measured V^E_{123} data. Finally, it may be stated that none of the relations is capable of predicting the ternary data exactly.

Registry No. 1,1,1-Trichloroethane, 71-55-6; *n*-hexane, 110-54-3; 1-propanol, 71-23-8; 1-butanol, 71-36-3; 1-pentanol, 71-41-0.

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Compressibility Isotherms of Simulated Natural Gases

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The compressibility isotherms of two samples of simulated natural gases containing, respectively, 88% and 80% methane have been measured at 298.15 and 323.15 K and pressures up to 160 bar by using a Burnett apparatus. The experimental data for the compressibility factor are compared with values calculated by the recently developed truncated virial equation of state for multicomponent gas mixtures for which the appropriate parameters were previously evaluated from experimental *pVT* data of pure gases and binary and ternary gas mixtures. It is found that the virial equation of state is capable of predicting the compressibilities of natural gases within 0.1% of the experimental values, provided the density and the composition are within the applicability range of the fitted parameters.

Introduction

A study of the compressibility isotherms of natural gases is useful both from a practical and a theoretical point of view. On the practical side, a knowledge of the compressibility isotherms of natural gases is essential in the gas industry for performing custody-transfer calculations. The theoretical interest in this subject arises from the fact that natural gases are multicomponent mixtures and the development of an equation of state of such mixtures needs proper evaluation of the interaction of dissimilar molecules. Therefore, a number of investigations is currently being carried out at several gas research laboratories as well as at some academic institutions to develop accurate equations of state of natural gases in order to compute the compressibility factor for given values of pressure, temperature, and composition. However, in order to test the validity of these equations, accurate compressibility data for natural gases of different compositions are necessary. Measurements on simulated natural gases have the advantage that an equation of state can be examined for any desired composition. It is, therefore, considered worthwhile to measure the compressibility isotherms of two samples of simulated natural gas of different compositions and to examine how well a truncated form of the virial equation of state for multicomponent mixtures, developed recently in this laboratory (*1*, *2*), agrees with the experimental results. The experimental data reported in this paper should also be useful in evaluating the performance of other existing equations of state as well as in the development of new equations of state for multicomponent gas mixtures.

Table I. Composition of the Simulated Natural Gases

compounds	composition, mol % sample A	sample B	applicability range of GERG eq
methane	88.269	80.078	>50
ethane	6.115	11.641	<10
propane	0.998	6.530	<5
butane	0.989	1.750	<1.5
nitrogen	2.693	0	<50
carbon dioxide	0.936	0	<30

Experimental Section

The compressibility isotherms were measured in a Burnett apparatus based on repeated expansions of the measuring gas from a principal vessel to an expansion vessel. Since the apparatus, shown schematically in Figure 1, has been described in detail in a previous publication (*3*), only important features will be outlined here. The principal vessel, a steel cylinder A of 12-mm i.d., 30-mm o.d., and 27-cm^3 inner volume, is connected via an expansion valve V1 to a Ruska differential pressure meter B that together with the connecting capillaries form the expansion volume. The chambers can be evacuated or filled with the measuring gas by a filling–evacuation system attached to the apparatus via valve V2. The oil side of the differential pressure meter is connected to a hydraulic oil pump that in turn is connected to a Michels pressure balance and to a specially designed 3-m mercury column. The complete assembly including the valves is placed in an oil thermostat C, the temperature of which can be maintained constant to within 1 mK of any desired temperature by means of a proportional–integral temperature regulating system.

The measurements were carried out on two samples of simulated natural gas received from the Royal Dutch Shell Laboratory, Amsterdam. The compositions of the samples, as specified by the laboratory, are given in Table I. The experimental data were taken at 298.15 and 323.15 K and at pressures ranging from 1.5 to 160 bar. In each Burnett run, the chambers are filled with the sample gas to a desired initial pressure that is measured by the pressure balance after bringing the differential pressure meter to its null position. The accuracy of pressure measurements by the pressure balance is better than 0.01%. The expansion valve V1 is then closed, and the expansion volume is evacuated to 10^{-4} mmHg by

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Table II. Density and Compressibility Factor of Simulated Natural Gases

sample A					sample B				
T, K	p, bar	ρ, mol dm^{-3}	Z_{exp}	Z_{cal}	T, K	p, bar	ρ, mol dm^{-3}	Z_{exp}	Z_{cal}
298.150	123.7313	6.3408	0.787 16	0.785 89	298.151	160.8010	9.5978	0.675 84	
	95.0471	4.6780	0.819 61	0.818 95		120.5697	7.0809	0.686 87	0.681 29
	73.1009	3.4513	0.854 41	0.853 84		94.4584	5.2241	0.729 39	0.724 26
	55.9103	2.5463	0.885 76	0.885 33		74.3982	3.8541	0.778 69	0.774 74
	42.4690	1.8786	0.911 95	0.911 68		58.1438	2.8435	0.824 87	0.822 04
	32.0584	1.3860	0.933 07	0.932 81		44.9516	2.0978	0.864 38	0.862 31
	24.0669	1.0225	0.949 44	0.949 33		34.3961	1.5477	0.896 48	0.894 94
	17.9914	0.7544_1	0.962 02	0.962 02		26.0912	1.1419	0.921 72	0.920 61
	13.4075	0.5565_9	0.971 72	0.971 65		19.6582	0.8424_6	0.941 29	0.940 39
	9.9652	0.4106_4	0.978 93	0.978 91		14.7331	0.6215_5	0.956 20	0.955 46
	7.3924	0.3029_6	0.984 29	0.984 34		10.9928	0.4585_7	0.967 02	0.966 85
	5.4763	0.2235_2	0.988 32	0.988 40		8.1828	0.3383_2	0.975 67	0.975 37
	4.0530	0.1649_1	0.991 43	0.991 41		6.0758	0.2496_1	0.981 92	0.981 74
	2.9965	0.1216_7	0.993 51	0.993 65		4.5040	0.1841_6	0.986 60	0.986 48
	2.2143	0.0897_6	0.995 10	0.995 31		3.3343	0.1358_7	0.989 97	0.990 00
	1.6360	0.0662_3	0.996 52	0.996 53		2.4662	0.1002_4	0.992 47	0.992 61
	1.2083	0.0488_6	0.997 58	0.997 44		1.8232	0.0739_5	0.994 48	0.994 54
						1.3472	0.0545_6	0.996 02	0.995 97
323.148	150.0941	6.6530	0.839 67		323.148	135.5652	6.6052	0.763 90	
	113.0900	4.9082	0.857 56	0.856 66		103.9848	4.8728	0.794 24	0.790 82
	85.8285	3.6210	0.882 19	0.881 58		80.2904	3.5949	0.831 26	0.828 77
	65.0463	2.6714	0.906 24	0.905 73		61.7284	2.6522	0.866 26	0.864 51
	49.0927	1.9709	0.927 10	0.926 70		47.1208	1.9566	0.896 32	0.895 06
	36.8880	1.4540	0.944 24	0.943 88		35.7143	1.4435	0.920 83	0.919 87
	27.6037	1.0727	0.957 74	0.957 49		26.9023	1.0650	0.940 19	0.939 41
	20.5867	0.7914_0	0.968 18	0.968 04		20.1613	0.7856_9	0.955 06	0.954 50
	15.3147	0.5838_6	0.976 25	0.976 09		15.0501	0.5796_5	0.966 35	0.966 00
	11.3678	0.4307_5	0.982 23	0.982 18		11.2011	0.4276_4	0.974 86	0.974 68
	8.4254	0.3177_9	0.986 76	0.986 76		8.3188	0.3155_0	0.981 36	0.981 19
	6.2369	0.2344_5	0.990 09	0.990 18		6.1668	0.2327_6	0.986 08	0.986 05
	4.6127	0.1729_7	0.992 54	0.992 73		4.5654	0.1717_2	0.989 50	0.989 67
	3.4107	0.1276_1	0.994 76	0.994 62		3.3775	0.1266_9	0.992 24	0.992 36
	2.5200	0.0941_5	0.996 24	0.996 02		2.4964	0.0934_7	0.994 08	0.994 35
	1.8604	0.0694_6	0.996 90	0.997 06		1.8450	0.0689_6	0.995 83	0.995 83
						1.3630	0.0508_7	0.997 17	0.996 92

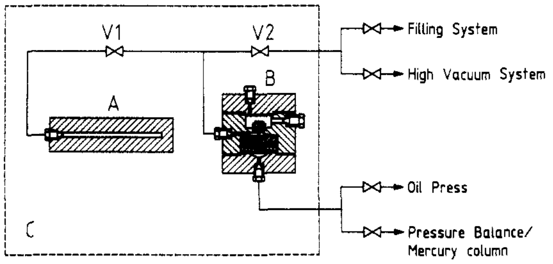

Figure 1. Schematic diagram of the Burnett apparatus.

opening valve V2 to the vacuum system. Subsequently, valve V2 is closed and valve V1 is opened so that the gas in chamber A expands into chamber B. The whole procedure is repeated until the lowest measurable pressure is reached. The pressures at the lower end of the expansions, namely, those below 5 bar, are measured with the same accuracy of 0.01% by the mercury column. The temperature of the thermostat is measured with an accuracy of 2 mK by means of a calibrated Pt resistance thermometer (IPTS 68).

Data Analysis

Each Burnett run consists of a series of pressures, p_0, p_1, p_2, ..., p_n, where n is the total number of expansions. At any pressure p_j, the compressibility factor $Z = pV/RT$ and the density $\rho = 1/V$ (V = molar volume) are determined by using the following relations

$$Z_j = p_j(Z_0/p_0)(N_\infty)^j\prod_{i=1}^{j}\xi_i \qquad (1)$$

$$\rho_j = p_j/Z_jRT \qquad (2)$$

in which (Z_0/p_0) is a run constant, N_∞ is the cell constant at zero pressure, R is the gas constant, T is the temperature, and ξ_i are correction terms to account for the pressure distortion of the experimental volume

$$\xi_i = (1 + ap_i)/(1 + bp_{i-1}) \qquad (3)$$

where a and b are the pressure distortion coefficients of the combined volumes of A and B and the volume of the steel cylinder A, respectively. The zero-pressure cell constant together with the pressure distortion coefficients a,b have been evaluated by calibrating the apparatus with pure argon. The calibrated values of the cell constant N_∞ = 1.355 41 ± 0.000 03 at T = 298.15 K and 1.355 45 ± 0.000 03 at T = 323.15 K. The values of a and b, which are independent of temperature in a small temperature interval, are as follows: $a = 2.37 \times 10^{-6}$ bar^{-1}, $b = 1.66 \times 10^{-6}$ bar^{-1}. The run constant (Z_0/p_0) for each run is determined by using the well-known Burnett relation (*3*)

$$p_0/Z_0 = \lim_{p_j\to 0} p_jN_\infty{}^j\left(\prod_{i=1}^{j}\xi_i\right) \qquad (4)$$

The required extrapolation to zero pressure is carried out by fitting the values of $F_j = p_jN_\infty{}^j(\prod_{i=1}^{j}\xi_i)$ of each run into successively 1, 2, 3, ... degree polynomials of the form $F = C_0 + C_1p + C_2p^2 + C_3p^3 + ...$ and evaluating the run constant from the calculated values of the coefficient C_0, following the procedure described elsewhere (*3*). Finally, the compressibility factor Z_j and the density ρ_j at each experimental pressure of p_j of individual runs are computed from (1) and (2) using appropriate values of p_0/Z_0, N_∞, and ξ_i.

Experimental Results

The values of the compressibility factor Z_j and the density ρ_j for the two samples of simulated natural gases as a function of the pressure and at the two different temperatures are recorded in Table II. The absolute accuracy of the density data is estimated to be better than 0.05%. The experimental data of a second run, taken on one of the two samples at 298.15 K, are found to agree with those of the first run within this accuracy.

The experimental values of Z can be fitted, by a least-squares analysis, to a polynomial in the density of the form

$$Z = 1 + B\rho + C\rho^2 + D\rho^3 + ... \tag{5}$$

where B, C, and D are virial coefficients. It turns out that the number of coefficients required for the best fit is not always the same but depends both on the composition and the temperature. The standard deviation for the best fit is found to vary between 0.6×10^{-4} and 1.3×10^{-4}, showing the high precision of the measurements and that the relative accuracy of the measurements is much larger than the absolute accuracy. The number of significant figures for Z and ρ given in Table II is appropriate to the accuracy of these fits; for this reason, one more digit is retained than would, strictly, be warranted by the absolute experimental accuracy mentioned earlier.

Although third or higher degree polynomials are ncessary to obtain the best fit, the compressibility isotherms for both samples can be represented within the precision of 0.1% by a truncated virial equation of state containing only two coefficients, namely B and C.

Comparison with the Virial Equation of State for Natural Gases

Recently, a new virial equation of state for natural gases has been developed at this laboratory with the active support and cooperation of several European gas companies that jointly form GERG (Groupe Européen de Récherches Gazières). This equation, the so-called GERG equation, shows great promise in predicting accurately (i.e., within 0.1%) the compressibility factor of natural gases in the temperature range 273-313 K, at pressures up to 120 bar and within certain restrictions as to the composition such as indicated in the last column of Table I. The equation is written in the form of a Leiden expansion of Z with second and third virial coefficients

$$Z = 1 + \rho\sum_k^n\sum_l^n B_{kl}x_kx_l + \rho^2\sum_k^n\sum_l^n\sum_m^n C_{klm}x_kx_lx_m \tag{6}$$

where ρ is the molar density of the system, x_k is the mole fraction of component k in the gas mixture, B_{kl} and C_{klm} are, respectively, the second and third virial coefficients that were previously evaluated for 13 different components from experimental pVT data of pure gases and $pVTx$ data of a large number of binary and ternary gas mixtures, the latter being obtained mainly from GERG. Its novelty lies in the fact that it turned out to be at all possible to find a set of values for the coefficients B_{kl} and C_{klm}, such that the accuracy of 0.1% aimed at is achieved. Details of the development of this equation of state and the evaluation of the parameters can be found elsewhere (*1*, *2*).

In testing the applicability of the GERG equation to the two samples of simulated natural gases, the virial coefficients B_{kl} and C_{klm} are to be considered constants; no further adjustments of them can be made. The compositions of the two samples of simulated natural gases given in Table I are such that one is inside and the other is outside the applicability range of eq 6 fitted to the available experimental data. As shown in Figure 2, for sample A, whose composition is within the applicability range, the calculated values of the compressibility factor Z at the two experimental temperatures and up to 120 bar are within 0.1% of those found in the present measurement; clearly, though, the fit to eq 6 is not yet the optimal one. The figure of 0.1% is about twice the estimated absolute accuracy of the experimental values. For this sample, the mean deviation and the root mean square deviation of the complete experimental data from the GERG equation are also found to be fairly low, namely, -2.4×10^{-4} and 4.5×10^{-4}, respectively.

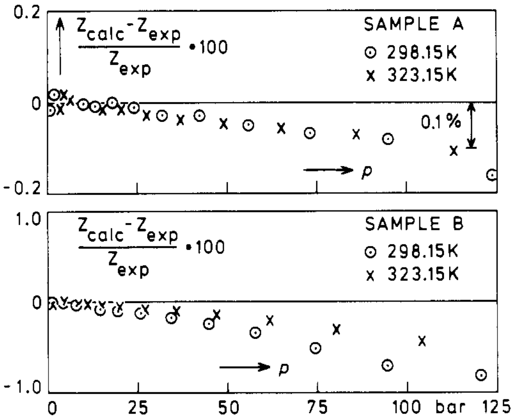

Figure 2. Comparison between the calculated and experimental values of the compressibility factor of two samples of simulated natural gases.

However, as one may expect, the agreement is less satisfactory for sample B whose composition is outside the applicability range of the GERG equation. As shown in Figure 2, for this sample the deviation of the experimental values from the corresponding calculated values for Z at higher pressures increases up to 0.8%. At lower pressures ($p < 25$ bar), however, the deviations for this sample also remain low, namely, within 0.1%.

We may, therefore, conclude that the new virial equation of state of the form (6), with parameters evaluated from the experimental pVT data of pure gases and binary and ternary gas mixtures, is capable of predicting the compressibility factor of a natural gas within 0.1% provided the density and the composition are within the applicability range for the fitted values of the parameters.

Acknowledgment

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Glossary

a,b	pressure distortion coefficients, bar^{-1}
B,C,D	virial coefficients
N	cell constant
p	pressure, bar
R	gas constant, m^3 bar/(mol K)
T	temperature, K
V	volume, cm^3 mol^{-1}
x	mole fraction
Z	compressibility factor

Greek Letters

ρ	density, mol m^{-3}
ξ	pressure distortion correction coefficient

Subscripts and Superscripts

0	initial condition
i,j	gas expansion number
k,l,m	component
n	total number of components
∞	infinite number of gas expansions

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Excess Second Virial Coefficients and Critical Temperatures of Methyl Acetate and Diethyl Sulfide

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For the system methyl acetate and diethyl sulfide, measurements are reported of excess second virial coefficients (at 50, 75, and 100 °C) and critical temperatures for 11 compositions. The efficacy of the correlations due to Tsonopoulos and to Hayden and O'Connell, both in its original form and incorporating a pseudocritical temperature, are discussed.

Introduction

The following equation relates the excess second virial coefficient, ϵ, to the change in pressure, ΔP, when equal volumes of two pure gases 1 and 2 at equal pressure are mixed at constant temperature (*1*).

$$\epsilon = 2RT\Delta P/(P^2 + P\Delta P) \tag{1}$$

$$\epsilon = B_{12} - \tfrac{1}{2}(B_{11} + B_{22}) \tag{2}$$

This method renders possible estimation of the unlike interaction second virial coefficient B_{12} with uncertainty comparable with that of B_{11} and B_{22}.

The fugacity coefficient ϕ_i for two components may be expressed in terms of virial coefficients.

$$\ln \phi_1 = (B_{11} + 2Y_2^2\epsilon)P/RT \tag{3}$$

B values are thus required directly for PVT calculations and for liquid/vapor equilibrium estimations.

Of greater importance is the use of the results to test the efficacy of correlations that have been proposed for the prediction of PVT behavior of mixtures since only a small proportion of all possible mixtures can be studied.

Almost all correlations are of the "corresponding states" type and require that B and T be "reduced" with use of critical or pseudocritical temperatures, pressures, and sometimes volumes.

While pseudocritical temperature has often been used as a fitting parameter for second virial coefficient correlations, as has been previously described (*2*), in this work an independent estimate of T_{12}^{c} (unlike interaction) has been obtained from the measurement of mixture critical temperatures as a function of composition.

Experimental Section

Apparatus. The apparatus for measurement of ϵ from the pressure charge on mixing was unchanged from that described previously (*3*).

The procedure for measurement of critical temperatures using the sealed-tube method has been described by McElroy et al. (*2*). Possible decomposition of the compounds at elevated temperatures was diminished by maintaining temperatures near critical for the minimum time needed for stable readings. No evidence of decomposition was noted, and no drift in critical temperature with increasing exposure to elevated temperatures was observed.

Materials. "Pure"-grade diethyl sulfide supplied by Koch-Light Laboratories, Ltd., was dried over calcium sulfate and distilled in a 50-cm spinning band (PTFE) column (Nester/Faust Manufacturing Corp. Model S-1179).

The methyl acetate supplied by May and Baker, Ltd., was purified in a similar manner, central cuts from the distillation being used in both cases. Gas chromatographic analysis indicated greater than 99.95% purity.

All reagents were thoroughly degassed and then distilled directly into either the virial coefficient apparatus or critical point tubes.

Theory

Pseudocritical Temperature. The thermodynamic conditions for a critical point in a binary system is that the second and third derivatives of free energy with respect to mole fraction be zero.

$$\left(\frac{\partial^2 G}{\partial Y^2}\right)_{T,P} = 0 \tag{4}$$

$$\left(\frac{\partial^3 G}{\partial Y^3}\right)_{T,P} = 0 \tag{5}$$

In the previous study (*2*), the combining rules

$$a_m = a_{11}Y_1^2 + a_{22}Y_2^2 + 2Y_1Y_2a_{12} \tag{6}$$

and

$$b_m = b_{11}Y_1^2 + b_{22}Y_2^2 + 2Y_1Y_2b_{12} \tag{7}$$

and the thermodynamic critical point condition were used in conjunction with the Redlich–Kwong equation of state to solve for a_{12} and hence for unlike-interactions critical temperature T_{12}^{c}. The Redlich–Kwong in common with the Peng–Robinson equation and others was developed from the van der Waals equation of state.

$$\frac{RV}{RT} = \frac{1}{V-b} - \frac{a}{V^2} \tag{8}$$

The first term in this equation is an approximation for the hard-sphere equation of state that was known to be in error by van der Waals himself. The accurate hard-sphere equation of state

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