[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE DEFENSE RESEARCH LABORATORY OF THE UNIVERSITY OF TEXAS]

Some Vapor Pressures and the Critical Constants of Trimethylamine

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Introduction

This laboratory has been interested[1] for some time in the thermodynamic properties of the methylamines. The data on trimethylamine are particularly meager. Only one investigation on the critical constants of trimethylamine is recorded and only certain ranges of temperature are covered by vapor pressure determinations. Hence, the purpose of this investigation was the complete determination of the critical data and the vapor pressures from 60° up to the critical point for this substance.

Previous Investigations

The critical temperature and pressure have been determined by Vincent and Chappuis[2] as 160.5° and 41 atm., respectively. No critical density datum is given. Simon and Huter[3] present a vapor pressure equation for the temperature range −90 to +12°. Thompson and Linnett,[4] as an incidental investigation, gave data for the range −6 to +11°. Aston, Sagenkahn, Szasz, Moessen and Zuhr[5] reported for the range −73 to +5°, and Swift and Hochanadel[6] covered the range 0 to 40° in their measurements. The data of Simon and Huter, of Aston, *et al.*, and of Swift and Hochanadel seem to cover adequately the range −90 to +40°.

In the investigation here reported, all pressure measurements were made with a dead-weight piston gage; because of the lower limit of about 5 atmospheres of the gage, measurements of the vapor pressure of trimethylamine were, of necessity, restricted to the range above 60°.

Method and Apparatus

The dead-weight piston gage has been described elsewhere.[7] Thermostat temperatures were controlled to ±0.005° by means of a platinum resistance thermometer in conjunction with a photoelectric cell relay and a Mueller bridge. The actual thermostat temperatures were simultaneously measured by this same resistance thermometer, recently calibrated by the National Bureau of Standards. Various-sized samples of liquid trimethylamine were introduced in the usual manner[7] into the glass liner and into the pressure bomb.

Five separate samples of trimethylamine were subjected to vapor pressure measurements. These vapor pressure determinations were made at different relative values of liquid and vapor volumes. At the lower temperatures, the vapor pressures were independent of volume over a fairly large range. But in the critical region (150° and above), the vapor pressures did depend slightly upon volume, becoming larger as the volume decreased. This change, however, was never greater than 0.2% of the value of the vapor pressure, indicating the presence of only a very small amount of impurity.

In the determination of the critical constants, the usual procedures[8] for the determination of compressibility isotherms were followed. Such isotherms were determined below and above the critical temperature, based upon some two hundred individual measurements in both the vapor and liquid regions.

Material Used

The trimethylamine was prepared from Eastman Kodak Co. trimethylamine hydrochloride, purified by the method described by Arthur and Felsing.[1j] The gaseous amine was liberated in an appropriate generator[9] by the treatment of the purified salts with an excess of 50% potassium hydroxide solution.

The liberated gas was passed through a "Drierite" column into a steel cylinder containing sodium ribbon. After twenty-four to forty-eight hours contact, the cylinder and contents were cooled to −78° and the hydrogen and air were removed by evacuation. The amine was distilled into the glass reservoir portion of the system, about one-fifth of the liquid amine being withdrawn by the vacuum pump. The remainder was distilled under vacuum into individual glass liners for the pressure bomb.

The Experimental Data

The vapor pressure data are presented in Table I.

TABLE I

EXPERIMENTAL VAPOR PRESSURES OF TRIMETHYLAMINE

Temp., °C.	Vapor press., mm.	Temp., °C.	Vapor press., mm.
60	4,393	140	22,037
70	5,587	150	25,972
80	7,015	155	28,155
90	8,703	158	29,547
100	10,682	159.5	30,266
110	12,972	160	30,507
120	15,592	160.15 Critical point	30,581
130	18,583		

The compressibility isotherms, upon which the critical constants are based, were determined at 130, 140, 150, 155, 158, 159.5, 159.9, 160.0, 160.1, 160.3 and 160.5°. The 199 individual determinations are not listed here[10]; they are presented graphically in Fig. 1, without showing the individual points on the graph.

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[1] (a) Felsing and Wohlford, THIS JOURNAL, **54**, 1442 (1932); (b) Felsing and Buckley, *J. Phys. Chem.*, **37**, 779 (1933); (c) Felsing and Jessen, THIS JOURNAL, **55**, 4418 (1933); (d) Felsing and Ashby, *ibid.*, **56**, 226 (1934); (e) Felsing and Phillips, *ibid.*, **58**, 1973 (1936); (f) Felsing and Kelso, *ibid.*, **60**, 1949 (1938); (g) Felsing and Patterson, *ibid.*, **60**, 2693 (1938); (h) Felsing and Kenner, *ibid.*, **61**, 2457 (1939); (i) Felsing and Ball, *ibid.*, **63**, 2525 (1941); (j) Arthur with Felsing, *ibid.*, **68**, 1883 (1946).

[2] Vincent and Chappuis, *Compt. rend.*, **101**, 427 (1885).

[3] Simon and Huter, *Z. Elektrochem.*, **41**, 28 (1935).

[4] Thompson and Linnett, *Trans. Faraday Soc.*, **32**, 681 (1936).

[5] Aston, *et al.*, THIS JOURNAL, **66**, 1171 (1944).

[6] Swift and Hochanadel, *ibid.*, **67**, 880 (1945).

[7] Kelso with Felsing, *ibid.*, **62**, 3132 (1940).

[8] (a) Kelso with Felsing, *ibid.*, **62**, 3132 (1940); (b) Beattie, *Proc. Am. Acad. Arts. Sci.*, **69**, 389 (1934); (c) Beattie, Ingersoll and Stockmayer, THIS JOURNAL, **64**, 546 (1942).

[9] Felsing and Thomas, *Ind. Eng. Chem.*, **21**, 1269 (1929).

[10] The complete experimental data are available from the American Documentation Institute, 1719 N Street, N. W., Washington, D. C., as Document 2724; photoprints $0.50 or microfilm $0.50.

Treatment of Data and Discussion

The vapor pressures were plotted to large scale and two vapor pressure equations were derived: one for the region 60 to 130° and the other for the region 130° to the critical point. The equations were determined by the least squares method and are found to be:

$$(1)\quad (60\text{–}130°):\ \log_{10} p\ (\text{mm.}) = -1202.2908/T + 7.250828$$

$$(2)\quad (130\text{–}160°):\ \log_{10} p\ (\text{mm.}) = -738.6065/T + 0.0029426\ T + 4.914884$$

where $T = 273.16 + t°$ C. The r. m. s. deviation of the calculated from the observed values using Eq. (1) is 0.089%; using Eq. (2), it is 0.026%.

The equation proposed by Swift and Hochanadel[6] for the range 0 to 40° also reproduces well our value at 60°.

The compressibility data above and below the critical point were plotted to very large scale; Fig. 1 is an exact copy except that the individual points are not reproduced. As an aid in establishing the critical volume use was made of the Cailletet and Mathias rule of rectilinear diameters; based upon the data of 158° and above, the equation becomes

$$(v_l + v_g)/2 = 26.308 - 0.13758t$$

where v_l and v_g are the specific volumes in ml./g. The following critical constants were obtained from the large scale graph: $t_c = 160.15 \pm 0.10°$; $p_c = 40.24 \pm 0.05$ atm. and $v_c = 4.28 \pm 0.05$ ml./g.

The liquid phase compressibilities and some compressibility data above this critical region will be reported in a later paper.

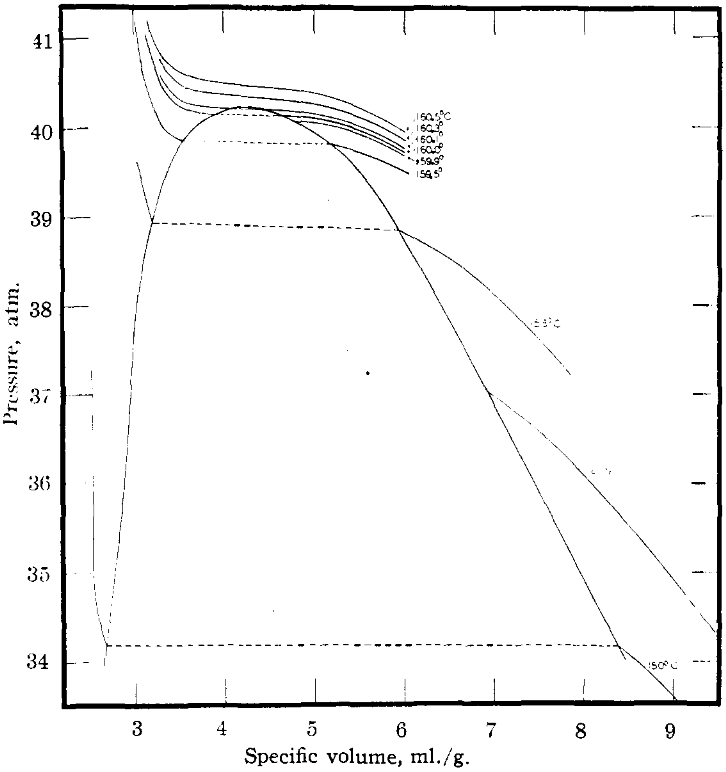

Fig. 1.—Isotherms near the critical point.

Acknowledgment.—This work was made possible by a grant from the Defense Research Laboratory, The University of Texas, under the sponsorship of the Bureau of Ordnance, Navy Department, Contract NOrd-9195.

Summary

1. Vapor pressures were determined for trimethylamine from 60° to the critical point; two equations have been established which cover the range measured.

2. Isotherm compressibility data have been determined at temperatures below and above the critical temperature. From these data the critical constants have been evaluated as $t_c = 160.15 \pm 0.10°$, $p_c = 40.24 \pm 0.05$ atm. and $v_c = 4.28 \pm 0.05$ ml./g.

AUSTIN, TEXAS RECEIVED JULY 26, 1949