

Virial Coefficients of Methane–Ethane Mixtures in the Temperature Range from 0 to 60°C Determined with an Automated Expansion Apparatus¹

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An automated expansion apparatus has been set up which can be used for PVT measurements on gases from 0 to 60 °C at pressures from 2 to 7 MPa. It consists of two chambers connected by an expansion valve. The ratio of the two volumes is 1:54. The measurements along one isotherm, which take 20 h, can be performed routinely and without operator attendance. The uncertainty of the compressibility factor is estimated to be 10^{-3} . The compressibility factors of binary mixtures of the main components of most natural gases, methane and ethane, were determined on high-grade gas, the mole fractions of ethane being 0.05, 0.15, and 0.25. Seven isotherms were measured of each of the mixtures. Data from the literature for the virial coefficients of the pure substances were used to establish a virial equation of state which approximates the measured compressibility factors with a standard deviation of 0.4×10^{-3} . This is substantially smaller than the uncertainty. The interaction virial coefficients were calculated from this equation of state. The results obtained are in good agreement with other available data.

KEY WORDS: compressibility factors; expansion apparatus; methane-ethane mixtures; PVT ; virial coefficients.

1. INTRODUCTION AND DEFINITION OF THE PROBLEM

At pressures which are not too high, the PVT behavior of gases can be represented by a virial-type equation of state. In the case of binary gas mixtures, the virial coefficients are often calculated from the known virial coefficients of the pure components by means of mixing rules. The quality

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of the equation of state can be improved if the interacting virial coefficients are known. Their experimental determination is very time-consuming, as a large number of PVT data are required for the determination of the second and third virial coefficients of binary gas mixtures with different mole fractions. To perform this measurement task, a fully automated measuring device was set up, allowing a completely computer-controlled determination of the compressibility factors $Z = pV/RT$ of gases. p is the pressure, V the molar volume, R the gas constant, and T the temperature.

2. TEST APPARATUS AND MEASUREMENTS

As the measurements have to be performed only in the gaseous single phase region, the expansion method was chosen for measuring the compressibility factor Z . The apparatus is a modified commercial Desgranges and Huot Z -meter described in detail elsewhere [1]. The apparatus can be used in the temperature range from 0 to 60°C at pressures up to 7 MPa. A schematic diagram of the apparatus is given in Fig. 1. The apparatus consists of two chambers A and B connected by an expansion valve V2. The ratio of the two volumes is determined from calibration measurements with a reference gas. The inlet valve V1, the expansion valve V2, and the exhaust valve V3 are pneumatically operated and computer-controlled. Only two states are possible. In state 1 the valves V2 and V4 are closed, whereas in state 2 the inlet valve V1 and the exhaust valve V3 are closed, but the expansion valve V2 is open. At the start of the experiment the

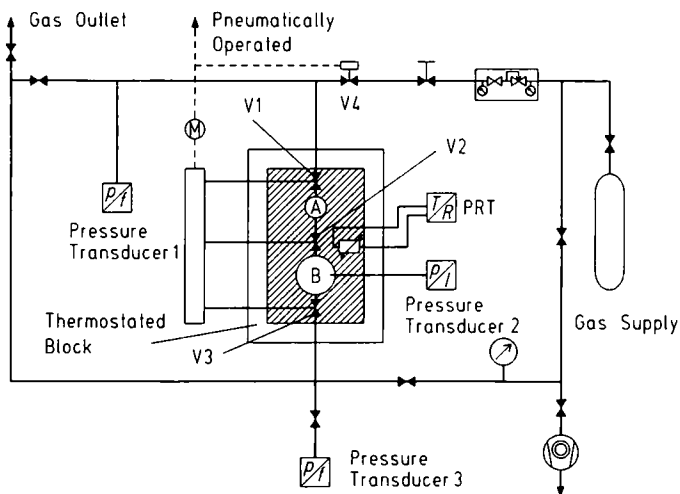


Fig. 1. Schematic diagram of the automated expansion apparatus.

smaller chamber A is filled via valve V4 with gas at a certain pressure, which is measured with the pressure transducer 1, made by Paroscientific (range, 12 MPa). Chamber B is filled with gas at atmospheric pressure, and the pressure is measured by the pressure transducer 3 (range, 0.11 MPa) also made by Paroscientific. When pressure and temperature equilibrium is reached, the apparatus changes over the state 2, meaning pneumatic operation. Gas expands from the high-pressure chamber B until pressure equilibrium is reached. The pressure prevailing after the expansion is then measured by the pressure transducer 2 (range, 0.3 MPa) made by Rosemount. The temperature of the pressure vessels is thermostated by means of circulating liquid. The set temperatures and pressures are controlled by the computer. The pressure transducers are calibrated against piston gauges. Pressure transducer 2 is calibrated at ambient pressure against transducer 2 after each expansion. The relative measuring uncertainty of the pressure transducers 1 and 3 is estimated to be 2×10^{-4} and that of pressure transducer 2 is 5×10^{-4} . The temperature is measured with a 100- Ω platinum resistance thermometer with an uncertainty of 10 mK.

3. CALCULATION OF THE COMPRESSIBILITY FACTOR

The temperatures T_1 and T_2 measured in states 1 and 2 are normally slightly different. But as the pressure p_{cx} after expansion is relatively small, less than 0.25 MPa, p_x can be corrected by means of the ideal-gas law,

$$p_x(T_1) = p_{\text{cx}}(T_2) T_1/T_2 \quad (1)$$

Therefore, for the following calculations, $T_1 = T_2 = T$.

In state 1 (i.e., the expansion valve V_2 is closed) for the gas in chamber A, the equation of state for real gases is valid:

$$pV_A = Z(p) n_A RT \quad (2)$$

In Eq. (2), p is the pressure in chamber A, V_A is the volume of chamber A, $Z(p)$ is the compressibility factor at the pressure p , n_A is the amount of substance in chamber A, and R is the temperature. For the gas in chamber B the analogous equation applies:

$$p_{\text{amb}} V_B = Z(p_{\text{amb}}) n_B RT \quad (3)$$

In state 2 valve V2 is open, and the pressure of the gas is p_{cx} in both chambers. The the following equation applies:

$$p_{\text{cx}}(V_A + V_B) = Z(p_{\text{cx}})(n_A + n_B) RT \quad (4)$$

Combining Eqs. (2), (3), and (4) yields

$$Z(p) = p / [(A + 1) p_{\text{ex}} / Z(p_{\text{ex}}) - A p_{\text{amb}} / Z(p_{\text{amb}})] \quad (5)$$

The volume ratio $A = V_{\text{B}} / V_{\text{A}} = 54$ has been determined from measurements with methane, the main component of the gas under investigation. If $\rho(T, p) = p / [Z(T, p) RT]$ is substituted, Eq. (5) yields

$$A = \{ [\rho(T, p) - \rho(T, p_{\text{amb}})] / [\rho(T, p_{\text{ex}}) - \rho(T, p_{\text{amb}})] \} - 1 \quad (6)$$

for calculation of the ratio A . The densities ρ are calculated from the equation of state of Pieperbeck et al. [2], the relative uncertainty of ρ being 0.3×10^{-3} .

For the calculation of Z from Eq. (5) the compressibility factors $Z(p_{\text{ex}})$ and $Z(p_{\text{amb}})$ must be known. They can be determined from a series of isotherm expansion measurements using an iteration method. In the first step, in Eq. (5) $Z(p_{\text{ex}})$ and $Z(p_{\text{amb}})$ are replaced by 1 and a series of $Z(p)$ values is evaluated. A virial equation,

$$Z(p) = 1 + a_1 p + a_2 p^2 + a_3 p^3 \quad (7)$$

is fitted to the preliminary $Z(p)$ values. From Eq. (7), improved approximations for $Z(p_{\text{amb}})$ and $Z(p_{\text{ex}})$ are calculated and are inserted into Eq. (5). The iteration is continued until the compressibility factor $Z(p)$ changes by less than 10^{-4} .

4. MEASUREMENT RESULTS AND CORRELATION EQUATIONS

The measurements were carried out on high-grade methane-ethane mixtures supplied by Messer Griesheim of Germany. Three mixtures were investigated, the mole fraction x_1 of ethane being 0.05, 0.15, and 0.25. For each mixture, the compressibility factors were determined on seven isotherms at temperatures between 0 and 60°C with pressures up to 7 MPa. The measurements on each isotherm were repeated seven times. The TpZ data are given in Table 1. From measurements on nitrogen and methane the uncertainty of the compressibility factor is estimated to be 10^{-3} .

For the correlation of the measured values, an approach with a virial equation of state was used, truncated after the third coefficient [3]:

$$Z = 1 + B(T)/V + C(T)/V^2 \quad (8)$$

For the virial coefficients of the mixture the following combination rules were used [3].

$$B(T) = B_{11}(T)x_1^2 + 2B_{12}(T)x_1x_2 + B_{22}(T)x_2^2 \quad (9)$$

Table I. Results of (TpZ) Measurements on Methane–Ethane Mixtures: $\Delta Z/Z = (Z_{\text{calc}} - Z)/Z$ [Z_{calc} calculated with Eq. (8)]

T_{01} (K)	p (MPa)	Z	$10^3 \Delta Z/Z$
$x_{\text{ethane}} = 0.25142$			
273.779	2.15230	0.91726	-0.1
273.879	3.13197	0.87774	-0.0
273.976	4.14510	0.83568	0.1
273.933	5.14695	0.79291	0.1
273.945	6.01028	0.75580	0.1
273.882	6.92543	0.71649	-0.1
283.242	2.16421	0.92627	-0.0
283.272	3.07317	0.89432	-0.1
283.371	4.09570	0.85774	0.0
283.359	5.17484	0.81853	0.2
283.339	5.98371	0.78948	-0.1
283.371	6.97107	0.75447	-0.2
294.309	2.18797	0.93450	0.4
294.382	3.07493	0.90775	0.4
294.408	4.06271	0.87777	0.3
294.419	5.05216	0.84786	0.1
294.422	6.04973	0.81790	0.1
294.260	6.95080	0.79126	-0.2
303.498	2.10970	0.94345	0.3
303.555	3.17150	0.91513	0.2
303.592	4.28856	0.88525	0.2
303.597	5.18919	0.86169	-0.1
303.610	6.03909	0.83939	0.0
303.594	6.99503	0.81583	-0.6
313.193	2.21167	0.94716	0.2
313.284	3.06156	0.92692	0.3
313.281	4.33788	0.89688	0.4
313.273	5.29252	0.87531	-0.0
313.272	6.04547	0.85854	-0.2
313.273	6.97551	0.83836	-0.3
313.273	6.95403	0.83897	-0.4
323.143	2.30013	0.95113	0.1
323.164	3.29721	0.93046	-0.1
323.215	4.27544	0.91037	-0.1
323.200	5.31120	0.88965	-0.1
323.189	6.22265	0.87200	-0.2
323.191	7.02400	0.85703	-0.2
333.289	2.25861	0.95730	0.1
333.307	3.15657	0.94084	-0.0
333.313	4.41945	0.91823	-0.2
333.300	5.26377	0.90327	0.1
333.307	6.18414	0.88790	-0.0
333.293	7.01254	0.87430	0.2

Table I. (Continued)

T_{90} (K)	p (MPa)	Z	$10^3 \Delta Z, Z$
$N_{\text{ethane}} = 0.15097$			
273.692	2.06513	0.93438	-0.3
273.822	3.17186	0.89833	-0.3
273.856	4.20589	0.86409	-0.2
273.866	5.08268	0.83510	-0.3
273.808	6.01173	0.80410	-0.1
273.795	6.94770	0.77416	-0.4
283.108	2.12702	0.94035	-0.4
283.238	3.09545	0.91266	-0.3
283.282	4.17350	0.88184	-0.1
283.289	5.09134	0.85562	0.2
283.274	6.12361	0.82659	0.6
283.235	6.97033	0.80354	0.8
294.260	2.09799	0.94891	-0.5
294.285	3.08927	0.92457	-0.4
294.318	4.08913	0.90032	-0.3
294.320	5.09327	0.87607	0.1
294.329	6.04476	0.85404	0.1
294.320	7.01477	0.83178	0.9
303.540	2.05540	0.95516	-0.3
303.614	3.12330	0.93214	-0.3
303.662	4.06463	0.91209	-0.2
303.647	5.09761	0.89041	-0.0
303.640	6.14821	0.86922	0.1
303.645	6.98230	0.85297	0.5
313.146	2.24043	0.95595	0.2
313.190	3.33003	0.93534	0.0
313.239	4.15424	0.91949	0.6
313.226	5.06796	0.90294	0.6
313.231	6.22174	0.88299	0.5
313.239	7.03092	0.86933	0.8
322.883	2.30692	0.95980	0.0
322.922	3.07797	0.94670	0.1
322.938	4.31900	0.92613	0.3
322.949	5.10757	0.91376	0.2
322.943	6.18126	0.89713	0.5
322.938	7.06038	0.88445	0.5
333.227	2.33162	0.96407	-0.0
333.248	3.11483	0.95233	0.1
333.300	4.20750	0.93686	-0.2
333.307	5.30598	0.92152	0.0
333.294	6.27914	0.90884	-0.0
333.287	6.97977	0.89976	0.3

Table I. (Continued)

T_{00} (K)	p (MPa)	Z	$10^3 \Delta Z/Z$
$x_{\text{ethane}} = 0.05297$			
273.633	2.03777	0.94532	1.4
273.732	3.04290	0.91959	0.8
273.795	4.14801	0.89086	0.8
273.859	5.16959	0.86511	0.2
273.881	6.05846	0.84274	0.2
273.828	6.94281	0.82100	0.1
283.139	2.11861	0.95141	-0.3
283.221	3.19662	0.92684	-0.4
283.283	4.18942	0.90461	-0.5
283.284	5.12446	0.88368	-0.2
283.274	6.08745	0.86301	-0.2
283.258	7.00566	0.84404	-0.2
294.218	2.16313	0.95748	-0.8
294.248	3.18830	0.93750	-1.0
294.372	4.29712	0.91647	-1.0
294.370	5.11445	0.90079	-0.6
294.334	6.01748	0.88476	-0.8
294.342	6.99967	0.86779	-0.7
302.726	2.12385	0.96240	-0.7
302.759	3.08948	0.94572	-0.9
302.805	4.33112	0.92467	-0.9
302.788	5.26595	0.90923	-0.8
302.780	6.20498	0.89445	-0.7
302.806	6.99552	0.88234	-0.4
302.791	7.01652	0.88241	-0.8
312.474	2.15052	0.96579	-0.1
312.511	3.15340	0.95033	-0.1
312.575	4.14389	0.93572	-0.2
312.578	5.32898	0.91862	0.0
312.573	6.16569	0.90749	-0.2
312.546	6.96824	0.89696	-0.0
323.136	2.30295	0.96783	-0.1
323.204	3.35706	0.95422	-0.4
323.215	4.09979	0.94413	0.1
323.207	5.24258	0.93031	-0.2
323.198	6.14870	0.91989	-0.4
323.222	7.04469	0.90995	-0.3
333.305	2.23783	0.97259	-0.3
333.316	2.09532	0.97427	-0.2
333.358	3.13661	0.96223	-0.4
333.360	4.22622	0.94998	-0.5
333.355	5.20199	0.93937	-0.3
333.362	6.11438	0.93049	-0.7
333.357	7.04085	0.92137	-0.4

B_{11} and B_{22} are the second virial coefficients of the pure components 1 and 2, x_1 and x_2 are the mole fractions of components 1 and 2 in the mixture, and B_{12} is the so-called interaction virial coefficient. The third virial coefficient C of a binary gas mixture may be written as

$$C(T) = C_{111}(T)x_1^3 + 3C_{112}(T)x_1^2x_2 + 3C_{122}(T)x_1x_2^2 + C_{222}(T)x_2^3 \quad (10)$$

C_{111} and C_{222} are the third virial coefficients of the pure components. C_{112} and C_{122} are the contributions from the interactions of unlike molecules.

For ethane, the virial coefficients were calculated with the following correlation equations fitted to data given in the literature [3].

$$B_{11} = a_0 + a_1 T^{-1} + a_2 T \quad (11)$$

$$C_{111} = b_0 + b_1 T^{-1} + b_2 T + b_3 T^2 \quad (12)$$

The second and third virial coefficients of methane were calculated with Eqs. (13) and (14) [2].

$$B_{22} = c_1 \tau^{0.75} + c_2 \tau \quad (13)$$

$$C_{222} = c_3 + c_4 \tau^{2.75}, \quad \text{where} \quad \tau = 273.15 \text{ K}/T \quad (14)$$

The interaction virial coefficients B_{12} as well as C_{112} and C_{122} were determined from our experiments. They are represented as

$$B_{12} = d_0 + d_1 \tau + d_2 \tau^{0.25} + d_3 \tau^{0.5} \quad (15)$$

$$C_{112} = e_0 + e_1 \tau + e_2 \tau^{0.25} \quad (16)$$

$$C_{122} = f_0 + f_1 \tau + f_2 \tau^{0.25} \quad (17)$$

The coefficients of Eqs. (11)–(17) are given in Table II. Equation (8) represents the measured values with a relative standard deviation of 0.4×10^{-3} , which is well within the uncertainty of measurement. The relative differences between measured and calculated compressibility factors are given in Table I. In nearly all cases they are smaller than 10^{-3} .

In Fig. 2 the interaction virial coefficients B_{12} calculated with Eq. (15) are compared with results of other research groups. It can be seen that B_{12} values calculated with the GERG equation [4] are in good agreement. They differ by not more than $0.001 \text{ m}^3 \cdot \text{kmol}^{-1}$ above 270 K, whereas C_{112} and C_{122} differ up to $0.003 \text{ m}^6 \cdot \text{kmol}^{-2}$.

The differences of the compressibility factors calculated with the GERG equation and Eq. (8) representing our measured values differ by

Table II. Coefficients of the Correlation Equations, Eqs. (11)–(17), for T in K, B in $\text{m}^3 \cdot \text{kmol}^{-1}$, and C in $\text{m}^6 \cdot \text{kmol}^{-2}$; Range of Validity, $273 \text{ K} < T < 333 \text{ K}$

i	a_i	b_i	c_i
0	0.38559172	1.0050531	-
1	-142.43254	-105.90460	0.01858026
2	$-0.31150596 \cdot 10^{-3}$	$-3.0728805 \cdot 10^{-3}$	-0.02190583
3	---	$3.1163465 \cdot 10^{-6}$	$5.967196 \cdot 10^{-6}$
4	---	---	$4.308001 \cdot 10^{-6}$
	d_i	e_i	f_i
0	26.6526030	2.13455836	-0.544747453
1	-10.6157215	0.806760775	-0.197666510
2	-73.7323037	-2.93328151	0.746661808
3	57.5857185	---	---

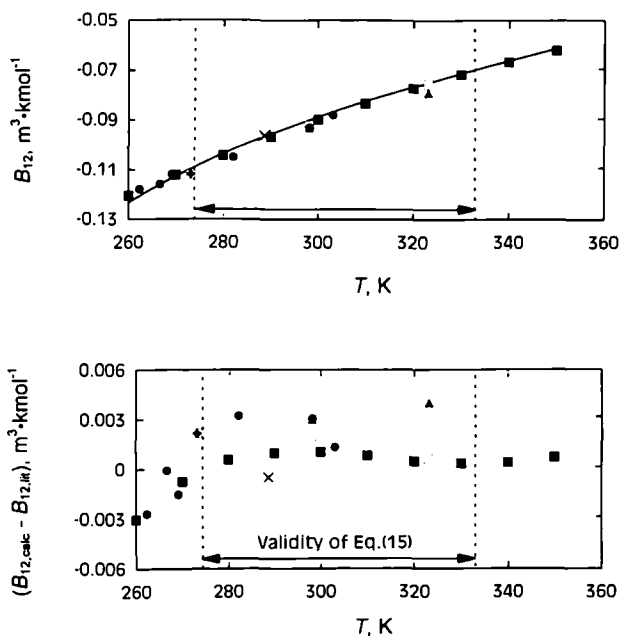


Fig. 2. Interaction virial coefficients $B_{1,2}$ determined by different authors and deviations $B_{12,\text{calc}} - B_{12,\text{lit}}$ of interaction virial coefficients taken from the literature from results calculated with Eq. (15). (—) This work; (■) GERG [4]; (▲) Dantzler et al. [5]; (□) Gunn [6], values given by Dantzler et al. [5]; (◆) Hoover et al. [7]; (×) Mason and Eakin [8]; (●) Wormald et al. [9].

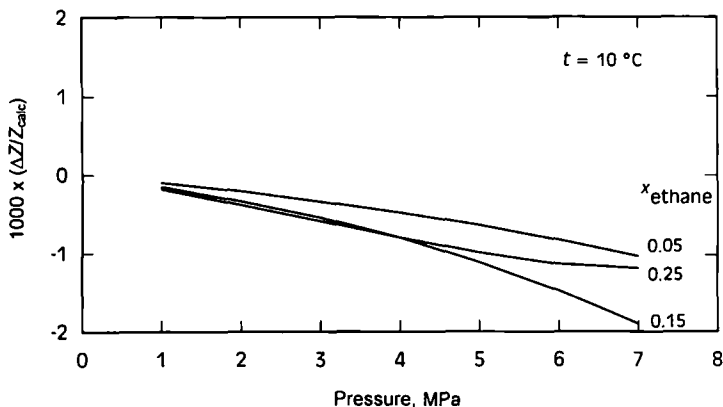


Fig. 3. Relative deviations $\Delta Z/Z_{\text{calc}} = (Z_{\text{GERG}} - Z_{\text{calc}})/Z_{\text{calc}}$ of compressibility factors Z_{calc} calculated with the correlation equation [Eq. (8)] from results calculated with the GERG equation [4]. Temperature: $t = 10^\circ\text{C}$.

less than 2×10^{-3} at 7 Pa and by less than 10^{-3} below 4 MPa. Figure 3 shows as an example the deviation of the compressibility factors for the temperature 10°C . The differences are within the combined uncertainties of the GERG equation and Eq. (8). The GERG equation also represents well the data for $x_{\text{ethane}} = 0.25$, though the validity of this equation is limited to mole fractions of ethane smaller than 0.2.

The compressibility factors measured by Haynes et al. [10] were compared with the compressibility factor calculated with Eq. (8) in the range where Eq. (8) holds. The validity of this equation is limited to pressures considerable lower than the pressure on the dew line at the same temperature. For temperatures between 280 and 320 K and mole fractions $x_{\text{ethane}} = 0.3147$, 0.4978, and 0.6547, 14 compressibility factors determined by Haynes were compared, the relative differences are smaller than 1.8×10^{-3} .

5. CONCLUSION

Experiments have shown that with the computer-controlled expansion apparatus described, a great number of compressibility factors can be measured completely automatically in the range from 0 to 60°C at pressures from 2 to 7 MPa. A measurement uncertainty of 10^{-3} can be achieved. The setup is suitable for the very time-consuming task of

determining compressibility factors for developing equations of state for gas mixtures. From these equations the interaction virial coefficients of binary mixtures can be derived.

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