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DETERMINATION OF PURITY BY FREEZING POINT DEPRESSION. PURITY AND FREEZING POINT OF HEXADECAFLUOROHEPTANE.

V. E. Anderson and G. D. Oliver

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Title: DETERMINATION OF PURITY BY FREEZING POINT DEPRESSION. PURITY AND FREEZING POINT OF HEXADECAFLUOROHEPTANE.

Authors: V. E. Anderson and
G. D. Oliver

CARBIDE AND CARBON CHEMICALS DIVISION
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ABSTRACT

The theory, apparatus, and experimental procedure for the determination of purity by the freezing point depression method are described. The accuracy, precision, and limitations of the method are discussed.

The purities and freezing points of hexadecafluoroheptane samples are given.

DETERMINATION OF PURITY BY FREEZING POINT DEPRESSION. PURITY AND FREEZING POINT OF HEXADECAFLUOROHEPTANE.

INTRODUCTION

The success of a purification program depends upon a knowledge of the purity at successive stages of the process. Also, information pertaining to purity is desirable prior to the determination of the physical properties of a compound. Since purity data were essential for the purification of hexadecafluoroheptane, this work was an integral part of that program[1].

Although the refractive index and ebulliometric data may serve as an indication of purity, a quantitative purity result may be obtained from the freezing point method.

In this report the freezing point method, including both the theory and apparatus, is described and the results obtained on hexadecafluoroheptane are presented.

THEORETICAL BASIS FOR THE METHOD

The well known equation,

$$\Delta T = \frac{1000\ K_f\ g}{MG} \qquad (1)$$

where K_f is the cryoscopic constant
g is the weight of the solute
M is the molecular weight of the solute
G is the weight of the solvent.

expresses the relationship between freezing point depression and concentration. Provided a solution obeys the ideal solution laws, only the main component will crystallize unless the temperature is at or below the eutectic temperature; therefore, the solution becomes increasingly more concentrated as freezing progresses. If the rate of crystallization is assumed to be constant, the rate of decrease of solvent as liquid is also constant. Consequently, the lowering of the freezing point at any given time during crystallization may be expressed by the equation,

$$\Delta T = \frac{1000\ K_f\ g}{M\ (G - AX)} \qquad (2)$$

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1. Blumkin, S., N. C. Orrick, J. W. Grisard, and J. D. Gibson, "Purification of Hexadecafluoroheptane", Carbide and Carbon Chemicals Division, K-25 Plant, K-557, February 22, 1950.

2. Glasgow, Streiff, and Rossini, "Determination of the Purity of Hydrocarbons by Measurement of Freezing Points", J. Research Natl. Bur. Standards, 35, 355 (1945), RP 1676.

where A is the rate of crystallization in grams per minute and X is the freezing time in minutes. The difference ($\Delta T'$) between the temperature at the onset of crystallization and the temperature at any subsequent time during freezing is given by the equation

$$\Delta T' = \frac{1000\ K_f\ g}{M\ (G - AX)} - \frac{1000\ K_f\ g}{GM} \qquad (3)$$

For any given sample A, K_f, g, M, and G are constants. By rearrangement of terms, equation (3) may be expressed in the form:

$$\frac{\Delta T'}{X} = \frac{A}{G}\ \Delta T' + \frac{1000\ K_f\ gA}{G^2\ M} \qquad (4)$$

This equation shows that $\Delta T'/X$ is a linear function of $\Delta T'$. The rate of crystallization and number of moles of impurity are computed from the slope and intercept, respectively.

Because of supercooling, the system does not reach equilibrium immediately. Hence, some material is frozen before equilibrium is attained, the amount of unfrozen material being equal to $G - AX_1$, where X_1 is the number of minutes required to attain equilibrium. X_1 can be determined accurately by visual inspection as the slope of the liquid cooling curve is very steep in comparison to the slope of the freezing curve at the onset of crystallization. In this case the slope of the line represented by equation (4) will be equal to $\frac{A}{G - AX_1}$ and the intercept $\frac{1000\ K_f\ gA}{(G - AX_1)^2 M}$.

The above derivation assumes the rate of crystallization to be constant. This assumption is usually valid; but the rate of crystallization will change with time if the material has a large K_f, a relatively high impurity, and a small temperature head.

Correction for a Variable Crystallization Rate

This laboratory has found that by treating the rate of crystallization as a variable instead of a constant, equation (4) will still be applicable.

$$\frac{\Delta T'}{X} = \frac{1000\ K_f gR}{MG^2} + \frac{R\ \Delta T'}{G} \qquad (5)$$

where R is the rate of crystallization.

If the rate of crystallization is assumed to be directly proportional to the temperature head, then

$$\frac{A}{H} = \frac{R}{Z} \qquad (6)$$

where A is the rate of crystallization at the onset of crystallization.
R is the rate of crystallization at X time.
H is the head of temperature at the onset of crystallization.
Z is the head of temperature at X time.

Equation (5) can now be written

$$\frac{\Delta T'}{X} = \frac{1000\ K_f\ gA\ \frac{Z}{H}}{MG^2} + \frac{A\ \frac{Z}{H}\ \Delta T'}{G} \qquad (7)$$

Plots of $\frac{\Delta T'}{X}$ vs. $\frac{Z}{H}$ and $\frac{Z}{H}$ vs. $\frac{Z}{H}\ \Delta T'$ give two straight lines. The constants $\frac{1000\ K_f\ gA}{MG^2}$ and $\frac{A}{G}$ are obtained by picking two values of $\frac{\Delta T'}{X}$ and $\frac{Z}{H}\ \Delta T'$ corresponding to any two values of $\frac{Z}{H}$ from the above straight lines and substituting in equation (7).

The accuracy is a direct function of the purity since dilute solutions obey Raoult's law more closely than concentrated ones; however, the precision decreases as the purity increases which is partially due to larger percentage errors in temperature measurements. Thus, there will be a region (dependent upon the K_f) where the purity can be obtained with optimum accuracy and precision.

Accuracy and Precision

The precision and accuracy can be evaluated from a plot (see figure 3) of the impurity vs. freezing point. Equation (1) can be written in the following form:

$$\Delta\ T = -\frac{K_f}{M_1}\ \frac{1000\ g\ M_1}{M_2 G} + T_o \qquad (8)$$

where T is the freezing point of the solution
T_o is the freezing point of the main component
M_1 is the molecular weight of the main component
M_2 is the molecular weight of the impurity.

A plot of T vs. $\frac{1000\ g\ M_1}{M_2 G}$ will give a straight line with a slope equal to $-\frac{K_f}{M_1}$. Observing the deviations of a given set of data points from a line drawn through the points with slope $-\frac{K_f}{M_1}$ will give information concerning the accuracy and precision. The randomness of distribution of the points about the line will be a test of the precision, while any trend of the points to deviate from linearity will be an indication of the inaccuracy.

Although this method enables one to make a quantitative estimate of the impurity in mole percent, no information pertaining to the kind, number, or relative proportions present can be gathered. Also, the impurity must be liquid-soluble, solid-insoluble or the results will be erroneous. If the freezing point of the pure material is known, it is necessary to measure only the freezing point of the sample to determine the purity. However, since the freezing point of a solution often cannot be determined accurately without the aid of a freezing curve, especially with much supercooling, this method is of value even though the freezing point of the pure material is known.

APPARATUS AND PROCEDURE

The apparatus consists of a double-walled freezing tube, ring stirrer and motor, high vacuum pump, platinum resistance thermometer, Mueller Bridge, and electric timer.

The freezing tube was surrounded by a silvered jacket which could be evacuated and maintained at any desired pressure. The rate of freezing was controlled by the pressure in the jacket. A high vacuum pump, connected to the tube by a ball and socket joint, was used for evacuating the system. Stirring was effected by means of a ring stirrer which operated with a reciprocating vertical stroke. Temperature measurements were made with a platinum resistance thermometer in conjunction with a Mueller Bridge. In most cases the refrigerant was a slush of trichloroethylene and solid carbon dioxide; liquid nitrogen was used for lower freezing points.

At the beginning of a run, 50 cc. of sample was weighed into the tube, the thermometer clamped into position, and a slow steady stream of nitrogen passed over the material to prevent condensation of water in the tube. After immersing the tube in the refrigerating bath, the sample cooled to approximately 10° above the freezing point, then the desired cooling rate was obtained by evacuation of the jacket. Temperature readings were recorded at one minute intervals until the stirrer showed signs of laboring; at that time the frozen material usually constituted 1/3 to 1/2 of the total. After stirring ceased, the liquid and solid were no longer in equilibrium; therefore, further temperature measurements were not read. The data were plotted and the impurity calculated by the procedure given previously. If the plots showed the data to be unsatisfactory, i.e., non-attainment of equilibrium for a sufficient period of time, the experiment was repeated using a different cooling rate and/or a different stirring rate.

PURITY RESULTS ON HEXADECAFLUOROHEPTANE

Measurements were made on a series of samples throughout the purification of hexadecafluoroheptane. The K_f was determined by measuring the freezing point depression and by the addition of Freon-113 or chlorotrifluoroethylene polymer of known molecular weight to a sample of hexadecafluoroheptane whose freezing point was known.

Plots of the temperature, expressed in resistance, vs. time, in minutes, and of the temperature difference divided by time vs. temperature difference are shown in figures 1 and 2, respectively, for a sample of hexadecafluoroheptane. By using these plots and equation (4), the purity was calculated to be 99.47 mole percent and the freezing point -51.90°C.

The bias of the experimental method of measuring the purity of hexadecafluoroheptane samples ranges from approximately -40% at 0.25 mole percent to + 4% at 7 mole percent as shown in figure 3. An estimation of the precision of the method may be obtained from the work of Glasgow, Strieff, and Rossini[2].

SUMMARY

A procedure has been described for determining the purity of compounds in mole percent. A method correcting for the change in the rate of crystallization caused by a variable temperature head has been outlined. The results are presented on a series of hexadecafluoroheptane samples obtained during the process of purification and an estimate of the precision is made.

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NOTEBOOK REFERENCES

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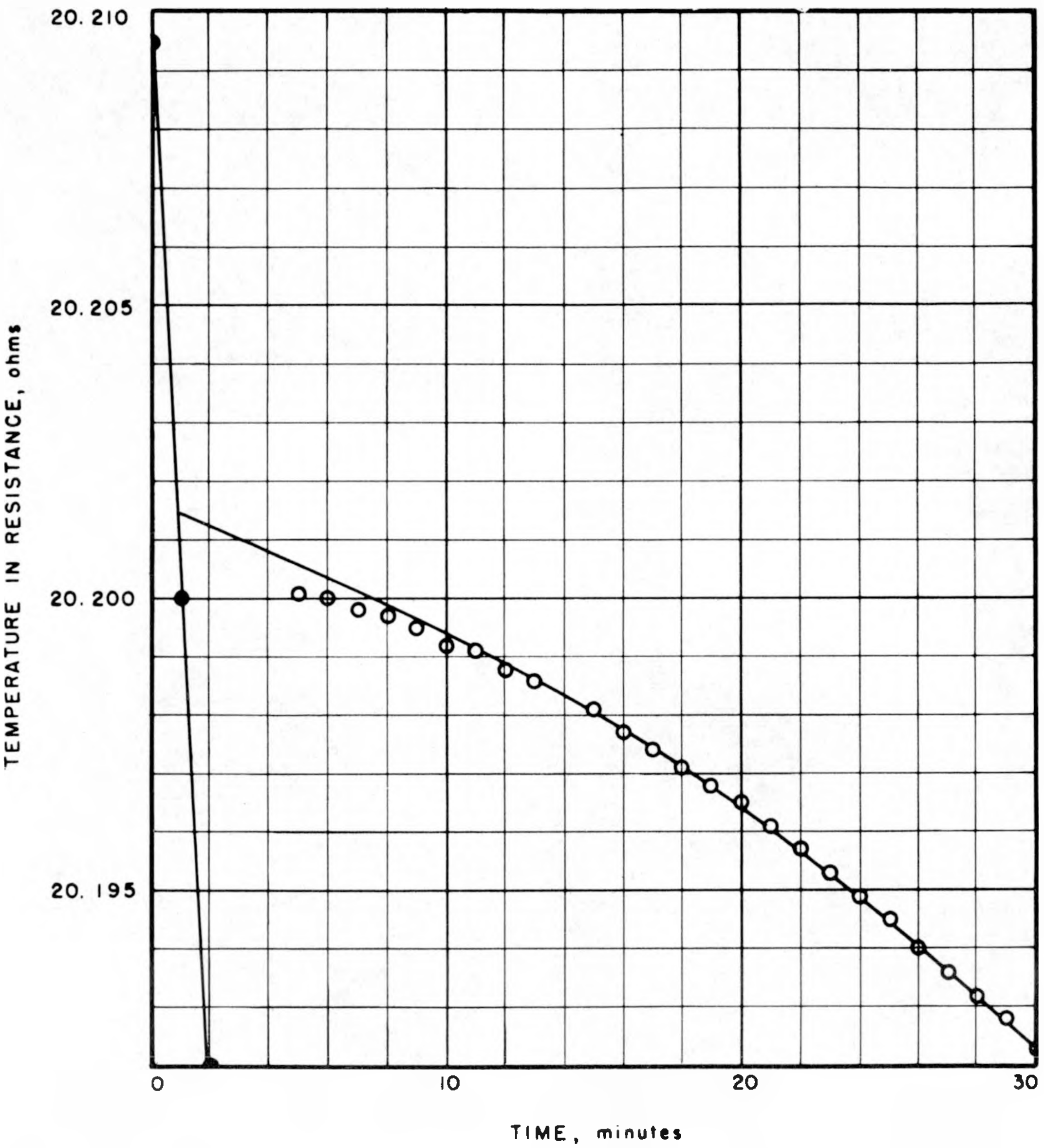
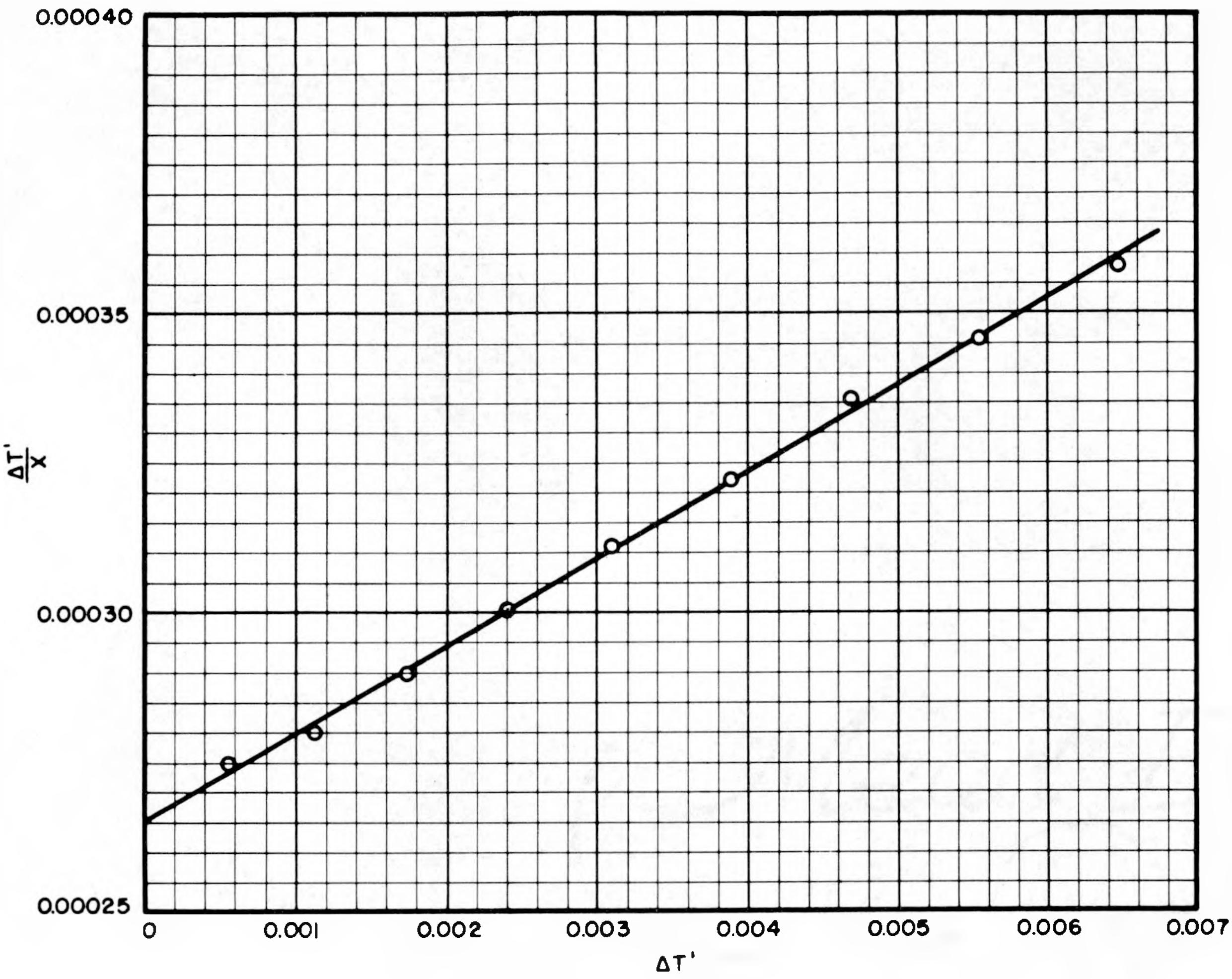


HEXADECAFLUOROHEPTANE FREEZING CURVE

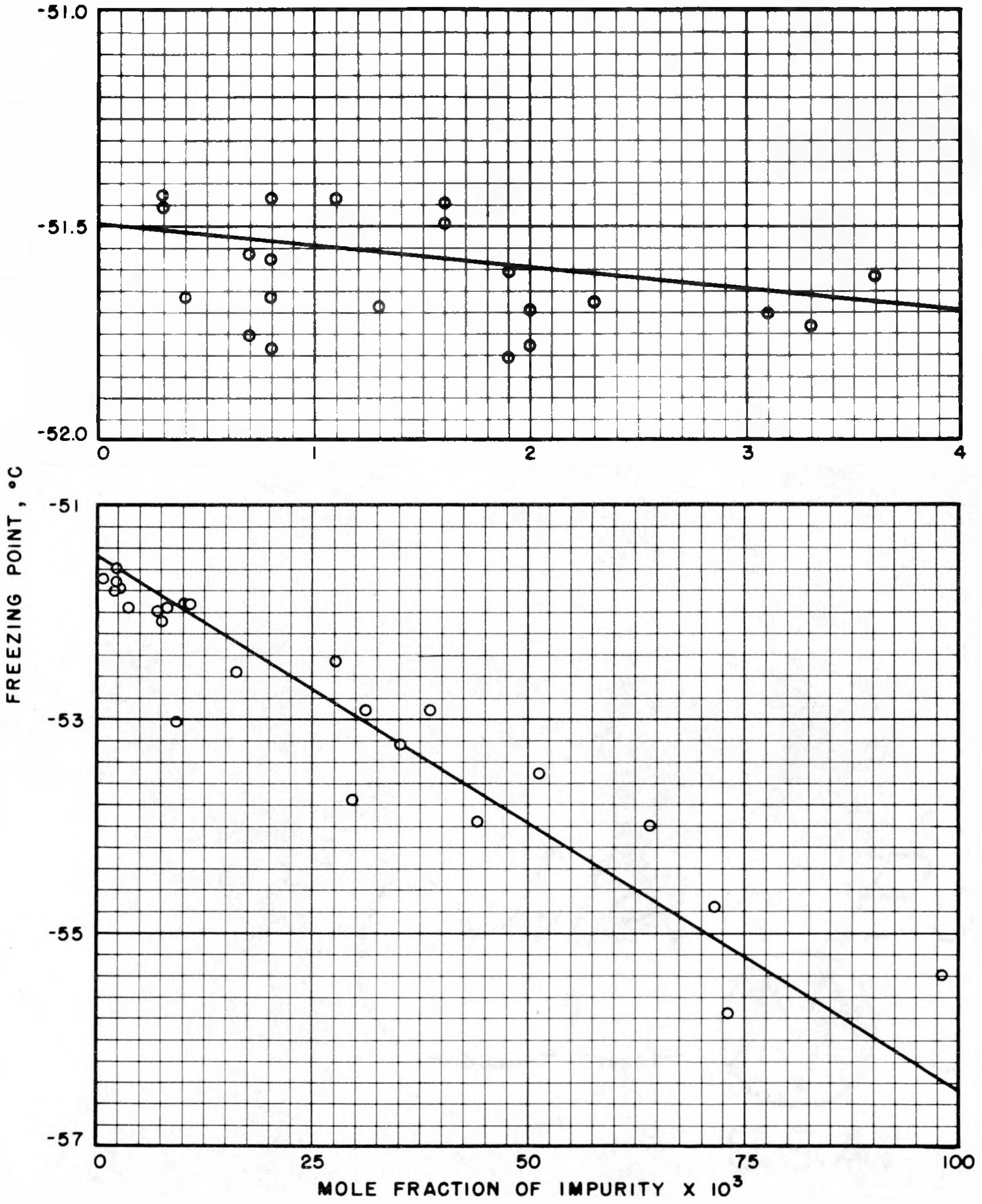
FIGURE 1

Ryder VEA
LDC-B-1050
1-13-50



TEMPERATURE DIFFERENCE DIVIDED BY TIME AS A FUNCTION OF TEMPERATURE DIFFERENCE

FIGURE 2



IMPURITY AS A FUNCTION OF FREEZING POINT
ON SAMPLES OF HEXADECAFLUOROHEPTANE

FIGURE 3

VEA
LDC-C-757
1-18-50