Compression Factors and Virial Coefficients of Ethene and Ethene + Ethane Mixtures

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Compression factors were measured using a weighing method for ethene + ethane at y(ethene) = 0.7 and 0.3, temperatures from 283.15 to 333.15 K, and pressures up to 6.0 MPa. Pure and unlike interaction second and third virial coefficients were determined and compared with predictive equations.

Introduction

With the growth of the petrochemical industry, worldwide production of ethene expanded rapidly into megatons per year. The measurement of large volume flows of ethene demanded for custody transfer and design purposes accurate knowledge of the compression factor, from which the thermodynamics properties such as enthalpy, entropy residuals, and fugacity coefficients can be determined.

The pVT behavior of ethene and mixtures with common natural gas components is also of interest in the application of the Groupe Europeen de Recherches Gazieres (GERG) virial coefficient procedures to natural and industrial gases (*1*, *2*).

By investigating (p, V, T, and n) properties of ethene, it's compression factors Z can be determined through the compression factor's definition

$$Z = pVM/RTm \quad (1)$$

It has been previously demonstrated (*1*) that directly measuring the pressure (p), volume (V), temperature (T), and mass (m) of a gas of molar mass M to determine Z is a straightforward and accurate way to obtain the compression factor.

Experimental Section

The experimental apparatus used in this experimental study and the procedures were unchanged from those reported in earlier work (*3*, *4*). In order to extend the temperature range, a refrigeration system was coupled to the air thermostat.

The gas samples were analyzed by gas chromatography and are shown in Table I. Eight to eleven compression factor measurements were taken for each cylinder at a given temperature.

Results

The compression factors for ethene and y C_2H_4 + $(1 - y)$ C_2H_6 have been measured at 10 K intervals in the temperature range from 283.15 to 333.15 K and pressures up to 6 MPa. The experimental results for pure ethene were fitted to the truncated virial equation as follows:

$$Z = pV/nRT = 1 + (B/V_m) + (C/V_m^2) \quad (2)$$

where B and C are second and third virial coefficients. The results for pure ethene are shown in Table II. The second and third virial coefficients derived from the compressibility factors are presented in Table III. The second virial coefficients for pure ethene are compared with the literature values of Douslin and Harrison (*5*), Michels and Geldermans (*6*), Ratzsch and Bittrich (*7*), and Thomas and Zander (*8*).

Table I. Compositions of Gases Used in This Study and Mean Molar Mass M

gas	component	mole fraction	M/(g mol^{-1})
ethane	C_2H_6	0.9967	30.063
	C_2H_4	0.0025	
	N_2	0.0008	
ethene	C_2H_4	0.9991	
	C_2H_2	0.0004	28.054
	CO_2	0.0002	
	O_2	0.0001	
	N_2	0.0001	

Table II. Compression Factor Z for Ethene

p/MPa	T/K	Z	p/MPa	T/K	Z
4.3031	283.17	0.5975	3.9166	283.15	0.6527
3.5168	283.15	0.7029	2.8938	283.13	0.7676
2.4806	283.14	0.8105	2.2066	283.17	0.8333
1.8352	283.15	0.8665	1.5985	283.15	0.8848
1.2982	283.14	0.9070	1.0089	283.10	0.9269
0.7199	283.15	0.9477			
5.2451	293.15	0.5501	4.7616	293.15	0.6170
4.3060	293.15	0.6691	3.7646	293.17	0.7230
3.3101	293.14	0.7645	2.9070	293.13	0.7977
2.4432	293.14	0.8373	1.9192	293.15	0.8758
1.0877	293.13	0.9285	0.7427	293.15	0.9514
6.0275	303.13	0.5503	5.0276	303.13	0.6163
4.8281	303.16	0.6749	3.9839	303.15	0.7450
3.3040	303.15	0.7953	2.7263	303.17	0.8371
2.1983	303.15	0.8726	1.7512	303.15	0.8999
1.3178	303.16	0.9251	1.0702	303.16	0.9394
0.7436	303.15	0.9568			
5.8421	313.15	0.6434	5.1546	313.15	0.6967
3.8457	313.15	0.7845	3.1693	313.15	0.8257
2.7600	313.15	0.8503	2.2434	313.16	0.8811
1.7842	313.15	0.9067	1.3849	313.15	0.9292
1.0755	313.15	0.9419	0.7381	313.16	0.9596
5.9465	323.16	0.6890	5.1644	323.17	0.7376
4.5158	323.16	0.7748	3.6365	323.17	0.8224
3.1111	323.15	0.8500	1.9203	323.15	0.9136
1.5147	323.17	0.9324	1.2408	323.14	0.9450
0.9233	323.15	0.9583	0.6829	323.14	0.9671
6.1592	333.15	0.7220	5.2521	333.15	0.7657
4.5245	333.16	0.8021	3.9100	333.13	0.8303
3.3910	333.14	0.8540	2.3234	333.16	0.9034
1.9420	333.15	0.9191	1.6096	333.14	0.9331
1.1714	333.15	0.9499	0.8010	333.15	0.9663

Excellent agreement is obtained with these works and with the $B(T)$ equation

$$B = b_0 + b_1/T + b_2/T_2$$

with the ethene coefficients below estimated by Levelt-Senger and Hastings (*9*).

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$$b_0 = 53.6535\ \text{cm}^3\ \text{mol}^{-1}$$

$$b_1 = -27398.0\ \text{cm}^3\ \text{mol}^{-1}\ \text{K}^{-1}$$

$$b_2 = -9.03445\text{E+6}\ \text{cm}^3\ \text{mol}^{-1}\ \text{K}^{-2}$$

The second virial coefficients are plotted in Figure 1. Also plotted are values from the literature and the values calculated from the Levelt-Senger and Hastings equation which evidently agrees closely with the results obtained.

The ethene third virial coefficients are plotted in Figure 2. Also plotted are the results obtained by Butcher and Dadson (*14*), Douslin and Harrison (*5*), and Trappeniers et al. (*15*) which are all in good agreement above about 313 K. Below that temperature the results of this work are generally larger in magnitude but in excellent agreement with the predictions of the Orbey and Vera (*16*) equation. This equation takes the form

$$C(p_c/RT_c)^2 = C^{(0)} + \omega C^{(1)} \tag{3}$$

with

$$C^{(0)} = 0.01407 + 0.02432/T_R^{2.8} - 0.00313/T_R^{10.5} \tag{4}$$

and

$$C^{(1)} = -0.02676 + 0.0177/T_R^{2.8} + 0.04/T_R^{3} - 0.003/T_R^{6} - 0.00228/T_R^{10.5} \tag{5}$$

The compression factors for y C_2H_4 + $(1 - y)$ C_2H_6 are presented in Table IV. The interaction second virial coefficients of the mixtures in this work were evaluated from the second virial coefficient for gas mixtures

$$B_m = \sum_{i=1}^{m}\sum_{j=1}^{m} y_i y_j B_{ij} \tag{6}$$

or for the binary mixtures

$$B_{12} = y_1^2 B_{11} + y_2^2 B_{22} + 2y_1 y_2 B_{12} \tag{7}$$

The B_m and C_m values obtained by fitting a quadratic equation to the compressibility factor as a function of molar density are reported in Table V.

A detailed study into whether a higher order equation might be justified has not been attempted.

Also reported are the unlike interaction second virial coefficient values B_{12} (two determinations at each temperature). The pure component B values used for the B_{12} calculation were, for ethene, the values in Table III and, for ethane, a fit to the data reported by Dymond and Smith (*13*) and McElroy et al. (*4*), the actual values used being listed in Table VI.

The averaged values of interaction second virial coefficients B_{12} are listed in Table VI and have been plotted in Figure 3 along with the values from the Tsonopoulos equation (*10*) and the Mak–Leilmezs equation (*11*). The Tsonopoulos equation for pure nonpolar components is

$$\frac{Bp_c}{RT_c} = f^{(0)}(T_R) + \omega_f^{(1)}(T_R) \tag{8}$$

Table III. Second and Third Virial Coefficients of Ethene

T/K	$\lim_{\rho\to 0} Z$	B/(cm^3 mol^{-1})	C/(cm^6 mol^{-2})
283.15	0.9982	−155.5	7920
293.15	0.9978	−144.6	7712
303.15	0.9988	−134.7	7245
313.15	0.9970	−126	7082
323.15	1.0000	−117.9	6567
333.15	0.9986	−109.7	6420

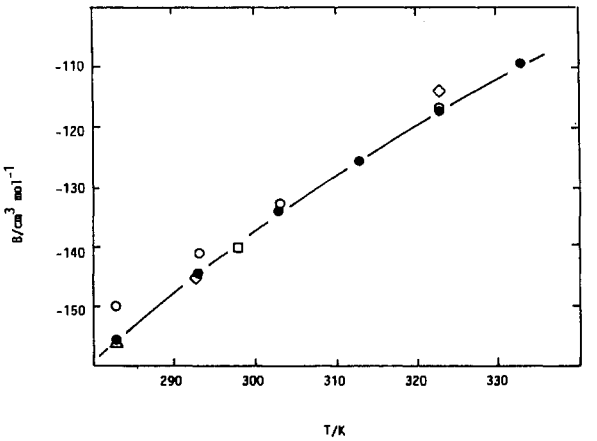

Figure 1. Second virial coefficients of ethene: ●, this work; △, D. R. Douslin and R. H. Harrison (*5*); ◇, M. Ratzsch and H. Bittrich (*7*); ○, W. Thomas and M. Zander (*8*); □, Michels and Geldermans (*6*); —, second virial coefficient calculated from the Levelt-Senger and Hastings equation (*9*).

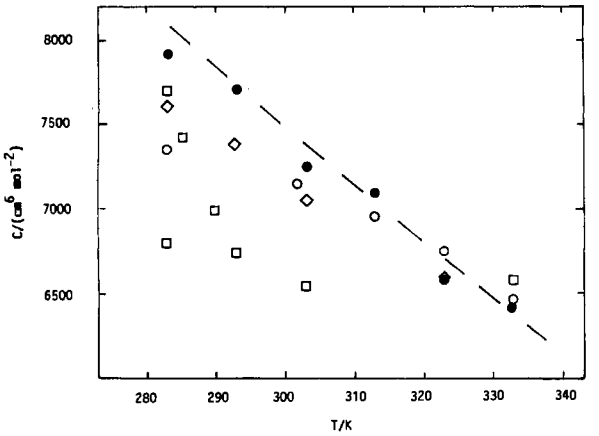

Figure 2. Third virial coefficients of ethene: ●, this work, ○, Butcher and Dadson (*14*); □, Trappeniers et al. (*15*); ◇, Douslin and Harrison (*5*); —, Orbey and Vera equation (*16*).

where

$$f^{(0)}(T_R) = 0.1445 - 0.33/T_R - 0.1385/T_R^2 - 0.0121/T_R^3 - 0.000607/T_R^8 \tag{9}$$

$$f^{(1)}(T_R) = 0.0637 + 0.331/T_R^2 - 0.423/T_R^3 - 0.008/T_R^8 \tag{10}$$

the reduced temperature $T_R = T/T_c$ and ω is the Pitzer acentric factor. The pseudocritical values $p_{c,12}$, $T_{c,12}$, and ω_{12} needed for application of the Tsonopoulos equation to interaction virial coefficients were calculated as follows:

$$T_{c,12} = (T_{c,1}T_{c,2})^{1/2}(1 - k_{12}) \tag{11}$$

$$p_{c,12} = \frac{4T_{c,12}(p_{c,1}V_{c,1}/T_{c,1} + p_{c,2}V_{c,2}/T_{c,2})}{(V_{c,1}^{1/3} + V_{c,2}^{1/3})^3} \tag{12}$$

$$\omega_{12} = 0.5(\omega_1 + \omega_2) \tag{13}$$

k_{12} is the characteristic interaction constant, but for ethene and ethane mixtures it is set to zero. The Tsonopoulos equation predicts B_{12} values with average and maximum deviations of 4.6 and 7.6 cm^3 mol^{-1} in the temperature range 283.15–333.15 K. While consistently slightly higher than the experimental values, the agreement is excellent, as illustrated in Figure 3.

Table IV. Compression Factor Z for y Ethene + $(1 - y)$ Ethene

p/MPa	T/K	Z	p/MPa	T/K	Z	p/MPa	T/K	Z	p/MPa	T/K	Z
					$y = 0.3628$						
3.4161	283.17	0.6117	3.1919	283.16	0.6600	2.8608	283.17	0.7106	2.5396	283.15	0.7553
2.1523	283.15	0.8007	1.8648	283.17	0.8343	1.5596	283.15	0.8650	1.2509	283.13	0.8935
0.9994	283.13	0.9121	0.7222	283.14	0.9148						
					$y = 0.6389$						
4.0158	283.13	0.5596	3.5928	283.14	0.6381	3.1861	283.15	0.6974	2.7237	283.15	0.7560
2.3756	283.16	0.7941	2.0123	283.16	0.8307	1.6793	283.16	0.8615	1.4448	283.14	0.8816
1.1737	283.16	0.9062	0.9689	283.14	0.9435						
					$y = 0.3734$						
4.4468	293.14	0.5023	4.0165	293.15	0.5976	3.5478	293.17	0.6733	3.0425	293.14	0.7338
2.6933	293.14	0.7741	2.3618	293.16	0.8072	2.0570	293.16	0.8367	1.7251	293.14	0.8662
1.3467	293.13	0.8977	0.7593	293.14	0.9435						
					$y = 0.7965$						
4.7667	293.16	0.5740	4.119	293.15	0.6526	3.6978	293.14	0.7085	3.0936	293.15	0.7667
2.6311	293.14	0.8077	2.2233	293.14	0.8416	1.8473	293.16	0.8709	1.4963	293.15	0.8972
1.2517	293.15	0.9147	1.0008	293.17	0.9315	0.7642	293.16	0.9484			
					$y = 0.3923$						
4.6880	303.14	0.5874	4.2982	303.14	0.6390	3.8059	303.14	0.6961	3.1890	303.14	0.7581
2.6747	303.14	0.8071	2.1263	303.15	0.8510	1.8201	303.15	0.8769	1.5146	303.14	0.8988
0.9964	303.14	0.9301	0.7329	303.14	0.9492						
					$y = 0.7761$						
5.6063	303.16	0.5501	5.0497	303.15	0.6182	4.4421	303.17	0.6835	3.8397	303.14	0.7351
2.7219	303.15	0.8261	2.2349	303.14	0.8612	1.7948	303.14	0.8911	1.4357	303.16	0.9124
1.0513	303.16	0.9338									
					$y = 0.3226$						
4.5415	313.14	0.6611	4.0449	313.13	0.7095	3.4409	313.15	0.7626	3.9989	313.14	0.7967
2.5786	313.15	0.8335	2.1605	313.17	0.8649	1.4404	313.15	0.9102	0.2084	313.16	0.9238
0.7031	313.16	0.9552									
					$y = 0.6516$						
5.0965	313.16	0.6545	4.5795	313.16	0.6983	4.0830	313.13	0.7389	3.6227	313.16	0.7727
3.0355	313.15	0.8142	2.5291	313.14	0.8498	1.736	313.17	0.9010	1.3386	313.16	0.9231
1.0884	313.17	0.9357	0.8133	313.16	0.9518						
					$y = 0.3753$						
4.4867	323.16	0.7220	3.8136	323.13	0.7719	3.2973	323.15	0.8073	2.4681	323.15	0.8624
2.0643	323.15	0.8870	1.7194	323.14	0.9087	1.4276	323.15	0.9243	0.9341	323.15	0.9509
0.6934	323.14	0.9623									
					$y = 0.6508$						
5.1581	323.15	0.7048	4.4764	323.15	0.7514	3.3726	323.15	0.8228	2.7931	323.15	0.8564
2.2947	323.15	0.8850	1.9894	323.15	0.9060	1.2213	323.15	0.9457	0.9528	323.14	0.9537
0.6812	323.14	0.9679									
					$y = 0.3104$						
4.2908	333.14	0.7641	3.6548	333.15	0.8034	3.1416	333.16	0.8342	2.6962	333.14	0.8590
2.2436	333.14	0.8854	1.8587	333.14	0.9073	1.5341	333.15	0.9217	1.2596	333.13	0.9352
1.0025	333.15	0.9504	0.7999	333.14	0.9624						
					$y = 0.6648$						
5.2102	333.16	0.7402	4.4469	333.15	0.7832	3.8077	333.14	0.8168	3.2708	333.16	0.8446
2.6604	333.15	0.8776	2.1984	333.16	0.8991	1.8040	333.15	0.9174	1.4616	333.15	0.9331
1.1258	333.17	0.9491	0.7710	333.15	0.9662						

Table V. Second Virial B_m, Third Virial Coefficient C_m, and Interaction Virial Coefficient B_{12} for y Ethene + $(1 - y)$ Ethane

T/K	ethene mole fraction	B_m/(cm^3 mol^{-1})	C_m/(cm^6 mol^{-2})	B_{12}/(cm^3 mol^{-1})
283.15	0.3628	−182.8	8260	−168.4
283.15	0.6389	−173.8	9250	−180.2
293.15	0.3734	−172.3	9700	−162.3
293.15	0.7965	−154.0	8680	−166.8
303.15	0.3923	−158.0	8890	−150.1
303.15	0.7761	−142.3	7700	−150.1
313.15	0.3226	−150.2	8370	−138.3
313.15	0.6514	−138.8	8040	−143.2
323.15	0.3753	−136.3	6900	−127.1
323.15	0.6508	−126.6	6520	−127.3
333.15	0.3104	−132.5	8290	−125.7
333.15	0.6648	−120.8	7360	−125.1

The Mak and Leilmezs correlation derives from the Peng and Robinson equation (*12*) but has similarities with the Tsonopoulos equation and so should be extendable to mixtures in a similar way. The equation has the following form:

$$\frac{Bp_c}{RT_c} = 0.778 - 0.45724\frac{\alpha}{T_R} \tag{14}$$

where

$$\alpha = \alpha^{(0)} + \omega\alpha^{(1)} \tag{15}$$

and

$$\alpha^{(0)} = -1.4524905 + 14.360017/T_R - 45.000285/T_R^2 + 78.907097/T_R^3 - 79.449258/T_R^4 + 45.841959/T_R^5 - 14.078304/T_R^6 + 1.7835426/T_R^7 \tag{16}$$

$$\alpha^{(1)} = -4.3816022 + 15.205023/T_R - 20.874489/T_R^2 + 12.697209/T_R^3 - 2.5851848/T_R^4 \tag{17}$$

We have extended its application to mixtures using eqs 11–13 and applying them just as for the Tsonopoulos equation.

Table VI. Unlike Interaction Second Virial Coefficients B and Third Virial Coefficients C for Ethane (1) + Ethene (2)

T/K	$-B_{11}$/(cm^3 mol^{-1})	$-B_{12}$/(cm^3 mol^{-1})	C_{111}/(cm^6 mol^{-2})	C_{222}/(cm^6 mol^{-2})	C_{112}/(cm^6 mol^{-2})	C_{122}/(cm^6 mol^{-2})
283.15	208	174.3	11 500	7960	3800	12 800
293.15	194	164.6	11 090	7640	9050	9 870
303.15	179	150.1	10 700	7330	8900	7 700
313.15	167	140.8	10 320	7020	6700	9 100
323.15	154	127.2	9 900	6700	5400	6 700
333.15	145	125.4	9 470	6400	7800	7 500

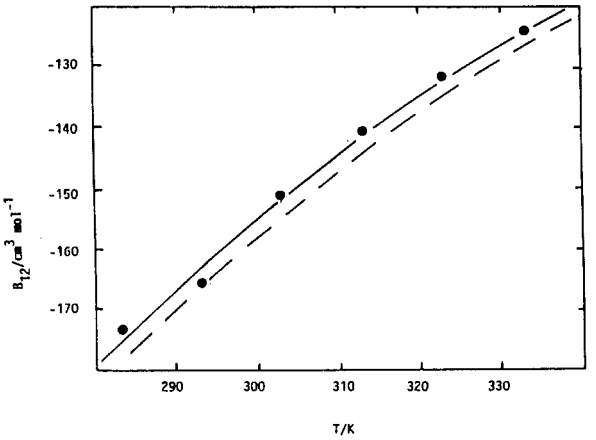

Figure 3. Unlike interaction second virial coefficients for ethane + ethene: ●, this work; —, Tsonopoulos (*10*); - - -, Mak and Leilmezs (*11*).

The Mak and Leilmezs equation predictions are also plotted in Figure 3, and the equation evidently does not fit the experimental data as well as the Tsonopoulos equation.

Unlike interaction third virial coefficients are listed in Table VI. C_{112} and C_{122} have been calculated from the C_m values and mole fractions, using the smoothed values of C_{111} and C_{222} listed in the table and the relation

$$C_m = y_1^3 C_{111} + 3y_1^2 y_2 C_{112} + 3y_1 y_2^2 C_{122} + y_2^3 C_{222} \qquad (18)$$

Since C_m, C_{111}, C_{222}, and the mole fractions are known, there are two unknowns, C_{112} and C_{122}, and because C_m has been measured for two compositions, the two equations can be solved for the two unknowns. This procedure necessarily results in an accumulation of errors in the C_{112} and C_{122} values. There are however very few measurements of unlike interaction third virial coefficients reported, and so the results are of interest. Efforts to reduce the uncertainty in C_{ijj} measurements are continuing.

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