure 7. It was designed for measuring freezing ranges. The thermometer was centered in a cylindrical glass freezing tube 2 cm in diameter and about 25 cm long, provided with a glass jacket that could be evacuated if desired. The thermometer was supported by a ground-in glass head provided with an outlet tube for the passage of air from the freezing-range cell. The tip of the thermometer was about 2 cm from the bottom of the cell, and the depth of the liquid in the cell was 20 cm. Just above the bottom of the cell was a glass bubbler of the type described by Branham and Sperling¹⁸ with orifices about 0.003 in. in diameter. The bubbler was provided with an inlet tube passing through the double-walled vessel and connected to a source of purified air dried over phosphorus pentoxide or conditioned to contain a desired partial pressure of water.

The freezing temperature of a portion of acid of high purity was measured as follows: While the acid was being melted in the apparatus it was stirred with air saturated with water at 0°C . It was then brought to a temperature about 10 degrees above the freezing temperature and thoroughly treated with air saturated with water at -25°C . Air saturated at this temperature contains a partial pressure of water vapor of about 0.5 mm of mercury, which is 10 times as much as is needed to cause virtually complete reversion of benzoic anhydride to benzoic acid.¹⁹ The cell was then transferred to an oil bath that was kept 8 degrees below the freezing point of the acid. The acid undercooled about 0.5 degree C. When crystals suddenly formed, the temperature rose to within a few millidegrees of the equilibrium temperature in less than 2 minutes. About 5 percent of the acid was allowed to freeze, and then the temperature of the oil bath was quickly raised to the freezing temperature of the acid and kept constant within 0.01 degree C. This prevented further formation of solid and allowed the thermometer to indicate the temperature of equilibrium. The freezing temperature under these conditions was 122.369_9°C . Next, the acid was stirred with air dried over phosphorus pentoxide until the temperature rose to a constant value at 122.374_0°C , representing equilibrium in contact with dry air. This required 40 minutes, and observations were continued for 30 minutes longer. Thereafter the air used for stirring contained a partial pressure of water vapor of 4.6 mm of Hg, corre-

¹⁷ Frank W. Schwab and Edward Wichers, *Precise Measurement of the Freezing Range as a Means of Determining the Purity of a Substance, Temperature—Its Measurement and Control in Science and Industry*, p. 256-264 (Reinhold Publishing Corporation, New York, N. Y., 1941).

¹⁸ J. R. Branham and E. O. Sperling, *Bubbler tip of Pyrex glass for difficult absorptions*, *J. Research NBS* **22**, 701 (1939) RP1214.

¹⁹ Frank W. Schwab and Edward Wichers, *Preparation of benzoic acid of high purity*, *J. Research NBS* **25**, 747 (1940) RP1351.

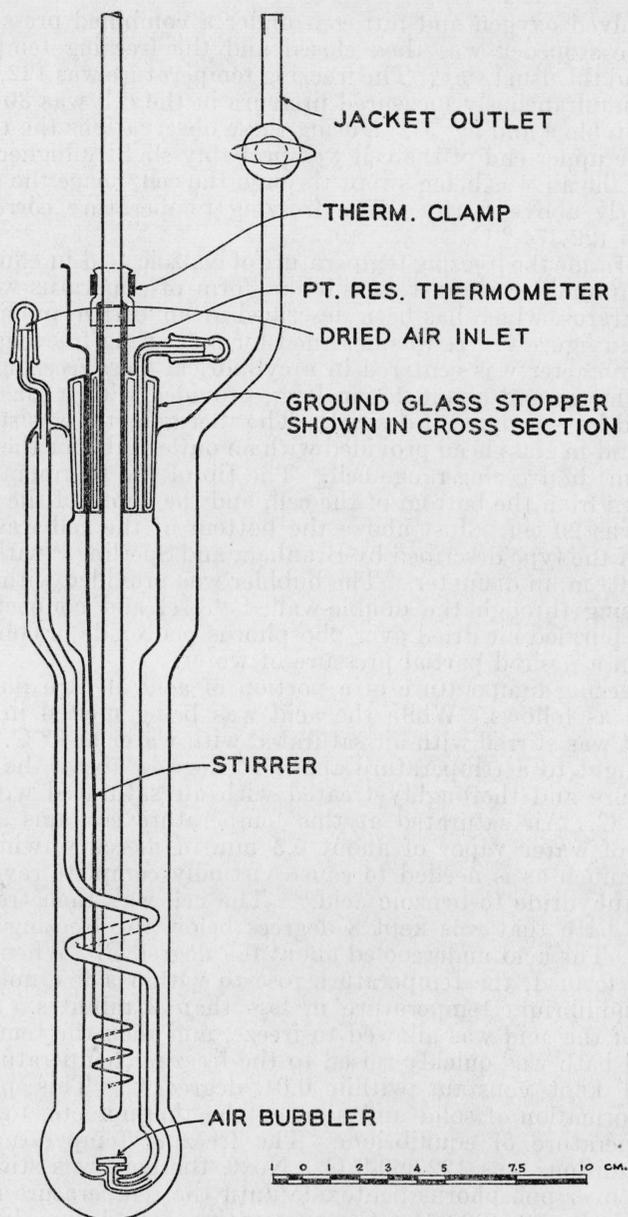


FIGURE 7.—Apparatus for measuring the freezing temperature in equilibrium with dry air and for determining the purity of the acid.

sponding to saturation with water vapor at 0°C , whereupon the freezing temperature fell to $122.343_{6}^{\circ}\text{C}$. The two temperatures observed, when the mixture of solid and liquid acid was in equilibrium with air containing partial pressures of water vapor of 4.6 and 0.5 mm of Hg, offered a means of extrapolating to the freezing temperature in

equilibrium with dry air. The extrapolated temperature was 122.373°C , which agrees sufficiently well with the observed temperature under dry air to indicate that the acid, when thus observed, did not contain a significant amount of benzoic anhydride.

After these observations were completed the purity of the acid was determined by measuring its freezing range in the same apparatus by a procedure previously described.²⁰ Its purity was found to be 99.998_4 mole percent. The presence of 0.001_6 mole percent of impurity caused an initial depression of the freezing temperature of 0.001_2 degree C, or of 0.001_3 degree C at the point in the freezing range when 5 percent of the substance is frozen. This correction was therefore applied to the observed freezing temperature of the acid ($122.374_0^{\circ}\text{C}$), giving a value for pure benzoic acid of $122.375_3^{\circ}\text{C}$, with an estimated uncertainty of ± 0.001 degree C.

VI. CHANGE IN THE SPECIFIC VOLUME OF BENZOIC ACID THAT ACCOMPANIES FREEZING

The change in volume when benzoic acid freezes is of interest in connection with its behavior in the sealed cells. No data were found on the density of solid benzoic acid at or near its freezing point, and no apparently reliable values for the density of the liquid at that temperature. Observations by Timmermans and Burriel²¹ on the liquid at 130° , 155° , and 180°C permit extrapolation to the freezing temperature. The respective values for the density are 1.07494, 1.05218, and 1.02942 g/ml. Extrapolation to the freezing temperature gives 1.0819 g/ml. In this calculation the freezing temperature given by Timmermans (122.45°C) was used so as to minimize the effect of possible systematic errors in the other temperatures.

There are no data for the density of the solid acid at temperatures higher than 23.3°C . The only available coefficient of expansion²² is for the interval between 15° and 30°C . This value is probably in error because its calculation involved Lumsden's²³ determination of the density at 15°C (1.266 g/cm^3), a value which appears to be less accurate than the one published by Hendricks and Jefferson²⁴ ($1.3211 \pm 0.0001\text{ g/cm}^3$ at 23.3°C). It was accordingly impossible to make any reasonably good extrapolation to the density of the solid acid at its melting point. The change of volume on freezing was, therefore, calculated from the recorded value for the heat of fusion per gram ΔH_f , 1,400 cc-atm, the observed pressure coefficient of the freezing temperature $\Delta T/\Delta P$, $0.038_6^{\circ}\text{C/atm}$, and the freezing temperature of the acid T , 395.6°K , by means of the Clausius-Clapeyron equation

$$\frac{\Delta P}{\Delta T} = \frac{\Delta H_f}{T(v_2 - v_1)}$$

²⁰ Frank W. Schwab and Edward Wichers, Precise Measurement of the Freezing Range as a Means of Determining the Purity of a Substance, Temperature—Its Measurement and Control in Science and Industry, p. 256-264 (Reinhold Publishing Corporation, New York, N. Y., 1941).

²¹ Jean Timmermans and F. Burriel, Recherches sur les propriétés de quelques combinaisons organiques, solides à la température ordinaire, Chimie & Industrie, Special No., p. 196-7, March (1931).

²² E. R. Smith, The determination of the coefficient of cubical expansion of solid benzoic acid by means of a gas-filled dilatometer, BS J. Research 7, 903 (1931) RP382.

²³ John Scott Lumsden, The physical properties of heptole, hexahydrobenzoic, and benzoic acids and their derivatives, J. Chem. Soc. 87, 90 (1905).

²⁴ S. B. Hendricks and M. E. Jefferson, Anisotropy of molecular crystals. I. Experimental, J. Optical Soc. of America 23, 269 (1933).

in which v_1 is the specific volume of the liquid form, and v_2 that of the solid. The shrinkage which occurs on freezing, thus calculated, is 0.138 cm³/g. The corresponding calculated value for the density of the solid at the freezing temperature is 1.27 g/cm³.

The foregoing calculated value for the density at 122.37° C and the value of Hendricks and Jefferson for the density at 23.3° C give as the coefficient of cubical expansion, for the 99-degree interval, 0.00040 per degree.

Acknowledgment is made for the advice and many helpful suggestions received from members of the Heat Division, in particular E. F. Mueller, C. S. Cragoe, H. F. Stimson, and C. H. Meyers. Thanks are also expressed to C. L. Gordon for preparing the drawings.

VII. APPENDIX

Calculation of Temperatures in Platinum Resistance Thermometry

By Frank W. Schwab and E. R. Smith

The Callendar equation has been used for more than a half century for the computation of temperatures. During all these years there was little need for a departure from its use, but recently when it was appreciated that precision platinum resistance thermometers might be calibrated at temperatures other than the ice, steam, sulfur, and oxygen points, it became clear that a direct application of the fundamental equations offers advantages.

The fundamental equations can be modified in a regular manner to improve their application to the computation of temperatures. For the range from 0° to 660° C, one modification of the fundamental equation is described in this section. In the range from -190° to 0° C, two forms are given, of which the second is the more suitable for solution by the use of a slide rule.

1. RELATION BETWEEN THE POWER SERIES, CALLENDAR, AND CALLENDAR-VAN DUSEN EQUATIONS

The international scale of temperature between 0° and 660° C is defined by the resistance R_t of a platinum resistance thermometer by means of the formula

$$R_t = R_0(1 + At + Bt^2), \quad (1)$$

for which the constants, R_0 , A , and B are determined from measurements of resistances at the melting point of ice, the boiling point of water, and the boiling point of sulfur. From -190° to 0° C, the temperature scale is obtained from the resistance by the formula

$$R_t = R_0[1 + At + Bt^2 + C(t-100)t^3], \quad (2)$$

in which the constants R_0 , A , and B are the same as in formula 1 and the constant C is found from a measurement of resistance at the boiling point of oxygen.²⁵

²⁵ Compt. rend., Eighth General Conference of Weights and Measures, (Paris, 1933).

National Bureau of Standards certificates for platinum resistance thermometers report only values for the constants R_0 , c , and δ for the Callendar formula

$$t = 100 \frac{R_t - R_0}{R_{100} - R_0} + \delta \left(\frac{t}{100} - 1 \right) \frac{t}{100},$$

in which the value to be used for $(R_{100} - R_0)$ is given by

$$(R_{100} - R_0) = 100cR_0.$$

The value of the constant β may also be given for use in the Callendar-Van Dusen equation

$$t = 100 \frac{R_t - R_0}{R_{100} - R_0} + \delta \left(\frac{t}{100} - 1 \right) \frac{t}{100} + \beta \left(\frac{t}{100} - 1 \right) \left(\frac{t}{100} \right)^3 \quad (3)$$

at temperatures below 0°C .

Equations 1 and 2 are the fundamental international equations. The constants for them can be computed from those of the equivalent forms of the Callendar and Callendar-Van Dusen equations. R_0 , of course, remains the same for all. The relationships between the constants are readily obtained by writing the complete fundamental equation, 2, in the form

$$\frac{R_t}{R_0} = 1 + At + Bt^2 + C(t - 100)t^3 \quad (4)$$

and the Callendar-Van Dusen equation in the equivalent form

$$\frac{R_t}{R_0} = 1 + c \left(1 + \frac{\delta}{100} \right) t - \left(\frac{c\delta}{10^4} \right) t^2 - \left(\frac{c\beta}{10^8} \right) (t - 100)t^3. \quad (5)$$

Since these equations are equivalent, comparison of coefficients gives

$$A = c \left(1 + \frac{\delta}{100} \right), B = -\frac{c\delta}{10^4}, C = \frac{-c\beta}{10^8}. \quad (6)$$

The constants of the Callendar and Callendar-Van Dusen equations in terms of those of the fundamental equations are

$$c = A + 100B, \delta = -\frac{10^4 B}{c}, \beta = -\frac{10^8 C}{c}. \quad (7)$$

2. INTERPOLATION OF TEMPERATURES BY USE OF THE POWER SERIES EQUATIONS

The power series equations can be expanded to make them more useful for the computation of temperatures by successive approximations. A simple graph together with a short table obviate more than one computation for a precision of the temperature within 0.001°C .²⁶

²⁶ All of the precisions of the computation of temperature referred to in this appendix are dependent only on the method of computation. Other errors, such as errors of calibration, have been discussed by Brickwedde and Hoge, and others. Harold J. Hoge and Ferdinand G. Brickwedde, *Intercomparison of platinum resistance thermometers between -190° and 445°C* , J. Research NBS **28**, 217 (1942) RP1454.

(a) IN THE RANGE FROM 0° TO 660° C

With a calculating machine, the fundamental equations can be used as conveniently as the Callendar and Callendar-Van Dusen equations to compute temperatures from resistances. For example, equation 1 can be written in the form

$$\left(\frac{R_t}{R_0} - 1\right) = t(A + Bt) \text{ and } t = \frac{(R_t/R_0) - 1}{A + Bt}. \quad (8)$$

If t_1 is a first estimation of the temperature,

$$t_2 = \frac{(R_t/R_0) - 1}{A + Bt_1}, \quad (9)$$

etc.

When the measured temperature is between 0° and 100° C, and the first estimated temperature, t_1 , is correct to within 1° C, one solution of equation 9 yields the correct temperature to the nearest 0.01° C. In the range between 100° and 660° C, two successive solutions are sufficient for this accuracy.

Better convergence can be obtained by the formula

$$t_2 = \frac{[(R_t/R_0) - 1] + Bt_1^2}{A + 2Bt_1} \quad (10)$$

which can be derived from equation 1 by the Newton-Raphson method of series approximation²⁷ or, less elegantly, by adding $R_0 Bt^2$ to each side of equation 1. With equation 10, if the first estimate of the temperature, t_1 , is correct to within 2° C, the first solution of the equation for t_2 yields the temperature correctly to within 0.001° C over the complete range of validity of equation 1. The first estimation for t_1 can be made to within 2° C from a rough plot of R_t with respect to t . To make this plot, values of R_t for $t=0^\circ, 100^\circ, 200^\circ \dots, 600^\circ$ C, can be quickly tabulated by little more than inspection of the fundamental formula $R_t = R_0(1 + At + Bt^2)$. The results are plotted on a scale such that 1 mm = 1 degree and 0.1 ohm for a 25-ohm thermometer. With sufficient accuracy the plot is taken as linear over each 100-degree interval. Then only one computation with equation 10 is needed to find the correct temperature to within the precision of calibration of a platinum resistance thermometer.

(b) IN THE RANGE FROM -190° TO 0° C.

Equation 2 can be solved approximately to obtain

$$t_2 = \frac{(R_t/R_0) - 1}{A + Bt_1 + C(t_1 - 100)t_1^2} \quad (11)$$

for temperatures below 0° C. For measurements with a 25-ohm thermometer and with an initial estimate of the temperature made correctly to within 1° C, the first temperature computed by equation 11 differs from the correct temperature by 0.003° C at -25° C and by

²⁷ See also, Scarborough, *Numerical Mathematical Analysis*, p. 178, Johns Hopkins Press (1930).

0.057° C at -190° C. The second computation, using the first as the estimated value, is correct to better than 0.001° C between 0° and -140° C and is in error by only 0.004° C at -190° C.

When equation 2 is treated by the Newton-Raphson method, there is obtained

$$t_2 = \frac{[(R_t/R_0) - 1] + Bt_1^2 + C(3t_1 - 200)t_1^3}{A + 2Bt_1 + C(4t_1 - 300)t_1^2} \quad (12)$$

This equation appears unwieldy but is quite simple to use with the aid of a modern calculating machine and will yield over the complete range of 0° to -190° C temperatures correct to the nearest 0.001° C on the first computation when the initial estimate, t_1 , is correct to within 2 degrees. If 0.005° to 0.01° C is sufficient precision, the initial estimate need be correct to within 5° C.

An equation of the same form as equation 12 but a little simpler in the final terms of the numerator and denominator can be found by adding $Bt^2 + nC(t-100)t^3$ to each side of equation 2, written in the form $(R_t/R_0) - 1 = At + Bt^2 + C(t-100)t^3$. Then, on solving approximately for t , there is obtained

$$t_2 = \frac{[(R_t/R_0) - 1] + Bt_1^2 + nC(t_1 - 100)t_1^3}{A + 2Bt_1 + (n+1)C(t_1 - 100)t_1^2} \quad (13)$$

By trial, it has been found that equation 13 gives as satisfactory convergence as equation 12 when n is assigned the value of 2.64, so that equation 13 becomes

$$t_2 = \frac{[(R_t/R_0) - 1] + Bt_1^2 + E[(t_1/100) - 1]t_1^3}{A + 2Bt_1 + F[(t_1/100) - 1]t_1^2} \quad (14)$$

in which $E=264C$ and $F=364C$.

The following procedure is recommended for the calculation of temperatures by means of either equation 12 or 14.

3. PROCEDURE FOR THE CALCULATION OF TEMPERATURES BY USE OF THE POWER SERIES EQUATIONS]

Obtain the initial estimate of the temperature, correct to within 2° C from a very simple graph of R plotted with respect to t . This graph is made to a scale of 1 mm = 1° C and 0.1 ohm. The point for $t = -190^\circ$ is connected by a straight line to the point for $t = -100^\circ$. The latter is connected by another straight line to the point for $t = 0^\circ$. The temperature corresponding to any resistance in the range covered can be read from the plot to within 2° C for use as t_1 with either equation 12 or 14. If equation 12 is to be used, values of the temperature functions useful for a quick computation are taken from table 11. If equation 14 is preferred, table 12 is used. In either case the following method is rapid.

TABLE 11.—Data for computing temperatures in platinum resistance thermometry by the equations ¹

$$t_2 = \frac{[(R_t/R_0) - 1] + Bt_1^2}{A + 2Bt_1}$$

and

$$t_2 = \frac{[(R_t/R_0) - 1] + Bt_1^2 + C(3t_1 - 200)t_1^3}{A + 2Bt_1 + C(4t_1 - 300)t_1^2}$$

in the ranges of temperature from 0° to 190° C and 0° to -190° C, respectively

	$\frac{t}{10^6}$	$-(4t-300)\frac{t^2}{10^{12}}$	$\frac{t^2}{10^7}$	$(3t-200)\frac{t^3}{10^{12}}$
0	0.000000	0.000000000	0.0000000	0.000000000
1	1	0	1	0
2	2	1	4	2
3	3	3	9	6
4	4	5	16	14
5	5	8	25	27
6	6	12	36	47
7	7	16	49	76
8	8	21	64	115
9	9	27	81	165
10	10	34	100	230
11	11	42	121	310
12	12	50	144	408
13	13	59	169	525
14	14	70	196	664
15	15	81	225	827
16	16	93	256	1016
17	17	106	289	1233
18	18	121	324	1481
19	19	136	361	1763
20	20	152	400	2080
21	21	169	441	2436
22	22	188	484	2832
23	23	207	529	3273
24	24	228	576	3760
25	25	250	625	4297
26	26	273	676	4886
27	27	297	729	5531
28	28	323	784	6234
29	29	350	841	7000
30	30	378	900	7830
31	31	407	961	8729
32	32	438	1024	9699
33	33	470	1089	10745
34	34	504	1156	11870
35	35	539	1225	13077
36	36	575	1296	14370
37	37	613	1369	15753
38	38	653	1444	17230
39	39	694	1521	18804

¹ See footnote at end of table.

TABLE 11.—Data for computing temperatures in platinum resistance thermometry by the equations ¹—Continued

$-t$	$-\frac{t}{10^6}$	$-(4t-300)\frac{t^2}{10^{12}}$	$\frac{t^2}{10^7}$	$(3t-200)\frac{t^3}{10^{12}}$
40	40	736	1600	20480
41	41	780	1681	22261
42	42	826	1764	24153
43	43	873	1849	26158
44	44	922	1936	28281
45	45	972	2025	30527
46	46	1024	2116	32900
47	47	1078	2209	35404
48	48	1134	2304	38044
49	49	1191	2401	40824
50	50	1250	2500	43750
51	51	1311	2601	46826
52	52	1374	2704	50056
53	53	1438	2809	53447
54	54	1505	2916	57002
55	55	1573	3025	60727
56	56	1643	3136	64627
57	57	1715	3249	68707
58	58	1790	3364	72972
59	59	1866	3481	77428
60	60	1944	3600	82080
61	61	2024	3721	86934
62	62	2107	3844	91995
63	63	2191	3969	97268
64	64	2277	4096	102760
65	65	2366	4225	108477
66	66	2457	4356	114423
67	67	2550	4489	120606
68	68	2645	4624	127031
69	69	2742	4761	133703
70	70	2842	4900	140630
71	71	2944	5041	147817
72	72	3048	5184	155271
73	73	3155	5329	162998
74	74	3264	5476	171005
75	75	3375	5625	179297
76	76	3489	5776	187882
77	77	3605	5929	196766
78	78	3723	6084	205956
79	79	3844	6241	215458
80	80	3968	6400	225280
81	81	4094	6561	235428
82	82	4223	6724	245910
83	83	4354	6889	256732
84	84	4488	7056	267902
85	85	4624	7225	279427
86	86	4763	7396	291314
87	87	4905	7569	303570
88	88	5049	7744	316203
89	89	5196	7921	329221

¹ See footnote at end of table.

TABLE 11.—Data for computing temperatures in platinum resistance thermometry by the equations¹—Continued

$-t$	$-\frac{t}{10^3}$	$-(4t-300)\frac{t^2}{10^{12}}$	$\frac{t^2}{10^7}$	$(3t-200)\frac{t^3}{10^{12}}$
90	90	5346	8100	342630
91	91	5499	8281	356439
92	92	5654	8464	370655
93	93	5812	8649	385287
94	94	5973	8836	400341
95	95	6137	9025	415827
96	96	6304	9216	431751
97	97	6473	9409	448122
98	98	6646	9604	464949
99	99	6821	9801	482239
100	100	7000	10000	500000
101	101	7182	10201	518241
102	102	7366	10404	536971
103	103	7554	10609	556198
104	104	7744	10816	575930
105	105	7938	11025	596177
106	106	8135	11236	616946
107	107	8335	11449	638247
108	108	8538	11664	660089
109	109	8744	11881	682480
110	110	8954	12100	705430
111	111	9167	12321	728947
112	112	9383	12544	753041
113	113	9602	12769	777721
114	114	9825	12996	802997
115	115	10051	13225	828877
116	116	10280	13456	855371
117	117	10513	13689	882489
118	118	10749	13924	910240
119	119	10989	14161	938634
120	120	11232	14400	967680
121	121	11479	14641	997389
122	122	11729	14884	1027770
123	123	11982	15129	1058833
124	124	12239	15376	1090589
125	125	12500	15625	1123047
126	126	12764	15876	1156217
127	127	13032	16129	1190111
128	128	13304	16384	1224737
129	129	13579	16641	1260106
130	130	13858	16900	1296230
131	131	14141	17161	1333118
132	132	14427	17424	1370781
133	133	14717	17689	1409230
134	134	15011	17956	1448475
135	135	15309	18225	1488527
136	136	15611	18496	1529397
137	137	15916	18769	1571097
138	138	16225	19044	1613636
139	139	16539	19321	1657027

¹ See footnote at end of table.

TABLE 11.—Data for computing temperatures in platinum resistance thermometry by the equations¹—Continued

$-t$	$-\frac{t}{10^6}$	$-(4t-300)\frac{t^2}{10^{13}}$	$\frac{t^2}{10^7}$	$(3t-200)\frac{t^3}{10^{12}}$
140	140	16856	19600	1701280
141	141	17177	19881	1746407
142	142	17502	20164	1792418
143	143	17832	20449	1839326
144	144	18165	20736	1887142
145	145	18502	21025	1935877
146	146	18843	21316	1985543
147	147	19189	21609	2036151
148	148	19538	21904	2087714
149	149	19892	22201	2140243
150	150	20250	22500	2193750
151	151	20612	22801	2248247
152	152	20978	23104	2303746
153	153	21349	23409	2360259
154	154	21724	23716	2417799
155	155	22103	24025	2476377
156	156	22486	24336	2536006
157	157	22874	24649	2596698
158	158	23266	24964	2658466
159	159	23663	25281	2721323
160	160	24064	25600	2785280
161	161	24469	25921	2850351
162	162	24879	26244	2916548
163	163	25294	26569	2983885
164	164	25713	26896	3052373
165	165	26136	27225	3122027
166	166	26564	27556	3192859
167	167	26997	27889	3264882
168	168	27434	28224	3338109
169	169	27876	28561	3412554
170	170	28322	28900	3488230
171	171	28773	29241	3565150
172	172	29229	29584	3643329
173	173	29690	29929	3722779
174	174	30155	30276	3803513
175	175	30625	30625	3885547
176	176	31100	30976	3968893
177	177	31580	31329	4053565
178	178	32064	31684	4139578
179	179	32554	32041	4226945
180	180	33048	32400	4315680
181	181	33547	32761	4405798
182	182	34051	33124	4497312
183	183	34561	33489	4590237
184	184	35075	33856	4684587
185	185	35594	34225	4780377
186	186	36118	34596	4877621
187	187	36648	34969	4976333
188	188	37182	35344	5076529
189	189	37721	35721	5178223
190	0. 000190	0. 000038266	0. 0036100	0. 005281430

¹ The constants R_0 , A , B , and C are determined by measurements of resistances at the melting point of ice, the boiling points of water, sulfur, and oxygen, respectively. The powers of 10 used in the computations as coefficients of the functions of t and of the constants B and C are such as to make the order of magnitude of the constant factors greater than 1 but less than 10 and to effect a simple regulation of decimal points.

TABLE 12.—Data for computing temperatures in platinum resistance thermometry by the equations¹

$$t_2 = \frac{[(R_t/R_0) - 1] + Bt_1^2}{A + 2Bt_1}$$

and

$$t_2 = \frac{[(R_t/R_0) - 1] + Bt_1^2 + E[(t_1/100) - 1]t_1^2}{A + 2Bt_1 + F[(t_1/100) - 1]t_1^2}$$

in the ranges of temperature from 0° to 190° C and 0° to -190° C, respectively.

$-t$	$-\frac{t}{10^6}$	$-\left(\frac{t}{100}-1\right)\frac{t^2}{10^6}$	$\frac{t^2}{2 \times 10^6}$	$\left(\frac{t}{100}-1\right)\frac{t^2}{10^6}$
0	0.000000	0.000000000	0.0000000	0.000000000
1	1	1	5	1
2	2	4	20	8
3	3	9	45	28
4	4	17	80	67
5	5	26	125	131
6	6	38	180	229
7	7	52	245	367
8	8	69	320	553
9	9	88	405	795
10	10	110	500	1100
11	11	134	605	1477
12	12	161	720	1935
13	13	191	845	2483
14	14	223	980	3128
15	15	259	1125	3881
16	16	297	1280	4751
17	17	338	1445	5748
18	18	382	1620	6882
19	19	430	1805	8162
20	20	480	2000	9600
21	21	534	2205	11206
22	22	590	2420	12991
23	23	651	2645	14965
24	24	714	2880	17142
25	25	781	3125	19531
26	26	852	3380	22146
27	27	926	3645	24997
28	28	1004	3920	28099
29	29	1085	4205	31462
30	30	1170	4500	35100
31	31	1259	4805	39026
32	32	1352	5120	43254
33	33	1448	5445	47796
34	34	1549	5780	52667
35	35	1654	6125	57881
36	36	1763	6480	63452
37	37	1876	6845	69395
38	38	1993	7220	75723
39	39	2114	7605	82453

¹See footnote at end of table.

TABLE 12.—Data for computing temperatures in platinum resistance thermometry by the equations ¹—Continued

$-t$	$-\frac{t}{10^6}$	$-\left(\frac{t}{100}-1\right)\frac{t^2}{10^9}$	$\frac{t^2}{2 \times 10^6}$	$\left(\frac{t}{100}-1\right)\frac{t^3}{10^9}$
40	40	2240	8000	89600
41	41	2370	8405	97179
42	42	2505	8820	105205
43	43	2644	9245	113695
44	44	2788	9680	122665
45	45	2936	10125	132131
46	46	3089	10580	142111
47	47	3247	11045	152620
48	48	3410	11520	163676
49	49	3577	12005	175297
50	50	3750	12500	187500
51	51	3928	13005	200303
52	52	4110	13520	213724
53	53	4298	14045	227782
54	54	4491	14580	242495
55	55	4689	15125	257881
56	56	4892	15680	273961
57	57	5101	16245	290753
58	58	5315	16820	308277
59	59	5535	17405	326553
60	60	5760	18000	345600
61	61	5991	18605	365439
62	62	6227	19220	386091
63	63	6469	19845	407577
64	64	6717	20480	429916
65	65	6971	21125	453131
66	66	7231	21780	477243
67	67	7497	22445	502274
68	68	7768	23120	528246
69	69	8046	23805	555180
70	70	8330	24500	583100
71	71	8620	25205	612028
72	72	8916	25920	641987
73	73	9219	26645	672999
74	74	9528	27380	705090
75	75	9844	28125	738281
76	76	10166	28880	772598
77	77	10494	29645	808063
78	78	10830	30420	844703
79	79	11171	31205	882540
80	80	11520	32000	921600
81	81	11875	32805	961908
82	82	12238	33620	1003490
83	83	12607	34445	1046370
84	84	12983	35280	1090575
85	85	13366	36125	1136131
86	86	13757	36980	1183064
87	87	14154	37845	1231401
88	88	14559	38720	1281167
89	89	14971	39605	1332391

¹ See footnote at end of table.

TABLE 12.—Data for computing temperatures in platinum resistance thermometry by the equations ¹—Continued

$-t$	$-\frac{t}{10^6}$	$-\left(\frac{t}{100}-1\right)\frac{t^2}{10^9}$	$\frac{t^2}{2 \times 10^6}$	$\left(\frac{t}{100}-1\right)\frac{t^3}{10^9}$
90	90	15390	40500	1385100
91	91	15817	41405	1439321
92	92	16251	42320	1495081
93	93	16693	43245	1552409
94	94	17142	44180	1611333
95	95	17599	45125	1671881
96	96	18063	46080	1734083
97	97	18536	47045	1797966
98	98	19016	48020	1863560
99	99	19504	49005	1930895
100	100	20000	50000	2000000
101	101	20504	51005	2070905
102	102	21016	52020	2143640
103	103	21536	53045	2218236
104	104	22065	54080	2294723
105	105	22601	55125	2373131
106	106	23146	56180	2453493
107	107	23699	57245	2535839
108	108	24261	58320	2620201
109	109	24831	59405	2706611
110	110	25410	60500	2795100
111	111	25997	61605	2885701
112	112	26593	62720	2978447
113	113	27198	63845	3073371
114	114	27811	64980	3170504
115	115	28434	66125	3269881
116	116	29065	67280	3371535
117	117	29705	68445	3475500
118	118	30354	69620	3581810
119	119	31013	70805	3690498
120	120	31680	72000	3801600
121	121	32357	73205	3915150
122	122	33042	74420	4031183
123	123	33738	75645	4149733
124	124	34442	76880	4270838
125	125	35156	78125	4394531
126	126	35880	79380	4520850
127	127	36613	80645	4649829
128	128	37356	81920	4781507
129	129	38108	83205	4915918
130	130	38870	84500	5053100
131	131	39642	85805	5193090
132	132	40424	87120	5335926
133	133	41215	88445	5481644
134	134	42017	89780	5630283
135	135	42829	91125	5781881
136	136	43651	92480	5936476
137	137	44483	93845	6094107
138	138	45325	95220	6254811
139	139	46177	96605	6418629

¹ See footnote at end of table.

TABLE 12.—Data for computing temperatures in platinum resistance thermometry by the equations¹—Continued

$-t$	$-\frac{t}{10^6}$	$-\left(\frac{t}{100}-1\right)\frac{t^2}{10^9}$	$\frac{t^2}{2 \times 10^6}$	$\left(\frac{t}{100}-1\right)\frac{t^3}{10^9}$
140	140	47040	98000	6585600
141	141	47913	99405	6755763
142	142	48797	100820	6929157
143	143	49691	102245	7105823
144	144	50596	103680	7285801
145	145	51511	105125	7469131
146	146	52437	106580	7655855
147	147	53374	108045	7846012
148	148	54322	109520	8039644
149	149	55280	111005	8236793
150	150	56250	112500	8437500
151	151	57231	114005	8641807
152	152	58222	115520	8849756
153	153	59225	117045	9061390
154	154	60239	118580	9276751
155	155	61264	120125	9495881
156	156	62300	121680	9718825
157	157	63348	123245	9945625
158	158	64407	124820	10176325
159	159	65478	126405	10410969
160	160	66560	128000	10649600
161	161	67654	129605	10892263
162	162	68759	131220	11139003
163	163	69876	132845	11389865
164	164	71005	134480	11644892
165	165	72146	136125	11904131
166	166	73299	137780	12167627
167	167	74464	139445	12435426
168	168	75640	141120	12707574
169	169	76829	142805	12984116
170	170	78030	144500	13265100
171	171	79243	146205	13550572
172	172	80468	147920	13840579
173	173	81706	149645	14135167
174	174	82956	151380	14434386
175	175	84219	153125	14738281
176	176	85494	154880	15046902
177	177	86781	156645	15360295
178	178	88082	158420	15678511
179	179	89394	160205	16001596
180	180	90720	162000	16329600
181	181	92058	163805	16662572
182	182	93410	165620	17000562
183	183	94774	167445	17343618
184	184	96151	169280	17691791
185	185	97541	171125	18045131
186	186	98945	172980	18403688
187	187	100361	174845	18767513
188	188	101791	176720	19136655
189	189	103234	178605	19511167
190	0.000190	0.000104690	0.0180500	0.019891100

¹ The constants R_0 , A , B , and C are determined by measurements of resistances at the melting point of ice, the boiling points of water, sulfur, and oxygen, respectively. E and F are equal to 264C and 364C, respectively. The powers of 10 used in the computations as coefficients of the functions of t , and of the constants B , E , and F are such as to make the order of magnitude of the constant factors greater than 1 but less than 10 and to effect a simple regulation of decimal points.

Set decimal point indicators at corresponding positions on the keyboard and middle dial of a calculating machine equivalent to the Marchant Model M. Set the value of A in the keyboard in its proper position for the decimal point and add it into the middle dial. This clears the keyboard. Set the value of $10^{-6}t_1$ in the keyboard properly with respect to its decimal point and multiply, by $2 \times 10^6 B$. This operation adds the product, $2Bt_1$, to A in the middle dial. Bring the carriage back to its original position, place the value of $10^{-12}(4t_1 - 300)t_1^2$ taken from table 11 if equation 12 is used, or the value of $10^{-9}[(t_1/100) - 1]t_1^2$ taken from table 12 if equation 14 is used, in the keyboard with proper account of the decimal point, multiply by $10^{12}C$ for equation 12, or by 10^9F for equation 14. This operation adds the third term of the denominator to the sum of the first two and shows the value of the whole denominator in the middle dial. Record this value on paper and clear the dials of the machine. The numerator is next obtained in the same manner but left in the middle dial while the denominator is set in the keyboard. Automatic division now yields the temperature correct to the nearest millidegree. With practice, the computation of a temperature, exclusive of the calculation of $(R_t/R_0) - 1$, can be made by this procedure in less than 2 minutes.

The powers of 10 used in the computations as coefficients of the functions of t_1 and of the constants B and C are such as to make the order of magnitude of the constant factors greater than 1 but less than 10 and to effect a simple regulation of decimal points. In table 11, for use with equation 12, the following are tabulated:

$10^{-6}t_1$ to be multiplied by $2 \times 10^6 B$ to obtain $2Bt_1$, as $2 \times 10^6 B$ is approximately 1.2.

$10^{-12}(4t_1 - 300)t_1^2$ and $10^{-12}(3t_1 - 200)t_1^3$ to be multiplied by $10^{12}C$ to obtain $C(4t_1 - 300)t_1^2$ and $C(3t_1 - 200)t_1^3$, since $10^{12}C$ is approximately 4.4.

$10^{-7}t_1^2$ to be multiplied by $10^7 B$ to obtain Bt_1^2 , as $10^7 B$ is approximately 6.

In table 12, for use with equation 14, the tabulation is analogous. With proper regard for signs, columns 2 and 4 of table 11 or table 12 can be used to calculate temperatures in the upper range from 0° to 190° C, if the table for computations of temperatures below 0° C is complete. These columns can be extended to 660° C, or a table of squares can be used.

Computations made with these modified fundamental equations involve the ratio of R_t to R_0 , both of which should therefore be measured with the same bridge. This ratio will be practically the same for the same temperature with any calibrated bridge, provided the calibration of a given bridge is consistent, i. e., of about the same fractional error in all the dials. The fundamental constants are assumed to be given correctly, i. e., the thermometer must have a proper calibration and this, of course, is true no matter what method of computation is used. The steam point does not appear in the equations and can even be eliminated from the calibration of the thermometer by the use of another fixed point in a suitable region of the temperature scale, such as the freezing point of benzoic acid, or by comparison with a thermometer which has been given a primary calibration.

WASHINGTON, December 29, 1944.