U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1676

*Part of Journal of Research of the National Bureau of Standards, Volume 35, November 1945*

# DETERMINATION OF THE PURITY OF HYDROCARBONS BY MEASUREMENT OF FREEZING POINTS[1]

By Augustus R. Glasgow, Jr., Anton J. Streiff,[2] and Frederick D. Rossini

## ABSTRACT

An improved and simplified procedure is described for determining the freezing points of hydrocarbons from time-temperature freezing and melting curves, and for calculating the purity when the freezing point for zero impurity is (a) known and (b) not previously known. A procedure for determining the cryoscopic constant is also described.

## CONTENTS

## I. INTRODUCTION

In connection with the work of this laboratory on the analysis, purification, and properties of hydrocarbons, the freezing point, determined from time-temperature freezing and melting curves, has been used to evaluate the purity of given samples of hydrocarbons. Since the previous reports on this subject [1, 2, 3],* improvements have been made in the apparatus and the procedure has been clarified and simplified. This report describes the present apparatus and procedure for determining the freezing point from time-temperature freezing and melting curves and for calculating the purity when

---

[1] This investigation was performed at the National Bureau of Standards as part of the work of the American Petroleum Institute Research Project 6 on the "Analysis, Purification, and Properties of Hydrocarbons."

[2] Research Associate on the American Petroleum Institute Research Project 6 at the National Bureau of Standards.

* Figures in brackets indicate the literature references at the end of this paper.

the freezing point for zero impurity is known and also when the freezing point for zero impurity is not previously known. A procedure for determining the cryoscopic constant is also described.

## II. PRINCIPLES INVOLVED

The definitions, abbreviations, and symbols used in this paper are the same as those given in the preceding report [2], to which the reader is referred for details not covered here.

For the equilibrium between a crystalline phase consisting of the major component alone and a liquid phase consisting of the major component and one or more other components, the thermodynamic relation between the temperature of equilibrium and the composition of the liquid phase, for an ideal or sufficiently dilute solution, is

$$-\ln N_1 = -\ln (1-N_2) = A(t_{f_0}-t)[1+B(t_{f_0}-t)+ \ . \ . \ .], \qquad (1)$$

where

$N_1$=the mole fraction of the major component in the liquid phase;

$N_2=(1-N_1)$=the sum of the mole fractions of all other components in the liquid phase;

$t_{f_0}$=the temperature, in degrees centigrade, of the freezing point of the major component when pure (that is, when $N_2=0$);

$t$=the given temperature of equilibrium, in degrees centigrade;

$A=\Delta H_{f_0}/RT_{f_0}^2$;

$B=1/T_{f_0}-\Delta C_{p_0}/2\Delta H_{f_0}$;

$R$=the gas constant, per mole;

$T_{f_0}=t_{f_0}+273.16$

$\Delta H_{f_0}$=the heat of fusion; per mole, of the major component in the pure state at the temperature $T_{f_0}$;

$\Delta C_{p_0}$=the heat capacity, per mole, of the pure liquid less that of the pure solid, for the major component in the pure state at the temperature $T_{f_0}$.

It is seen that the three constants ($t_{f_0}$, $A$, and $B$) in eq 1 are properties only of the major component, so that the relation between the temperature of equilibrium and the mole fraction of solute is the same for all solutes, of which there may be more than one in the same solution, provided they remain in the liquid phase and form with the major component an ideal solution.

If $r$ is the fraction crystallized of the total number of moles of all components in the system, then, as previously shown [2],

$$t=t_{f_0}-a/[\{1-(b/a)\}-r], \qquad (2)$$

where $a$ and $b$ are constants for the given sample. Equation 2 gives the relation between the temperature of equilibrium and the fraction of material crystallized.

When the experiment is one performed according to the procedure described in the present report, the rate of crystallization or melting of the major component is substantially constant with time, and, as previously shown [2],

$$r=k(z-z_f), \tag{3}$$

where $k$ is a constant characteristic of the given experiment, $z$ is any given time, and $z_f$ is the time at which freezing begins or melting is complete. Furthermore,

$$t=t_{f_0}-a'/[1-k'(z-z_f)], \tag{4}$$

where $a'$ and $k'$ are constants [2]. Equation 4 gives the relation between the temperature of equilibrium and the time during the part of the experiment in which equilibrium between the liquid and solid phases of the major component exists.

## III. APPARATUS AND MATERIALS

The freezing-point apparatus in its present form is shown in figures 1, 2, and 3, which give, respectively, the assembly, the details of the freezing tube,[3] and the details of the stirring assembly. With the stirrer shown in figure 3, the vertical stroke is usually made 1½ inches over-all, and the rate about 120 strokes per minute.

The thermometric system consists of a 25-ohm platinum resistance thermometer, a resistance bridge (Müeller-type)[4] in which the main coils are thermostated, and a highly sensitive galvanometer, adjusted so that 1 mm on the scale is equivalent to from 0.0001 to 0.0005 degree centigrade.

The apparatus also includes a vacuum system and a stop watch or clock.

The cooling and warming baths used are listed in table 1.

TABLE 1.—*Cooling and warming baths used*

| Type of experiment | Range of freezing points | Cooling or warming bath |
|---|---|---|
| | °*C* | |
| Freezing | +30 to −50 | Slush of solid carbon dioxide in a 50-50 mixture of carbon tetrachloride and chloroform. |
| Do | −50 to −170 | Liquid air, or preferably, liquid nitrogen. |
| Melting | +30 to −10 | Water maintained constant (±1 degree centigrade) at 10 to 25 degrees centigrade above the freezing point of the sample. |
| Do | −10 to −90 | Ice and water.[a] |
| Do | −90 to −170 | Slush or solid carbon dioxide in a 50-50 mixture of carbon tetrachloride and chloroform.[a] |

[a] See the discussion at the end of section V.

---

[3] Acknowledgment is gratefully made of the assistance of F. W. Rose, Jr. (formerly Research Associate on the API Research Project 6, and since October 1940, with the Houdry Process Corporation, Marcus Hook, Pa.), in fixing the details of the first design of the freezing tube shown in figure 2.

[4] Leeds & Northrup No. 8069, type G-2.

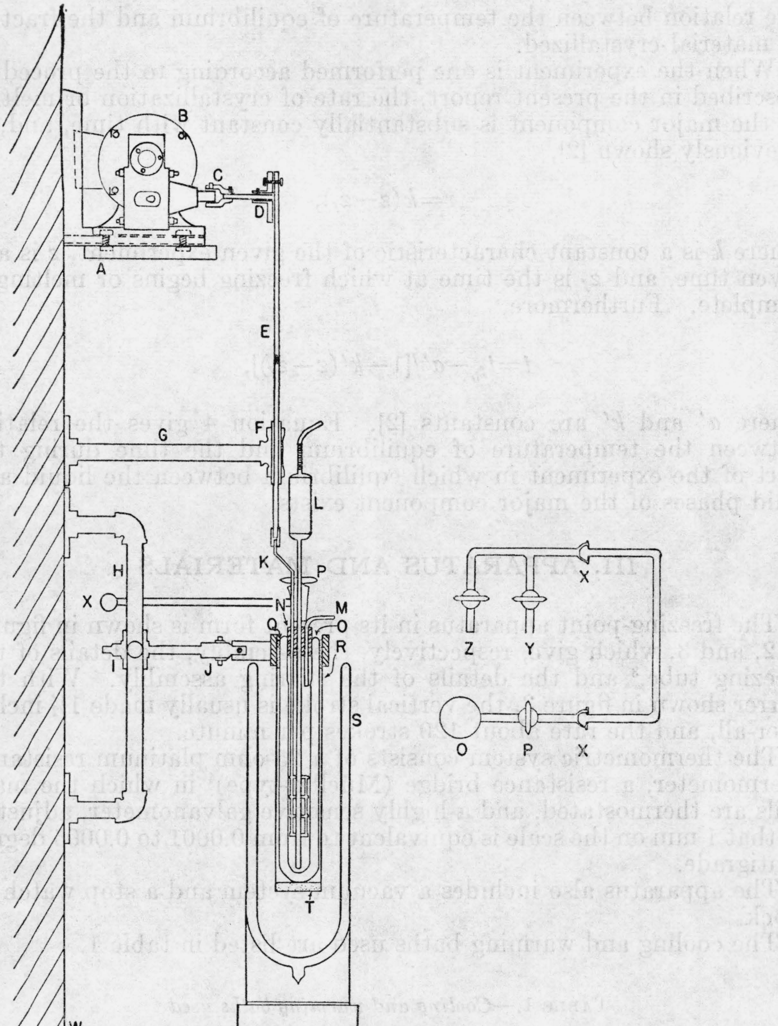

**Figure 1.**—*Assembly of the freezing-point apparatus.*

*A*, Bracket for motor, with rubber pad; *B*, motor, with reduction gears, to give 120 rpm; *C*, coupling; *D*, wheel; *E*, steel rod; *F*, bearing; *G*, support for bearing; *H*, support for freezing tube; *I*, adjustable clamp holder; *J*, clamp for freezing tube; *K*, stirrer; *L*, thermometer; *M*, tube for inlet of dry air; *N*, cork stopper, with holes as shown, plus a small hole for the "seed" wire; *O*, freezing tube, with silvered jacket; *P*, stopcock on freezing tube; *Q*, asbestos collar; *R*, brass cylinder, 12½ inches long and 2⅛ inches inside diameter, with Bakelite collar; *S*, Dewar flask, for cooling or warming bath; *T*, asbestos pad at bottom of cylinder *R*; *U*, wood-block support; *V*, table top; *W*, wall; *X*, spherical joint, 18/7; *Y*, connection to vacuum; *Z*, connection to air, through drying tube.

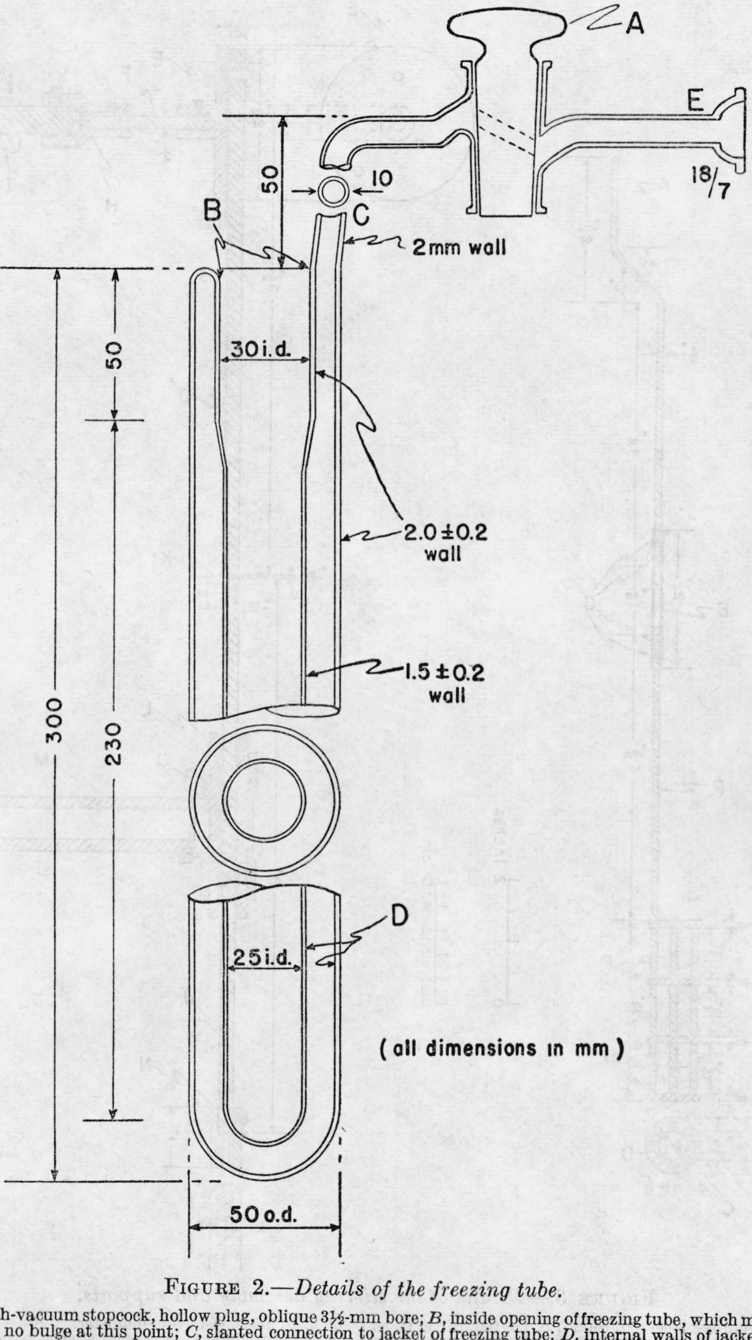

FIGURE 2.—*Details of the freezing tube.*

*A*, High-vacuum stopcock, hollow plug, oblique 3½-mm bore; *B*, inside opening of freezing tube, which must have no bulge at this point; *C*, slanted connection to jacket of freezing tube; *D*, internal walls of jacket of freezing tube, silvered; *E*, spherical joint, 18/7.

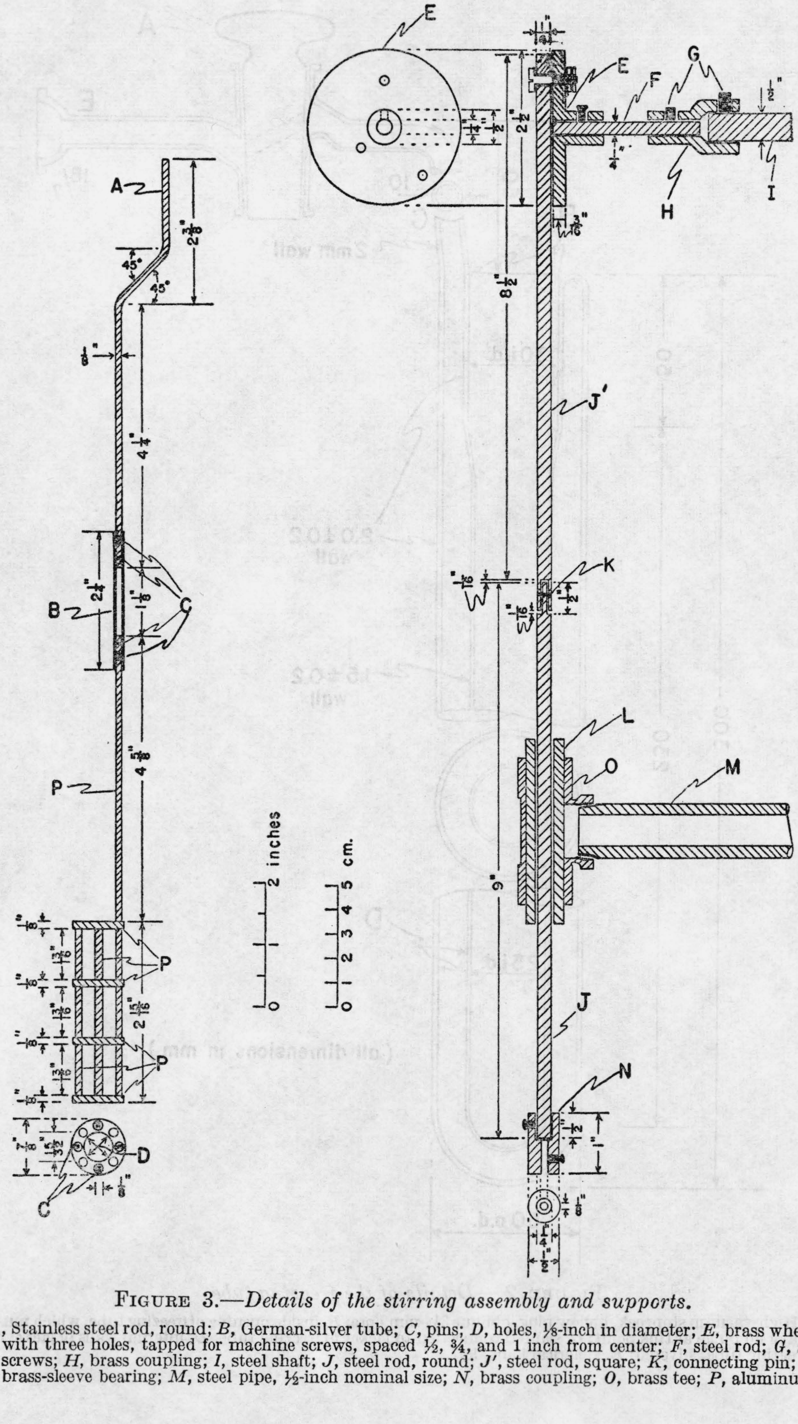

FIGURE 3.—*Details of the stirring assembly and supports.*

*A*, Stainless steel rod, round; *B*, German-silver tube; *C*, pins; *D*, holes, ⅛-inch in diameter; *E*, brass wheel, with three holes, tapped for machine screws, spaced ½, ¾, and 1 inch from center; *F*, steel rod; *G*, set screws; *H*, brass coupling; *I*, steel shaft; *J*, steel rod, round; *J'*, steel rod, square; *K*, connecting pin; *L*, brass-sleeve bearing; *M*, steel pipe, ½-inch nominal size; *N*, brass coupling; *O*, brass tee; *P*, aluminum.

## IV. EXPERIMENTAL PROCEDURE FOR A FREEZING EXPERIMENT

The procedure for performing a freezing experiment is as follows:

The apparatus is assembled, with no refrigerant and no sample of hydrocarbon yet in place, but with a stream (10 to 20 ml a minute) of dry air flowing. The jacket of the freezing tube is filled with air freed of carbon dioxide and water.

As required, the operator must be prepared to induce crystallization in the hydrocarbon sample as soon as possible after the temperature has passed below the freezing point of the sample. In some cases, crystallization may be induced by introducing, into the hydrocarbon sample at the appropriate time, a small metal rod, which has been kept at liquid air temperatures. In other cases, crystallization may be induced by introducing, into the hydrocarbon sample at the appropriate time, crystals of the hydrocarbon on the coiled end of a small metal rod. These crystals are made by placing several milliliters of the hydrocarbon in a small test tube (incased in a thin metal tube) immersed in a refrigerant whose temperature is below the freezing point of the hydrocarbon.

The Dewar flask surrounding the freezing tube is filled with the appropriate refrigerant. The thermometer and stopper are temporarily removed and the hydrocarbon sample (50 ml of liquid) is introduced. When the hydrocarbon is volatile or normally gaseous at room temperature, the freezing tube is cooled before introducing the sample in order to minimize loss by evaporation. The flow of dry air into the freezing tube is continued in order to keep out water vapor. The stirrer is started and the sample is allowed to cool down to within about 15 degrees centigrade of the freezing point, when evacuation of the jacket of the freezing tube is begun.

The time and the resistance of the thermometer are observed at even intervals of 0.1 ohm (about 1 degree centigrade) to determine the rate of cooling. When a cooling rate is obtained that will give a change of 1 degree in about 2 to 3 minutes, in the range of about 5 to 10 degrees above the freezing point, the stopcock controlling the jacket of the freezing tube is closed. (The optimum rate of cooling will vary with the hydrocarbon being examined.)

When the temperature reaches a point about 5 degrees above the expected freezing point, the time is recorded to 1 second (or 0.01 minute), at which the resistance of the termometer equals certain preselected values (every 0.1 or 0.05 ohm). At the appropriate time (see above), crystallization is induced. The beginning of crystallization will be accompanied by a halt in the cooling of the liquid. After recovery from under cooling is substantially complete, the resistances, including the reading of the scale of the galvanometer at full sensitivity as well as the scale reading with no current through the galvanometer, are recorded at intervals of about 1 minute. These observations, together with the sensitivity of the galvanometer system in terms of ohms per millimeter of scale reading, yield a sensitivity near 0.0001 degree centigrade in the measurement of temperature. These observations are continued until the stirrer begins laboring.

Then the stirrer is stopped and comparison of "N" and "R" readings is made through the commutator. These latter readings are made at fixed intervals of about 1 minute, alternately for "N" and "R," and the difference between the two at any given instant of time is determined from a plot of the several values against time.

## V. EXPERIMENTAL PROCEDURE FOR A MELTING EXPERIMENT

The procedure for performing a melting experiment is exactly the same as for a freezing experiment, up to the point where the stirrer begins laboring. When the stirrer shows signs of laboring, a comparison of "N" and "R" readings is made through the commutator, as in the previous section, except that the stirrer is still operating. When the laboring of the stirrer becomes quite pronounced, the cooling bath is replaced by the appropriate warming bath, and, simultaneously, further evacuation of the freezing tube is begun, with the stirrer still operating. After evacuation for an appropriate length of time (3 to 10 minutes), the stopcock on the freezing tube is closed, and observations of time and resistance are continued along the equilibrium portion of the melting curve as along the equilibrium portion of the freezing curve. When melting is substantially complete, as evidenced by a marked change in the rate of change of resistance, the time is recorded when the resistance reaches certain preselected values at even intervals of 0.05 ohm (0.5 degree centigrade). The experiment is concluded when the temperature has reached a point 5 to 10 degrees above the freezing point.

For substances having freezing points in the range −135° to −170° C, the melting experiment may be performed by letting the cooling bath of liquid air remain in position and evacuating the jacket of the freezing tube as much as possible. This will make the thermal conductivity across the jacket so small that the energy introduced by the stirrer may be used to provide the energy of melting. A similar procedure may be used for melting experiments with substances having freezing points in the range from about −50 to −80° C, utilizing the bath of solid carbon dioxide in a 50-50 mixture of carbon tetrachloride and chloroform.

## VI. EVALUATION OF THE FREEZING POINT FROM A FREEZING CURVE

To locate zero time (the time at which crystallization would have begun in the absence of undercooling), a preliminary plot is made of the time-resistance observations covering the liquid cooling line and the equilibrium portion of the freezing curve. For this plot, as shown in figure 4, the time scale is taken so that 1 cm is equivalent to 1 minute and the resistance scale (for a 25-ohm thermometer) so that 1 cm is equivalent to 0.02 ohm (0.2 degree centigrade). Usually the extent of undercooling is small enough that no correction for zero time need be made, in which case zero time can usually be determined by a visual extrapolation, on this plot, of the equilibrium portion of the freezing curve back to its intersection with the liquid-cooling line. However, if undercooling is appreciable, correction for its effect on the time may be required (see part II–2 of reference [1]).

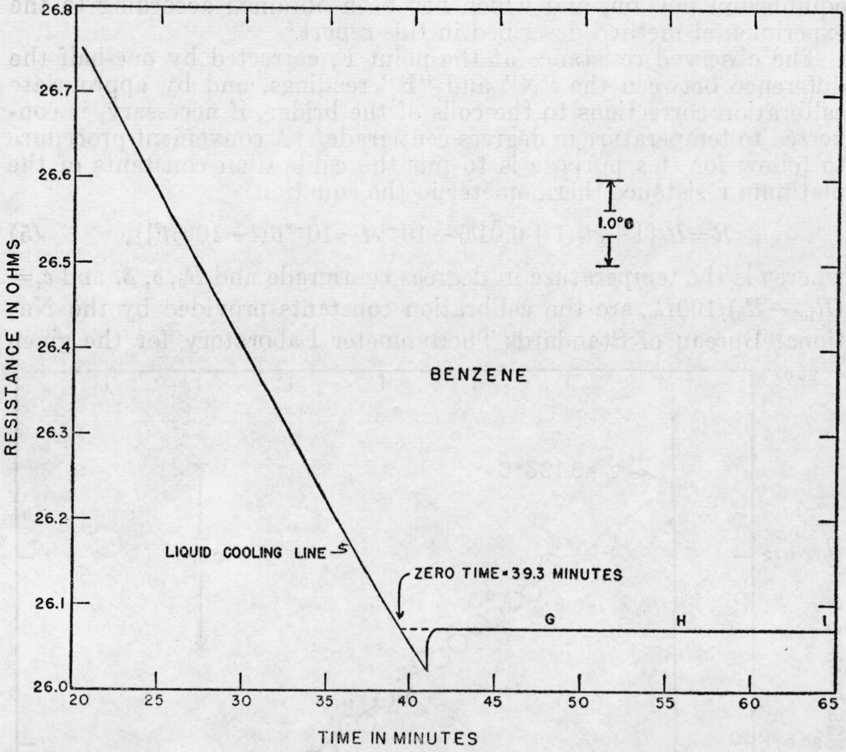

FIGURE 4.—*Time-temperature cooling curve for determining "zero" time in an experiment on a sample of benzene.*

The scale of ordinates gives the resistance in ohms of the platinum resistance thermometer, and the scale of abscissas gives the time in minutes. GHI represents the equilibrium portion of the freezing curve. Zero time is given by the intersection of the liquid cooling line with GHI extended. The same data are plotted in figure 5 with a magnified scale of temperature.

In order to locate accurately the resistance corresponding to the freezing point, the time-resistance observations are plotted as shown in figure 5, with the same time scale as before but with the scale of temperature magnified 10 to 200 times. The equilibrium portion of the curve, GHI, is extended back to its intersection at F with the liquid line by the simple geometrical construction shown in figure 6 (taken from reference [2]), selecting, for this purpose, three points (near the ends and the middle) of the equilibrium portion of the curve. The point F gives the resistance corresponding to the freezing point. (For details regarding the identification of the equilibrium portion of the curve, and the geometrical construction for determining the freezing point, see reference [2].)

If there is any doubt about the location of the equilibrium portion of the time-temperature curve, the criterion described on pages 210 and 211 of reference [2] may be applied. This procedure [2] involves plotting values of $(z-z_m)/(R-R_m)$ versus $(z-z_m)$, where $(R_m, z_m)$ is an arbitrary fixed point near the middle of the equilibrium portion and $(R, z)$ is any other point on the curve. This plot yields a straight line for that portion of the time-termperature curve representing the equilibrium portion, and which has been obtained according to the experimental method described in this report.[5]

The observed resistance at the point F, corrected by one-half the difference between the "N" and "R" readings, and by appropriate calibration corrections to the coils of the bridge, if necessary, is converted to temperature in degrees centigrade. A convenient procedure to follow for this purpose is to put the calibration constants of the platinum resistance thermometer in the equation

$$R=R_0\{1+ct[(1+0.01\delta)-10^{-4}\delta t-10^{-8}\beta(t-100)t^2]\}, \tag{5}$$

where $t$ is the temperature in degrees centigrade and $R_0$, $\delta$, $\beta$, and $c$,$=(R_{100}-R_0)/100R_0$, are the calibration constants provided by the National Bureau of Standards Thermometer Laboratory for the given

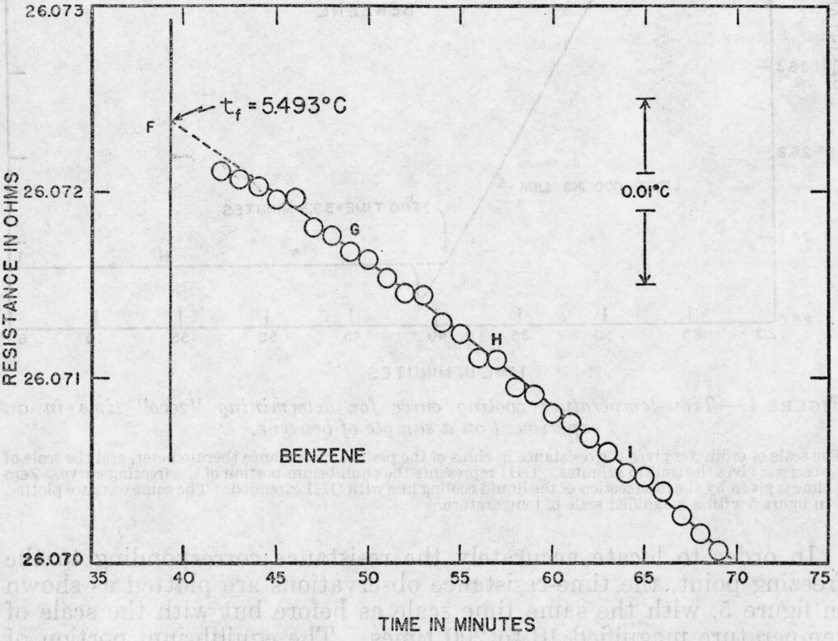

FIGURE 5.—*Time-temperature cooling curve for determining the freezing point of a sample of benzene.*

The scale of ordinates gives the resistance in ohms of the platinum resistance thermometer, and the scale of abscissas gives the time in minutes. GHI represents the equilibrium portion of the freezing curve. The freezing point F is determined as described in the text (see [2]). These data are the same as those plotted in figure 4.

thermometer. The foregoing equation with four constants is used for the range −190° to 0° C. For the range above 0° C, $\beta$ is taken as zero, and the equation is simplified to

$$R=R_0\{1+ct[(1+0.01\delta)-10^{-4}\delta t]\}. \tag{6}$$

With this equation, values of $R$ are calculated to 0.00001 ohm, for unit degrees in the range of interest. (If determinations are to be

---

[5] This plot of $(z-z_m)/(R-R_m)$ versus $(z-z_m)$ may also be used to evaluate $t_f$ and $t_{f_0}$, as described on pages 210 and 211 of reference [2].

made on many different hydrocarbons, time will be saved by making up at the start a table of such values of $R$ for unit degrees in the entire range). Linear interpolation between unit degrees may be used without significant error to obtain the temperature corresponding to the given resistance. A table of this kind covering the range −190° to 50° C can be put on a sheet 14 by 17½ inches in size.

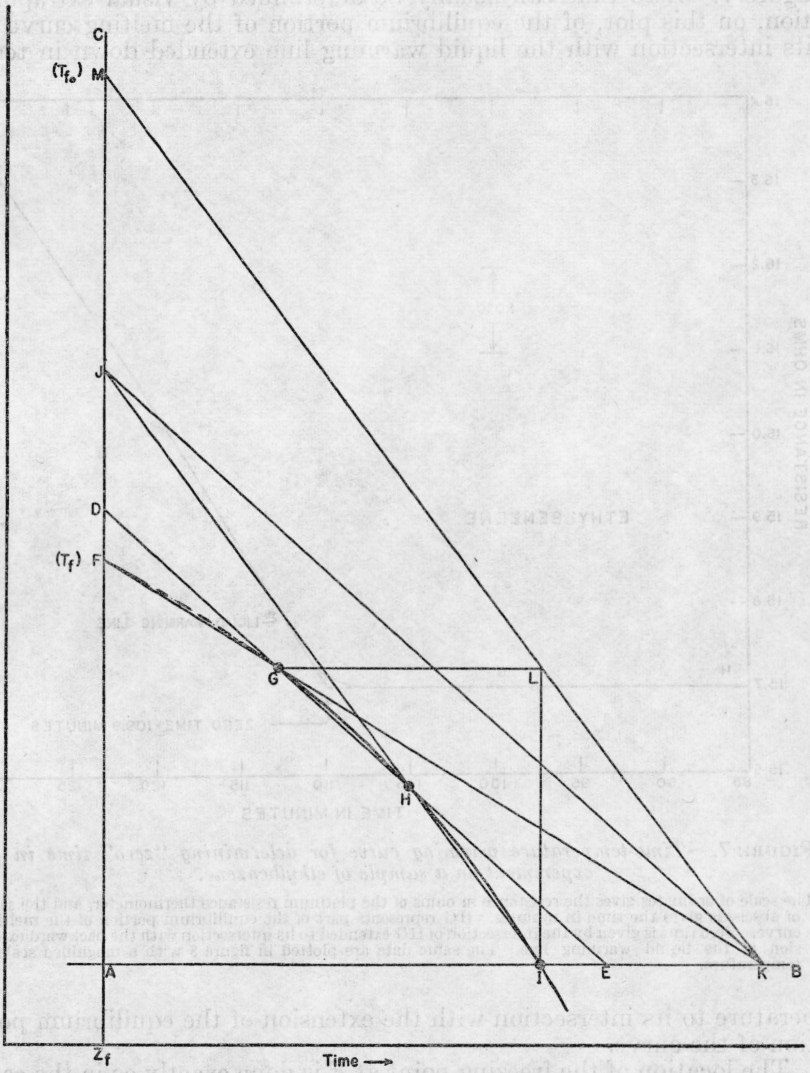

FIGURE 6.—*Geometrical construction for determining the freezing point.*

Given G, H, and I as any three points on the equilibrium portion of the freezing curve, preferably spaced approximately as shown. Construction to determine $t_f$: Draw AC parallel to the temperature axis at "zero" time (the time at which crystallization would have begun in the absence of undercooling). Draw AB through I parallel to the time axis. Draw a line through G and H intersecting AB at E and AC at D. Draw a line through H and I intersecting AC at J. Draw a line through J parallel to DE, intersecting AB at K. Draw a line through K and G, intersecting AC at F. F is the desired point, representing the freezing point of the given sample. Construction to determine $t_{f_0}$: Draw a line through G parallel to AB and a line through I parallel to AC, the two lines intersecting at L. Draw a line through points K and L, intersecting AC at M. M is the desired point, representing the freezing point for zero impurity, $t_{f_0}$.

## VII. EVALUATION OF THE FREEZING POINT FROM A MELTING CURVE

Zero time is determined from a preliminary plot (as for the freezing curve) of the time-resistance observations covering the equilibrium portion of the melting curve and the liquid warming line, as shown in figure 7. Zero time can usually be determined by visual extrapolation, on this plot, of the equilibrium portion of the melting curve to its intersection with the liquid warming line extended down in temperature to its intersection with the extension of the equilibrium portion of the curve.

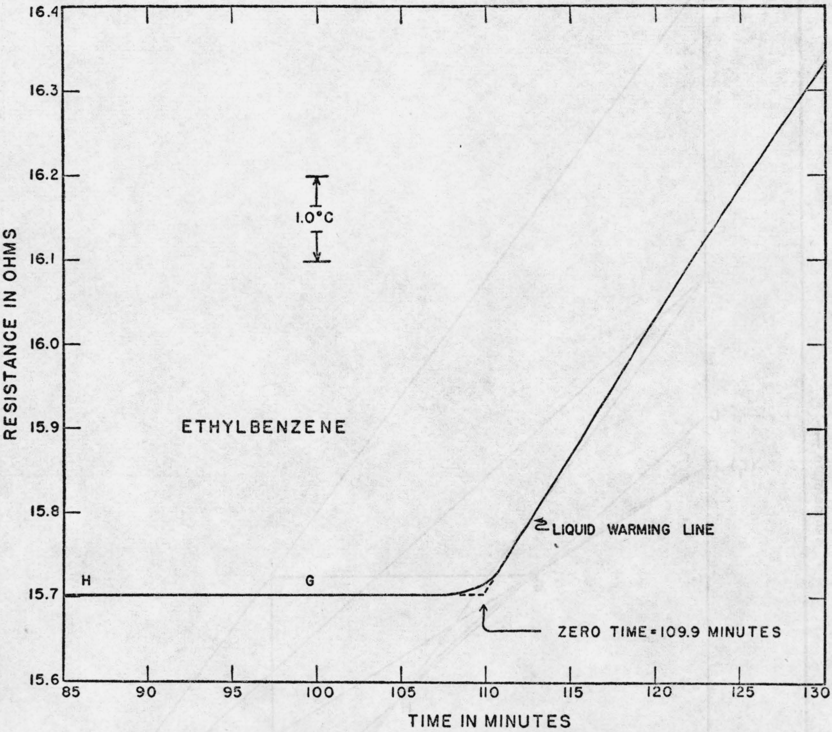

FIGURE 7.—*Time-temperature warming curve for determining "zero" time in an experiment on a sample of ethylbenzene.*

The scale of ordinates gives the resistance in ohms of the platinum resistance thermometer, and the scale of abscissas gives the time in minutes. HG represents part of the equilibrium portion of the melting curve. Zero time is given by the intersection of HG extended to its intersection with the backward extension of the liquid warming line. The same data are plotted in figure 8 with a magnified scale of temperature.

The location of the freezing point at F is done exactly as in the case of the freezing experiment, except that the geometrical construction is made to the right, as in figure 8. See figure 6 and reference [2] for details.

The conversion of resistance to temperature is made as previously described.

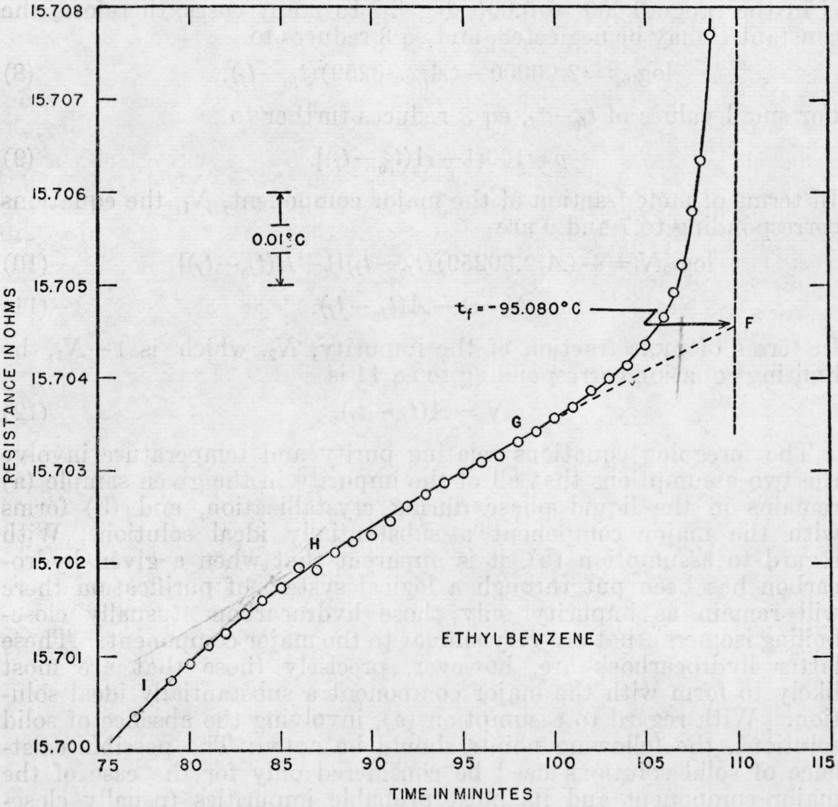

FIGURE 8.—*Time-temperature warming curve for determining the freezing point of a sample of ethylbenzene.*

The scale of ordinates gives the resistance in ohms of the platinum resistance thermometer, and the scale of abscissas gives the time in minutes. IHG represents the equilibrium portion of the melting curve. The freezing point F is determined as described in the text (see [2]). These data are the same as those plotted in figure 7.

## VIII. CALCULATION OF THE PURITY WHEN THE FREEZING POINT FOR ZERO IMPURITY IS KNOWN

When the values of the freezing point for zero impurity and the cryoscopic constants are known, the measured value of the freezing point may be used to calculate the purity of the given sample by means of the equation

$$\log_{10}p = 2.00000 - (A/2.30259)(t_{f_0} - t_f)[1 + B(t_{f_0} - t_f)]. \qquad (7)$$

In eq 7, $p$ is the purity in mole percent, $t_f$ is the freezing point, $t_{f_0}$ is the freezing point for zero impurity, and $A$ and $B$ are the cryoscopic constants [6] defined in section II.

For many hydrocarbons of low molecular weight, the value of the constant $A$ lies in the range 0.005 to 0.06 deg$^{-1}$ and that of the constant

---

[6] Selected "best" values of the cryoscopic constants of the more important hydrocarbons of the various classes are being compiled for publication in a joint investigation of the Thermochemical Laboratory and the American Petroleum Institute Research Project 44 at the National Bureau of Standards.

$B$ in the range 0.000 to 0.005 deg$^{-1}$. In many cases, therefore, the constant $B$ may be neglected, and eq 3 reduces to

$$\log_{10}p = 2.00000 - (A/2.30259)(t_{f_0} - t_f). \tag{8}$$

For small values of $t_{f_0} - t_f$, eq 8 reduces further to

$$p = 100[1 - A(t_{f_0} - t_f)]. \tag{9}$$

In terms of mole fraction of the major component, $N_1$, the equations corresponding to 7 and 9 are

$$\log_{10}N_1 = -(A/2.30259)(t_{f_0} - t_f)[1 + B(t_{f_0} - t_f)] \tag{10}$$

$$N_1 = 1 - A(t_{f_0} - t_f). \tag{11}$$

In terms of mole fraction of the impurity, $N_2$, which is $1 - N_1$, the limiting equation corresponding to eq 11 is

$$N_2 = A(t_{f_0} - t_f). \tag{12}$$

The foregoing equations relating purity and temperature involve the two assumptions that all of the impurity in the given sample (a) remains in the liquid phase during crystallization, and (b) forms with the major component a substantially ideal solution. With regard to assumption (b), it is apparent that when a given hydrocarbon has been put through a logical system of purification there will remain as impurity only those hydrocarbons (usually close-boiling isomers) that are very similar to the major component. These latter hydrocarbons are, however, precisely those that are most likely to form with the major component a substantially ideal solution. With regard to assumption (a), involving the absence of solid solutions, the following points should be noted: The possible existence of solid solutions need be considered only for the case of the major component and its most probable impurities (usually close-boiling isomers); among hydrocarbons of low molecular weight, close-boiling isomeric impurities fortunately seldom possess the required shape and size of the molecule to favor the formation of solid solutions. However, when there are known cases where a given hydrocarbon and its most probable impurity (for the given process of purification) form solid solutions, or otherwise do not conform to the requirements for the ideal relations, and if it is desired to translate into purity the freezing points of such systems, observations should be made on known mixtures of such hydrocarbons for the purpose of evaluating the actual relation between freezing point and purity. In general, in those cases where the identity of the impurity is known, the actual relation between purity and freezing point may be determined experimentally from known mixtures. In such cases, the observed relation, rather than the theoretically calculated relation for the ideal solution, should be used if the former is found to differ significantly from the latter.

## IX. CALCULATION OF THE PURITY WHEN THE FREEZING POINT FOR ZERO IMPURITY IS NOT PREVIOUSLY KNOWN

When for the given compound under examination, the freezing point for zero impurity is not previously known, its value may be determined by application of the procedures previously described [1, 2].

The first of these procedures may be performed simply as follows: The time of crystallization is determined as described in part II–3 of reference [1]. If this experiment is not identical with the one from which the freezing point has been determined, the time of crystallization for the latter is related to that for the former (with the same quantity of sample in both experiments) as follows:

$$(z_{xln})_1/(z_{xln})_2 = (\Delta t/\Delta z)_2/(\Delta t/\Delta z)_1, \tag{13}$$

where $z_{xln}$ is the time of crystallization in minutes, $\Delta t/\Delta z$ is the cooling rate (or the negative of the warming rate) of the liquid phase at the freezing point in degrees per minute or ohms per minute, and the subscripts 1 and 2 identify the two experiments.[7]

Taking the rate of crystallization to be substantially constant [1], the fraction, $r$, crystallized at any time $z_r$ is

$$r = (z_r - z_f)/z_{xln} \tag{14}$$

where $z_f$ is "zero" time or the time at which crystallization begins (with no significant amount of undercooling). In the proper application of eq 9 and 10, it is necessary that the rate of introduction of energy by stirring be small in comparison with the total rate of heat flow to or from the sample.[8] If the stirring energy is significantly large, appropriate correction for it must be made in evaluating the time of crystallization, as described in part II–3 of reference [1]. The time $z_r$ is selected as far as possible down the equilibrium portion of the curve (see GHI in fig. 5 and 8). Then the freezing point for zero impurity is

$$t_{f_0} = t_f + \left(\frac{1-r}{r}\right)(t_f - t_r), \tag{15}$$

where $t_r$ is the equilibrium temperature at the time $z_r$. It is desirable to make the determination of $t_{f_0}$ from several experiments on the same or different samples of the highest purity.

When the value of the freezing point for zero impurity is thus determined, and a value of the cryoscopic constant (or constants) is known, the calculation of the purity is made by means of the appropriate equations given in the preceding section.

Whenever the value of the cryoscopic constant $A$ is not known, a value for it may be determined as described in the following section.

The second procedure for determining $t_{f_0}$ is described on pages 205–207 of reference [2]. This procedure, which requires no additional experimental data, is applicable only to those experiments in which the time-temperature observations extend over a sufficiently large fraction (of the order of ¼ to ½) of material crystallized. The geometrical construction for determining $t_{f_0}$ by this procedure is illustrated in figure 6. If the point M lies off the available plotting space,

---

[7] If the resistance-time curve at the freezing point, for either a melting or a freezing experiment, is not sufficiently linear to permit reasonably accurate evaluation of the slope directly from the resistance-time plot, the slope at the freezing point may be readily evaluated, from the data of either the freezing or the melting experiment, by plotting, as a function of time, values of the slope of successive chords of the resistance-time curve taken as the difference in successive readings of resistance divided by the time interval in minutes, and extrapolating these slopes to the "zero" time, $z_f$, at the freezing point.

[8] The energy of stirring may be readily determined by having the substance and container at the temperature of the jacket (0°, −80°, or −185° C), taking observations of resistance, with stirring, for a period of 10 minutes, stopping the stirrer for a period of 5 minutes, again taking observations of resistance, with stirring, for another period of 10 minutes, etc. The cessation of stirring in a given period produces, between the two periods adjacent to it, an offset (decrease) of the resistance (temperature) curve with respect to time. The actual displacement of the resistance-time line between the two stirring periods, measured at the middle of the period of no stirring, divided by 5, the number of minutes in which the stirrer was halted, gives the value of the stirring energy in terms of the change of resistance (temperature) per minute, of the given system.

its value may be determined analytically as follows [2]: Given the three points G, H, and I on the equilibrium curve, having values of time equal to $z_G$, $z_H$, and $z_I$ (with point H having been selected midway between G and I in point of time, so that $z_G - z_H = z_H - z_I$) and values of temperature (resistance) equal to $t_G$, $t_H$, and $t_I$, respectively. Then (see footnote 5)

$$t_{f_0} = t_G + (t_G - t_I)/(u-1), \tag{16}$$

where

$$u = (t_H - t_I)/(t_G - t_H). \tag{17}$$

In general, it is desirable to utilize both of the foregoing procedures where possible. The two procedures should give the same result within the respective limits of uncertainty. (See fig. 5 in reference [2].)

## X. DETERMINATION OF THE CRYOSCOPIC CONSTANT

When enough of the given compound is available, the cryoscopic constant may be determined directly by measuring the lowering of the freezing point caused by the addition to it of a measured amount of an appropriate solute. The amount of the given compound required is about 40 ml, and its purity should be about 97 or more mole percent. The solute required to be added is one that will form with the given compound a substantially ideal solution (with no solid solutions), its purity should be about 97 or more mole percent, and the amount required is about 2 ml. Preferably, the solute added should be isomeric with the given compound and the impurity in the solute should not include any significant amount of the given compound. Furthermore, the solute added must be one that does not form a eutectic mixture with the given compound at the resulting concentration in the solution formed. In general, eutectic mixtures of this low concentration will be likely to occur only for solutes that have freezing points much higher than the given substance.[9]

Let H be the given hydrocarbon compound under examination. Measurement is made of the freezing point, $t_f^p$, of a sample of "pure" H, according to the procedure described in the preceding sections of this report. To a weighed amount of 40 ml of pure H is added 2 ml of the given solute, with the weight of the solute being determined from the increase in weight. The solution thus formed is one in which the concentration of the hydrocarbon H is about 5 mole percent less than in the pure H. Measurement is made of the freezing point, $t_f^s$, of the solution. Let

$m^p$ = the mass of the pure H used in making the solution of H.

$m^q$ = the mass of the solute, Q.

$M^p$ = the molecular weight of pure H, taken to be that given by the molecular formula of H;

$M^q$ = the molecular weight of the solute, Q, taken to be that given by the molecular weight of Q;

$N^p$ = the mole fraction of H in pure H;

$N^s$ = the mole fraction of H in the solution formed from H and Q, calculated from the masses and molecular weights. If H and Q are isomeric, the mole fraction is identical with the weight fraction.

---

[9] For example, *p*-xylene (fp=13.26° C) forms with ethylbenzene (fp=−94.95° C) a eutectic mixture in which there is about 3½ mole percent of *p*-xylene.

Then the following relations hold

$$-\ln N^{p}=A(t_{f_0}-t_f^{\,p}) \tag{18}$$

$$-\ln N^{s}=A(t_{f_0}-t_f^{\,s}) \tag{19}$$

$$-\ln (N^{s}/N^{p})=A(t_f^{\,p}-t_f^{\,s}) \tag{20}$$

$$A=-2.3026\ [\log_{10}(N^{s}/N^{p})]/(t_f^{\,p}-t_f^{\,s}). \tag{21}$$

For many compounds, the value of $t_f^{\,p}-t_f^{\,s}$ in the foregoing experiments will be, for the amounts indicated, about 1° to 2° C, and the uncertainty in the resulting value of the cryoscopic constant should be not more than several percent. (See reference [3]).

In case 40 ml of the given compound in a purity of about 97 percent is not available for making up a solution as described above, the cryoscopic constant, $A$, may be determined, without contaminating the sample, from a value of the heat of fusion estimated by a comparison with observations on a substance whose heat of fusion is known [1]. The procedure is as follows: Select a similar compound F whose heat of fusion is known and whose freezing point is within about 15° C of that of the compound G whose heat of fusion is to be estimated. Perform a complete time-temperature freezing experiment on the substance F, and likewise on the substance G, using substantially the same number of moles in each case and the same jacket temperature. For each of the experiments, the corrected time of crystallization is determined. Then, approximately,

$$(\Delta Hm)_{\mathrm{G}}=(\Delta Hm)_{\mathrm{F}}\frac{(\Delta t/\Delta z)_{\mathrm{G}}(z_{xln})_{\mathrm{G}}}{(\Delta t/\Delta z)_{\mathrm{F}}(z_{xln})_{\mathrm{F}}}. \tag{22}$$

The foregoing relation will yield a value for the heat of fusion, and hence the cryoscopic constant, which will in most cases be uncertain by not more than about 20 percent of itself. The accuracy of this procedure can be improved by using two reference substances, one of freezing point above and the other below that of the given substance, and appropriately interpolating.

Where possible, the method of determining the cryoscopic constant by direct measurement of the lowering of the freezing point is to be preferred over the approximate method described in the preceding paragraph. For use in the ideal systems discussed in this report, the most accurate values of the cryoscopic constants are usually derived from heats of fusion measured calorimetrically.

## XI. DISCUSSION

Duplicate determinations of the freezing point of a given sample made by a given operator with the apparatus and procedure described in sections III to VII will usually differ by not more than 0.002 to 0.005 degree centigrade, except for very impure samples and for compounds having rather small values of the cryoscopic constant $A$. It follows that duplicate determinations would yield values of purity (in mole percent) differing usually by not more than 0.2 to 0.5 times the cryoscopic constant $A$ (in deg$^{-1}$).

Determinations of the freezing point of a given sample made in different laboratories with the apparatus and procedure described in sections III to VII should normally differ by not more than about 0.01 to 0.02 degree centigrade, if the resistance bridges and the platinum resistance thermometers have been properly calibrated, as with constants certified by the National Bureau of Standards, and measurements of the ice point are made at appropriate intervals.

Assuming that the impurity remains entirely in the liquid phase during crystallization and forms with the major component a substantially ideal solution, the uncertainty in the value of the purity of a given sample determined with the present apparatus and procedure will include (a) an uncertainty in the value of the freezing point $t_f$, which uncertainty has been discussed above, and (b) an uncertainty in the given value of $t_{f_0}$. For substances having a large value of the cryoscopic constant $A$, the uncertainty in $t_{f_0}$ will usually be near 0.01 to 0.03 degree centigrade, if the sample available for measurement has a purity of about 99.8 or more mole percent. For substances having a small value of the cryoscopic constant $A$, the uncertainty in $t_{f_0}$ may be near 0.05 to 0.10 degree centigrade, when the determination is made on a sample having a purity of about 99.8 or more mole percent. The uncertainty in the value of $t_{f_0}$ will, of course, decrease with increase in the purity of the sample. As discussed in section VIII, calculations relating to systems of known components should be based, when possible, upon actual experimental observations on known mixtures of such compounds.

For those compounds that have one or more metastable forms whose freezing points can be determined, it becomes necessary to ascertain for which crystalline form the determined freezing point has been obtained. For those cases where the freezing point (for zero impurity) of metastable form II is more than a few degrees below that of the stable form I, there is little difficulty in identifying the forms, as it would usually require a rather impure sample of form I to have a freezing point below that of a pure sample of form II. When the difference in the freezing points (for zero impurity) of the two forms is less than several degrees, and especially when the difference is less than one degree, the problem of identifying the forms is somewhat more involved. However, except in the most complicated case, it is possible to determine the value of $t_{f_0}$ yielded by the given experiment (as outlined in section IX) and to identify the crystalline form from the value of $t_{f_0}$.

Measurements of freezing points of actual "best" samples, with evaluation of freezing points for zero impurity, together with determinations of cryoscopic constants as required, have been made, according to the method and procedures described in this report, on approximately 80 different purified hydrocarbons of the paraffin, alkylcyclopentane, alkylcyclohexane, alkylbenzene, monoolefin, diolefin, and cyclomonoolefin series in connection with the work at this Bureau of the American Petroleum Institute Research Project 6 on the purification and properties of hydrocarbons. Determinations of the purity of the NBS Standard Samples of hydrocarbons are also being made by the procedures described in this report. Complete details of this experimental work will appear in other reports from the National Bureau of Standards [7].

## XII. REFERENCES

[1] B. J. Mair, A. R. Glasgow, Jr., and F. D. Rossini, J. Research NBS **26,** 591 (1941) RP1397.
[2] W. J. Taylor and F. D. Rossini, J. Research NBS **32,** 197 (1944) RP1585.
[3] A. J. Streiff and F. D. Rossini, J. Research NBS **32,** 185 (1944) RP1584.
[4] G. K. Burgess, J. Research NBS **1,** 635 (1928) RP22.
[5] E. W. Washburn, J. Am. Chem. Soc. **32,** 653 (1910).
[6] G. N. Lewis and M. Randall, Thermodynamics and the free energy of chemical substances (McGraw-Hill Book Co., Inc., New York, N. Y., 1923).
[7] American Petroleum Institute Research Project 6 and Hydrocarbon Standard Samples Laboratory; National Bureau of Standards. Unpublished data.

WASHINGTON, May 20, 1945.