

where n_i and q_i are the numbers and bond energies of the i -th bond in the molecule and $(\Delta H_A)_j$ the heat of formation of the j -th gaseous atoms produced by complete decomposition of the compound. The bond energies for C—NO₂ were calculated from the heat of formation of C(NO₂)₄(3) assuming that the bond energies in both molecules, CNF and C(NO₂), are approximately the same. The difference of the two heats of formation, the measured one - 5.57 kcal./mole and the estimated one ± 0 kcal./mole, is probably due to the fact that the C—Cl bond is influenced by the three nitro groups and vice versa. Using the same bond energies for C—NO₂ in CNF as in C(NO₂)₄, the bond energy for Cl—C in CNF was calculated from the measured heat of formation to be 72.8 kcal./mole as compared with 78.3 kcal./mole for the reported value (10).

Probably the largest source of error is the determination of the arsenic oxide formed by converting Cl₂ in Cl. Another source of error is the estimation of the nitric acid formed from the CNF compound besides the nitric acid formed by oxidation of nitrogen. Some data are still unavailable on the combustion of chlorine compounds in the presence of arsenious acid. If these errors lie in the range of 5 cal. per mole, the heat of formation changes approximately within 1 kcal./mole.

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Compressibilities of Liquid Methyl Borate

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No liquid density data for methyl borate has been reported other than some orthobaric values. The present work measured compressibilities of liquid methyl borate from 180 to 209.79° C. and pressures from 17.00 to 40.00 atmospheres.

VAPOR PRESSURES of methyl borate have been measured by Webster and Dennis (7), Hansen and Hughes (4), and Griskey, Gorgas, and Canjar (3). The third set of investigators also measured compressibilities of the superheated vapor. No liquid density data were reported other than some orthobaric densities given by Hansen and Hughes (4).

The present work used an apparatus that was a modification of the design of Keyes (5) and Beattie (1). A detailed description of the apparatus has been published by Cherney, Marchman, and York (2) except for certain changes reported by Li and Canjar (6).

The methyl borate was prepared from 99.9% pure material in the apparatus depicted in Figure 1. A third of the material was distilled in the presence of sodium from flask B to flask 2 where it was condensed. Next, the middle third of the original sample was distilled and

condensed in flask 3. This portion was solidified by a dry ice-acetone mixture, evacuated, melted, resolidified, again evacuated, and melted once more. The sample was then transferred to ampules (4, 5), condensed by the dry ice-acetone mixture, evacuated, solidified, and sealed.

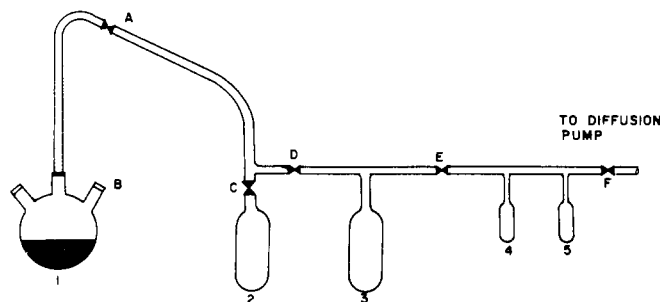


Figure 1. Methyl borate charging apparatus

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Table I. Methyl Borate Liquid Compressibility Data

Temp., °C.	Press., Atm.	Density,
		Gram Moles/Liter
180.00	17.00	5.380
	20.00	5.408
	25.00	5.445
	30.00	5.476
	35.00	5.504
202.17	40.00	5.530
	25.00	4.821
	30.00	4.899
	35.00	4.975
209.79	40.00	5.031
	28.50	4.597
	30.00	4.647
	35.00	4.754
	40.00	4.824

The compressibility data are given in Table I. No comparison is possible since no other such data exist.

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Pressure-Volume-Temperature Behavior of Methyl Alcohol in the Gaseous and Liquid States

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P-V-T data available in the literature for methyl alcohol have been used to develop a reduced density correlation for this substance. The critical constants used are those determined by Young (22): $T_c = 513.2^\circ \text{K.}$, $P_c = 78.50 \text{ atm.}$, and $\rho_c = 0.272 \text{ gram/cc.}$ In order to extend the *P-V-T* information for methyl alcohol over the complete range of temperatures up to $T_R = 2.0$ and pressures up to $P_R = 40$, the Nelson-Obert compressibility factor charts (14) and the available reduced density correlations for water (21) and ammonia (6) have been used. The resulting reduced density plots for methyl alcohol are capable of reproducing experimental values within 1.1%.

CONTINUED INTEREST in the transport and thermodynamic properties of polar and nonpolar substances requires that their *P-V-T* behavior be accurately known over a wide range of temperatures and pressures. Lydersen, Greenkorn, and Hougen (13) have made an extensive study using 82 different substances, and they have utilized the critical compressibility factor, z_c , as the third correlating parameter in order to represent the *P-V-T* behavior of both polar and nonpolar substances. In their studies, they classified all substances in the following four categories: $0.28 < z_c < 0.30$, $0.26 < z_c < 0.28$, $0.24 < z_c < 0.26$, and $z_c = 0.231$, to represent the *P-V-T* behavior of water which is highly polar and exhibits strong hydrogen bonding tendencies. Despite the fact that the critical compressibility factor has been applied extensively for the correlation of the *P-V-T* behavior of substances, little effort has been made to extend these studies to polar substances having values of $z_c < 0.231$, and particularly in the compressed gaseous and liquid regions. In this regard, methyl alcohol with $z_c = 0.219$ represents a polar molecule with strong hydrogen bonding tendencies.

Hobson and Weber (10) produced unique saturation density envelopes for substances having similar z_c values. Their conclusions are well demonstrated for a number of substances having values ranging from $z_c = 0.219$ for methyl

alcohol to $z_c = 0.291$ for nitrogen. Hall and Ibele (7), in their compressibility studies of polar gases, introduced the dipole moment as an additional parameter to account for the polar contributions of molecules, and they developed correction charts to account for the deviation from a standard compressibility chart obtained from the *P-V-T* data of the rare gases. Lydersen, Greenkorn, and Hougen (13) plotted z_c values against the reduced dipole moment, $\mu(P_c)^{1/2}/RT_c$, and concluded that no suitable correlation exists between these variables.

Thodos and coworkers comprehensively investigated the *P-V-T* behavior of substances of similar critical compressibility factors. For the monatomic gases, argon, krypton, and xenon (9), and the diatomic gases, nitrogen, oxygen, and carbon monoxide (3), the critical compressibility factor of which ranges from $z_c = 0.290$ for xenon to $z_c = 0.294$ for carbon monoxide, a single correlation of reduced density vs. reduced temperature, with constant reduced pressure as a parameter, applies equally well for the dense gaseous and liquid states. Similar reduced density correlations have been developed specifically for carbon dioxide (11), ammonia (6), and water (21) having z_c values of 0.275, 0.242, and 0.231, respectively.

To cover the complete spectrum of *P-V-T* behavior, methyl alcohol, with $z_c = 0.219$, was selected for investiga-