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Compression Factors and Virial Equation of State Coefficients for the System Carbon Monoxide + Ethane

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Compression factors were measured using a weighing method for carbon monoxide + ethane mixtures at 10 K intervals from 298.15 to 343.15 K and at pressures up to 10 MPa. Unlike interaction second and third virial coefficients were determined and compared with predictive relationships.

Introduction

Carbon monoxide and ethane are components in both natural and synthetic fuel gases as well as in a large range of other industrial gas mixtures. In representing the pressure–volume–temperature (pVT) behavior of multicomponent mixtures, the coefficients obtained from fitting the behavior of binary systems are of major significance and coupled with the pure substance behavior are often all that are required.

No measurements of the pVT behavior of the CO + C_2H_6 system appear to have been reported in the literature. Most commonly pVT behavior is correlated using the virial equation, and no virial coefficients have been recorded in the major compilations of Dymond and Smith (*1*) and of Warony and Stecki (*2*) or apparently in more recent publications.

In the compilation of second and third virial coefficients produced by the Groupe Europeen de Recherches Gazieres (GERG) (*3*), carbon monoxide and ethane are components covered, but unlike interaction virial coefficients for CO + C_2H_6 have not been included. This is because the maximum carbon monoxide mole fraction considered is $x(\mathrm{CO}) = 0.03$, and so the contribution of cross terms with other components would in most cases be very small.

A later publication by the GERG group, "Standard GERG Virial Equation for Field Use" (*4*), points out however that synthetic fuel gases may have higher carbon monoxide concentrations, and so determination of the appropriate coefficients is desirable. The GERG virial coefficient compilation represents such a major coherent set of data that extension of its application to a much broader range of components and concentration ranges is a very worthwhile objective.

The virial coefficients B and C are typically obtained by fitting the virial equation to compression factors Z, measured as a function of pressure and temperature:

$$Z = pV/RT = 1 + (B_m/V) + (C_m/V)^2 \qquad (1)$$

The most widely used experimental procedure for determining Z is the method due to Burnett (*5*) which is indirect and requires a succession of pressure measurements. One of its advantages and a reason for its popularity is that direct determination of the number of moles of gas n is not required. Prior to the availability of mass comparators, direct accurate determination of the mass of gas by weighing and from that the number of moles was a difficult problem.

Since even at high pressures the mass of a high-pressure cylinder is very large compared to the mass of gas within, determination of the mass of gas by direct weighing was not a recommended approach. A mass comparator, however, after loading of a large mass (such as a steel pressure vessel) allows very accurate measurement of incremental mass changes. The advent of such devices therefore made direct mass of gas determination much more attractive, and so in this work Z is obtained from measurement of T, p, V, M, and m. The molar mass is known for pure substances and can be determined if impurity levels are known. For mixtures the composition must be known, or if it is not then M for the mixture can be obtained by a fit to the data. For example, eq 1 may be rewritten to read

$$pV/mRT = (1/M) + (B_m\rho/M^2) + (C_m\rho^2/M^3) \qquad (2)$$

where ρ is density and M, as well as B_m and C_m, is a fitting parameter.

Table 1. Purity of the Gases

gas	component	y	$M/(\mathrm{g{\cdot}mol^{-1}})$
ethane	C_2H_6	0.9990	
	N_2	0.0008	
	O_2	0.0002	30.04
carbon monoxide	CO	0.9996	
	N_2	0.0003	
	O_2	0.0001	28.01

Experimental Section

The apparatus has been described previously (*6*, *7*), and only a basic review will be given here. A "monel" metal cylinder of nominal volume 500 $\mathrm{cm^3}$ was accurately calibrated by weighing it filled with water. The volume change as a function of pressure was also determined. Four high-precision Bourdon-tube pressure gauges (Mensor Model 2792) with full-scale readings of 20.0, 6.5, 2.7, and 1 MPa with claimed accuracies of 0.001 of the full-scale reading were used simultaneously with a 13.0-MPa full-scale digital pressure meter, Digiquartz Model 1002 K-1, with a claimed accuracy of 0.0001 of full scale. All gauges were calibrated with a Budenburg Model 280L dead weight tester. Temperature was measured with a platinum resistance thermometer and an Automatic Systems Laboratory resistance bridge, and the International Temperature Scale ITS-90 was employed. Mass was determined with a Sartorius Model 1683 MP8 mass comparator with a capacity of 10 kg and resolution of 1 mg.

The ethane gas was "ultrahigh purity" grade supplied by New Zealand Industrial Gases and the carbon monoxide ultrahigh purity grade supplied by Matheson Gas Products. The gas compositions are recorded in Table 1.

Results and Discussion

The compression factors determined using

$$Z = pVM/RTm \qquad (3)$$

for $C_2H_6(1) + CO(2)$ and with M determined using the molar masses of Table 1 are reported in Table 2.

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Table 2. Amount of Substance Density and Compression Factors for C_2H_6 (1) + CO (2) + N_2 (3) + (1 − x_1 − x_2 − x_3) O_2

p/MPa	T/K	ρ_n/(mol·m^{-3})	Z	p/MPa	T/K	ρ_n/(mol·m^{-3})	Z
$x_1 = 0.3656, x_2 = 0.6338, x_3 = 0.0005$							
6.977	293.14	3344.5	0.8558	3.198	293.14	1416.0	0.9265
5.995	293.15	2816.7	0.8732	2.654	293.15	1157.3	0.9407
5.140	293.16	2371.5	0.8893	2.190	293.16	945.1	0.9506
4.400	293.14	1997.9	0.9037	1.802	293.15	770.5	0.9597
3.753	293.15	1682.0	0.9154	1.480	293.15	629.0	0.9655
$x_1 = 0.4165, x_2 = 0.582\,82, x_3 = 0.0006$							
8.093	303.15	3847.8	0.8344	2.728	303.14	1154.1	0.9377
6.917	303.14	3216.2	0.8533	2.241	303.15	937.1	0.9489
5.912	303.15	2690.5	0.8719	1.834	303.16	757.7	0.9601
5.043	303.15	2249.1	0.8895	1.496	303.14	614.7	0.9655
3.892	303.14	1693.5	0.9118	1.216	303.16	495.5	0.9737
3.306	303.16	1421.2	0.9228				
$x_1 = 0.3550, x_2 = 0.644\,43, x_3 = 0.0005$							
7.479	313.15	3218.1	0.8926	3.142	313.15	1274.0	0.9473
6.294	313.15	2669.8	0.9055	2.566	313.16	1029.0	0.9575
5.297	313.15	2214.8	0.9185	2.089	313.14	831.4	0.9651
4.454	313.14	1839.7	0.9298	1.697	313.15	670.5	0.9719
3.742	313.14	1530.7	0.9389				
$x_1 = 0.3556, x_2 = 0.6438, x_3 = 0.0005$							
6.218	323.15	2517.8	0.9192	1.985	323.15	760.1	0.9721
5.200	323.15	2079.1	0.9308	1.598	323.16	608.8	0.9771
4.349	323.14	1722.2	0.9398	1.287	323.15	488.9	0.9796
3.631	323.15	1427.1	0.9469	0.938	323.15	353.8	0.9864
3.033	323.15	1180.8	0.9561	0.702	323.15	264.1	0.9897
2.457	323.15	948.5	0.9642				
$x_1 = 0.4819, x_2 = 0.5173, x_3 = 0.0006$							
10.402	333.15	4505.9	0.8334	4.276	333.15	1679.9	0.9190
8.763	333.15	3719.8	0.8505	3.546	333.16	1373.8	0.9319
7.421	332.16	3082.8	0.8716	2.939	333.16	1127.6	0.9410
6.165	333.15	2507.1	0.8877	1.548	333.15	574.5	0.9726
5.140	333.15	2051.5	0.9045	1.237	333.15	457.0	0.9776
$x_1 = 0.4676, x_2 = 0.5316, x_3 = 0.0006$							
10.592	343.15	4283.9	0.8666	2.688	343.14	981.8	0.9595
8.807	343.15	3502.6	0.8813	2.141	343.14	774.4	0.9688
7.349	343.15	2873.3	0.8964	1.703	343.15	611.7	0.9757
6.033	343.16	2317.3	0.9125	1.355	343.15	483.5	0.9822
4.965	343.15	1877.9	0.9268	0.999	343.15	354.7	0.9871
4.092	343.15	1527.8	0.9388	0.736	343.15	259.7	0.9929
3.368	343.14	1243.7	0.9493				

Table 3. Second and Third Mixture Virial Coefficients of C_2H_6 (1) + CO (2) + N_2 (3) + (1 − x_1 − x_2 − x_3) O_2

T/K	x_1	$\lim_{\rho_n \to 0} Z$	$-B_{mix}$/(cm^3·mol^{-1})	C_{mix}/(cm^6·mol^{-2})
293.15	0.365 63	1.0002	56.88 ± 1.6	4133 ± 400
303.15	0.416 53	1.0019	60.58 ± 1.4	4460 ± 330
313.15	0.354 96	1.0004	45.66 ± 1.3	3796 ± 320
323.15	0.355 57	1.0007	42.38 ± 1.7	4025 ± 600
333.15	0.481 93	1.0016	55.84 ± 1.7	4141 ± 340
343.15	0.467 62	1.0044	48.90 ± 0.4	3916 ± 200

Second and third virial coefficients obtained from the best fit of the quadratic equation (1) are listed in Table 3. Polynomials of higher order were also tested, but no significant improvement to the fit was evident, and so a quadratic equation was deemed to be satisfactory.

The unlike interaction second virial coefficients were evaluated from the mixture values using the relation

$$B_m = \sum_{i=1}^{m}\sum_{j=1}^{m} y_i y_j B_{ij} \qquad (4)$$

The values obtained using pure component values obtained from the GERG correlation are listed in Table 3 and plotted in Figure 1 along with the correlations of Tsonopoulos (*8*) and of Mak and Lielmezs (*9*). In both these correlations $T_{c,12}$ has the form

$$T_{c,12} = (T_{c,1}T_{c,2})^{0.5}(1 - k_{12}) \qquad (5)$$

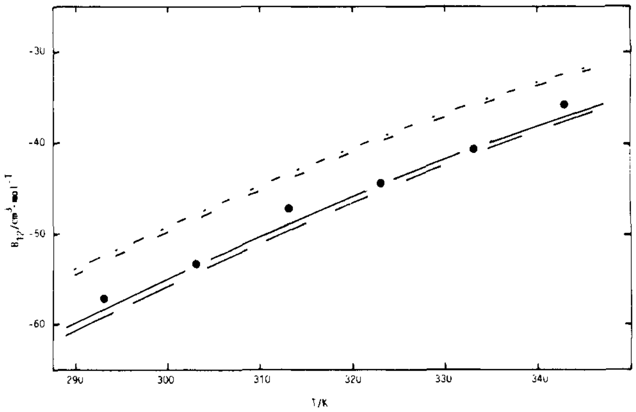

Figure 1. Unlike interaction second virial coefficient of CO + C_2H_6: ●, this work; – – –, Tsonopoulos (*6*) with k_{12} = 0; - - -, Tsonopoulos (*6*) with k_{12} = 0.042; —, Mak and Lielmezs (*7*) with k_{12} = 0; – – –, Mak and Lielmezs with k_{12} = 0.042.

Most compilations of association parameters set k_{12} = 0 for the system CO + C_2H_6. The Mak and Lielmezs correlation is based to a degree on the Peng–Robinson equation of state (*10*) and a k_{ij} value for use in the equation

$$a_{ij} = (a_{ii}a_{jj})^{0.5}(1 - k_{ij,PR}) \qquad (6)$$

A value of $k_{ij,PR}$ = 0.026 obtained from the data tabulated by Knapp et al. (*11*) has been reported (*12*).

Table 4. Unlike Interaction Virial Coefficients for C_2H_6 (1) + CO (2)

T/K	$-B_{12}$/(cm^3·mol^{-1})	C_{112}/(cm^6·mol^{-2})	C_{122}/(cm^6·mol^{-2})
293.15	56.97	6422	3434
303.15	53.38	6315	3372
313.15	47.15	6032	3199
323.15	44.63	6309	3641
333.15	40.74	5174	2729
343.15	35.60	4997	2833

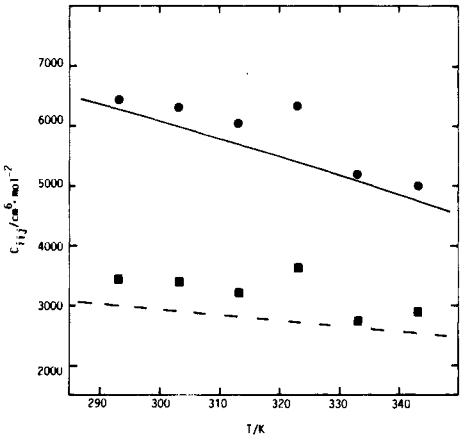

Figure 2. Unlike interaction third virial coefficients of C_2H_6 (1) + CO (2): ●, this work, C_{122}; ■, this work, C_{112}; - - -, Orbey–Vera (*12*), C_{122}; —, Orbey–Vera, C_{122}.

The coefficients a and b in the Peng–Robinson equation obey the relations

$$a_{ii} = 0.477235R^2T_{c,i}^{\ 2}/P_{c,i} \quad (7)$$

$$b_{ii} = 0.077796RT_{c,i}/P_{c,i} \quad (8)$$

$$\alpha = [1 + k_i(1 - T_R^{\ 0.5})]^2 \quad (9)$$

and so with simple combining rules for the coefficients it is possible to obtain an estimate of k_{12} knowing $k_{12,PR}$. The value obtained, $k_{12} = 0.042$, was tried in both the Tsonopoulos correlation and that of Mak and Lielmezs to see whether an improved fit to the B_{12} results could be effected.

It is clear from Figure 1 that the two correlations tested fit the results quite well with k_{12} set to zero. The Mak and Lielmezs relation gives the best fit, but the difference is probably not significant. A slightly improved fit could evidently be obtained by a nonzero k_{12} but with a value well below 0.042.

Third interaction virial coefficients were obtained from the mixture values listed in Table 3 using the correlations proposed by McGregor et al. (*13*) for the determination of third cross virial coefficients using one binary mixture sample only. The proposed relations were

$$C_m = \sum_i y_iC_{iii} + \sum_i \sum_{j=i+1} y_iy_j\delta C_{ij} \quad (10)$$

and

$$\delta C_{ij} = 3C_{iij} - 2C_{iii} - C_{jjj} = 3C_{ijj} - C_{iii} - 2C_{jjj} \quad (11)$$

Rearranging these equations for a binary system gives for C_{112} and C_{122}

$$C_{112} = C_m/3y_1y_2 + C_{111}(2 - 1/y_2)/3 + C_{222}(1 - 1/y_1)/3 \quad (12)$$

and

$$C_{122} = C_m/3y_1y_2 + C_{222}(2 - 1/y_1)/3 + C_{111}(1 - 1/y_2)/3 \quad (13)$$

The third virial coefficients for pure CO and C_2H_6 were taken from the correlation reported in the GERG technical report no. 2 (*3*). The resulting C_{112} and C_{122} values are recorded in Table 4.

Unlike interaction third virial coefficients may be predicted using the Orbey and Vera (*14*) correlation. This is a corresponding states procedure requiring unlike interaction critical point and acentric factor values. The same procedures as were used in correlating B_{12} values were used. The Orbey–Vera correlation has the form

$$C_{ij} = (RT_{c,ij}/p_{c,ij})^2[C^0 + \omega_{ij}C^1] \quad (14)$$

where

$$C^0 = 0.01407 + 0.02432T_r^{-2.8} - 0.00313T_r^{-10.5} \quad (15)$$

$$C^1 = -0.02676 + 0.0177T_r^{-2.8} + 0.04T_r^{-3.0} - 0.003T_r^{-6.0} - 0.00228T_r^{-10.5} \quad (16)$$

and ω_{ij} is the acentric factor.

The unlike interaction terms C_{iij} are obtained (*14*) using

$$C_{112} = (C_{111} + 2C_{12})/3 \quad (17)$$

$$C_{122} = (C_{222} + 2C_{12})/3 \quad (18)$$

The predictions of the Orbey–Vera correlation extended to unlike interaction terms in this way are plotted in Figure 2. Evidently the agreement with experiment is good.

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