[CONTRIBUTIONS FROM THE JET PROPULSION LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

The Critical Point of Nitromethane

BY D. N. GRIFFIN

Introduction

Up to the present time only calculated values have been available for the critical temperature of nitromethane. The critical point of nitromethane has now been determined experimentally.

Methods for obtaining calculated values for the critical constants are based on other physical constants such as boiling points, surface tensions, and molecular weights. Guldberg[1] and Guye[2] proposed the following rule for obtaining the approximate critical temperature from the boiling point of a substance

$$T_b = 2/3(T_c) \qquad (1)$$

where T_b is the absolute boiling point and T_c the absolute critical temperature. Ramsay and Shields[3] proposed the equation

$$\gamma(Mv)^{2/3} = K(t_c - t\ 6) \qquad (2)$$

where γ is the surface tension, M the molecular weight, v the specific volume, K a universal constant, t_c (°C.) the critical temperature, and t (°C.) the ambient temperature. Boyd and Copeland[4] used the Ramsay–Shields equation in conjunction with their own data on the surface tension of nitromethane and obtained a critical temperature of 623°K. (350°C). Other empirical methods for determining the critical constants have been proposed to give greater accuracy than the Guldberg–Guye rule. Taft and Stareck[5] considered

$$T_f + T_b = T_c \qquad (3)$$

where T_f is the absolute freezing point, to be more useful than the Guldberg–Guye rule whereas Lautié[6] proposed

$$4(T_c/T_b) + 10(T_b/T_c) = 12.69 \qquad (4)$$

Mei-Chio Chen and Dji-Bin Hu[7] related the critical temperature to the molecular weight as well as to the boiling point in their equation

$$T_c = 10^{1.59/\sqrt{M}}T_b \qquad (5)$$

where M is the molecular weight.

The values of the critical temperature of nitromethane as given in Table I were obtained by applying equations (1) through (5).

TABLE I

COMPARISON OF VARIOUS CALCULATED VALUES OF THE CRITICAL POINT OF NITROMETHANE

Equation		T_c (°K.)	t_c (°C.)
Guldberg–Guye	(1)	562	289
Ramsay–Shields (by Boyd and Copeland)	(2)	623	350
Taft and Stareck	(3)	619	346
Lautié	(4)	640	367
Mei-Chio Chen and Dji-Bin Hu	(5)	597	324

Experimental Methods

Experimental methods of determining the critical point are based on the physical transition that takes place at the critical point. If a glass tube is partially filled with a liquid and sealed, the meniscus formed between the liquid and gas phases may be seen to disappear when the system is heated above the critical region, and will reappear when cooled back down through the critical region. The disappearance of the meniscus marks the transition of the liquid to a single gas phase at or near the critical point. Although usually sharply defined, this phenomenon does not necessarily mark the true critical point; instead, it might be considered to occur in the critical region. If the quantity of liquid placed in the tube is either too great or too small, the meniscus will disappear at a temperature below the true critical temperature. This effect is described later in this section. It has also been observed that even after the transition to a single gas phase at the apparent critical point, the density of the gas is not uniform throughout the tube but remains greater in the lower portions. Winkler and Maass[8] reported that the density difference for a fixed available space decreases with a rise in temperature, but is measurable up to at least 10° above the critical point.

When a pure liquid and its vapor co-exist in a closed system, the pressure exerted at a given temperature, that is, the vapor pressure of the liquid at that temperature, is independent of the total quantity of the substance present. Above the critical point, only one phase can exist; hence the pressure, at constant volume, will vary according to the quantity of the substance present. These facts may be applied to the determination of critical constants.

If a plot is made of pressure *vs.* temperature for a sample heated in a constant-volume system, a point of discontinuity in the curve will mark the transition from a liquid–vapor system to a single-phase system. However, this point of discontinuity will correspond to the critical point only if the proper size of sample is used, for if a sample of insufficient size is chosen, it will pass entirely into the vapor phase at some temperature below the critical temperature. Similarly, if a sample is too large, it will expand and entirely fill the tube with liquid before the critical point is reached. If the proper size of sample is chosen, the densities of the liquid and vapor phases become equal at the critical point, and they become a single phase without any discontinuity appearing in the pressure–temperature curve. This density is known as the critical density. Because of the indefiniteness of the point of discontinuity near the critical point, it is necessary to interpolate to the critical density by choosing samples having mean bulk densities both greater and less than the critical density.

Ipatieff and Monroe[9] used the bomb technique to determine the critical points for several substances. To obtain the critical point, they plotted pressure *vs.* temperature. The resultant curve gave a region of discontinuity in the critical region. They stated that they observed no effect

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[1] Guldberg, *Z. physik. Chem.*, **5**, 374 (1890).

[2] Guye, *Bull. soc. chim.*, **4**, 262 (1890).

[3] Ramsay and Shields, *Z. physik. Chem.*, **12**, 433 (1893).

[4] Boyd and Copeland, THIS JOURNAL, **64**, 2540 (1942).

[5] Taft and Stareck, *J. Phys. Chem.*, **34**, 2307 (1930).

[6] Lautié, *Bull. soc. chim.*, **2**, 2234 (1935).

[7] Mei-Chio Chen and Dji-Bin Hu, *J. Chinese Chem. Soc.*, **10**, 212 1943).

[8] Winkler and Maass, *Can. J. Res.*, **9**, 613 (1933).

[9] Ipatieff and Monroe, *Ind. Eng. Chem., Anal. Ed.*, **14**, 171 (1942).

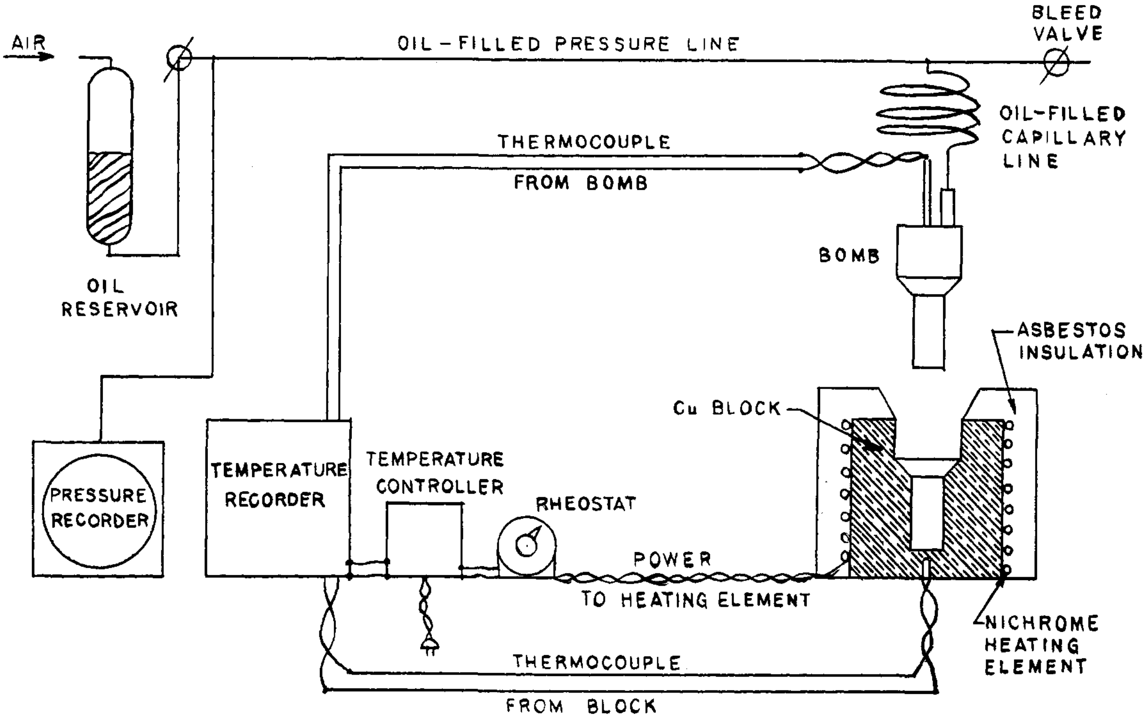

Fig. 1.—Diagram of thermal decomposition apparatus.

when the size of sample was varied, but their method of representing the data graphically failed to show the actual point of discontinuity in each case.

The bomb technique was also used to obtain the critical point of nitromethane. A plot was made of log p *vs.* $1/T$ for each test and compared with a similar plot of the vapor pressure of nitromethane. In each case, a straight line was produced, corresponding to the vapor pressure up to a point at which a sharp break occurred indicating a transition to a single-phase system. The temperature at which the break occurred, and the nature of the curve above that temperature, depended upon the size of the sample used. A plot was then made of these transition points *vs.* sample size. A maximum in the curve occurred at 315°, which was considered to be the true critical temperature t_c. The critical density d_c was obtained from the weight of the sample at this point, and the volume of the bomb, whereas the vapor pressure corresponding to the critical temperature was the critical pressure p_c.

Description of Data and Results

Samples of purified nitromethane, varying from 1.5 to 3.5 ml. in volume (1.71 to 3.98 g.), were placed in a stainless-steel bomb having an internal volume of 8.2 ml., and were heated by means of an electrically heated copper block into which the bomb fitted (Fig. 1). The temperature was recorded by a thermocouple located within the bomb and attached to a Leeds and Northrup Micromax recording potentiometer. The pressure was recorded by a Brown Bourdon-type recording gage connected to the bomb by an oil-filled capillary line.

The data used for the vapor pressure of nitromethane were experimental values obtained in work done in the Department of Chemical Engineering of the California Institute of Technology.[10] Experimental values were obtained to above 500 p.s.i.a.; hence extrapolated values up to the critical point were considered valid (Fig. 2).

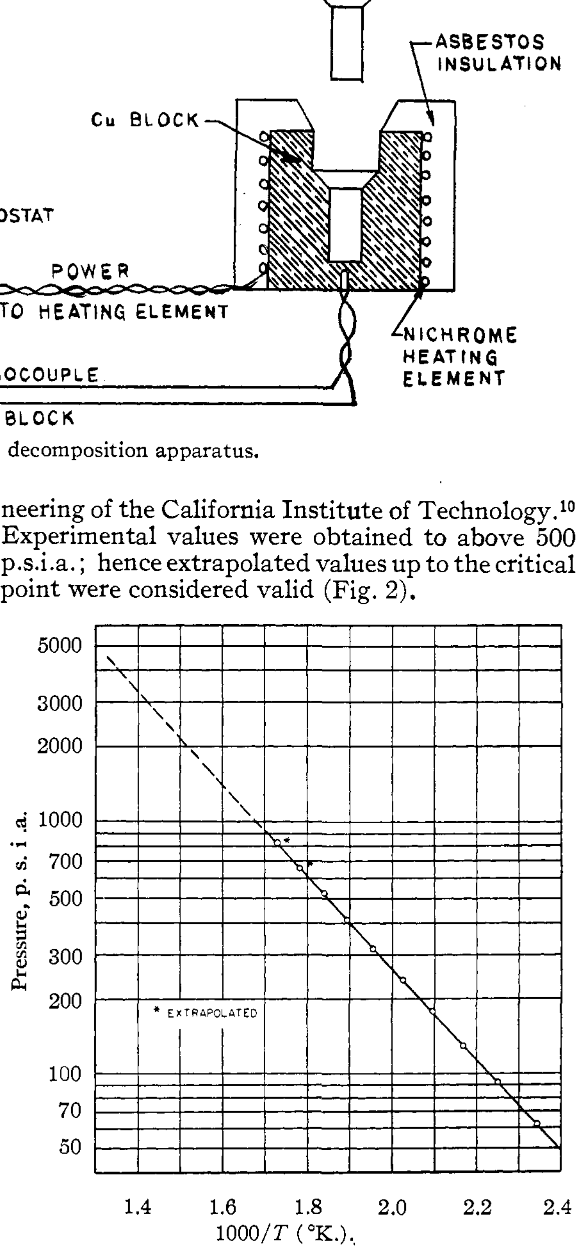

Fig. 2.—Vapor pressure of nitromethane.

When log p was plotted against $1/T$ for samples

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(10) Unpublished data.

between 1.5 and 2.3 ml. in volume (1.17 and 2.62 g.), the curve at the temperatures above the transition point fell below the vapor pressure line, indicating that all the sample in each case passed into the vapor phase before the critical temperature was reached (Fig. 3). Thus the samples were too small; *i.e.*, the mean bulk densities were less than the critical density for nitromethane. In the case of samples between 2.6 and 3.5 ml. in volume (2.96 and 3.98 g.), the pressures developed above the transition point were in excess of the extrapolated vapor pressure, indicating that the internal volume of the apparatus was entirely filled with expanded liquid (Fig. 4). These samples were therefore too large; *i.e.*, the mean bulk densities were greater than the critical density. A 2.5 ml. (2.84-g.) sample was used, and the resultant log p *vs.* $1/T$ curve showed only a slight deflection in the critical region and had the maximum observed temperature of the transition point (Fig. 5). The mean bulk density of this sample was therefore nearly equal to the critical density.

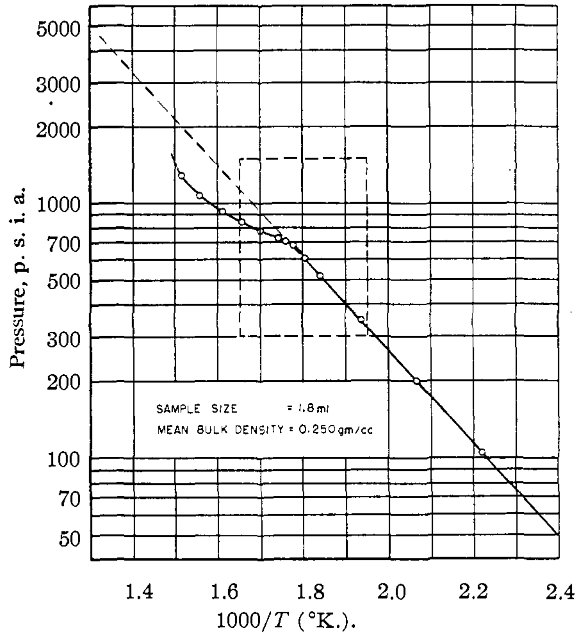

Fig. 3.—Pressure effect in critical region of sample of nitromethane having mean bulk density less than critical density.

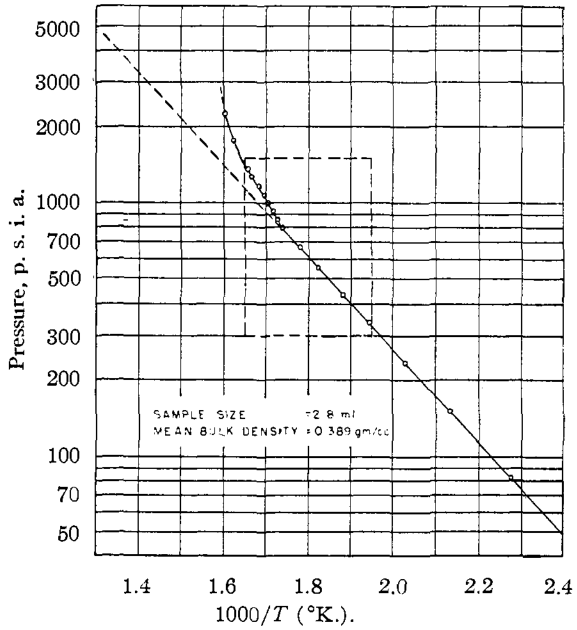

Fig. 4.—Pressure effect in critical region of sample of nitromethane having mean bulk density greater than critical density.

At temperatures above the critical temperature, slow decomposition of the nitromethane caused an upward trend in the log p *vs.* $1/T$ curves irrespective of the size of the samples used. This effect is evident in Figs. 3, 4 and 5.

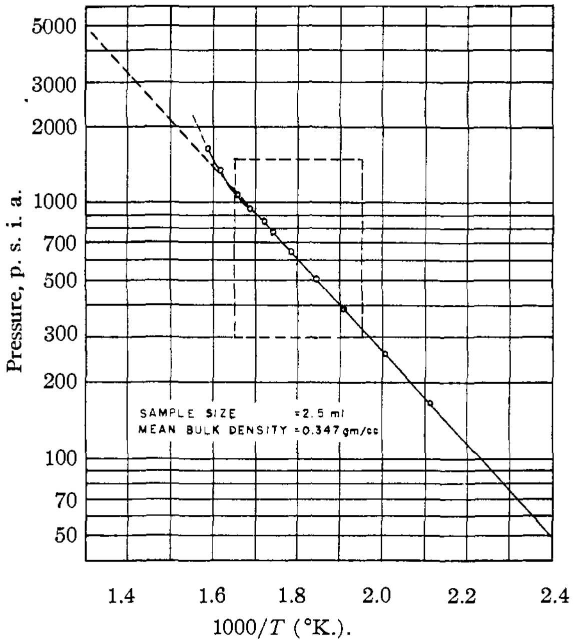

Fig. 5.—Pressure effect in critical region of sample of nitromethane having mean bulk density nearly equal to critical density.

To obtain the true critical point, a plot was made of the temperature of the transition points *vs.* sample size (Fig. 6). The maximum in the curve occurred at 315° (588°K.) and at a sample size of 2.535 ml. (2.885 g.). This point gives a critical temperature of 315° and a critical density of 0.352 g./cc. The critical pressure, which corresponds to the vapor pressure at the critical temperature, is 915 p.s.i.a.

Summary

This method offers a means of determining graphically the values for t_c, p_c and d_c for liquids

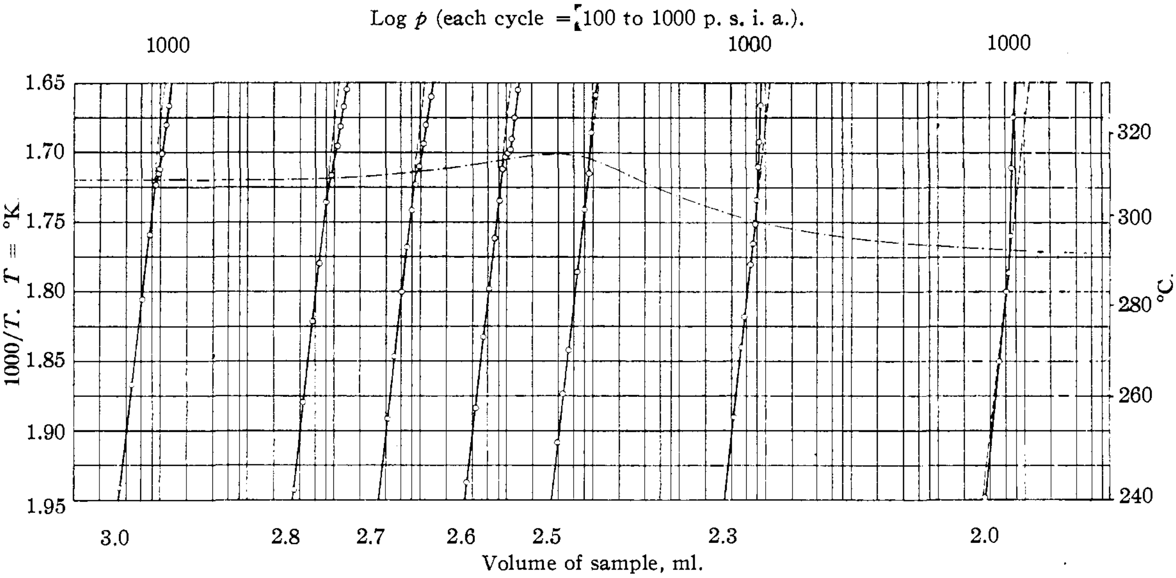

Fig. 6.—Critical point of nitromethane, obtained by interpolating to maximum of critical region: – – – – –, vapor pressure of NM (extrapolated); ——, experimental data; —·—·—·—, linear plot of points of deviation.

having high critical temperatures. It is apparently limited in accuracy only by the accuracy of the instruments used in measuring temperature and pressure.

The following critical constants were obtained for nitromethane: $t_c = 315 \pm 1°$, $p_c = 915 = \pm 15$ p.s.i.a., and $d_c = 0.352 \pm 0.004$ g./cc.

Pasadena, California Received October 22, 1948

[Contribution No. 253 from the Chemical Department, Experimental Station, E. I. du Pont de Nemours & Co.]

The Structure of Neoprene. II.[1] Determination of End-Groups by Means of Radiosulfur

By W. E. Mochel and J. H. Peterson

It is now generally agreed that in the free radical polymerization of vinyl compounds and dienes, fragments of the initiator become combined as end-groups in the polymer molecules.[2] The polymerization catalysts, so-called, are compounds that decompose under polymerization conditions to form free radicals, which in turn become the true, primary initiators. In some cases it has been postulated, on the basis of kinetics studies, that the catalyst first combines with the monomer to produce a complex which subsequently rearranges to an activated molecule,[3] but the structure of the resulting polymer would also involve the catalyst or some fragment as a terminal group. However, not all polymer molecules need have the primary initiator as an end-group. For example, it has recently been demonstrated[4] that the mercaptans used as regulators, or modifiers, particularly in diene polymerizations, are chain transfer agents[5] which likewise become attached as end-groups on the polymer molecules. Other possibilities must also be considered, such as chain transfer with monomer and termination of two chains by mutual interaction without combination[6] to yield additional types of end-groups.

Determination of the end-groups in neoprene (polychloroprene) was therefore undertaken to obtain further knowledge about the structure and formation of this synthetic elastomer. The general purpose chloroprene polymer, Neoprene

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(1) Part I, Mochel, Nichols and Mighton, This Journal, **70**, 2185 (1948).

(2) Kamenskaya and Medvedev, *Acta Physicochim., U. R. S. S.*, **13**, 576 (1940); Price and co-workers, This Journal, **63**, 2798 (1941); **64**, 1103, 2508 (1942); **65**, 517 (1943); Kern and Kammerer, *J. prakt. Chem.*, **161**, 81 (1942); Bartlett and co-workers, This Journal, **65**, 543 (1943); **67**, 812, 816 (1945); Blomquist, Johnson and Sykes, *ibid.*, **65**, 2446 (1943); Pfann, Williams and Mark, *J. Polymer Sci.*, **1**, 14 (1946).

(3) Schulz and Staudinger, *Z. physik. Chem.*, **39B**, 246 (1938); Cuthbertson, Gee and Rideal, *Proc. Roy. Soc. (London)*, **A170**, 300 (1939); Schulz and Blaschke, *Z. physik. Chem.*, **B51**, 75 (1942).

(4) Price and Adams, This Journal, **67**, 1674 (1945); Snyder, Stewart, Allen and Dearborn, *ibid.*, **68**, 1422 (1946); Wall, Banes, and Sands, *ibid.*, **68**, 1429 (1946); Smith, *ibid.*, **68**, 2059, *et seq.* (1946); Kolthoff and Harris, *J. Polymer Sci.*, **2**, 41, *et seq.* (1947).

(5) Flory, This Journal, **59**, 241 (1937); Mayo, *ibid.*, **65**, 2324 (1943).

(6) Melville, *J. Chem. Soc.*, 274 (1947); Burnett and Melville, *Nature*, **156**, 661 (1945); Flory, This Journal, **59**, 251 (1937).