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METHOD FOR DETERMINING INDIVIDUAL HYDROCARBONS IN MIXTURES OF HYDROCARBONS BY MEASUREMENT OF FREEZING POINTS^{1 2}

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ABSTRACT

A method is described for determining individual hydrocarbons in mixtures of hydrocarbons by the measurement of freezing points. Experimental data are given for the determination of the four C₈ aromatic hydrocarbons. The uncertainty of the determination of each hydrocarbon is near ± 1 percent of the total sample.

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I. INTRODUCTION

This paper describes a general method for determining individual hydrocarbons in mixtures of hydrocarbons by measurement of freezing points. The method is based on the fact that the amount of a hydrocarbon H in an unknown mixture of hydrocarbons can be determined by measurement of the lowering of the freezing point of a sample of pure H caused by the addition to it of a given amount of the unknown mixture. If the unknown mixture contains none of the hydrocarbon H, the lowering of the freezing point will have its greatest value, which will be substantially that called for by the ideal or dilute solution laws; whereas, if the unknown is composed entirely of the hydrocarbon H, the lowering of the freezing point will be zero.

In the exact application of the method, it is important to show that the solution of the hydrocarbon H with the unknown is, within the desired limits, ideal or sufficiently dilute, so that the ideal law of the lowering of the freezing point may be applied. If the solution of the hydrocarbon H with the unknown is not ideal or sufficiently dilute, it will be necessary to separate the unknown mixture beforehand by

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an appropriate fractionating process into two or more portions, each of which will form substantially ideal, or sufficiently dilute, solutions with the appropriate pure hydrocarbons.

II PREPARATION OF THE SAMPLE

In order to utilize the freezing point observations in the desired manner, it is important that each mixture of hydrocarbons examined be one that forms an ideal or sufficiently dilute solution with each of the hydrocarbons to be determined. In general, this requires that the unknown mixture of hydrocarbons be composed preponderantly of hydrocarbons of a similar or nearly similar type, as for example, (a) a mixture of paraffins plus cycloparaffins or of either of these separately, or (b) a mixture of olefins, or (c) a mixture of aromatics. Such mixtures will in general be ones most likely to follow, within the desired limits, the ideal law of the lowering of the freezing point. On the other hand, mixtures containing hydrocarbons of different type (considering for this purpose paraffins and cycloparaffins to be of similar type) may be expected to show significant departures from the behavior of an ideal solution. Such mixtures would require appropriate fractionation by type before proceeding with measurements of the lowering of the freezing point.

The method of analysis described in this paper places no restriction or limitation on the boiling range of the material to be examined, although obviously the precision is likely to be better for a narrow-boiling fraction than for a very wide-boiling fraction, such as the entire gasoline fraction.

The amount of hydrocarbon material required is, for each determination, about 40 ml of the "pure" hydrocarbon and 2 to 3 ml of the unknown.

III. METHOD

Given an unknown mixture of hydrocarbons of similar type, it is required to determine the amount of a given hydrocarbon H which is in the unknown mixture. Measurement is made of the freezing point of a sample of "pure" H, and also the freezing point of a dilute solution of the unknown mixture in "pure" H. The molecular weight of the unknown is determined, if necessary, by measuring the lowering of the freezing point of another hydrocarbon, of the same type as the unknown mixture but which is not a component of the unknown mixture, on the addition to this other hydrocarbon of a measured small amount of the unknown. Let

N^p = the mole fraction of the hydrocarbon H in the given lot of "pure" H. (This will be slightly less than unity, in general.)

N^s = the mole fraction of the hydrocarbon H in the solution made by adding a small amount of the unknown to "pure" H.

N^u = the mole fraction of the hydrocarbon H in the unknown mixture.

m^p = the mass of the sample of "pure" H used in making the solution of "pure" H and the unknown.

m^u = the mass of the unknown used in making the solution of "pure" H and the unknown.

M^p = the molecular weight of "pure" H, taken to be that given by the molecular formula of hydrocarbon H.

M^u = the molecular weight of the unknown, determined, if necessary, from a lowering of the freezing point as mentioned above.

t_{f_0} = the freezing point of hydrocarbon H for zero impurity, in degrees centigrade.

t_f^p = the freezing point of the given lot of "pure" H, which, in general, will be slightly lower than t_{f_0} .

t_f^s = the freezing point of the solution of "pure" H with the unknown.

It follows that

$$N^p \frac{m^p}{M^p} + N^u \frac{m^u}{M^u} = N^s \left(\frac{m^p}{M^p} + \frac{m^u}{M^u} \right), \quad (1)$$

which is equivalent to

$$N^u = N^s - \left(\frac{m^p}{m^u} \right) \left(\frac{M^u}{M^p} \right) (N^p - N^s). \quad (2)$$

The values of N^p and N^s are given by the following relations [1, 2, 3]:

$$-\ln N^p = A(t_{f_0} - t_f^p)[1 + B(t_{f_0} - t_f^p)] \quad (3)$$

$$-\ln N^s = A(t_{f_0} - t_f^s)[1 + B(t_{f_0} - t_f^s)], \quad (4)$$

where

$$A = \Delta H_{f_0} / RT_{f_0}^2, \quad (5)$$

$$B = 1/T_{f_0} - \Delta C_{p_0} / 2\Delta H_{f_0}, \quad (6)$$

T_{f_0} = the freezing point in degrees Kelvin of pure H with zero impurity,

R = the gas constant per mole,

ΔH_{f_0} = the heat of fusion of pure H at T_{f_0} ,

ΔC_{p_0} = the heat capacity of pure H in the liquid state less the heat capacity of pure H in the solid state, at T_{f_0} .

In eq 2, which gives explicitly the value of the desired quantity N^u , the values of N^p and N^s are computed from eq 3 and 4, respectively, using the measured values of t_f^p and t_f^s , with the given value of t_{f_0} . It should be noted that for high precision the difference between t_f^p and t_f^s must be as precise as possible, whereas the value selected for t_{f_0} is of secondary importance, since it is used primarily as a reference point. In fact, if the sample H is sufficiently pure with N^p very nearly equal to unity, then eq 2, 3, and 4 may be simplified without significant error by substituting 1 for N^p and t_f^p for t_{f_0} , as follows:

$$N^u = N^s - \left(\frac{m^p}{m^u} \right) \left(\frac{M^u}{M^p} \right) (1 - N^s) \quad (2a)$$

$$-\ln N^p = 0; N^p = 1 \quad (3a)$$

$$-\ln N^s = A(t_f^p - t_f^s)[1 + B(t_f^p - t_f^s)]. \quad (4a)$$

In eq 2 (and 2a), the masses m^p and m^u are obtained from weighings on a balance, the molecular weight M^p is taken as known and equal to that of the hydrocarbon H, and the molecular weight of the unknown mixture, M^u , is determined as follows:

Given a hydrocarbon G which is not a component of the unknown mixture but which forms with it a substantially ideal or sufficiently dilute solution. Measurement is made of the freezing point of a lot of "pure" G, which should contain not more than 0.005 mole fraction of impurity, and of the freezing point of a dilute solution of the unknown in G. Let

t_f^p = the freezing point of the lot of "pure" G,

t_f^s = the freezing point of a dilute solution of the unknown in G,

m^p = the mass of "pure" G in the solution,

m^u = the mass of the unknown in the solution,

M^p = the molecular weight of G, taken as known from its molecular formula,

M^u = the molecular weight of the unknown mixture.

If the freezing point of "pure" G, t_f^p , is not too much below the freezing point of G for zero impurity, t_{f_0} , then the molecular weight of the unknown is obtained with sufficient accuracy from the following equations:

$$-\ln N^s = A(t_f^p - t_f^s)[1 + B(t_f^p - t_f^s)] \quad (7)$$

and

$$M^u = M^p(m^u/m^p)N^s/(1 - N^s). \quad (8)$$

In eq 7, the constants A and B are the same as before, except that they now apply to pure hydrocarbon G.

The possible precision of the method in the case of the four C_8 aromatics is as follows. It is necessary to determine the difference between t_f^p and t_f^s within $0.01^\circ C$, if the amount of the given compound is to be determined to within 0.005 mole fraction, when the relative amounts of the "pure" hydrocarbon and the unknown are selected so as to give a lowering of about $2^\circ C$ when none of the given compound is present in the unknown.

IV. EXPERIMENTAL PROCEDURE AND RESULTS

The use of this method is here illustrated by application to the four C_8 aromatic hydrocarbons. Since it has been shown [8, 9]⁴ that the four C_8 aromatic hydrocarbons follow the ideal solution laws as regards the liquid-solid equilibrium, it appeared desirable, for this system, to use as known test mixtures simply the four pure components in turn, determining in each case a component different from the one being examined so that the known would contain none of the component being determined. In these experiments, the lowering of the freezing point would, for the given molal ratios used, be a maximum, and departures from the theoretical values would be more easily recognized.

In the experimental part of the work, the determination of freezing points was made with the apparatus and procedure described in reference [3], with the following additions to the procedure:

⁴ Figures in brackets indicate the literature references at the end of this paper.

(a) For best results in the case of solutions, it was found necessary to extend the observations on the equilibrium portion of the time-temperature freezing or melting curve to cover the largest possible fraction of the material crystallized or melted.

(b) Instead of a visual extension of the equilibrium portion of the curve to "zero" time on freezing (the time at which crystallization would have begun in the absence of undercooling), or to the corresponding time on melting, the geometrical method described in a recent report of the API Research Project 44 at this Bureau was used [4].

For certain hydrocarbons, it is found that the time-temperature freezing curve obtained in the manner referred to has no portion recognizable as representing thermodynamic equilibrium between solid and liquid. In such cases, the time-temperature melting curve is used.

To test the over-all accuracy of the method, determinations were made of the amount of ethylbenzene, of *p*-xylene, and of *m*-xylene in "pure" *o*-xylene (0.9940 mole fraction pure), and the amount of *o*-xylene in "pure" *p*-xylene (0.9948 mole fraction pure). The amounts determined (see table 1) were, respectively, 0.0090, -0.0012, 0.0138, and 0.0034 mole fraction, which values are to be compared with zero as the theoretical value.

A convenient way of tabulating the experimental results and calculations is illustrated in table 1, where the columns give, in order, the following quantities wherever appropriate (see footnotes to the table for further explanation): the freezing point for zero impurity, $N_2=0$; the resistance in ohms of the given platinum resistance thermometer at the given freezing point; the difference in resistance of the platinum resistance thermometer at the given freezing point and at the freezing point for zero impurity; the change in resistance with temperature for the given thermometer at the given mean temperature; the value of $t_{f_0}-t_f$, obtained as the quotient $(R_{f_0}-R_f)/(dR/dt)$; the value of A as defined by eq 5; the value of B as defined by eq 6; the ratio of the masses of the "pure" substance and the unknown; the ratio of the molecular weights of the unknown and the "pure" substance; and the mole fraction of the given hydrocarbon in the "pure" substance, in the solution, and in the unknown. Table 1 also gives the values of A and B , as defined by eq 5 and 6, respectively, for benzene.

For these small differences, the calculation of the value of the lowering of the freezing point may be made most conveniently and precisely by taking the difference in the two values of the resistance, R , of the resistance thermometer, and dividing by the value of dR/dt for the mean temperature. (If a thermoelement is used, the difference in the two values of the emf, E , is divided by the appropriate value of dE/dt .) For a platinum resistance thermometer for which the constants R_0 , δ , β , and c ($= (R_{100}-R_0)/R_0$) are given,

$$dR/dt=R_0c[(1+0.01\delta)-(2\times 10^{-4})\delta t-(4\beta\times 10^{-8})(t-75)t^2].$$

The foregoing equation is applicable for temperatures below 0° C. For temperatures above 0° C, the equation is simplified to

$$dR/dt=R_0c[(1+0.01\delta)-(2\times 10^{-4})\delta t].$$

With these equations, values of dR/dt for unit values of t covering the range of interest may be tabulated and linear interpolation used for obtaining values for intermediate temperatures.

Application of the method has also been made [9] to the determination of the amounts of each of the four C_8 aromatic hydrocarbons in five different unknown mixtures consisting of C_7 , C_8 , and C_9 aromatic hydrocarbons, and the amounts of ethylbenzene and *p*-xylene in seven other different unknown mixtures consisting of C_7 , C_8 , and C_9 aromatics. For each of the first five of these unknowns, the following independent data were available to serve for comparison with the results obtained by the method of measuring freezing points:

(a) From analytical distillation data the relative amounts of the C_7 , C_8 , and C_9 aromatics (from which values the mean molecular weights could be calculated, as well as the percentage of the sum of the four C_8 aromatics).

(b) From analytical distillation data, the percentage of *o*-xylene in each of the unknowns.

The results obtained on one of the unknowns by the present method are given in table 1.

TABLE 1.—*Experimental data on the determination of the four C_8 aromatics in an unknown mixture of aromatics*

Material	t_f	R_f	$R_{f_0}-R_f$	dR/dt	$t_{f_0}-t_f$
ETHYLBENZENE					
$N_2=0$ ^a	°C -94.950	Ohms 15.7212	Ohms 0.0000	Ohms/degree 0.10509	°C 0.000
"Pure" ^b		15.7176	.0036	0.10509	.034
"Pure"+ <i>o</i> -xylene.....		15.5094	.2118	.10514	2.014
"Pure"+unknown.....		15.5360	.1853	.10514	1.762
<i>p</i> -XYLENE					
$N_2=0$ ^a	13.260	26.8621	0.0000	-----	0.000
"Pure" ^b		26.8411	.0210	0.10116	.208
"Pure"+ <i>o</i> -xylene.....		26.5995	.2626	.10120	2.595
"Pure"+unknown.....		26.6547	.2074	.10119	2.050
<i>m</i> -XYLENE					
$N_2=0$ ^a	-47.890	20.6183	0.0000	-----	0.000
"Pure" ^b		20.4836	.1347	0.10314	1.306
"Pure"+ <i>o</i> -xylene.....		20.2735	.3448	.10318	3.342
"Pure"+unknown.....		20.3611	.2572	.10316	2.493
<i>o</i> -XYLENE					
$N_2=0$ ^a	-25.190	22.9503	0.0000	-----	0.000
"Pure" ^b		22.9271	.0232	0.10234	.227
"Pure"+ <i>p</i> -xylene.....		22.7149	.2354	.10238	2.299
"Pure"+unknown.....		22.7489	.2014	.10237	1.967
BENZENE					
$N_2=0$ ^a	5.530	-----	-----	-----	-----

See footnotes at end of table.

TABLE 1.—Experimental data on the determination of the four C₈ aromatics in an unknown mixture of aromatics—Continued

Material	A	B	m^2/m^u	M^u/M^p	N^p	N^a	N^u
ETHYLBENZENE							
$N_2=0^a$	Degree ⁻¹ 0.03454	Degree ⁻¹ 0.00424			Mole fraction 1.0000	Mole fraction	Mole fraction
"Pure" ^b					0.9988		
"Pure"+ <i>o</i> -xylene.....			13.871	1.0000	.9988	0.9322	0.0090
"Pure"+unknown.....			14.072	1.0085	.9988	.9405	.1136
<i>p</i> -XYLENE							
$N_2=0^a$	0.02509	0.00276			1.0000		
"Pure" ^b					0.9948		
"Pure"+ <i>o</i> -xylene.....			16.099	1.0000	.9948	0.9365	-0.0012
"Pure"+unknown.....			17.236	1.0085	.9948	.9496	.1641
<i>m</i> -XYLENE							
$N_2=0^a$	0.02761	0.00337			1.0000		
"Pure" ^b					0.9644		
"Pure"+ <i>o</i> -xylene.....			16.762	1.0000	.9644	0.9109	0.0138
"Pure"+unknown.....			16.334	1.0085	.9644	.9329	.4142
<i>o</i> -XYLENE							
$N_2=0^a$	0.02660	0.00312			1.0000		
"Pure" ^b					0.9940		
"Pure"+ <i>p</i> -xylene.....			17.442	1.0000	.9940	0.9403	0.0034
"Pure"+unknown.....			17.091	1.0085	.9940	.9487	.1688
BENZENE							
$N_2=0^a$	0.01523	0.00274			1.0000		

^a This row, labeled $N_2=0$, gives values for the substance with zero impurity, that is, having $N_2=0$, where N_2 is the sum of the mole fractions of all the impurities. The indicated freezing point for zero impurity is the accepted value, taken from the tables of the API Research Project 44 at the National Bureau of Standards.

^b This row, labeled "Pure", gives values for the material actually used for the "Pure" sample. Its purity is given in the column headed N^p .

The molecular weight of the unknown, determined from the lowering of the freezing point in benzene, is 107.31, which is to be compared with the value 107.06 determined from the data of the analytical distillation. In a check experiment, the molecular weight of a sample of pure ethylbenzene was determined from the lowering of the freezing point in benzene to be 106.45, as compared with the theoretical value of 106.16. The sum of the percentages of the four C₈ aromatics was determined to be 86.1 ± 2.4 percent by volume by measurement of freezing points, which value is to be compared with 85.0 ± 0.5 percent by volume obtained from the data of the analytical distillation. The amount of *o*-xylene determined by measurement of freezing points is 16.9 ± 1.2 percent by volume, which is to be compared with the value 17.6 ± 1.0 percent by volume obtained from the data of the analytical distillation.

Figure 1 shows a time-temperature freezing curve used to determine the freezing point of a solution of the unknown in *o*-xylene. Figure 2 shows a time-temperature melting curve used to determine

the freezing point of a solution of the unknown in ethylbenzene. Figure 3 shows a time-temperature freezing curve used to determine the freezing point of a solution of the unknown in benzene, for the determination of molecular weight.

V. DISCUSSION

From the results of the data so far obtained, it appears that, with the method and procedure described here, individual aromatic hydrocarbons can be determined in a mixture of aromatic hydrocarbons with an uncertainty for each compound near ± 1 percent of the sample.

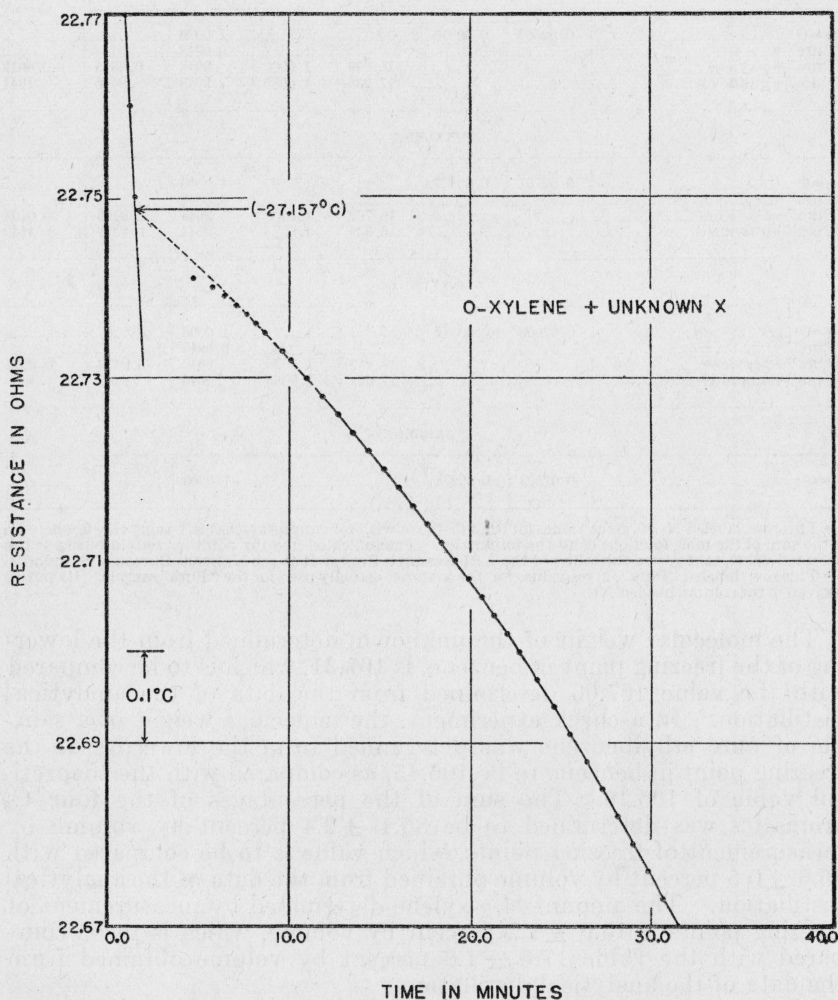


FIGURE 1.—Time-temperature freezing curve for *o*-xylene plus an "unknown" mixture of aromatic hydrocarbons.

The scale of ordinates gives the resistance of the platinum resistance thermometer in ohms; The scale of abscissas gives the time in minutes.

Previous measurements [3] have shown that mixtures of paraffins and cycloparaffins in dilute solution follow the ideal solution law of the lowering of the freezing point. It follows, therefore, that the present method can be used to determine individual paraffin or cycloparaffin hydrocarbons in mixtures of paraffin and cycloparaffin hydrocarbons.

Although no information is available with regard to olefin hydrocarbons and other types, there appears to be no reason why the method can not be used to determine individual olefins in a mixture of olefins, etc.

When the present investigation was nearing conclusion, references were found to the following three papers in the literature that men-

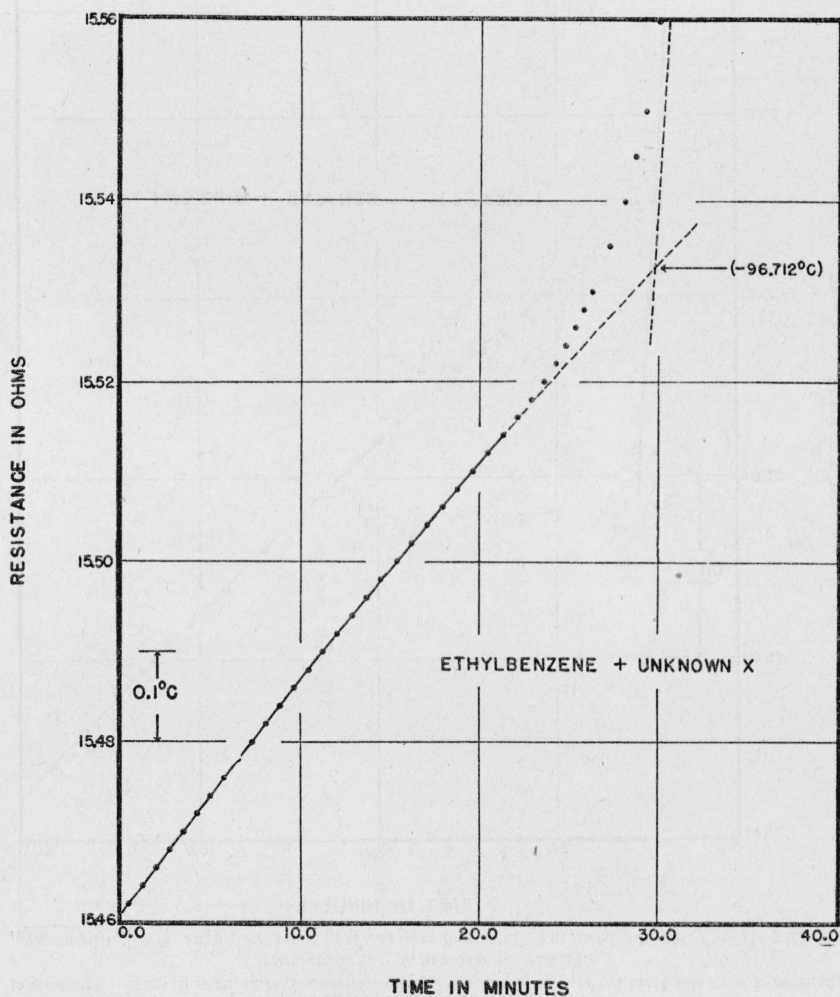


FIGURE 2.—Time-temperature melting curve for ethylbenzene plus an "unknown" mixture of aromatic hydrocarbons.

The scale of ordinates gives the resistance of the platinum resistance thermometer in ohms. The scale of abscissas gives the time in minutes.

tion or describe a method of analysis similar in principle to that described in the present paper: Norris and Rubinstein [5], Norris and Vaala [6], and Ibing [7]. The first two of these papers [5, 6] are concerned with other problems and barely mention the method. In the third paper, Ibing [7] describes his procedure and apparatus in detail, uses in his calculations only the simple limiting form of the law of the lowering of the freezing point, and does not define the freezing point nor tell how he determined it from his time-temperature observations.

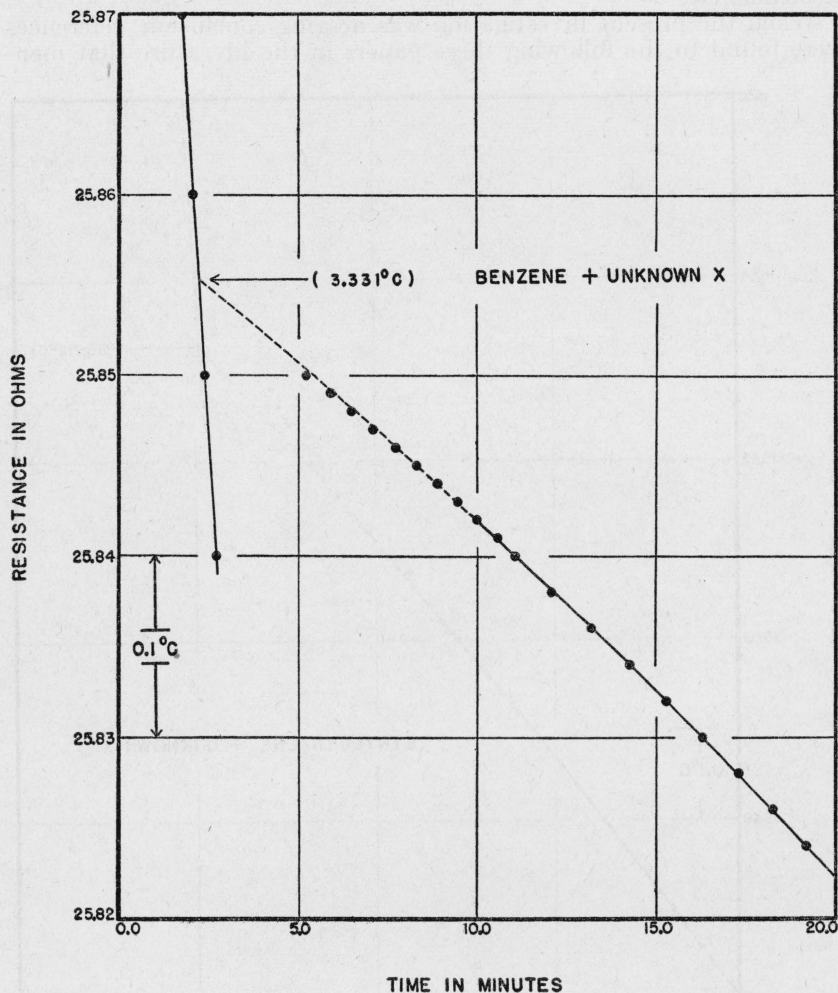


FIGURE 3.—Time-temperature freezing curve for benzene plus an "unknown" mixture of aromatic hydrocarbons.

The scale of ordinates gives the resistance of the platinum resistance thermometer in ohms. The scale of abscissas gives the time in minutes.

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