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Second and Third Virial Coefficients for Methane + Ethane and Methane + Ethane + Carbon Dioxide at (300 and 320) K

Huaiwen Hou,[†] **James C. Holste,*** **and Kenneth R. Hall**

Department of Chemical Engineering, Texas A&M University, College Station, Texas 77843

Kenneth N. Marsh and Bruce E. Gammon

Thermodynamics Research Center, Texas A&M University, College Station, Texas 77843

Measurements of pVT made using the Burnett technique at (300 and 320) K are reported for methane, ethane, three x_1 methane + $(1 - x_1)$ ethane mixtures with $x_1 = 0.30623$, 0.49971, and 0.70090, and two x_1 methane + x_2 ethane + $(1 - x_1 - x_2)$ carbon dioxide mixtures with $x_1 = 0.32125$, $x_2 = 0.34099$ and $x_1 = 0.24759$, $x_2 = 0.56013$. Second virial coefficients have been calculated from these results for the pure fluids, and the binary and ternary mixtures. Cross second and third virial coefficients have been derived, including the cross third virial coefficient which describes the simultaneous unlike interaction between methane, ethane, and carbon dioxide. The experimental results were used to test an approximation to the virial equation which greatly simplifies calculations for multicomponent mixtures and which requires only experimental virial coefficients for binary mixtures. Values calculated using the model agree with experimental values within the estimated uncertainties. The results are compared with literature values, where available.

Introduction

Natural gases often contain concentrations of carbon dioxide. Removal of carbon dioxide from gas streams is necessary because its presence leads to lower energy content and inefficiencies in combustion. Because methane and ethane are the major components in natural gas, the separation of carbon dioxide from methane and ethane is important. Accurate densities over a pressure and temperature range for CH_4, C_2H_6, and CO_2 and their mixtures are necessary for process design, operation calculations, and custody transfer.

Many theoretical and empirical models have been proposed to predict multicomponent mixture properties from few-component mixture properties. Testing such models requires results for multicomponent mixtures. However, the infinite number of possible multicomponent mixtures makes it impossible to study each mixture experimentally. A feasible procedure is to choose some typical, useful multicomponent mixtures as representative. In this work, we have studied two $CH_4 + C_2H_6 + CO_2$ mixtures.

Many experimental studies have been made on pure CH_4, C_2H_6, and CO_2 (Dymond and Smith, 1980; Sychev et al., 1987a,b; Holste et al., 1987) and some studies on their binary mixtures (see references in the Discussion). There have been a number of measurements from which both cross second and third virial coefficients for $CH_4 + C_2H_6$ can be derived (Haynes et al., 1985; Blanke and Weiss, 1995; see also references in the review by Hiza et al. (1982)). However, accurate and consistent third virial coefficients are scarce for this mixture, thereby limiting the applicability of the virial equation. In this work, we have measured the second and third virial coefficients for three $CH_4 + C_2H_6$ mixtures.

The virial equation is commonly used to describe the behavior of gases and gas mixtures. One form of the virial equation represents the compressibility factor Z as a power series in the molar density ρ:

$$Z = p/(\rho RT) = 1 + B\rho + C\rho^2 + ... \tag{1}$$

where B, C, ... are the second, third, and higher virial coefficients, respectively. For many gases, eq 1, when truncated after the third term, provides a good representation of Z up to about two-thirds of the critical density.

The mixing rules for the second and third virial coefficients of an n-component mixture are:

$$B(x) = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j B_{ij} \tag{2}$$

$$C(x) = \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{k=1}^{n} x_i x_j x_k C_{ijk} \tag{3}$$

where B_{ij} and C_{ijk} are the cross second and third virial coefficients, respectively, and $B(x)$ and $C(x)$ are the mixture coefficients. Equation 3, when applied to a ternary mixture, contains a factor C_{123} which arises from simultaneous interactions of three unlike molecules. This coefficient cannot be determined from measurements on binary mixtures without assumptions because only two species are present and the triple unlike interaction cannot occur. In this work, we have determined at two temperatures the cross third virial coefficient which describes the simultaneous interactions among methane, ethane, and carbon dioxide.

Experimental Section

Measurements were made with a Burnett apparatus described previously by Holste et al. (1987). Figure 1 is a schematic diagram of the apparatus, which consists of two thermostated cells, V_A and V_B, and a diaphragm-type differential pressure indicator (DPI). Cell V_A is filled with the sample fluid, and the equilibrium pressure is measured. The sample is then expanded into the previously evacuated

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* To whom correspondence should be addressed.

[†] Deceased.

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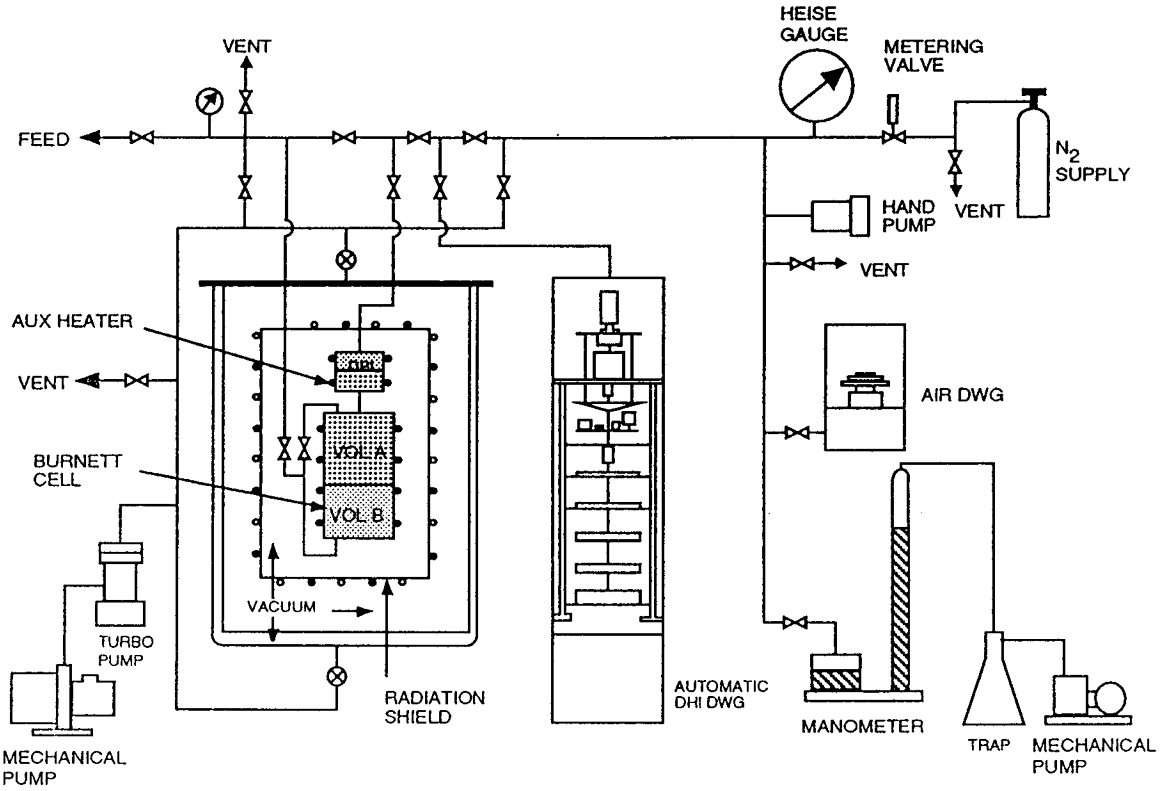

Figure 1. Schematic diagram of the Burnett apparatus.

cell V_B, and the equilibrium pressure is measured again. The sequence of evacuation of V_B, expansion of the sample from V_A into $V_A + V_B$, and measurement of equilibrium pressure is repeated until a predetermined minimum pressure is reached.

The temperature of the apparatus is controlled automatically within ±3 mK of the set point. The temperature is measured with a Minco platinum resistance thermometer embedded in the wall between cells V_A and V_B. The accuracy of the temperature measurement is better than ±5 mK on ITS-90. The temperature gradient between the upper end of cell V_A and the lower end of cell V_B is monitored with a differential thermopile. The gradient is less than 10 mK when the equilibrium pressure is recorded.

Pressures greater than 4 MPa are measured with a DH Instrument automatic pneumatic dead-weight gauge (DWG), and pressures between (0.1 and 4) MPa are measured with a Ruska air-lubricated dead-weight gauge. A mercury manometer measures pressures below 0.1 MPa. The precision of the measured pressure is ±0.001% or ±10 Pa (whichever is greater) using techniques described by Holste et al. (1977). The accuracy of the measured pressure is better than ±0.015%.

The mixture samples were prepared gravimetrically in thoroughly cleaned, dried, and evacuated 16 dm^3 aluminum cylinders. The amounts of mixtures prepared ranged from 46 mol (1.35 kg) for the ethane-rich ternary mixture to 56 mol (1.10 kg) for the ethane-lean binary mixture. Sample masses were determined within ±5 mg using an HCE 25 Voland balance. This mass measurement contributes less than ±0.000 01 uncertainty in the mole fraction. Immediately after weighing, the components were mixed thoroughly using mixers located inside the cylinders. The mixer design is given in Brugge et al. (1992).

The methane used was from Scientific Gas Products with a claimed purity of better than 0.9999 mole fraction, the ethane was from Matheson with a claimed purity of better than 0.99 mole fraction, and the carbon dioxide was from Scott Specialty Gases with a claimed purity of better than 0.9999 mole fraction. Each of these gases was used without further purification. Gas chromatography indicated the following mole fractions for the ethane feedstock: ethane, 0.9972; ethene, 0.0021; nitrogen, 0.0005; methane, 0.0002. The various impurities in the feedstocks contribute maximum uncertainties of ±0.0005 to the mixture mole fractions. This contribution is significantly larger than that contributed by the mass measurement; therefore, it is the overall uncertainty in the mixture composition. All uncertainties given in this work represent 95% confidence limits.

Analysis

Burnett runs consist of a series of isothermal pressure measurements made after expansions of the fluid from a primary volume into a smaller, evacuated volume. For each expansion, the ratio of the density before and after the expansion is

$$N_i = (V_A + V_B)_i/(V_A)_{i-1} = \rho_{i-1}/\rho_i \tag{4}$$

Therefore,

$$\rho_i = \rho_m \prod_{l=i+1}^{m} N_l \tag{5}$$

where N is the cell constant, m is the total number of expansions, ρ_i is the density after the ith expansion, and ρ_m is the density at the lowest pressure (the last expansion). The ideal-gas value is a good starting value for iterative calculations to establish ρ_m. The cell volume distorts with pressure, and the cell constant relative to the zero pressure value is

$$N_i = N_\infty\left[\frac{1 + \gamma_{(A+B)}p_i}{1 + \gamma_A p_{i-1}}\right] \tag{6}$$

Table 1. Experimental Pressures p and Derived Compressibility Factors Z for Burnett Isotherms for CH_4 (1) + C_2H_6 (2) + CO_2 (3)[a]

p/MPa	Z	p/MPa	Z	p/MPa	Z	p/MPa	Z	p/MPa	Z	p/MPa	Z
$x_1 = 0.0$, $x_2 = 1.0000$, $x_3 = 0.0$											
$T = 300.00$ K											
Set 1											
3.94952*	0.58119*	2.36125	0.79821	1.17072	0.90842	0.53863	0.95941	0.24022	0.98218	0.10572	0.99221
3.16389	0.70592	1.68594	0.86346	0.79865	0.93892	0.36059	0.97309	0.15954	0.98822		
Set 2											
3.68429*	0.63000*	2.09994	0.82447	1.02171	0.92081	0.46645	0.96498	0.20734	0.98465		
2.86587	0.74270	1.48219	0.88166	0.69374	0.94726	0.31164	0.97680	0.13757	0.98985		
$T = 320.00$ K											
Set 1											
3.96164	0.70798	2.10199	0.86218	0.99626	0.93795	0.45008	0.97258	0.19920	0.98798		
2.94588	0.79758	1.45988	0.90720	0.67214	0.95869	0.29990	0.98184	0.13202	0.99206		
Set 2											
6.57180*	0.35466*	3.97761	0.70642	1.46817	0.90664	0.45285	0.97241	0.13285	0.99200		
5.88199*	0.45577*	2.96008	0.79643	1.00214	0.93756	0.30177	0.98172				
5.02774*	0.58924*	2.11321	0.86137	0.67620	0.95844	0.20044	0.98791				
$x_1 = 0.30623$, $x_2 = 0.69377$, $x_3 = 0.0$											
$T = 300.00$ K											
Set 1											
4.82487	0.69568	2.57892	0.85344	1.29902	0.93350	0.55671	0.97052	0.24668	0.98706	0.10827	0.99434
3.59995	0.78638	1.79686	0.90084	0.83048	0.95564	0.37123	0.98046	0.16355	0.99144		
Set 2											
4.49823	0.72117	2.35680	0.86722	1.11302	0.94000	0.50218	0.97345	0.22214	0.98836	0.09743	0.99491
3.31687	0.80564	1.63312	0.91040	0.75033	0.96003	0.33453	0.98241	0.14721	0.99230		
$T = 320.00$ K											
Set 1											
7.64572*	0.62039*	4.29669	0.79964	2.12146	0.90606	0.99714	0.95781	0.43625	0.98138	0.19210	0.99184
5.84073	0.71753	3.05637	0.86169	1.44793	0.93684	0.65453	0.97193	0.28979	0.98767	0.12716	0.99461
Set 2											
6.84059	0.66295	3.72594	0.82866	1.80384	0.92069	0.82344	0.96456	0.36617	0.98439	0.16098	0.99317
5.14370	0.75518	2.61979	0.88266	1.22452	0.94684	0.55025	0.97646	0.24300	0.98967	0.10650	0.99548
$x_1 = 0.49971$, $x_2 = 0.50029$, $x_3 = 0.0$											
$T = 300.00$ K											
Set 1											
5.29681	0.76228	2.68204	0.88577	1.25097	0.94821	0.56163	0.97705	0.24793	0.98993	0.10864	0.99560
3.82265	0.83336	1.84430	0.92275	0.84077	0.96546	0.37366	0.98478	0.16422	0.99334		
Set 2											
6.52288	0.70151	3.44733	0.85087	1.64423	0.93140	0.74566	0.96942	0.33063	0.98655	0.14516	0.99411
4.82156	0.78557	2.40229	0.89826	1.11176	0.95409	0.49742	0.97970	0.21924	0.99110		
$T = 320.0$ K											
Set 1											
7.39244	0.74573	3.76676	0.87195	1.77112	0.94093	0.79859	0.97364	0.35324	0.98840	0.15493	0.99492
5.34240	0.81641	2.60202	0.91249	1.19338	0.96044	0.53193	0.98249	0.23410	0.99232	0.10244	0.99664
Set 2											
6.87664	0.76305	3.46577	0.88250	1.61892	0.94609	0.72772	0.97600	0.32144	0.98944	0.14089	0.99538
4.94091	0.83058	2.38476	0.91996	1.08880	0.96395	0.48433	0.98407	0.21295	0.99302		
$x_1 = 0.70090$, $x_2 = 0.29910$, $x_3 = 0.0$											
$T = 300.00$ K											
Set 1											
6.52297	0.79989	3.20570	0.90217	1.47922	0.95535	0.66125	0.98016	0.29140	0.99128	0.12759	0.99619
4.61931	0.85820	2.18978	0.93358	0.99154	0.97018	0.43945	0.98684	0.19292	0.99423		
Set 2											
6.38718	0.80396	3.13121	0.90448	1.44280	0.95646	0.64457	0.98067	0.28396	0.99151	0.12432	0.99629
4.51707	0.86138	2.13715	0.93520	0.96678	0.97093	0.42831	0.98717	0.18800	0.99438		
$T = 320.0$ K											
Set 1											
7.22467	0.83133	3.47190	0.91674	1.58730	0.96186	0.70689	0.98303	0.31100	0.99254	0.13609	0.99674
5.04687	0.87975	2.35830	0.94334	1.06156	0.97450	0.46934	0.98874	0.20581	0.99506		
Set 2											
7.13224	0.83328	3.42369	0.91788	1.56425	0.96242	0.69641	0.98328	0.30633	0.99265	0.13402	0.99678
4.97941	0.88130	2.32471	0.94415	1.04596	0.97488	0.46234	0.98890	0.20271	0.99514		

Table 1 (Continued)

p/MPa	Z	p/MPa	Z	p/MPa	Z	p/MPa	Z	p/MPa	Z	p/MPa	Z
$x_1 = 1.0000$, $x_2 = 0.0$, $x_3 = 0.0$											
$T = 300.00$ K											
Set 1											
8.43910	0.87250	3.94308	0.93553	1.78184	0.97022	0.78960	0.98670	0.34664	0.99414	0.15154	0.99744
5.79514	0.90770	2.65952	0.95590	1.18810	0.98005	0.52356	0.99117	0.22926	0.99612	0.10011	0.99831
Set 2											
7.72441	0.88138	3.59382	0.94100	1.61902	0.97290	0.71636	0.98793	0.31427	0.99469	0.13735	0.99768
5.29345	0.91502	2.41962	0.95978	1.07858	0.98187	0.47480	0.99199	0.20782	0.99649		
$T = 320.00$ K											
Set 1											
11.10990*	0.88352*	5.13106	0.93685	2.31548	0.97013	1.02600	0.98654	0.45049	0.99405	0.19695	0.99739
7.56549	0.91180	3.45720	0.95617	1.54385	0.97988	0.68038	0.99104	0.29797	0.99606	0.13012	0.99828
Set 2											
10.25215	0.88937	4.72697	0.94138	2.12800	0.97248	0.94169	0.98763	0.41321	0.99454	0.18060	0.99761
6.97906	0.91747	3.18066	0.95950	1.41772	0.98149	0.62423	0.99177	0.27326	0.99638	0.11930	0.99842
$x_1 = 0.32125$, $x_2 = 0.34099$, $x_3 = 0.33776$											
$T = 300.00$ K											
Set 1											
6.35019	0.71354	3.33336	0.85957	1.58133	0.93585	0.71528	0.97148	0.31679	0.98747	0.13902	0.99452
4.67989	0.79666	2.31563	0.90460	1.06761	0.95714	0.47682	0.98108	0.21001	0.99171		
Set 2											
5.02421	0.77995	2.51500	0.89594	1.16575	0.95311	0.52187	0.97927	0.23009	0.99091		
3.60308	0.84728	1.72302	0.92989	0.78216	0.96878	0.34696	0.98627	0.15236	0.99399		
$T = 320.00$ K											
Set 1											
6.06532	0.79438	2.99862	0.90126	1.38488	0.95524	0.61919	0.98017	0.27286	0.99130	0.11947	0.99620
4.31421	0.85592	2.04964	0.93324	0.92841	0.97015	0.41151	0.98685	0.18064	0.99424		
Set 2											
6.08822	0.79357	3.01161	0.90082	1.39125	0.95503	0.62212	0.98007	0.27416	0.99125	0.12004	0.99618
4.33153	0.85531	2.05887	0.93293	0.93276	0.97001	0.41348	0.98679	0.18151	0.99422		
$x_1 = 0.24756$, $x_2 = 0.56013$, $x_3 = 0.19231$											
$T = 300.00$ K											
Set 1											
4.70055	0.73048	2.44421	0.87173	1.15083	0.94205	0.51860	0.97436	0.29928	0.98876		
3.45008	0.81220	1.69057	0.91345	0.77522	0.96140	0.34535	0.98301	0.15192	0.99257		
Set 2											
5.32538	0.68576	2.86682	0.84730	1.37168	0.93047	0.62246	0.96914	0.27603	0.98645	0.12119	0.99407
3.98874	0.77817	2.00213	0.89647	0.92789	0.95359	0.41527	0.97953	0.18304	0.99104		
$T = 320.00$ K											
Set 1											
5.54672	0.75486	2.82425	0.88205	1.32053	0.94649	0.59351	0.97628	0.26213	0.98959	0.11487	0.99545
4.01646	0.82802	1.94498	0.92021	0.88808	0.96431	0.39499	0.98428	0.17363	0.99312		
Set 2											
6.36283	0.71454	3.33430	0.85926	1.58191	0.93557	0.71566	0.97134	0.31699	0.98740	0.13911	0.99449
4.68270	0.79665	2.31629	0.90426	1.06809	0.95693	0.47710	0.98098	0.21014	0.99166		

[a] Asterisks indicate data excluded from maximum-likelihood estimates to permit M of eq 7 to be 3.

where N_∞ is the zero-pressure cell constant while $\gamma_{(A+B)}$ and γ_A are pressure distortion coefficients which are calculated from the physical properties of the construction material. Substituting eqs 5 and 6 into the virial equation of state

$$p_i(\mathrm{calc}) = RT\sum_{k=1}^{M} B_k \rho_i^k \qquad (1a)$$

produces

$$p_i(\mathrm{calc}) = RT\sum_{k=1}^{M} B_k\left\{\rho_m N_\infty^{m-i}\prod_{l=i+1}^{m}\left[\frac{1+\gamma_{(A+B)}p_l}{1+\gamma_A p_{l-1}}\right]\right\}^k \qquad (7)$$

where R (=8.314 471 J·K^{-1}·mol^{-1}) is the gas constant, M is the number of terms in the virial equation (Brugge et al., 1992), and B_k is the kth virial coefficient ($B_1 = 1$). The parameters B_k, N_∞, and ρ_m were determined using a Burnett-isochoric reduction procedure applying the Britt and Leucke (1973) maximum-likelihood algorithm as developed by Embry (1980) and refined by Setzmann (1985). The densities associated with each pressure measurement are calculated from eq 5.

In this study, the pressure ranges are limited and M is 3 in the analysis. Values of γ_A and $\gamma_{(A+B)}$ in eq 6 are 2.29 × 10^{-5} MPa^{-1} and 2.13 × 10^{-5} MPa^{-1}, respectively at both (300 and 320) K. The second virial coefficient value changes only by about 0.05 cm^3·mol^{-1} if the pressure distortion effects are omitted from eq 7.

Table 2. Experimental Values of the Second *B* and Third *C* Virial Coefficients for CH_4 (1) + C_2H_6 (2) + CO_2 (3) Calculated by the Maximum-Likelihood Method (*N* Is the Number of Measurements)

	set	N	p_{min}/MPa	p_{max}/MPa	$100S^a$	N_∞	$B/(cm^3 \cdot mol^{-1})$	$\sigma_B/(cm^3 \cdot mol^{-1})$	$C/(cm^6 \cdot mol^{-2})$	$\sigma_C/(cm^6 \cdot mol^{-2})$
						$T = 300$ K				
$x_2 = 1.000$	1	10	0.1057	3.164	0.0027	1.515082	−182.72	0.05	10612	23
	2	9	0.1376	2.866	0.0021	1.515078	−182.60	0.07	10531	36
	1 + 2	19	0.1057	3.164	0.0031	1.515092	−182.74	0.02	10614	12
$x_1 = 0.30623$	1	11	0.1083	4.825	0.0028	1.515010	−129.86	0.04	7340	14
$x_2 = 0.69377$	2	11	0.0974	4.498	0.0022	1.515015	−129.89	0.04	7352	15
	1 + 2	22	0.0974	4.825	0.0024	1.515012	−129.87	0.01	7346	5
$x_1 = 0.49971$	1	11	0.1086	5.297	0.0014	1.514972	−100.82	0.02	5557	7
	2	11	0.1452	6.523	0.0015	1.514972	−100.86	0.02	5579	6
	1 + 2	22	0.1086	6.523	0.0019	1.514978	−100.87	0.01	5580	3
$x_1 = 0.70090$	1	11	0.1276	6.523	0.0040	1.514963	−74.47	0.07	4055	19
$x_2 = 0.29910$	2	11	0.1243	6.387	0.0050	1.514939	−74.40	0.06	4038	18
	1 + 2	22	0.1243	6.523	0.0042	1.514951	−74.44	0.02	4047	7
$x_1 = 1.0000$	1	12	0.1001	8.439	0.0030	1.514952	−42.23	0.04	2411	8
	2	11	0.1374	7.724	0.0026	1.514944	−42.22	0.04	2407	10
	1 + 2	23	0.1001	8.439	0.0027	1.514949	−42.23	0.01	2410	3
$x_1 = 0.32125$	1	11	0.1390	6.350	0.0019	1.514956	−98.11	0.04	4995	9
$x_2 = 0.34099$	2	10	0.1524	5.024	0.0020	1.514940	−97.97	0.07	4949	24
$x_3 = 0.33776$	1 + 2	21	0.1390	6.350	0.0028	1.514955	−98.08	0.01	4985	6
$x_1 = 0.24756$	1	11	0.1519	4.701	0.0014	1.514992	−121.47	0.02	6594	7
$x_2 = 0.56013$	2	10	0.1212	5.325	0.0010	1.515026	−121.60	0.03	6638	8
$x_3 = 0.19231$	1 + 2	21	0.1212	5.325	0.0022	1.515014	−121.56	0.01	6624	4
						$T = 320$ K				
$x_2 = 1.000$	1	10	0.1320	3.962	0.0020	1.515031	−159.33	0.04	9737	16
	2	10	0.1329	3.978	0.0010	1.515018	−159.32	0.03	9730	13
	1 + 2	20	0.1320	3.978	0.0015	1.515025	−159.32	0.01	9733	7
$x_1 = 0.30623$	1	11	0.1272	5.841	0.0014	1.514973	−112.63	0.04	6630	13
$x_2 = 0.69377$	2	12	0.1065	6.841	0.0022	1.514931	−112.52	0.02	6606	5
	1 + 2	23	0.1065	6.841	0.0023	1.514951	−112.57	0.01	6616	4
$x_1 = 0.49971$	1	12	0.1024	7.392	0.0040	1.514938	−87.07	0.04	5052	11
$x_2 = 0.50029$	2	11	0.1409	6.877	0.0048	1.514947	−87.07	0.09	5055	23
	1 + 2	23	0.1024	7.392	0.0042	1.514942	−87.07	0.02	5052	6
$x_1 = 0.70090$	1	11	0.1361	7.225	0.0026	1.514895	−63.71	0.05	3704	14
$x_2 = 0.29910$	2	11	0.1340	7.132	0.0050	1.514936	−63.85	0.08	3733	22
	1 + 2	22	0.1340	7.225	0.0044	1.514918	−63.79	0.02	3721	7
$x_1 = 1.0000$	1	11	0.1301	7.565	0.0034	1.514917	−35.30	0.08	2254	21
	2	11	0.1193	6.979	0.0036	1.514934	−35.34	0.07	2260	21
	1 + 2	22	0.1193	7.565	0.0035	1.514926	−35.32	0.02	2257	8
$x_1 = 0.32125$	1	11	0.1195	6.065	0.0043	1.514936	−84.58	0.06	4511	20
$x_2 = 0.34099$	2	11	0.1200	6.088	0.0047	1.514948	−84.65	0.09	4523	28
$x_3 = 0.33776$	1 + 2	22	0.1195	6.088	0.0045	1.514941	−84.61	0.02	4515	9
$x_1 = 0.24756$	1	11	0.1149	5.547	0.0067	1.514946	−105.16	0.09	5939	32
$x_2 = 0.56013$	2	11	0.1391	6.363	0.0025	1.514931	−105.16	0.04	5936	12
$x_3 = 0.19231$	1 + 2	22	0.1149	6.363	0.0047	1.514939	−105.16	0.02	5935	8

[a] $S = [\{\sum_{i=1}^{m}(p_i^{exp} - p_i^{calc})^2/(p_i^{calc})^2\}/(m - M - 1)]^{1/2}$. m = number of observations, and $M = 3$; see eq 7.

Results and Discussion

Measurements were made on CH_4, C_2H_6, three x_1 CH_4 + $(1 - x_1)$ C_2H_6 mixtures with $x_1 = 0.30623$, 0.49971, and 0.70090 and two x_1 CH_4 + x_2 C_2H_6 + $(1 - x_1 - x_2)$ CO_2 mixtures with $x_1 = 0.32125$, $x_2 = 0.34099$ and $x_1 = 0.24756$, $x_2 = 0.56013$. Two repetitions were made for each isotherm for each mixture to verify internal consistency. Because the equilibrium pressures were measured at temperatures differing slightly and at random from the set point, the experimental pressures, which are given in Table 1, were obtained by multiplying the recorded pressures by $T_{set\ point}/T_{exp}$. These adjustments, which rarely exceed 0.01%, assume that $(\partial Z/\partial T)_\rho(T_{exp} - T_{set\ point})$ is negligible. Table 2 contains the experimental values of the second and third virial coefficients calculated by the maximum-likelihood method, using a computer program developed by Setzmann (1985).

The effects of the impurities in ethane were determined using eq 2 and the Tsonopoulos (1974) modification of the correlation of Pitzer and Curl (1957). The second virial coefficient of a C_2H_4 + C_2H_6 mixture with $x(C_2H_4) = 0.0021$ is about 0.1 $cm^3 \cdot mol^{-1}$ larger than that of pure C_2H_6 at 300 K. Similarly, for N_2 + C_2H_6 with $x(N_2) = 0.0005$ and CH_4 + C_2H_6 with $x(CH_4) = 0.0002$, the increases at 300 K are about (0.12 and 0.04) $cm^3 \cdot mol^{-1}$, respectively. The combined effect of all three impurities will be less than 0.3 $cm^3 \cdot mol^{-1}$, which is the same as the estimated uncertainty in our measurements (±0.3 $cm^3 \cdot mol^{-1}$). For the mixtures containing ethane, the mixture second virial coefficients will be affected less than that of the pure ethane because of ethane dilution. Estimation of the effects on third virial coefficients caused by the impurities is relatively difficult. We believe, however, the effects are not significant.

To compare our results with other measurements, we fit our virial coefficients for pure methane and ethane with respect to temperature using the forms $B = B_0 + B_1/T$ and $C = C_0 + C_1/T$. Figures 2 and 3 show the comparisons of other measurements with our results. For methane, the results of Kleinrahm et al. (1988) are in closest agreement with our values. The largest absolute differences between the two sets of second and third virial coefficients are 0.03 $cm^3 \cdot mol^{-1}$ and 12 $cm^6 \cdot mol^{-2}$, respectively, which are well within our experimental uncertainty. For ethane, the results of Holste et al. (1982), which were made on a different sample of ethane of higher purity, show differences of less than 0.03 $cm^3 \cdot mol^{-1}$ and 34 $cm^6 \cdot mol^{-2}$ for the second and third virial coefficients, respectively.

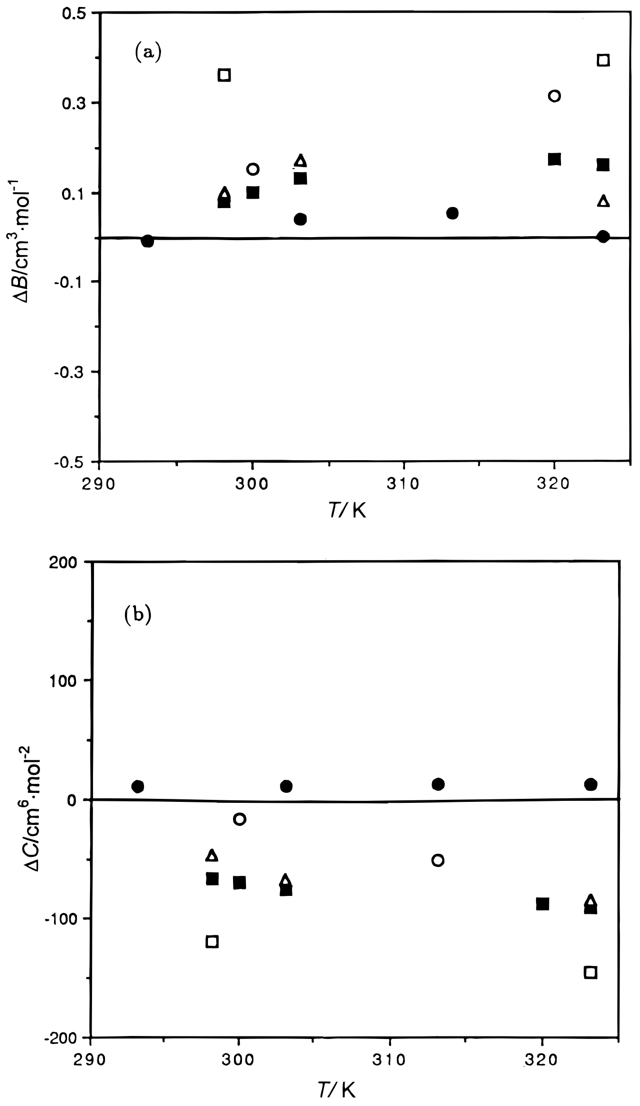

Figure 2. Comparison of other reported second and third virial coefficient measurements for CH_4 with this work: (a) $\Delta B = B$(ref) − B(this work); (b) $\Delta C = C$(ref) − C(this work); ○, Hwang (1988); ●, Kleinrahm et al. (1988); □, Trappeniers et al. (1979); ■, Goodwin (1974); △, Douslin et al. (1964).

Table 3. Pure and Cross Second Virial Coefficients for CH_4 (1) + C_2H_6 (2) + CO_2 (3)

	B_{ij}/(cm^3·mol^{-1})			B_{ij}/(cm^3·mol^{-1})	
	T = 300 K	T = 320 K		T = 300 K	T = 320 K
B_{11}	−42.22	−35.17	B_{12}	−89.02	−76.71
B_{22}	−189.92	−159.42	B_{13}	−63.24	−54.02
B_{33}	−121.56	−104.54	B_{23}	−122.41	−105.65

Hwang (1988) and Brugge et al. (1989) recently have measured mixture virial coefficients for CH_4 + CO_2 and C_2H_6 + CO_2 and the virial coefficients of CH_4, C_2H_6, and CO_2. The present results, along with the above measurements, provide a consistent set of pure and cross second and third virial coefficients of eqs 2 and 3, which appear in Tables 3 and 4. The experimental results are given in Table 5. For C_2H_6 + CO_2, two experimental results have exceptionally large deviations, especially the third virial coefficients. Therefore, we have excluded those values when determining the cross virials by fitting eq 2, 3, or 10.

Haynes et al. (1985) have made (p, V_m, x, T) measurements for CH_4 + C_2H_6. Using our pure and cross second and third virial coefficients, we calculated the mixture virial coefficients of CH_4 + C_2H_6 at the same compositions as those of Haynes et al. and then used eq 1 to calculate compressibility factors at their experimental conditions. Comparisons of the calculated and experimental compressibility factors are shown in Figure 4. In the low density range (ρ < 5 mol·dm^{-3}), our results agree with those of Haynes et al. from 0 to 0.2%. Equation 1 is not valid at higher densities when truncated after three terms.

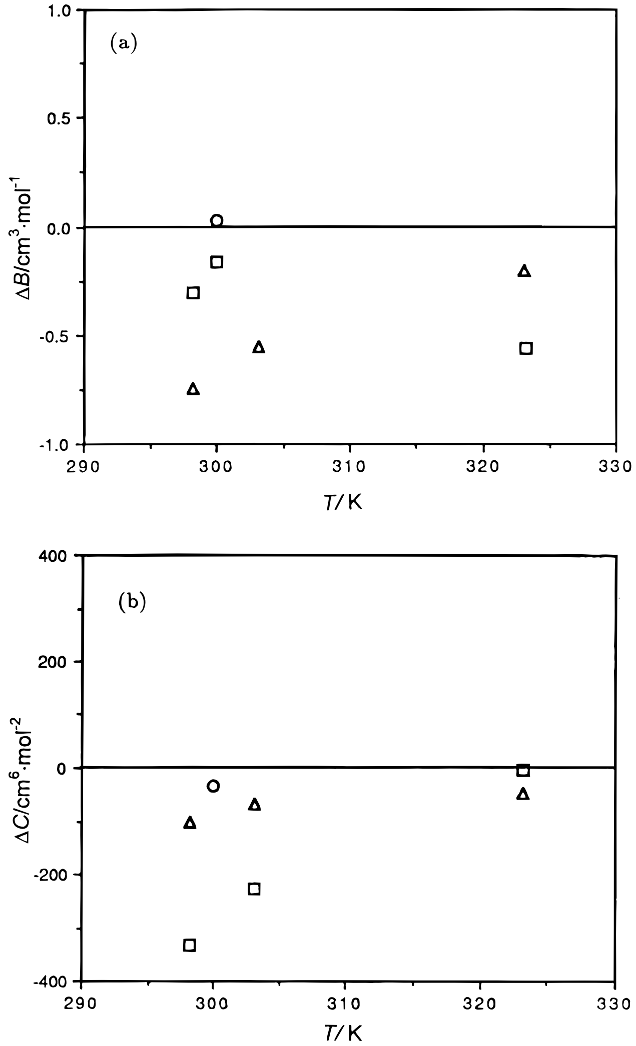

Figure 3. Comparison of other reported second and third virial coefficient measurements for C_2H_6 with this work: (a) $\Delta B = B$(ref) − B(this work); (b) $\Delta C = C$(ref) − C(this work); ○, Holste et al. (1982); □,Goodwin et al. (1976); △, Douslin and Harrison (1973).

Table 4. Pure and Cross Third Virial Coefficients for CH_4 (1) + C_2H_6 (2) + CO_2 (3): Comparisons of Eq 3 and the MHEMHS Model (Eqs 11−13)

	C_{ijk}/(cm^6·mol^{-2})			
	T = 300 K		T = 320 K	
	Eq 3	Eqs 8−10[a]	Eq 3	Eqs 8−10[a]
C_{111}	2409	2404	2229	2240
C_{222}	10598	10628	9692	9693
C_{333}	4928	4896	4411	4399
C_{112}	3765	3896	3594	3504
C_{113}	2851	2841	2641	2559
C_{122}	6778	6638	5902	5989
C_{133}	3632	3671	3195	3278
C_{223}	8283	7915	6963	6905
C_{233}	5670	6004	5075	5140
C_{123}	4283	4753	4204	4122

[a] Determined using only measurements for binary mixtures.

Table 5. Comparisons of Experimental Virial Coefficients for CH_4 (1) + C_2H_6 (2) + CO_2 (3) with Values Calculated Using Eq 2 or 3 and the MHEMHS Model (Eq 13)

				T = 300 K					T = 320 K				
ref	x_1	x_2	x_3	$B(x)$/ ($cm^3 \cdot mol^{-1}$)	ΔB^a(eq 2)/ ($cm^3 \cdot mol^{-1}$)	$C(x)$/ ($cm^6 \cdot mol^{-2}$)	ΔC^b(eq 3)/ ($cm^6 \cdot mol^{-2}$)	ΔC^b(eq 10)^c/ ($cm^6 \cdot mol^{-2}$)	$B(x)$/ ($cm^3 \cdot mol^{-1}$)	ΔB^a(eq 2)/ ($cm^3 \cdot mol^{-1}$)	$C(x)$/ ($cm^6 \cdot mol^{-2}$)	ΔC^b(eq 3)/ ($cm^6 \cdot mol^{-2}$)	ΔC^b(eq 10)^c/ ($cm^6 \cdot mol^{-2}$)
d	0	1	0	−182.74	0.18	10614	16	−14	−159.32	0.10	9733	41	40
d	0.30623	0.69377	0	−129.87	−0.04	7346	6	32	−112.57	0.06	6616	4	−17
d	0.49971	0.50029	0	−100.87	−0.03	5580	−2	−2	−87.07	−0.03	5052	−1	−2
d	0.70090	0.29910	0	−74.44	−0.01	4047	−1	−31	−63.79	−0.09	3721	0	19
d	1	0	0	−42.23	−0.01	2410	1	6	−35.32	−0.15	2257	28	17
e, f	1	0	0	−42.08	0.14	2394	−15	−10	−35.01	0.16	2205	−24	−35
e, f	0.90010	0	0.09990	−46.97	−0.18	2579	27	32	−39.21	0.04	2353	−4	6
e, f	0.70142	0	0.29858	−58.06	0.04	2884	−16	−17	−49.24	0.01	2644	−6	12
e, f	0.32393	0	0.67607	−87.71	−0.02	3823	−2	−7	−75.22	−0.09	3439	19	3
e, f	0.09888	0	0.90112	−110.51	−0.12	4568	10	24	−94.79	0.07	4037	−32	−41
e−g	0	0	1	−121.70	−0.14	4927	−1	31	−104.70	−0.16	4423	12	24
f, h	0	1	0	−182.70	0.22	10580	−18	−48	−159.36	0.06	9652	−40	−41
f	0	0.89957	0.10043	−171.59	−0.22	10008[i]	115[i]	173[i]	−149.40	−0.25	9112	216[i]	228[i]
f	0	0.74834	0.25166	−156.75	−0.51	8831	3	99	−135.66	0.03	7796	−2	14
f	0	0.50755	0.49245	−137.51	0.28	7062[i]	−158[i]	142[i]	−119.32	−0.09	6321	3	3
f	0	0.26022	0.73978	−126.14	−0.10	5852	3	−72	−108.73	−0.05	5176	5	−9
f	0	0.09633	-0.90367	−121.80	0.47	5184	−8	−54	−104.83	0.41	4623	−13	−18
e, f	0	0	1	−121.70	−0.14	4927	−1	31	−104.70	−0.16	4423	12	24
d	0.32125	0.34099	0.33776	−98.08	0.21	4985	11	−95	−84.61	0.03	4515	6	24
d	0.24756	0.56013	0.19231	−121.56	0.00	6624	−15	−31	−105.15	0.07	5935	−8	1
					rmsd = 0.21		11	45		0.14		19	23

[a] ΔB is the value of $B(x) - B(x)$(calc). The calculated value is from eq 2. [b] ΔC is the value of $C(x) - C(x)$(calc). The calculated value is from eq 3 or 10. [c] The coefficients of the MHEMHS model are determined from measurements on binary mixtures. [d] This work. [e] Hwang (1988). [f] Brugge et al. (1989). [g] Hiza et al. (1982). [h] Holste et al. (1982). [i] Values not used in the determination of pure and cross virial coefficients using eqs 2 and 3.

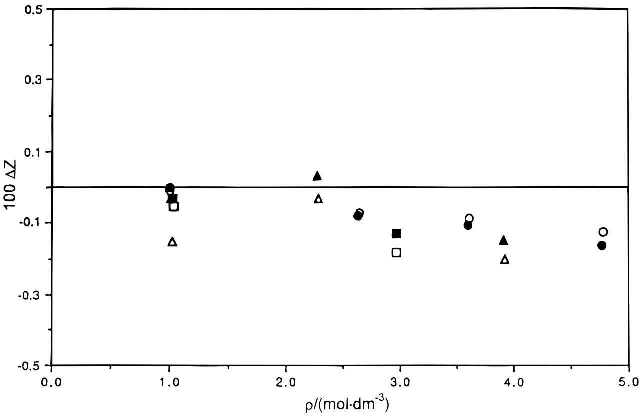

Figure 4. Comparison of compressibility factors for CH_4 (1) + C_2H_6 (2): $\Delta Z = Z^{exp} - Z^{calc}$, where Z^{exp} are the experimental values reported in Haynes et al. (1985) and Z^{calc} are calculated using the virial coefficients given in Tables 3 and 4 and eqs 1−3; ○, $x_1 = 0.68526$, $T = 300$ K; ●, $x_1 = 0.68526$, $T = 320$ K; □, $x_1 = 0.50217$, $T = 300$ K; ■, $x_1 = 0.50217$, $T = 320$ K; △, $x_1 = 0.34528$, $T = 300$ K; ▲, $x_1 = 0.34528$, $T = 320$ K.

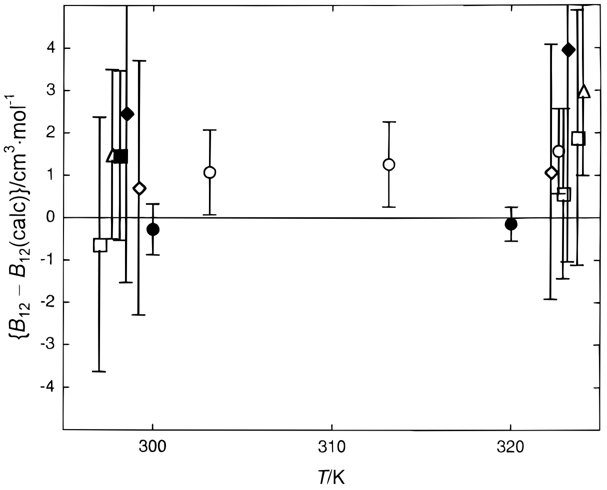

Figure 5. Deviations of cross second virial coefficients for methane + ethane from eq 8: ●, This work; ■, Gunn (1958); ○, McElroy and Fan (1994); ◆, Dantzler and Knobler (1968); △, Siebert and Knobler (1983); □, ◇, Michels and Nederbragt (1939).

Measurements on $CH_4 + C_2H_6$ in the temperature range studied have been reported by Michels and Nederbragt (1939), Gunn (1958), Dantzler and Knobler (1968), Siebert and Knobler (1983), and McElroy and Fan (1994). The experimental values, including those of this work, were weighted by either the authors' or our estimated experimental uncertainties to obtain the following equation:

$$B_{12}(\mathrm{calc})/(\mathrm{cm^3 \cdot mol^{-1}}) = 109.86 - 59748/(T/\mathrm{K}) \quad (8)$$

The deviations are shown in Figure 5. All the results are in agreement within the estimated uncertainties. Blanke and Weiss (1995) have recently reported pVT data for the mixture $CH_4 + C_2H_6$ and an equation for the second and third mixture virial coefficients. Their B_{12} values of (−88.74 and −76.72) $\mathrm{cm^3 \cdot mol^{-1}}$ at (300 and 320) K, respectively, are in excellent agreement with the values given in Table 3. Their C_{112} values of (4245 and 4188) $\mathrm{cm^6 \cdot mol^{-2}}$ and C_{122} values of (4640 and 4215) $\mathrm{cm^6 \cdot mol^{-2}}$ at (300 and 320) K differ considerably from the values given in Table 4. They note that their values differ from the GERG equation (Jaeschke, 1991) by up to 3000 $\mathrm{cm^6 \cdot mol^{-2}}$.

Second virial coefficients for $CH_4 + CO_2$ in the temperature range studied have been reported by Reamer et al. (1942), Ohgaki et al. (1982), Martin et al. (1987), Hwang (1988), Brugge et al. (1989), Esper et al. (1989), McElroy et al. (1990), and Mallu and Viswanath (1990). The experimental values were weighted by either the authors' or our estimated uncertainties to obtain the following equation:

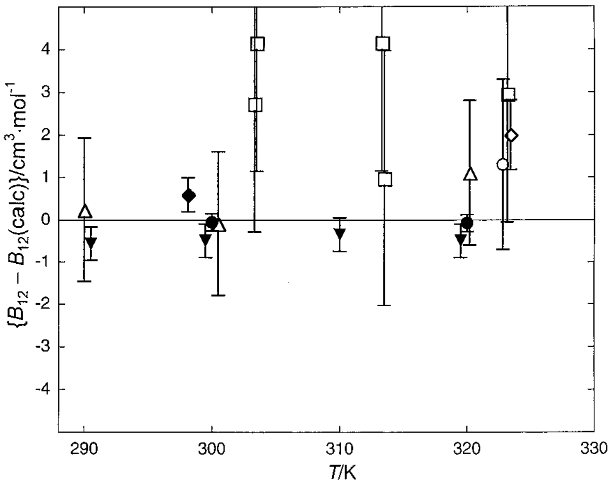

Figure 6. Deviations of cross second virial coefficients for methane + carbon dioxide from eq 9: ●, this work; ▼; Esper et al.(1989); □, McElroy et al. (1990); ○, Reamer et al (1942); △, Martin et al. (1987); ◆, Ohgaki et al. (1981); ◇, Mallu and Viswanath (1990).

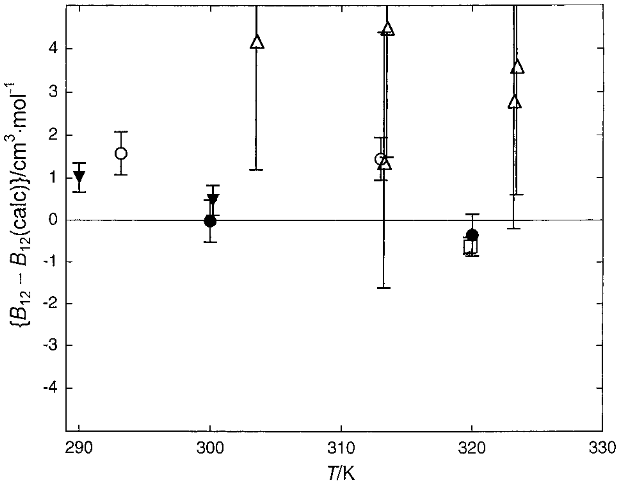

Figure 7. Deviations of cross second virial coefficients for ethane + carbon dioxide from eq 10: ○, this work; ▼; Holste et al (1982); □, Weber (1992); ○, Jaeschke (1987); △, McElroy et al. (1990).

$$B_{12}(\mathrm{calc})/(\mathrm{cm^3 \cdot mol^{-1}}) = 83.84 - 44138/(T/\mathrm{K}) \quad (9)$$

The deviations are shown in Figure 6. Except for some values by McElroy et al. (1990), all the results are in agreement within the estimated uncertainties. Measurements on the second virial coefficients for $C_2H_6 + CO_2$ in the temperature range studied have been reported by Holste et al. (1982), Jaeschke (1987), Brugge et al. (1989), McElroy et al. (1990), and Weber (1992). The experimental values were weighted by either the authors' or our estimated uncertainties to obtain the following equation:

$$B_{12}(\mathrm{calc})/(\mathrm{cm^3 \cdot mol^{-1}}) = 140.42 - 77857/(T/\mathrm{K}) \quad (10)$$

The deviations are shown in Figure 7. Except for some values by McElroy et al. (1990), all the results are in agreement within the estimated uncertainty.

McGregor et al. (1987) have proposed a model for cross third virial coefficients which provides a simplified mixing rule for mixture third virial coefficients. This model, the MHEMHS model, assumes that

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

where δC_{ij} are the MHEMHS cross terms. Equation 11 leads to

$$3C_{ijk} - C_{iii} - C_{jjj} - C_{kkk} = (\delta C_{ij} + \delta C_{ik} + \delta C_{jk})/2 \quad (12)$$

and produces the MHEMHS mixing rule

$$C(x) = \sum_{i=1}^{n} x_i C_{iii} + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} x_i x_j \delta C_{ij} \quad (13)$$

which is formally identical to the standard mixing rule for second virial coefficients (eq 2)

$$B(x) = \sum_{i=1}^{n} x_i B_{ii} + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} x_i x_j \delta B_{ij} \quad (14)$$

with

$$\delta B_{ij} = 2B_{ij} - B_{ii} - B_{jj} \quad (15)$$

Equation 13 contains far fewer terms for multicomponent mixtures than does eq 3.

Equations 11−13 allow the calculation of cross third virial coefficients from measurements on a single composition for a binary mixture and for a ternary mixture from a single composition measurement for each of the three binary mixtures. We used the MHEMHS model to determine cross third virial coefficients for $CH_4 + C_2H_6 + CO_2$ from the experimental results reported here and previously (Hwang, 1988; Brugge et al., 1989). To test the applicability of the model, only binary data are used in the determination. The results are given in Table 4. The values obtained from binary mixtures using the MHEMHS model differ from those obtained from binary and ternary mixtures using the virial equation by approximately the same magnitude as the accuracies of the measurements.

Table 5 contains the comparisons of the experimental second and third virial coefficients for two $CH_4 + C_2H_6 + CO_2$ mixtures with results calculated using the exact mixing rule and using the MHEMHS approximation. The two methods give essentially equivalent results even though only measurements for binary mixtures are used to determine the parameters in the MHEMHS model, while measurements for ternary mixtures are required for the ordinary mixing rule.

Conclusions

Virial coefficients were determined for CH_4, C_2H_6, three $CH_4 + C_2H_6$ mixtures, and two $CH_4 + C_2H_6 + CO_2$ mixtures at (300 and 320) K using a Burnett apparatus. Cross second and third virial coefficients were calculated for the ternary system at the same temperatures. The results were used to test a simplified model for the third virial coefficient (MHEMHS), and the model was satisfactory.

Acknowledgment

This paper is dedicated to the memory of Huaiwen Hou, a valued friend and co-worker.

Literature Cited

Blanke, W; Weiss, R. Virial Coefficients of Methane-Ethane Mixtures in the Temperature Range from 0 to 60 °C Determined with an Automated Expansion Apparatus. *Int. J. Thermophys.* **1995,** *16*, 643−653.

Britt, H. I.; Leucke, R. H. The Estimation of Parameters in Nonlinear Implicit Models. *Technometrics* **1973**, *15*, 233−247.

Brugge, H. B.; Holste, J. C.; Hall, K. R. A Flexible Foil, Gravity Driven Mixer for Preparation of Gas Mixtures. *Rev. Sci. Instrum.* **1992**, *63*, 5802−5803.

Brugge, H. B.; Hwang, C.-A.; Rogers, W. J.; Holste, J. C.; Hall, K. R.; Lemming, W.; Esper, G. J.; Marsh, K. N.; Gammon, B. E. Experimental Cross Virial Coefficents for Binary Mixtures of Carbon Dioxide with Nitrogen, Methane and Ethane at 300 and 320 K. *Physica A* **1989**, *156*, 382.

Dantzler, E. M.; Knobler, C. M.; Windsor, M. L. Interaction Virial Coefficients in Hydrocarbon Mixtures. *J. Phys. Chem.* **1968,** *72*, 676−684.

Douslin, D. R.; Harrison, R. H.; Moore, R. T. *P-V-T* Relations for Methane. *J. Chem. Eng. Data* **1964**, *9*, 358−363 .

Douslin, D. R.; Harrison, R. H. Pressure, volume, temperature relations of ethane. *J. Chem. Thermodyn.* **1973**, *5*, 491−512.

Dymond, J. H.; Smith, E. B. *The Virial Coefficients of Pure Gases and Mixtures: A Critical Compilation*; Claredon Press: Oxford, 1980.

Embry, D. L. Analysis of Burnett-Isochoric Data. M.S. Thesis, Texas A&M University, College Station, TX, 1980.

Goodwin, R. D. The Thermophysical Properties of Methane, From 90 to 500 K at Pressures to 700 Bar. *Natl. Bur. Stand. (U. S.), Tech. Note* **1974**, No. 653.

Goodwin, R. D.; Roder, H. M.; Straty, G. C. Thermophysical Properties of Ethane, from 90 to 600 K at Pressures to 700 *Bar. Natl. Bur. Stand. (U. S.), Tech. Note* **1976**, No. 684.

Gunn, R. D. The Volumetric Properties of Nonpolar Gaseous Mixtures. M.S. Thesis, University of California, Berkeley, CA, 1958.

Haynes, W. M.; McCarty, R. D.; Eaton, B. E.; Holste, J. C. Isochoric (p, V_m, x, T) measurements on (methane + ethane) from 100 to 320 K at pressure to 35 MPa. *J. Chem. Thermodyn.* **1985**, *17*, 209−232.

Hiza, M. J.; Kidnay, A. J.; Miller, R. C. *Equilibrium Properties of Fluid Mixtures; A Bibliography of Experimental Data on Selected Fluids;* IFI/Plenum: New York, 1982.

Holste, J. C.; Eubank, P. T.; Hall, K. R. Optimum Use of a Differential Pressure Transducer for High-Precision Measurements. *Ind. Eng. Chem. Fundam.* **1977**, *16*, 378−380.

Holste, J. C.; Hall, K. R.; Eubank, P. T.; Esper, G.; Watson, M. Q.; Warowny, W.; Bailey, D. M.; Young, J. G.; Bellomy, M. T. Experimental (p, V_m, T) for pure CO_2 between 220 and 450 K. *J. Chem. Thermodyn.* **1987**, *19*, 1233−1250.

Holste, J. C.; Young, J. G.; Eubank, P. T.; Hall, K. R. Interaction Second Virial Coefficients and Binary Interaction Parameters for the CO_2 - C_2H_6 Systems between 250 and 300 K. *AIChE J.* **1982**, *28*, 807−812.

Hwang, C.-A. PVT Measurements of Carbon Dioxide + Methane Mixtures and an Equation of State Development. Ph.D. Dissertation, Texas A&M University, College Station, TX, 1988.

Jaeschke, M. Determination of the Interaction Second Virial Coefficients for the Carbon Dioxide - Ethane System from Refractive Index Measurements. *Int. J. Thermophys.* **1987**, *8*, 81−95.

Jaeschke, M.; Audibert, S.; van Caneghem, P.; Humphreys, A. E.; Janssen-van Rosmalen, R.; Pellel, Q.; Schouten, J. A.; Michels, J. P. J. Simplified GERG Virial Equation for Field Use. *SPE Prod. Eng.* **1991** (Aug), 343.

Kleinrahm, R.; Duschek, W.; Wagner, W.; Jaeschke, M. Measurement and correlation of the (pressure, density, temperature) relation of methane in the temperature range from 273.15 K to 323.15 K at pressures of up to 8 MPa. *J. Chem. Thermodyn.* **1988**, *20*, 621−631.

Mallu, B. V.; Viswanath, D. S. Compression factors and second virial coefficients for H_2, CH_4, $\{xCO_2 + (1\text{-}x)CH_4\}$. *J. Chem. Thermodyn.* **1990**, *22*, 997−1006.

Martin, M. L.; Trengrove, R. D.; Harris, K. R.; Dunlop, P. J. Virial Coefficients of Gases, Ethane + Methane. *Int. Data Ser. Sel. Data Mixtures, Ser. A* **1987**, 57.

McElroy, P. J.; Fan, J. Compression factors and virial coefficients of (methane + ethane). *J. Chem. Thermodyn.* **1994**, *26*, 617−623.

McElroy, P. J.; Kee, L. L.; Renner, C. A. Excess Second Virial Coefficients for Binary Mixtures of Carbon Dioxide with Methane, Ethane, and Propane. *J. Chem. Eng. Data* **1990**, *35*, 3124−317.

McGregor, D. R.; Holste, J. C.; Eubank, P. T.; Marsh, K. N.; Hall, K. R.; Schouten, J. An Interaction Model for Third Virial Coefficients which Provides Simplified Equations for Mixtures. *Fluid Phase Equilib.* **1987**, *35*, 153−164.

Michels, A.; Nederbragt, G. W. Isotherms of Methane-Ethane Mixtures at 0 °C, 25 °C, and 50 °C, up to 60 Atmospheres. *Physica A* **1939,** *6*, 656−662.

Ohgaki, K; Mizuhaya, T.; Katayama, T. The Interaction Second Virial Coefficients for Seven Binary Systems Containing Carbon Dioxide, Methane, Ethylene, Ethane, and Propylene at 25 °C. *J. Chem. Eng. Jpn.* **1981**, *14*, 71−72.

Pitzer, K. S.; Curl, R. F., Jr. The Volumetric and Thermodynamic Properties of Fluids, III. Empirical Equation for the Second Virial Coefficient. *J. Am. Chem. Soc.* **1957**, *79*, 2369−2370.

Reamer, H. H.; Olds, R. H.; Sage, B. H.; Lacey, W. N. Phase Equilibria in Hydrocarbon Systems Methane + Carbon Dioxide System in the Gaseous Region. *Ind. Eng. Chem.* **1944,** *36*, 88−90.

Reamer, H. H.; Olds, R. H.; Sage, B. H.; Lacey, W. N. Phase Equilibria in Hydrocarbon Systems. Volumetric Behavior of Ethane-Carbon Dioxide System. *Ind. Eng. Chem*. **1945,** *37,* 688−691.

Setzmann, U. Computer Programs for the Analysis of Burnett-Isochoric Data. Department of Chemical Engineering, Texas A&M University, College Station, TX, 1985 (unpublished).

Siebert, E. D.; Knobler, C. M. Second Virial Coefficients of Gases Binary Normal Alkane Mixtures (C_1 to C_5). *Int. Data Ser. Sel. Data Mixtures, Ser. A* **1983**, 16.

Sychev, V. V.; Vasserman, A. A.; Zagoruchenko, V. A.; Kozlov, A. D.; Spiridonov, G. A.; Tsymarny, V. A. *Thermodynamic Properties of Methane, National Standard Reference Data Service of the USSR: A Series of Property Tables, No. 3.* Hemisphere Publishing Corp.: New York, 1987a.

Sychev, V. V.; Vasserman, A. A.; Kozlov, A. D.; Zagoruchenko, V. A.; Spiridonov, G. A.; Tsymarny, V. A. *Thermodynamic Properties of Ethane, National Standard Reference Data Service of the USSR: A Series of Property Tables, No. 4.* Hemisphere Publishing Corp.: New York, 1987b.

Trappeniers, J. J.; Wassenaar, T.; Abels, J. C. Isotherms and Thermodynamic Properties of Methane at Temperatures between 0 and 150 °C and at Densities up to 570 Amagat. *Physica A* **1979**, *98*, 289−297.

Tsonopoulos, C. An Empirical Correlation of Second Virial Coefficients. *AIChE J*. **1974**, *20*, 263−272.

Weber, L. A. Measurements of the Virial Coefficients and Equation of State of the Carbon Dioxide + Ethane System in the Supercritical Region. *Int. J. Thermophys*. **1992**, *13*, 1011−1032.

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