Density of an Equimolar Mixture of Ethane and Methyl Chloride

We have measured the density of an equimolar gas mixture of C_2H_6—CH_3Cl between 323.15 and 473.15 K at pressures to 14.0 MPa. Interaction second virial coefficients and dew-point pressures are extracted from the measurements. Intermolecular force constants for the Lennard-Jones and Stockmayer models are determined optimally for like and unlike pair interactions. Recent methods of prediction for second virial coefficients, both pure and interaction, are tested against experiment.

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SCOPE

Few high-accuracy (better than ±0.05%), density measurements are available for nonpolar/polar gas mixtures over extended ranges of pressure and temperature. Densities (or compressibility factors) are measured to a precision (reproducibility) of ±0.01% in modern PVT apparatus; but at reduced temperatures near unity and less, uncertainties due primarily to adsorption errors cause wide differences between precision and estimated accuracy.

Methyl chloride has a high dipole moment but does not hydrogen bond. The methyl chloride/ethane mixture is representative of haloalkane/alkane mixtures, with ethane the homomorph of methyl chloride. Thus the present mixture is a particularly simple nonpolar/polar mixture and a logical beginning for a long-term program of nonpolar/polar measurements. Because of the years of effort and high costs required for each such mixture, it is our rationale to do a few representative mixtures with care.

CONCLUSIONS AND SIGNIFICANCE

The Burnett mixing technique is shown to yield a mixture mol fraction to ±0.0007 (3σ). Measured densities for the equimolar mixture are considered accurate to ±0.04% with a contribution of more than ±0.03% coming from uncertainties in our adsorption error correction method.

Interaction second virial coefficients are calculated from the present mixture second virial coefficients and those of the pure components as published earlier. These values of B_{12} have uncertainties, thrice the standard deviation, ranging from 14.4 to 1.8 cm^3/mol for temperatures from 323.15 to 473.15 K (50 to 200°C); they are not sufficiently accurate to demonstrate the temperature dependency of k_{12}, the binary interaction constant. Experimental dew-point pressures with uncertainties ranging from 10 to 80 kPa provide a cricondentherm at 399.2 K and 7.55 MPa.

The intermolecular pair potentials for C_2H_6/C_2H_6 and C_2H_6/CH_3Cl via the Lennard-Jones model represent well the B_{11} and B_{12} macroscopic measurements, while the Stockmayer model is likewise adequate for the CH_3Cl/CH_3Cl interaction, at least over the present temperature range. Temperature-dependent and orientation-dependent effects for the Stockmayer potential energy for two methyl chloride molecules are also illustrated.

The modern predictive methods for pure component second virial coefficients of Tsonopoulos (1974, 1975, 1978, 1979), Hayden and O'Connell (1975), and Tarakad and Danner (1977) provide reasonable *a priori* estimates for ethane and for methyl chloride. They do not, however, generally provide estimates within our 3σ uncertainty limits for the experimental B_{ii} values. A fair yardstick of predictive ability is $\langle|\Delta|/3\sigma\rangle$, where at each temperature Δ is the difference between the predicted and experimental B_{ii}. Although our 3σ values for methyl chloride are far higher than those for ethane at the same temperature, this yardstick is roughly 3.3, 4.9, and 6.0, respectively, for the three predictive methods above. The constancy of this yardstick for a given predictive method regardless of the compound shows that "the compounds which are difficult to measure accurately are the same ones which are difficult to predict accurately." This truism is traceable obviously to molecular effects, such as polarity.

The yardstick $\langle|\Delta|/3\sigma\rangle$ for prediction of B_{12} is 1.97 (Hirschfelder et al., 1954), 4.03 (O'Connell-Prausnitz, 1967), 0.55 (Tsonopoulos with $k_{12} = 0.03$), 2.19 (Hayden-O'Connell), and 0.62 (Tarakad-Danner with $k_{12} = 0.06$). The correlations of Tsonopoulos and of Tarakad-Danner require k_{12}; the above values are optimal to minimize $\langle|\Delta|/3\sigma\rangle$.

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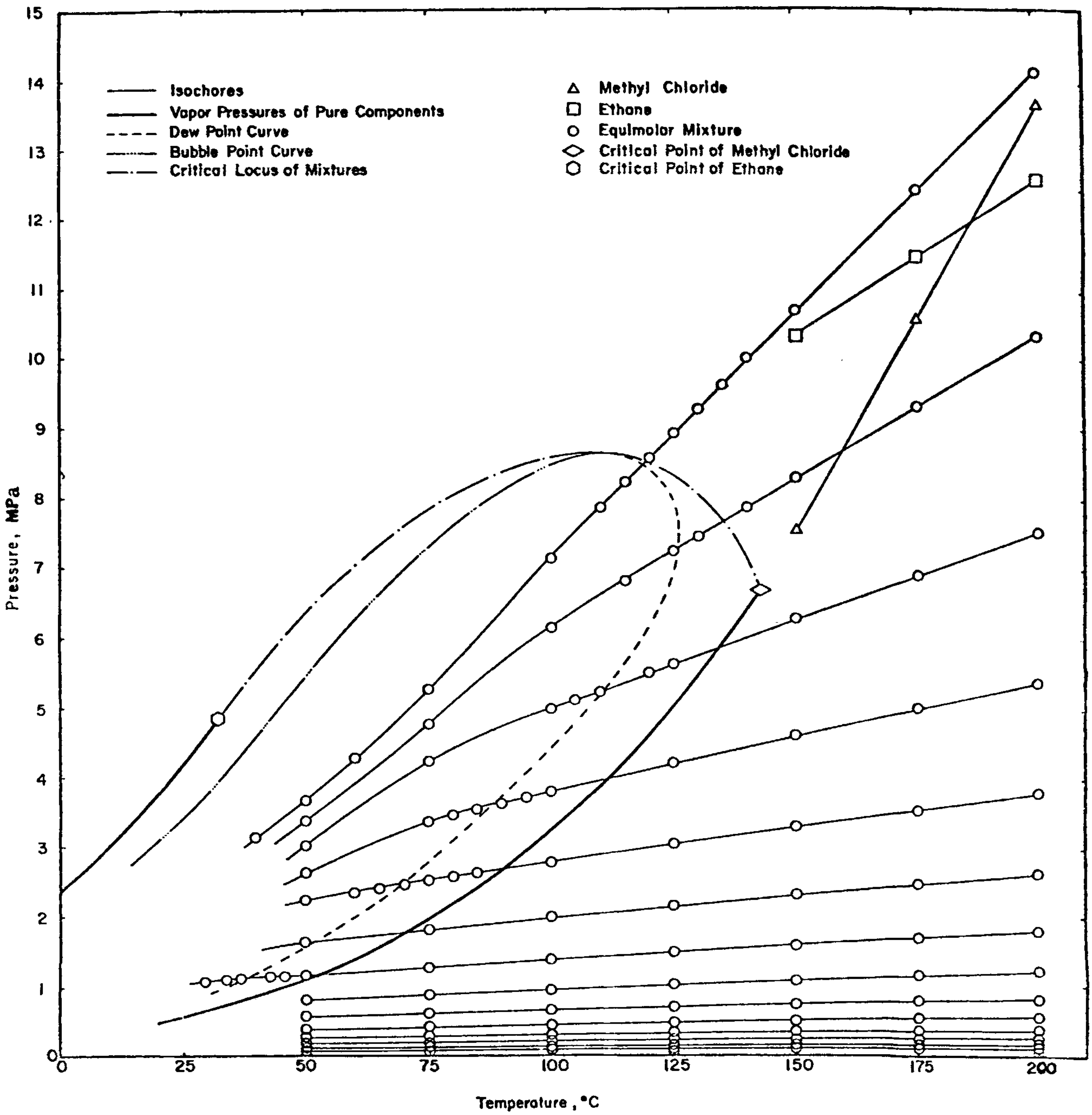

Figure 1. ***P-T*** **surface of the ethane/methyl chloride equimolar mixture. The bubble-point curve and critical locus are drawn arbitrarily, but consistent with the present measurements, to illustrate the relative position of the two-phase region. A near critical isochore is shown for methyl chloride and the upper portion of an ethane isochore is shown only to demonstrate the differences between isochoric slopes.**

A comprehensive experimental study of the volumetric properties of an equimolar mixture of the nonpolar/polar system of ethane/methyl chloride (chloromethane) is presented. The density of the two pure fluids over the same approximate range of pressure and temperature, along with the vapor pressure of methyl chloride, has appeared recently elsewhere (Mansoorian et al., 1981). Intermolecular potential parameters are calculated from the mixture data. The ability of prediction methods to estimate the interaction second virial coefficients for such a nonpolar/polar system also is tested.

EXPERIMENT

The Burnett-isochoric (B-I) density apparatus was described previously (Mansoorian et al., 1977; Mansoorian, 1978). This apparatus operates from ambient temperature to about 500 K and is separate from our cryogenic B-I apparatus (90–300 K) described in two recent articles in this journal (Holste et al., 1980, 1982).

The entire (P, ρ, T) surface for the equimolar mixture of ethane/methyl chloride was measured from a single sample using Burnett expansions at the maximum temperature of 473.15 K to couple the isochores shown in Figure 1. The maximum density isochore is near the critical density of the mixture as shown by the critical locus and equimolar isopleth of Figure 1.

TABLE 1. PRESSURES OF ETHANE AND OF METHYL CHLORIDE BEFORE AND AFTER MIXING (MPA)

Compound	423.15 K	448.15 K	473.15 K
Ethane	10.32454	11.46312	12.59759
Methyl chloride	7.53529	10.57726	13.67332
Mixture	10.68408	12.41921	14.12959

Burnett Mixing

The equimolar mixture was formed by the Burnett mixing technique (Hall and Eubank, 1974) from ethane (99.99 + mol% purity) and purified methyl chloride (99.975 mol% purity with 0.020 mol% Freon 12 as the principal impurity). Pure ethane was fed into the previously evacuated volume ($V_A + V_C$) (Figure 2) at 323.15 K and the appropriate pressure. Table 1 provides pressures measured along this ethane isochore (see Figure 1) at 423.15, 448.15, and 473.15 K. Valve 1 was then closed and volume ($V_B + V_C$) evacuated. The temperature bath was returned to 423.15 K; ($V_B + V_C$) was filled with methyl chloride and pressures were measured along the isochore of Figure 1 at 423.15, 448.15, and 473.15 K (see Table 1). Valves 2 and 5 were opened next, and the magnetic pump began circulation at 423.15 K. After 2 h, valves 2 and 5 were closed and the temperature raised to 473.15 K. Since an equal pressure change was expected from equal compositions in the two chambers, ($V_A + V_C$) and V_B, a pressure change upon opening valve 2 would indicate incomplete mixing. Further mixing was performed at 423.15 K until no change of pressure could be detected at 473.15 K; we can detect pressure changes of about 30 ppm. The pressures of the mixture at 423.15, 448.15, and 473.15 K (see Figure 1 and Table 1) were measured next to calculate the composition.

Mass balance equations derived previously (Hall and Eubank, 1974) allow calculation of the mixture compositions:

$$y_1 = (P_1 Z_m \xi_A / N_A P_m Z_1 \xi_{ABC}) \tag{1}$$

$$y_1 = 1 - (N_A - 1) P_2 Z_m \xi_{BC} / N_A P_m Z_2 \xi_{ABC} \tag{2}$$

and

$$y_1 = (P_1 \xi_A / Z_1)[(P_1 \xi_A / Z_1) + (N_A - 1)(P_2 \xi_{BC} / Z_2)]^{-1} \tag{3}$$

At a given temperature T, P_1 is the pressure of pure ethane (1), P_2 is the pressure of pure methyl chloride (2), and P_m is the pressure of the mixture of Table 1. The corresponding compressibility factors are Z_1, Z_2, and Z_m. Cell distortions with pressure require the slight correction factor ξ, the ratio of the cell volume at pressure P to that at zero pressure. At these temperatures

$$\xi = 1 + (3.13 \times 10^{-3})(P/\text{kPa}) \tag{4}$$

The volume ratio $N_A = (V_A + V_B + V_C)/V_A$ at zero pressure and 473.15 K was 1.490859 ± 14 × 10^{-6}, whereas $[(V_A + V_B + V_C)/(V_A + V_C)]$ was 1.483476 ± 10 × 10^{-6} as determined by previous calibrations with helium. Zero pressure volume ratios in this apparatus change less than 20 ppm over the entire temperature range of 323–473 K.

Since Z_1 and Z_2 are available from the previous pure component measurements (Mansoorian et al., 1981) and Z_m values follow from the present mixture observations, Eqs. 1–3 provide a consistency check of the mixture composition at each of the temperatures—423.15, 448.15, and 473.15 K.

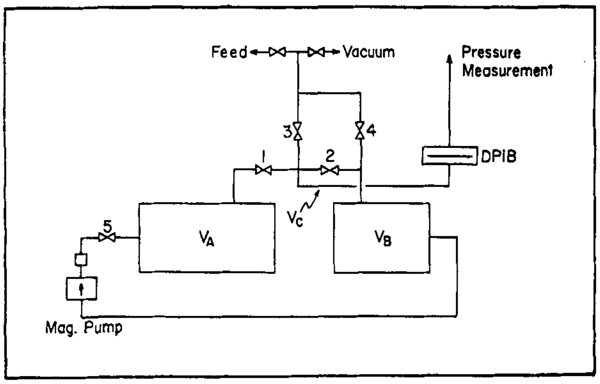

Figure 2. Burnett-isochoric cell with mixing capability. DPIB is a differential pressure indicator separating the experimental fluid from the pressure measurement fluid (here nitrogen).

TABLE 2. COMPOSITION OF ETHANE IN THE MIXTURE

	y_1 Calculated From		
Temp., K	Eq. 1	Eq. 2	Eq. 3
423.15	0.4971	0.4970	0.4970
448.15	0.4975	0.5001	0.4988
473.15	0.4976	0.4996	0.4986

Table 2 shows that Eq. 1 provides the most consistent compositions at the different temperatures, while Eqs. 2 and 3 yield a 0.26 and 0.20 mol% variation, respectively. Because our ethane densities (or Z_1 are considered accurate to 0.02%, whereas our methyl chloride densities (or Z_2) are judged accurate to only 0.11% (Mansoorian et al., 1981), the best compositions should result from Z_1 and Z_m. As discussed below, Z_m is considered accurate to 0.04% because adsorption errors for the mixture are roughly (1/7) those estimated for pure methyl chloride. Figure 1 shows the present methyl chloride isochore to be near critical and only slightly above the critical temperature of 316.27 K. The value of $y_1 = 0.4975 \pm 0.0007$ is based on statistical averaging (Mickley et al., 1957) of the last three columns of Table 2 with the uncertainty equal to thrice the standard deviation of the best values.

Adsorption

The Burnett cells were refinished to a mirror surface of 303 stainless steel prior to the mixture measurements. Physical adsorption errors in the density observations were corrected by a modified Langmuir model. The adsorption correction method, which has been discussed thoroughly by Mansoorian et al. (1981), has an estimated accuracy of 85%. The only differences between the adsorption treatment for pure methyl chloride and for the mixture are the exponent x in the modified Redlich-Kwong equation of state for the mixture was found to be 0.97 and the value of the Langmuir model constants. These constants for the mixture are given in Table 3 for the adsorption isotherm

$$(\rho - \rho^*)/\rho = K_A^{(l)} P_j^{(l)} / [1 + b^{(l)} P_j^{(l)}] \tag{5}$$

where $(\rho - \rho^*)/\rho$ is the fraction of molecules adsorbed, the superscript l indicates the isotherm, and the subscript j the isochore. For a given density and temperature, the ordinate of Figure 3 (ΔP) is added to the measured pressure to correct for adsorption. The maximum correction is about 0.22% (at 348.15 K) or a maximum error of 0.034% could remain in the pressures (or densities at set pressures) due to adsorption.

RESULTS

Compressibility Factors

The method of Hall and Canfield (1967) was used to reduce the raw B-I data (Mansoorian, 1978) by least squares regression with correction for adsorption to produce the smoothed compressibility factors of Table 4, which are considered accurate to ±0.04%. The thermodynamic properties of internal energy, enthalpy, Helmholtz energy, Gibbs energy, and entropy were computed over the same ranges of pressure and temperature by our UHAGS computer program. These tables* are based on the reference state of a perfect gas mixture at 100 kPa and 273.16 K.

TABLE 3. CONSTANTS OF MODIFIED LANGMUIR MODEL FOR THE MIXTURE

Model Constant, MPa^{-1}	Temp., K			
	323.15	348.15	373.15	398.15
$-b$	0.4020	0.2705	0.1894	0.1061
$K_A \times 10^4$	5.857	3.523	1.530	0.808

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* Supplemental material.

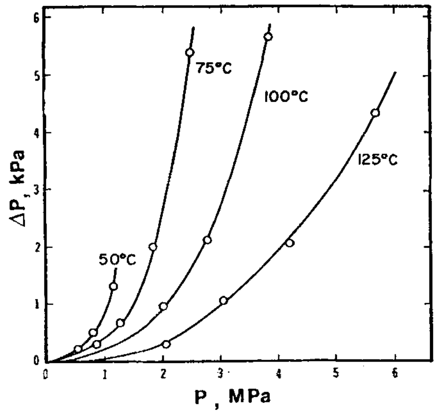

Figure 3. Changes of pressure of the mixture due to adsorption. $\Delta P \equiv P$ (corrected for adsorption) $-P$ (measured).

Virial Coefficients

Second and third virial coefficients, B_m and C_m, respectively, for the mixture are presented in Table 5 for use in the Leiden expansion

$$Z_m = 1 + B_m\rho + C_m\rho^2 + D_m\rho^3 + \ldots \tag{6}$$

The error bands for B_m and C_m are thrice the standard deviations produced by the Hall-Canfield routine. At each temperature, the computer program determines the optimal of virial coefficients (Lee et al., 1978). For 423.15, 448.15, and 473.15 K, statistically significant values of the fourth virial coefficient D_m can be determined, although the standard deviations are only a few times less than the absolute values of D_m itself. Below 423.15 K the data of Table 4 do not extend to such high pressure, since the dew-point curve is intersected first, and fewer terms in Eq. 6 are required to represent Z_m within 0.03%.

Values of the interaction second virial coefficient, B_{12}, were calculated from the statistical equation

$$B_{12} = (B_m - y_1^2B_{22} - y_2^2B_{22})/2y_1y_2 \tag{7}$$

TABLE 5. VIRIAL COEFFICIENTS OF THE ETHANE/METHYL CHLORIDE MIXTURE

T, K	$-B_m$, cm^3/mol	$\sigma(B)$	C_m, cm^6/mol^2	$\sigma(C)$	D_m, cm^9/mol^3
323.15	228.2	1.5	28105	2528	——
348.15	190.9	0.5	16610	471	——
373.15	162.4	0.4	12333	227	——
398.15	139.0	0.2	9691	100	——
423.15	121.7	0.2	9323	117	-2.06×10^5
448.15	106.6	0.2	8501	126	-1.88×10^5
473.15	93.3	0.2	7698	127	-1.52×10^5

with $y_1 = 0.4975$ and $B_{11}(T)$ for ethane together with $B_{22}(T)$ for methyl chloride taken from Mansoorian et al. (1981) and reproduced in Table 6. Figure 4 provides the temperature dependency of B_{11}, B_{22}, B_m, and B_{12}, while Table 6 contains the values of B_{12} with their standard deviations. The standard deviation in B_{12}, which results from the previous standard deviations in B_m, B_{11}, B_{22}, and y_1, is calculable from a simple error propagation formula based on Eq. 7 and derivatives thereof. The present uncertainties in y_1 and B_{11} produce negligible contributions to the uncertainty in B_{12}, which is higher than desired at 323.15 and 348.15 K. Had these values of B_{12} been obtained by our direct experimental method (Hall and Eubank, 1973; Holste et al., 1980, 1982), the uncertainties (thrice the standard deviation) would have been less than a unit cm^3/mol over the present temperature range.

Dew Points

The mixture isochores are nearly linear in the homogeneous region with observable change in slope upon passing into the heterogeneous region at the dew-point envelope (Eubank et al., 1980). Smoothed dew-point pressures are presented in Table 7 with double dew points at 393.15 and 398.15 K. The approximate cricondentherm is 399.2 K and 7.55 MPa.

TABLE 4. SMOOTHED COMPRESSIBILITY FACTORS OF THE ETHANE/METHYL CHLORIDE MIXTURE

	Compression Factor, Z_m						
P, MPa	473.15 K	448.15 K	423.15 K	398.15 K	373.15 K	348.15 K	323.15 K
0	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000
0.1	0.99763	0.99714	0.99654	0.99579	0.99475	0.99338	0.99147
0.2	0.99525	0.99427	0.99306	0.99156	0.98947	0.98671	0.98288
0.3	0.99288	0.99140	0.98958	0.98732	0.98416	0.98000	0.97422
0.4	0.99050	0.98853	0.98609	0.98306	0.97882	0.97323	0.96548
0.5	0.98813	0.98565	0.98259	0.97877	0.97344	0.96641	0.95668
1.0	0.97622	0.97120	0.96495	0.95708	0.94609	0.93149	0.91152
1.5	0.96430	0.95665	0.94707	0.93489	0.91785	0.89505	
2.0	0.95236	0.94201	0.92895	0.91216	0.88865	0.85688	
2.5	0.94042	0.92729	0.91059	0.88886	0.85837	0.81671	
3.0	0.92847	0.91247	0.89197	0.86496	0.82691		
3.5	0.91654	0.89759	0.87310	0.84042	0.79412		
4.0	0.90463	0.88265	0.85398	0.81520	0.75989		
4.5	0.89277	0.86766	0.83460	0.78928			
5.0	0.88095	0.85264	0.81499	0.76265			
5.5	0.86920	0.83760	0.79515	0.73532			
6.0	0.85755	0.82259	0.77511				
6.5	0.84600	0.80762	0.75491				
7.0	0.83459	0.79274	0.73460				
7.5	0.82333	0.77798	0.71426				
8.0	0.81227	0.76339	0.69399				
8.5	0.80142	0.74903	0.67393				
9.0	0.79082	0.73497	0.65424				
10.0	0.77051	0.70801	0.61687				
11.0	0.75161	0.68311					
12.0	0.73438	0.66086					
13.0	0.71905	0.65088					
14.0	0.70579						

TABLE 6. EXPERIMENTAL SECOND VIRIAL COEFFICIENTS

	Ethane (1)		Methyl Chloride (2)		Interaction	
T, K	$-B_{11}$, cm^3/mol	$\sigma_{B_{11}}$, cm^3/mol	$-B_{22}$, cm^3/mol	$\sigma_{B_{22}}$, cm^3/mol	$-B_{12}$, cm^3/mol	$\sigma_{B_{12}}$, cm^3/mol
323.15	156.25	0.10	341.5	3.4	206.6	4.8
348.15	132.81	0.15	287.1	1.9	171.1	2.3
373.15	113.52	0.10	237.7	0.8	148.6	1.2
398.15	97.28	0.10	205.0	0.5	126.3	0.7
423.15	83.94	0.09	179.0	0.4	111.5	0.6
448.15	72.00	0.13	157.8	0.3	97.9	0.6
473.15	61.80	0.08	139.5	0.3	85.6	0.6

TABLE 7. SMOOTHED DEW POINTS OF THE MIXTURE

T, K	P, MPa
313.15	1.21 ± 0.01
323.15	1.55 ± 0.01
333.15	2.01 ± 0.01
343.15	2.49 ± 0.01
353.15	3.05 ± 0.01
363.15	3.72 ± 0.01
373.15	4.41 ± 0.02
383.15	5.19 ± 0.03
393.15	6.19 ± 0.04
393.15	8.41 ± 0.03
398.15	6.95 ± 0.06
398.15	7.97 ± 0.08

COMPARISON WITH INTERMOLECULAR THEORY

The second virial coefficients of ethane were reproduced well over the entire range of temperature by the Lennard-Jones potential function with $\epsilon_{11}/k = 212.0$ K and $\sigma_{11} = 0.4721$ nm. The maximum deviation was 0.75 cm^3/mol at 398.15 K, and the average absolute deviation was 0.42 cm^3/mol. Corrected second virial coefficients of methyl chloride were fitted to the Stockmayer potential ($\epsilon_{22}/k = 375.0$ K, $\sigma_{22} = 0.3318$ nm, and $t_2^* = 0.654$) with a maximum deviation of 3.8 cm^3/mol at 348.15 K and an average absolute deviation of 1.1 cm^3/mol.

Hirschfelder et al. (1954) have shown the effective total energy of interaction between a polar and a nonpolar molecule to be of the same form as that for two nonpolar molecules, and thus they suggest the Lennard-Jones potential for the unlike interaction. Table 8 compares the present values of B_{12} with those calculated from the Lennard-Jones potential following optimal fit resulting in $\epsilon_{12} = 228$ K and $\sigma_{12} = 0.492$ nm. The value of B at a given temperature may be reproduced by a given potential model from a variety of combinations of the force constants, ϵ/k and σ. Figure 5 provides the locus of the force constants to reproduce exactly the experimental B for a given temperature. Families of isothermal curves are given for ethane and for ethane/methyl chloride using the Lennard-Jones potential. Were the data and the potential model perfectly correct, these isotherms would all cross at the same point. That they do not leads theoreticians to select somewhat different force constants from the same data and potential function.

Figure 6 illustrates the ability of the selected potential functions to reproduce the experimental second virial coefficients. Here, $B^* \equiv (3B/2\pi\tilde{N}\sigma^3)$, $T^* \equiv (kT/\epsilon)$, $t^* \equiv (\mu^2/\sqrt{8}\epsilon\sigma^3)$, and μ is the dipole moment (6.23×10^{-30} C·m for methyl chloride).

The dipole-dipole energy has a substantial contribution to the total energy of interaction for a pair of polar molecules. In the Stockmayer potential

$$U(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] - \frac{\mu^2}{r^3}(2\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2\cos\phi) \quad (8)$$

the dipole-dipole term is angle dependent with a minimum value of $-(2\mu^2/r^3)$ for the end-on position. Figure 7 compares the total intermolecular energy of two methyl chloride molecules in this position with that in the absence of dipole-dipole interaction. As shown by Rushbrooke (1940), an average effective value of dipole term of Eq. 8 over all angles is equivalent to a temperature-dependent average free energy. Cook and Rowlinson (1953) used this method to obtain the average

$$\epsilon_d(r, T) = -\frac{1}{3}\left[\frac{\mu^4}{r^6kT}\right] + \frac{7}{450}\left[\frac{\mu^8}{r^{12}(kT)^3}\right] + \ldots, \quad (9)$$

where subscript d denotes the dipole energy. Then the total energy becomes

$$U(r) = 4\epsilon\left[(\sigma/r)^{12}\left(1 + \frac{56t^{*4}}{225T^*}\right) - (\sigma/r)^6\left(1 + \frac{2t^{*2}}{3T^*}\right)\right] \quad (10)$$

As noted by Hirschfelder et al. (1942), methyl chloride does not exhibit extreme polar behavior despite a sizable dipole moment. The effective averaged total energies, for the maximum and the minimum temperatures of this work, are shown in Figure 7 for comparison. The canonical average, as concluded by Rowlinson (1958), yields incorrect, twice larger values for the dipole-dipole contribution.

COMPARISON WITH PREDICTIVE METHODS

Modern *a priori* predictive methods allow estimation of the measured pure and interaction second virial coefficients.

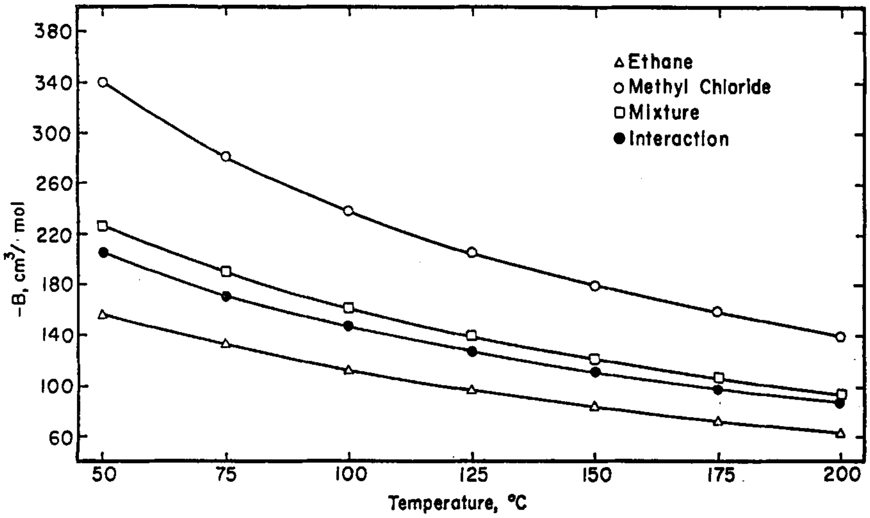

Figure 4. Comparison of the second virial coefficients of the ethane/methyl chloride system.

TABLE 8. EXPERIMENTAL AND CALCULATED LENNARD-JONES INTERACTION SECOND VIRIAL COEFFICIENTS OF THE ETHANE/METHYL CHLORIDE MIXTURE ($\epsilon_{12}/k = 228$ K, $\sigma_{12} = 0.492$ nm)

	Interaction Second Virial Coefficient, cm^3/mol		
T, K	$-B_{\text{obs.}}$	$-B_{\text{calc.}}$	$-(B_{\text{obs.}} - B_{\text{calc.}})$
323.15	206.6 ± 14.4	201.9	4.7
348.15	171.1 ± 6.9	174.1	−3.0
373.15	148.6 ± 3.6	150.7	−2.1
398.15	126.3 ± 2.1	130.7	−4.4
423.15	111.5 ± 1.8	113.6	−2.1
448.15	97.9 ± 1.8	98.6	−0.7
473.15	85.6 ± 1.8	85.6	0.0

Pure Components

The highly regarded methods of Tsonopoulos (1974, 1975, 1978, 1979), Hayden and O'Connell (1975), and Tarakad and Danner (1977) were used to provide estimates of the second virial coefficient of methyl chloride and of its nonpolar homomorph, ethane. Table 9 shows that the predictive methods do not generally provide estimates within the experimental uncertainties of 3σ, and a correlation between accurate measurement and accurate prediction. For ethane, the average of ratios of absolute deviation of the prediction to our 3σ uncertainty, $\langle |\Delta|/3\sigma \rangle$, are 3.35, 4.79, and 6.49 for the correlations of Tsonopoulos, Hayden-O'Connell, and Tarakad-Danner, respectively. The analogous values for methyl chloride are 3.34, 5.06, and 5.49, respectively.

Interaction Second Virial Coefficients for the Mixture

Hirschfelder et al. (1954) proposed the following combination rules:

$$\sigma_{12} = \frac{1}{2}(\sigma_{11} + \sigma_{22})\eta^{-1/6} \tag{11}$$

and

$$\epsilon_{12} = (\epsilon_{11}\epsilon_{22})^{1/2}\eta^2 \tag{12}$$

where

$$\eta = \left[1 + \frac{\alpha_1\mu_2^2}{4\sigma_{11}^3\sigma_{22}^3(\epsilon_{11}\epsilon_{22})^{1/2}}\right] \tag{13}$$

and α_1 is the polarizability of the nonpolar molecule. For ethane, a polarizability of 4.47×10^{-30} m^3 yielded a value of 1.026 for the factor η. Use of this value in Eqs. 11 and 12 produced the following force constants:

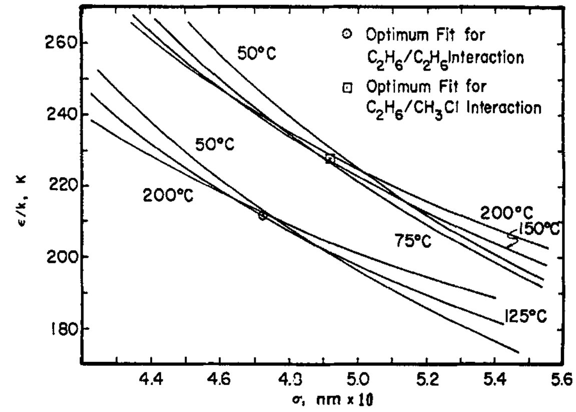

Figure 5. Pairs of the Lennard-Jones parameters to provide the experimental second virial coefficient at the indicated temperature.

$$\sigma_{12} = 0.4002 \text{ nm}$$

$$\epsilon_{12} = 297 \text{ K}$$

These force constants were then used, together with a table of reduced second virial coefficients for the Lennard-Jones (6–12) potential, to calculate the B_{12} values of the third column of Table 10.

O'Connell and Prausnitz (1967) developed a correlation for prediction of B_{12}, which is similar to that of Pitzer and Curl (1957) for pure components. The acentric factor ω_{12} was taken as the arithmetic average of that of the nonpolar compound and that of the nonpolar homomorph of the polar compound. Here, ω_{12} is identical to that of ethane (0.105). Calculated values of B_{12} via the O'Connell-Prausnitz correlation appear in the fifth column of Table 10. The correlations of Hirschfelder-Curtiss-Bird and O'Connell-Prausnitz, considered obsolete by many, contain no adjustable parameters (e.g., k_{12}) and so provide completely *a priori* predictions that here are seen to be respectable.

The correlation of Tsonopoulos, applied above to the pure components, requires the binary interaction parameter k_{12}. Table 11 shows the optimum value of k_{12} to fit exactly the experimental B_{12} for each of our seven temperatures. The standard deviation σ_k is $(\sigma_{B_{12}}/|dB_{12}/dk_{12}|)$, where this derivative is the variation of B_{12} with the assumed k_{12} via the Tsonopoulos correlation near $k_{12} = 0.03$. A graph of the optimum values of k_{12} with $3\sigma_k$ uncertainties vs. temperature does not show conclusively that k_{12} is a monotonic, decreasing function of temperature, as was shown by Holste et al. (1982) for CO_2/C_2H_6 from 250 to 300 K with more precise data. Table 11 does nothing to contradict that conclusion, but the present uncertainties $3\sigma_k$ are too large for definite conclusions to be drawn.

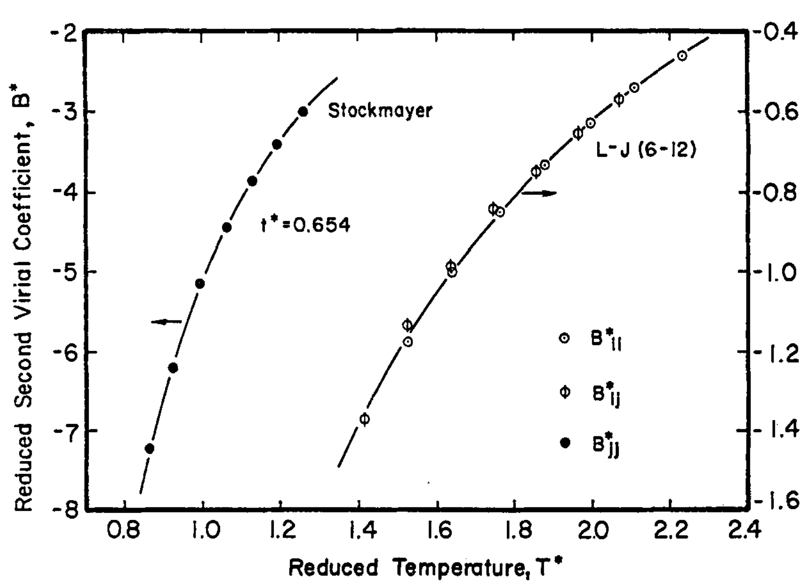

Figure 6. Reduced second virial coefficients of the systems under study.

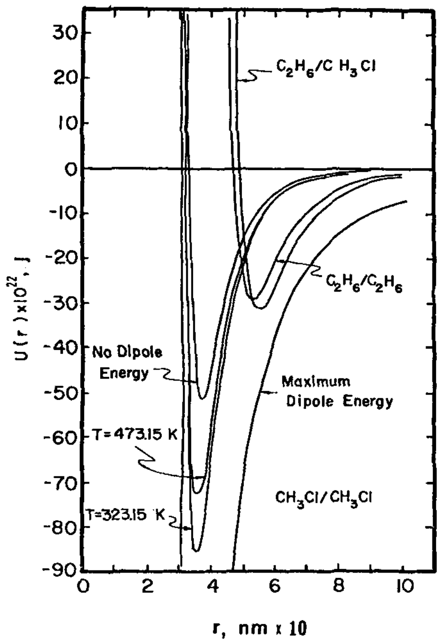

Figure 7. Intermolecular potentials for binary interactions.

Treating k_{12} as a constant independent of temperature, Table 11 provides the statistical values of $\bar{k}_{12}$ and $3\bar{\sigma}_k$. We then selected $k_{12} = 0.03$ as the best average value. Table 11 provides B_{12} values for the Tsonopoulos correlation with $k_{12} = 0.03$ and 0.05. With $k_{12} = 0.03$, the calculated values are within $3\sigma_{B_{12}}$, the given experimental uncertainties, for all but one temperature. Previously, Tsonopoulos (1979) suggested that $k_{12} \cong 0.05$ for haloalkane/hydrocarbon binaries. Here, Table 10 shows $k_{12} = 0.03$ to be significantly better.

Table 10 further provides comparisons of the experimental B_{12} with the correlation of Hayden-O'Connell, which has no adjustable parameters for ethane/methyl chloride, and with the correlation of Tarakad-Danner, which uses k_{12}. Calculation of k_{12} from the recommended formula of Tarakad-Danner (based on pure component critical volumes) yields $k_{12} = 1.640 \times 10^{-4}$, or effectively, $k_{12} \cong 0$. The predicted values of B_{12} are too negative—even at the higher temperatures where better agreement between experiment and prediction is expected. Use of $k_{12} = 0.03$ improves the prediction somewhat (Table 10), and $k_{12} = 0.06$ provides a near optimal fit to minimize $\langle |\Delta|/3\sigma_{B_{12}} \rangle$.

In summary the average ratios of absolute deviation of the various prediction methods for B_{12} to our 3σ uncertainty, $\langle |\Delta|/3\sigma \rangle$, are 1.97 (Hirschfelder-Curtiss-Bird), 4.03 (O'Connell-Prausnitz), 1.59 (Tsonopoulos with $k_{12} = 0.05$), 3.71 (Tsonopoulos with $k_{12} = 0$), 0.55 (Tsonopoulos with $k_{12} = 0.03$), 2.19 (Hayden-O'Connell), 5.83 (Tarakad-Danner with $k_{12} = 1.640 \times 10^{-4}$) 2.88 (Tarakad-Danner with $k_{12} = 0.03$), and 0.62 (Tarakad-Danner with $k_{12} = 0.06$). These ratios first support the conclusions above and, second, when compared with the like ratios for the pure components (same correlation) show the correlations for B_{12} appear somewhat better than they do for the pure second virial coefficients. This illusion is caused by adjusting k_{12} and the higher experimental uncertainties in B_{12} compared to B_{11} and B_{22}. This, in turn, is caused by the indirect determination of B_{12} via Eq. 7 and the propagation of errors in B_m, B_{11}, B_{22}, and y_1. Direct measurement of B_{12} avoids this accumulation of errors.

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TABLE 9. EXPERIMENTAL AND PREDICTED SECOND VIRIAL COEFFICIENTS FOR ETHANE AND FOR METHYL CHLORIDE

T, K	Experimental	Tsonopoulos	Δ	Hayden-O'Connell	Δ	Tarakad-Danner	Δ
Ethane, $-B(cm^3/mol)$							
323.15	156.25 ± 0.30	157.25	1.00	158.04	1.79	152.68	−3.57
348.15	132.81 ± 0.45	133.82	1.01	134.82	2.01	129.16	−3.65
373.15	113.52 ± 0.30	114.56	1.04	115.49	1.97	110.64	−2.88
398.15	97.28 ± 0.30	98.45	1.17	99.16	1.88	95.16	−2.12
423.15	83.94 ± 0.27	84.80	0.86	85.18	1.24	82.21	−1.73
448.15	72.00 ± 0.39	73.07	1.07	73.07	1.07	71.19	−0.81
473.15	61.80 ± 0.24	62.90	1.10	62.50	0.70	61.74	−0.06
Methyl Chloride, $-B(cm^3/mol)$							
323.15	341.5 ± 10.2	328.13	−13.37	367.43	25.93	329.51	−11.99
348.15	287.1 ± 5.7	274.03	−13.07	303.77	16.67	271.38	−15.72
373.15	237.7 ± 2.4	232.91	−4.79	255.10	17.40	228.78	−8.92
398.15	205.0 ± 1.5	200.56	−4.44	217.07	12.07	196.18	−8.82
423.15	179.0 ± 1.2	174.40	−4.60	186.80	7.80	170.37	−8.63
448.15	157.8 ± 0.9	152.78	−5.02	162.34	4.54	149.37	−8.43
473.15	139.5 ± 0.9	134.61	−4.89	142.30	2.80	131.99	−7.51

$\Delta \equiv -B(\text{calc.}) - [-B(\text{exp.})]$.

TABLE 10. EXPERIMENTAL AND PREDICTED INTERACTION SECOND VIRIAL COEFFICIENTS FOR ETHANE (1)/METHYL CHLORIDE (2) VALUES ARE $-B_{12}$ (CM^3/MOL)

T, K	Experimental	H-C-B	Δ	O-P	Δ	C.T.[a]	Δ	C.T.[b]	Δ	C.T.[c]	Δ	H-O	Δ	T-D[d]	Δ	T-D[c]	Δ	T-D[e]	Δ
323.15	206.6 ± 14.4	177.0	−29.6	219.6	13.0	195.5	−11.1	218.0	11.4	204.4	−2.2	188.0	−18.6	215.7	9.0	203.7	−2.9	192.0	−14.6
348.15	171.1 ± 6.9	155.0	−16.1	187.8	16.7	166.7	−4.4	186.1	15.0	174.3	3.2	161.8	−9.3	187.4	16.3	176.8	5.7	166.4	−4.7
373.15	148.6 ± 3.6	136.4	−12.2	161.7	13.1	143.2	−5.4	160.2	11.6	149.9	1.3	140.2	−8.4	163.9	15.3	154.4	5.8	145.1	−3.5
398.15	126.3 ± 2.1	120.9	−5.4	140.0	13.7	123.8	−2.5	138.9	12.6	129.8	3.5	121.9	−4.4	144.1	17.8	135.6	9.3	127.1	−0.8
423.15	111.5 ± 1.8	107.5	−4.0	121.7	10.2	107.4	−4.1	121.1	9.6	112.8	1.3	106.3	−5.2	127.3	15.8	119.5	8.0	111.7	0.2
448.15	97.9 ± 1.8	95.9	−2.0	106.1	8.2	93.5	−4.4	105.9	8.0	98.4	0.5	92.8	−5.1	112.8	14.9	105.6	7.7	98.5	0.6
473.15	85.6 ± 1.8	85.8	−0.2	93.7	8.1	81.5	−4.1	92.8	7.2	85.0	0.4	81.0	−4.6	100.1	14.5	93.5	7.9	86.9	1.3

k_{12} values: $a = 0.05$, $b = 0$, $c = 0.03$, $d = 1.640 \times 10^{-4}$, $e = 0.06$.

$\Delta \equiv -B(\text{calc.}) - [-B(\text{exp.})]$. H-C-B = Hirschfelder, Curtiss, and Bird (1954). O-P = O'Connell and Prausnitz (1967). C.T. = Tsonopoulos (1974, 1975, 1978, 1979). H-O = Hayden and O'Connell (1975).

T-D = Tarakad and Danner (1977).

TABLE 11. OPTIMUM BINARY INTERACTION PARAMETERS FOR THE TSONOPOULOS CORRELATION

T	k_{12} (optimum) $\pm 3\sigma_k$	
323.15	0.024 ± 0.032	
348.15	0.038 ± 0.018	
373.15	0.032 ± 0.011	$\bar{k}_{12} = 0.031$
398.15	0.039 ± 0.007	
423.15	0.029 ± 0.007	$\overline{3\sigma_k} = 0.017$
448.15	0.028 ± 0.007	
473.15	0.026 ± 0.008	

$\bar{k}_{12} \equiv \Sigma_i[(k_{12})_i(\sigma_k)_i^{-2}]/\Sigma(\sigma_k)_i^{-2}$
$\bar{\sigma}_k^2 \equiv \Sigma[(\sigma_k)_i^2/(N-1)]; N = 7$

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NOTATION

B_{11}, B_{22} = second virial coefficient for ethane and methyl chloride, respectively, cm^3/mol
B_{12} = interaction second virial coefficient, cm^3/mol
B^* = dimensionless second virial coefficient, $(3B/2\pi\tilde{N}\sigma^3)$
b = secondary Langmuir adsorption constant, (MPa)$^{-1}$
C = third virial coefficient, (cm^3/mol)^2
D = fourth virial coefficient, (cm^3/mol)^3
k = Boltzmann constant, 1.38054×10^{-23} J·K^{-1}
k_{12} = binary interaction constant
N_A = the volume ratio $(V_A + V_B + V_C)/V_A$
$\tilde{N}$ = Avogadro number, R/k
P = pressure, kPa or MPa
R = gas constant, 8.31441 J/K·mol
r = distance between molecular centers of mass, nm
T = temperature, K or °C = (K −273.15)
T^* = dimensionless temperature, $T/(\epsilon/k)$
t^* = dimensionless dipole moment, $\mu^2/\sqrt{8}\epsilon\sigma^3$
U = intermolecular pair potential, J
V = volume, m^3
y = mol fraction
Z = compressibility factor, $P/\rho RT$

Greek Letters

α = polarizability, m^3
Δ = $-B$ (calc.) $-$ $[-B(\text{exp})]$ of Tables 9 and 10
ϵ = intermolecular energy parameter, J
η = factor defined by Eq. 13
θ = angle in Eq. 8
μ = dipole moment, C·m
ξ = cell distortion factor
ρ = molar density, mol/cm^3
σ = standard deviation (letter subscripted)
σ = intermolecular collision diameter, nm (number subscripted)
ϕ = angle in Eq. 8
ω = acentric factor of Pitzer and Curl

Subscripts

A,B,C = various volumes in Burnett cell
d = dipole contribution
i = counter index
j = isochore number
m = mixture
1 = light component (ethane)
2 = heavy component (methyl chloride)

Superscripts

l = isotherm number
$*$ = dimensionless value

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