Measurement of the Volumetric Properties of a Nitrogen–Methane–Ethane Mixture at 275, 310, and 345 K at Pressures to 60 MPa

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The volumetric properties of a nitrogen–methane–ethane mixture are determined experimentally by a Burnett apparatus at 275, 310, and 345 K at pressures to 60 MPa. Compression factors are calculated by fitting simultaneously the isothermal pressure series to the Burnett relation and the virial equation. Densities and compression factors at integral pressures are calculated from the experimental data. The composition of the mixture is 12.09 mol % nitrogen, 62.65 mol % methane, and 25.26 mol % ethane.

Burnett Apparatus

The gas-phase *PVT* properties are obtained by the Burnett method (*1*) in which only temperature and pressure measurements are required. The apparatus is identical with the one described by Mollerup (*2*) and Mollerup and Angelo (*3*). The Burnett cell consists of two thick-walled vessels of unspecified volume, here approximately 125 and 275 cm^3, connected to each other by means of an expansion valve. The Burnett cell is located in a thermostat, and the larger volume is connected to the pressure measuring system by means of a diaphragm differential pressure indicator. The pressure is measured on either an oil dead-weight piston gauge or an air dead-weight piston gauge depending upon the pressure range.

The larger vessel in the Burnett apparatus is evacuated and filled with the gas or the gas mixture to be studied. After isothermal conditions are obtained, the temperature and the pressure are measured. The smaller volume is evacuated, the vacuum line is closed, the expansion valve is then opened, and the pressure is allowed to equalize between the two vessels. The temperature and pressure are measured again after isothermal conditions are obtained, which generally takes 2–4 h. Pressure is measured after the expansion valve has been closed very slowly with the diaphragm differential pressure in the nill position. The smaller volume is evacuated, and these expansions are continued until a low pressure is reached.

Reduction of Burnett Data

The result of the experiment is a series of decreasing pressures P_1, P_2, ..., P_i, ..., P_I at constant temperature. It is shown by Burnett that the pressures from an expansion series must satisfy the relation

$$Z_i/Z_j = (P_i/P_j)N^{i-j} \tag{1}$$

where N is the apparatus constant defined as

$$N = \frac{V_a + V_b}{V_a} \tag{2}$$

Table I. Compression Factors at Experimental Pressures

T = 275 K		T = 310 K		T = 345 K	
P, MPa	Z	P, MPa	Z	P, MPa	Z
60.3323	1.40133	58.8209	1.33432	60.4997	1.35183
44.3317	1.12433	45.7080	1.13031	45.7907	1.14590
21.8519	0.71643	26.4295	0.84618	30.2968	0.95534
18.7941	0.67281	23.1511	0.80801	25.6100	0.90442
13.6758	0.63289	16.9269	0.76488	19.3984	0.86322
12.5994	0.63667	15.5051	0.76377	17.2088	0.85764
10.2027	0.66691	12.2129	0.77889	13.7111	0.86103
9.55204	0.68092	11.3265	0.78746	12.3185	0.86638
7.87985	0.72676	9.07678	0.81705	9.94839	0.88123
7.37756	0.74266	8.43206	0.82737	8.96567	0.88938
6.04984	0.78753	7.55172	0.84256	7.23856	0.90621
5.64237	0.80183	6.74823	0.85737	6.52872	0.91394
4.57155	0.83992	6.25872	0.86677	5.26013	0.92879
4.24485	0.85160	5.58835	0.88004	4.73398	0.93529
3.40009	0.88178	4.97627	0.89249	3.80234	0.94722
3.14539	0.89084	4.60498	0.90018	3.41574	0.95231
2.49670	0.91380	4.09772	0.91082	2.73539	0.96145
2.30283	0.92063	3.63801	0.92058	2.45381	0.96529
1.81505	0.93771	3.36132	0.92650	1.96004	0.97211
1.67051	0.94275	2.97936	0.93472	1.75592	0.97496
1.30996	0.95526	2.63800	0.94212	1.40017	0.97996
1.20377	0.95893	2.43336	0.94656	1.25273	0.98204
0.940413	0.96799	2.15164	0.95270	0.997969	0.98566
0.863159	0.97065	1.90105	0.95818	0.892186	0.98716
0.672615	0.97717	1.75123	0.96146	0.710278	0.98976
0.616838	0.97907	1.54572	0.96597	0.634498	0.99085
0.479751	0.98375	1.36347	0.96997	0.504788	0.99271
0.439668	0.98511	1.25485	0.97235	0.450730	0.99349
0.341538	0.98844	1.10615	0.97562	0.358488	0.99482
0.312882	0.98942	0.974540	0.97852	0.319910	0.99537
0.222301	0.99249	0.896301	0.98024	0.254389	0.99632
		0.789299	0.98260	0.227040	0.99671
		0.694774	0.98468		
		0.638830	0.98591		
		0.562005	0.98761		
		0.494428	0.98910		
		0.399567	0.99119		
		0.283916	0.99374		

Several schemes for least-squares reduction of Burnett data are possible. In this work we have applied the method of Dalton et al. (*4*) but replaced the Newton–Raphson optimization routine by a Levenberg–Marquardt routine.

It is assumed that the experimental data are subject to random errors only and that the virial equation is able to accurately represent the isothermal compression factors as a function of density. Furthermore, the apparatus constant must be independent of pressure; otherwise an explicit expression for the pressure dependence must be known. In this work we have neglected the pressure dependence of the apparatus constant, as discussed elsewhere by Mollerup and Angelo (*3*).

Several isothermal expansion series can be reduced simultaneously. If we denote the number of expansion series by M and the number of expansions in series m by Im, then series m contains the pressures P^*_{1m}, P^*_{2m}, ..., P^*_{Im}.

The densities are calculated by minimizing the residual sum of squares

$$F = \sum_{m=1}^{M}\left(\sum_{i=1}^{I} w_i(P^*_i - P_i)^2\right)_m \tag{3}$$

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Table II. Parameters Determined by a Least-Squares Fit of the Experimental Pressures to the Objective Function at Pressures below 15 MPa

		av rel pressure residual	
parameter	std error	absolute	biased
T = 275 K, M = 2, Im = 15 and 16			
$B_1 = -7.70919098 \times 10^{-2}$	2.1×10^{-4}	1.9×10^{-4}	-2.0×10^{-5}
$B_2 = 4.16530923 \times 10^{-3}$	4.9×10^{-5}		
$B_3 = -1.25146299 \times 10^{-5}$	3.4×10^{-6}		
T = 310 K, M = 4, Im = 14, 7, 11, and 6			
$B_1 = -5.68611322 \times 10^{-2}$	2.8×10^{-4}	7.1×10^{-5}	-1.3×10^{-5}
$B_2 = 3.27721423 \times 10^{-3}$	8.4×10^{-5}		
$B_3 = 1.56289130 \times 10^{-5}$	7.9×10^{-6}		
T = 345 K, M = 2, Im = 16 and 16			
$B_1 = -4.15926573 \times 10^{-2}$	5.5×10^{-4}	3.7×10^{-4}	-1.4×10^{-5}
$B_2 = 2.69779585 \times 10^{-3}$	2.2×10^{-4}		
$B_3 = 5.13872163 \times 10^{-5}$	2.6×10^{-5}		

$N = 1.412825 - 4.667 \times 10^{-7} T$ (K), std error = 1.0×10^{-4}

gas constant = 8.31434 Pa·m^3/(mol·K)

Table III. Error Analysis. Maximum Error Contributions

T, K	exptl pressures, % (Pa)	data reduction, %	apparatus const, %	sum of errors, %	geometric mean, %
275	0.05 (300)	0.1	0.1	0.25	0.15
310	0.05 (300)	0.05	0.1	0.20	0.12
345	0.05 (300)	0.15	0.1	0.30	0.19

where P^*_i is the experimental pressure and P_i the calculated pressure that must satisfy the Burnett relation eq 1, that is

$$P_{im} = \frac{Z_{im}}{Z_{1m}} P_{1m} N^{1-im} \tag{4}$$

or

$$\rho_{im} = \rho_{1m} N^{1-im} \tag{5}$$

The compression factor $Z = P/\rho RT$ is calculated from the virial equation of state

$$Z_{im} = 1 + \sum_{j=1}^{J} B_j \rho_{im}^j \tag{6}$$

The parameters in the least-squares data reduction procedure are the virial coefficients B_j and, if desired, the apparatus constant N and the initial pressures P_{1m}. If the initial pressures P_{1m} are not parameters to be estimated, they are assumed to be exact and thus $P_{1m} = P^*_{1m}$. The weight factor w_i is a function of the observed pressure

$$w_i = \frac{1}{\sum_j (a_j + b_j P_i)^2} \tag{7}$$

where a_j and b_j are constants that depend on the barometer, the differential pressure indicators, and the dead-weight gauge used.

Preparation of the Gas Mixture

The gas mixture is prepared gravimetrically in a 4-L steel sample cylinder using a Voland Corporation HCE 10 balance and class S weights. The pure gases were delivered from Dansk Ilt & Brint. The purity of the nitrogen is 99.995 mol %, of methane 99.995 mol %, and of ethane 99.95 mol %. The gases were used without further purification. The prepared gas mixture contained 135.344 g of nitrogen, 401.597 g of methane, and 303.504 g of ethane. The molar composition of the gas is thus 12.09 mol % nitrogen, 62.65 mol % methane, and 25.26 mol % ethane.

Results and Discussion

Table I shows the experimental pressures and the calculated compression factors. This data reduction scheme is applied at experimental pressures up to 15 MPa. The compression factors at higher pressures are then calculated by direct application of eq 5. The apparatus constant is a weak function of the temperature determined from regression of the data and all previous data (*1*).

The parameters and standard errors of the parameters are shown in Table II.

The various error contributions are summarized in Table III. The total experimental error of the calculated compression factors may be as high as 0.3% if all errors add up. An error of 0.3% represents the worst case. If the error contributions are combined geometrically, the maximum errors are reduced by one-third. The largest errors are encountered at the highest density or in the vicinity of the minimum in the compression factors. The sum of the error contributions is the maximum error encountered and the geometric mean is the average error in the calculated compression factor.

Table IV shows calculated densities and compression factors at integral pressures up to 15 MPa.

Table IV. Interpolated Densities and Compression Factors

	T = 275 K		T = 310 K		T = 345 K	
P, MPa	density, mol/L	Z	density, mol/P	Z	density, mol/P	Z
0.1	0.04388	0.99662	0.03888	0.99779	0.03491	0.99855
0.2	0.08806	0.99324	0.07794	0.99559	0.06992	0.99710
0.4	0.17735	0.98646	0.15657	0.99118	0.14026	0.99422
1.0	0.45278	0.96595	0.39673	0.97796	0.35370	0.98563
2.5	1.1967	0.91369	1.0263	0.94511	0.90348	0.96466
5.0	2.6519	0.82462	2.1748	0.89200	1.8703	0.93198
6.0	3.3248	0.78927	2.6701	0.87184	2.2737	0.91998
7.0	4.0547	0.75506	3.1853	0.85264	2.6854	0.90876
7.5	4.4404	0.73871	3.4498	0.84348	2.8940	0.90347
8.0	4.8389	0.72307	3.7186	0.83468	3.1043	0.89842
9.0	5.6668	0.69462	4.2675	0.81824	3.5290	0.88907
10.0	6.5179	0.67101	4.8279	0.80363	3.9579	0.88083
12.5	8.5785	0.63729	6.2456	0.77651	5.0348	0.86554
15.0	10.341	0.63438	7.6181	0.76393	6.0922	0.85836

Registry No. N_2, 7727-37-9; CH_4, 74-82-8; C_2H_6, 74-84-0.

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Density, Isothermal Compressibility, and the Volume Expansion Coefficient of Liquid Chlorodifluoromethane for Temperatures of 310–400 K and Pressures up to 10 MPa

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The density measurements at given temperatures and pressures for liquid chlorodifluoromethane were carried out with the variable-volume method using a metal bellows. The results cover the high-density region from 510 to 1197 kg/m^3 along ten isotherms between 310 and 400 K for fourteen pressures from 1.5 to 10.0 MPa. The experimental uncertainty in the density measurements was estimated to be no greater than 0.2%. On the basis of the present results the density derivatives were calculated, and numerical values of the volume expansion coefficient and the isothermal compressibility are tabulated as a function of temperature and pressure.

Introduction

As a part of volumetric property measurements for the mixtures of the R 22 + R 114 system, we have measured density of liquid chlorodifluoromethane, one of the pure components of the R 22 + R 114 system, at given temperatures and pressures. The *PVTX* properties of this system in the supercritical region (*1*) and the composition dependence of critical parameters (*2*) were reported in our previous publications. In this paper, we report the experimental results of density for chlorodifluoromethane in the liquid region along ten isotherms between 310 and 400 K for fourteen pressures from 1.5 to 10.0 MPa. The values of the volume expansion coefficient and isothermal compressibility are also reported. The purity of the sample used was 99.99 wt % chlorodifluoromethane ($CHClF_2$, R 22).

Experimental Section

The density measurements of this work have been made with the variable-volume method using a metal bellows. The apparatus and experimental procedures used here were described in detail in a previous publication (*3*). A metal bellows made of stainless steel (AM 350) was chosen as a vessel in which the sample of known mass was filled and whose volume could be varied. Dimensions of the bellows were 75 mm in length, 0.15 mm in thickness, 30 mm in outer diameter, and 4.3 cm^2 in effective area. The bellows hung vertically downward in a pressure vessel made of 304 stainless steel and traveled longitudinally upward to a maximum distance of 16 mm. The volume of the bellows at the reference position was about 27 cm^3. The volume change of the bellows was detected by measuring the bellows displacement with the aid of a linear variable differential transformer with a resolution of less than 1 μm. The inner volume of the bellows and its variation with the bellows displacement were calibrated with an uncertainty of ±0.2%.

Nitrogen gas was supplied into the pressure vessel, and it surrounded the bellows. When the pressure of the nitrogen gas was increased or reduced, the bellows was compressed or expanded. The pressure of the nitrogen gas was measured with two different air-piston pressure gauges (Ruska, Models 2465 and 2470), depending on the pressure range. The precision of the two air-piston pressure gauges used was guaranteed by the supplier to be 0.015% for high pressures above 5 MPa and 0.010% for low pressures below 5 MPa, respectively. These pressure gauges were used also as the device for generating a constant pressure. Even if the bellows is held in balance, the pressure of the sample confined in the bellows is different from that of the nitrogen gas exerted on the bellows, mainly because of the reaction of the bellows against the compression. Prior to the experiments, the difference of the internal and external pressure of the bellows was calibrated in the experimental range of temperatures and pressures to be studied with an uncertainty of ±0.5 kPa. The pressure of the sample was set at the values desired within ±2 kPa.

In the body of the pressure vessel, a well was drilled for inserting a 25-Ω platinum resistance thermometer (Chino, Model R 800-2) calibrated with a precision of 2 mK on IPTS-68. The temperature was measured with the aid of this thermometer by a thermometer bridge (Tinsley, Type 5840). The resistance of the thermometer at the triple point of water was measured periodically. The pressure vessel was immersed in a circulating silicone oil bath (425 × 285 × 470 mm in inner dimensions). The temperature detected at the well drilled in the pressure vessel was set at the values desired within ±3 mK, and it was kept constant within a fluctuation of ±3 mK during the measurements of a given isotherm.

The mass of the sample prepared in a supply vessel was weighed with a precision chemical balance (Chyo, Model C_2-3000) with an uncertainty of 2 mg, and then the sample was supplied to the bellows, being evacuated up to around 0.5 mPa, from the supply vessel. After thermodynamic equilibrium of the sample was confirmed, temperature, pressure, and bellows position were measured. The uncertainty in the density mea-

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