Liquid Phase PVTx Properties of Carbon Tetrachloride–Octamethylcyclotetrasiloxane Binary Mixtures

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Measurements are reported for the compressions of pure carbon tetrachloride, octamethylcyclotetrasiloxane, and three of their mixtures from atmospheric to near freezing pressures at temperatures from 273 to 413 K. Nine isothermal equations of state were tested for precision in description of the data. Calculated excess volumes of mixing are reported. Comparison is made with available PVT data and isothermal and adiabatic compressibility results at atmospheric and elevated pressures.

Important advances toward better understanding of the liquid state have been made recently as a result of studies which use as a starting point the hard-sphere model. The structure of a real fluid is determined primarily by the repulsive forces between the molecules while the attractive forces may be considered a uniform potential field which holds the molecules together. The methods for describing the attractive forces become increasingly important in the compressed liquid region.

These theories, when dealing with mixtures, are sensitive to the difference in molecular sizes. A mixture which has been studied at atmospheric pressure because of the spherical symmetry of its components as well as the large disparity in their size is carbon tetrachloride–octamethylcyclotetrasiloxane (OMCTS).

We here describe measurements of the compressions of the two pure components and three of their mixtures. These data allow testing of isothermal equations of state as well as detailing the effect of pressure on the excess volume and hence the Gibbs free energy.

Experimental Program and Results

Apparatus. The experimental technique used to study the liquid phase PVT properties of CCl_4, OMCTS, and three binary mixtures is a modification of the bellows technique originated by Bridgman (*7*). A flexible metal bellows, filled with sample and sealed, is exposed to an external hydrostatic load in a high pressure cell under which the bellows shortens until the internal pressure is equal (except for a small fraction of an atmosphere depending on the stiffness of the bellows) to the external pressure. The change in length of the bellows is a measure of the volume change or compression of the sample. The rapidity with which the measurements can be made after thermal equilibrium is attained, the absence of hysteresis, and the need for comparatively few corrections make the bellows volume detection cell technique highly desirable.

The equipment used in the present investigation has been used in two previous studies. Snyder has measured liquid phase PVT properties of *n*-decane, *n*-dodecane, *n*-tetradecane, *n*-hexadecane, two binary mixtures, and one ternary mixture (*48*). Benson has measured liquid phase PVT properties of *n*-octane (*3*). Since details of the experimental apparatus and technique are available in the earlier studies, only the major points will be discussed herein.

The system has a pressure capability of 200 000 psi and a temperature capability of 150 °C. Two Heise gauges, one 0–1500 psi gauge and one 0–50 000 psi gauge, were used for pressure measurements below 50 000 psi. These were temperature compensated and accurate to 0.1% of full scale (*19*). For pressures above 50 000 psi, a Manganin cell pressure transducer was used. A Hallikainen constant temperature bath and Hallikainen Thermitrol controller were used to control the temperature of the PVT cell. The temperature of the bath was measured to ±0.01 °C with a platinum resistance thermometer previously calibrated by the National Bureau of Standards on the 1948 International Practical Temperature Scale. All isotherms were run at the set point temperature with measured variations of ±0.003 °C about the set point. A Leeds and Northrup Model G-2 Mueller bridge and a Model 2284d galvanometer and scale were used for the necessary resistance measurements. Information by Bedford and Kirby (*1*) allows the IPTS 48 thermometer constants to be converted to IPTS 68 thermometer constants and the temperature on the IPTS 68 scale to be calculated from the PRT resistance measurements. The experimental temperatures reported in this work are based on IPTS 68 after being converted from IPTS 48 thermometer constants.

Data Reduction. The change in volume of the sample in the bellows relative to the volume at some reference pressure, usually atmospheric pressure, as pressure is applied to the system is a function of the following: the vacuum corrected weight of the sample in the bellows, W_{vc}; the density of the sample at the reference pressure, $\rho(P_0,T)$; the temperature and pressure corrected cross-sectional area of the bellows, $A(P,T)$; and the change in length of the bellows with pressure, $\Delta L_B(P,T)$. Appropriate temperature and pressure corrections were applied to $\Delta L_B(P,T)$ and $A(P,T)$ to obtain the true compression of the sample as represented by eq 1.

$$k(P,T) = [v(P_0,T) - v(P,T)]/v(P_0,T) = \Delta L_B(P,T) \cdot A(P,T) \cdot \rho(P_0,T)/W_{vc} \quad (1)$$

The quantity $[v(P_0,T) - v(P,T)]/v(P_0,T) = k(P,T)$ is the compression of the sample where $v(P,T)$ is the specific volume at pressure P and temperature T and $v(P_0,T)$ is the specific volume at reference pressure P_0 and temperature T. The relative volume is defined by eq 2.

$$v(P,T)/v(P_0,T) = 1 - k(P,T) \quad (2)$$

With the exception of the density at atmosphere pressure, all terms on the right hand side of eq 1 were obtained during the course of this study. The atmospheric pressure density was determined by Herring (*20*) to $\pm 1 \times 10^{-5}$ g cm^{-3} using a hydrostatic weighing technique.

An error analysis technique used by the National Bureau of Standards, and detailed by Mickley (*37*), indicates that errors in the PVT measurements made with this system are no greater than ±0.0006 cm^3 of compression per cm^3 of sample. Experimental reproducibility is ±0.0002 cm^3 cm^{-3} or better.

Materials. The samples used in this study were prepared by Herring for use in the related density determinations at atmospheric pressure. The preparation of the samples is described in detail by Herring elsewhere (*20*). The Silicone Products Division of General Electric generously denoted the OMCTS used in the density and PVT measurements. The purity was stated to be better than 99.95% with the chief contaminant being water,

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probably present at the 100–300 ppm level (*51*). The purity of OMCTS is greatly affected by a trace of alkali or, to a lesser extent, strong acid. The alkali causes polymerization to either higher cyclics or linear polymers and/or rearrangement of the cyclic tetramer (*51*). Care was taken during the handling of the OMCTS to ensure the cleanliness of all glassware. The water impurity was effectively removed during degassing of the OMCTS. No other purification was attempted.

Fisher Certified Reagent (99 mol %) CCl_4 was used as the stock material for the distillation with P_2O_5 using a Nester/Faust annular Teflon spinning band distillation column. Each of nine 300-ml batches of CCl_4–P_2O_5 was refluxed for several hours and then distilled at a 200:1 reflux ratio. A 140-ml heart cut was removed, sealed in a light-proof bottle, and stored at −20 °C. Both refractive index and GLC testing of the nine batches showed no discernible differences among them. The purity of the final mixture of the nine batches of CCl_4 was checked using a Varian Aerograph GLC and 12 stock solutions with predetermined contaminant $CHCl_3$ in ratios of 1:40 000 $CHCl_3/CCl_4$ to 1:500 $CHCl_3/CCl_4$. The Fisher Certified Reagent contained 1 part $CHCl_3$ to 4000 parts CCl_4 (99.9+ % pure). The purified sample had 1 part $CHCl_3$ to 11 000 parts CCl_4 (99.99+ % pure) (*20*).

The purified and degassed pure components were used to prepare three binary mixtures of approximately 0.25, 0.50, and 0.75 mol fraction CCl_4. The laboratory temperature was controlled at 18.5 °C in order to minimize evaporation losses. The OMCTS freezing point is 17.5 °C. The mixtures were prepared using sealed glass containers to also minimize evaporation losses. After each mixture was prepared, it was immediately loaded into the density apparatus, and a 50-ml sample was removed for use in the PVT experiment. The final calculation of the mole fraction included an evaporation loss correction (*20*).

Experimental PVT Results. The isothermal compression and relative volume data for CCl_4, OMCTS, and three binary mixtures have been deposited; see paragraph at end of paper regarding supplementary material. No smoothing of the data has been done to the supplementary material. The isotherms deposited in addition to the maximum pressure on the isotherm are listed in Table I.

The maximum pressure on an isotherm was the lowest of three pressures: (a) the freezing pressure of the sample less a 10% safety margin; (b) the pressure at which the bellows compressed 40% of its uncompressed length; or (c) 200 000 psi at 150 °C, the limit of the cell. If either a or b was exceeded, the bellows would be permanently deformed.

The liquid–solid phase transition as a function of temperature and pressure has been measured for CCl_4 (*23*) but no work has been reported in the literature for OMCTS or binary mixtures of CCl_4 and OMCTS. The isothermal liquid–solid phase transition as a function of pressure for OMCTS was measured in this investigation at 50, 100, and 150 °C using an uncalibrated bellows in the PVT apparatus. No liquid–solid phase transition measurements were made on the binary mixtures since it was felt that the freezing pressures of the mixtures could safely be taken as linear functions with volume fractions of the pure component freezing pressures at each temperature.

Empirical Equations of State, Data Fitting, and Thermodynamic Analysis

Once the experimental PVT data have been fitted to an equation of state and a set of parameters determined, thermodynamic properties of the fluid can be calculated. However, the choice of an empirical equation of state to model the PVT data can be made only after an extensive analysis of the fitted data points and the models available. The problem is compounded by the fact that the compressibility equations commonly used to describe the pressure–volume behavior of the liquid phase are isothermal, and the temperature dependence of the parameters must be further determined empirically. The temperature dependence is necessary if derivatives of P and V are needed with respect to T for the calculation of certain thermodynamic quantities.

Table I. Compression Isotherms Deposited (Unsmoothed Data)

System	Temp (°C)	Max P (psig)
OMCTS	39.99	7 520
	59.99	14 050
	79.99	20 960
	100.00	24 090
	120.01	28 010
	140.02	30 920
CCL_4(1) + OMCTS(2)	39.99	9 960
x_1 = 0.249 15	59.99	16 460
	79.99	22 010
	100.00	28 010
CCl_4(1) + OMCTS(2)	39.99	12 980
x_1 = 0.501 24	59.99	19 960
	79.99	24 960
	100.00	30 950
CCl_4(1) + OMCTS(2)	39.99	15 970
x_1 = 0.749 29	59.99	22 000
	79.99	28 040
	100.00	33 990
CCl_4	0.00	6 550
	19.99	12 470
	39.99	19 070
	59.99	25 020
	79.99	32 590
	100.00	38 020
	120.01	43 640
	140.02	49 010

The minimization of the standard deviation of the fitted data points and of the parameters is the usual criterion for discriminating between various models available to determine which model provides the "best" fit. However, these parameters will usually not be good estimates unless the choice of the model is appropriate for the data and leads to randomly distributed, essentially stochastically independent residuals, and the fitting procedure itself leads to negligibly biased parameters (*31*).

Nine compressibility equations which have been used by other investigators to represent the isothermal pressure–volume behavior of a number of fluids are presented in this section. A generalized least-squares technique, a modification of Deming's procedure, is used to provide parameter estimates for the PVT data of this study using the nine compressibility equations. In generalized least squares, the fitting is done with error assumed in both the dependent and independent variables.

The data fitting is examined using several statistical techniques and a decision as to the "best" equation is made using the information thus obtained. The compressibility equations are fit to temperature and composition using assumed analytic forms. The temperature correlated compressibility equation parameters for CCl_4 are used to compare the PVT data of this study with four earlier investigations. The temperature correlated parameters for CCl_4 are also used to compare calculated and literature values for the isothermal and adiabatic bulk moduli.

Isothermal Compressibility Equations. The study of empirical isothermal compressibility equations and their applicability to specific liquid systems has received much attention. In most cases the empirical model, expressed as a pressure–volume equation, is treated as an interpolating and smoothing device and until recently little attention was given to discrimination between the chosen model and other models available. The conclusion to use a specific model has in the past been based on a "reasonable" fit of the data and little consideration was given to a comparison of compressibility equations and of sta-

Table II. Empirical Isothermal Compressibility Equations

Equation	Acronym	Form: $z = p/K_0;\ p = P - P_0;\ x \equiv V_0/V;\ \psi = K_0K'';\ \gamma \equiv [K_0'^2 - 2\psi]^{1/2}$	n
Usual Tait	UTE	$z = (K_0' + 1)^{-1}[\exp\{(K_0' + 1)(1 - x^{-1})\} - 1]$	2
First-order Murnaghan	ME_1	$z = (xK_0' - 1)/K_0'(\chi K_0' - 1)/K_0'$	2
First-order Birch	BE_1	$z = (^3/_2)[x^{7/3} - x^{5/3}][1 + (^3/_4)(K_0' - 4)(x^{2/3} - 1)]$	2
Linear secant modulus	LSME	$1/x = 1 - \{z/[1 + (^1/_2)(K_0' + 1)z]\}$	2
Second-order Murnaghan	ME_2	$z = 2(x^\gamma - 1)/[\gamma(x^\gamma + 1) - K_0'(x^\gamma - 1)]$	3
Second-order Birch	BE_2	$z = (^3/_2)[x^{7/3} - x^{5/3}][1 + (^3/_4)(K_0' - 4)(x^{2/3} - 1)^2]$ $+ (^1/_{24})\{143 + 9K_0'(K_0' - 7) + 9\psi\}(x^{2/3} - 1)^2]$	3
Third-degree Slater	3SE	$z = (1 - x^{-1}) + (^1/_2)(K_0' + 1)(1 - x^{-1})^2 + (^1/_6)(K_0'^2 + 3K_0' + 2 + \psi)(x - 1)$	3
Third-degree Davis–Gordon	3DGE	$z = (x - 1) + (^1/_2)(K_0' - 1)(x - 1)^2 + (^1/_6)(K_0'^2 - 3K_0' + 2 + \psi)(x - 1)^3$	3
Quadratic secant modulus	QSME	$1/x = 1 - \{z/[1 + (^1/_2)(K_0' + 1)z - (^1/_{12})(K_0'^2 - 2\psi - 1)z^2]$	3

tistical goodness-of-fit criteria. The problem of model discrimination is compounded by the presence of systematic errors in the data and systematic error generated by the choice of a poor model. The task becomes one of choosing a set of compressibility equations which can be critically examined using several goodness-of-fit criteria and a set of meaningful physical parameters obtained from the study.

Nine compressibility equations are presented in Table II, four two-parameter and five three-parameter equations (*2, 18, 30, 31, 32*). The two-parameter equations are written in terms of two physical quantities K_0 and K_0' where $K_0 = K|_{p=0}$, $K_0' = (\partial K/\partial P)_T|_{p=0}$, and $p = P - P_0$, a reduced pressure variable. The isothermal bulk modulus, K, is defined as:

$$K \equiv -V(\partial P/\partial V)_T \tag{3}$$

and is related to the isothermal compressibility, β_T, by eq 4.

$$\beta_T \equiv K^{-1} \tag{4}$$

The additional parameter in the three-parameter equations is ψ, where $\psi = K_0K_0''$ and $K_0'' = (\partial^2K/\partial P^2)_T|_{p=0}$. Although V_0 can be considered as an additional parameter, throughout this study V_0 was assumed to be a constant fixed by experiment, i.e., the atmospheric density measurements of Herring (*20*). As z decreases below unity, all of the isothermal equations of state begin to coalesce in form (*32*). For an error level of 2×10^{-4} in the relative volume, roughly the uncertainty of the relative volume measurements of this study, discrimination between equations is difficult for z levels much below $z = 0.1$. As z increases, discrimination among the equations becomes more pronounced.

The isothermal P–V equations presented in Table II can be extended to P–V–T or P–V–x equations by writing the parameters K_0, K_0', and, for three-parameter equations, ψ, as temperature or composition dependent functions. The form of the temperature or composition dependence has little or no theoretical justification and has in the past been written as a second degree polynomial in temperature or composition (*4, 56*).

Statistical Analysis of the Data. The results of a statistical analysis of the fitted PVT data were used to discriminate among the nine isothermal compressibility equations presented in Table II. Only equations pertinent to the interpretation of Tables III, IV, and VI will be given herein as details are available elsewhere (*2, 8, 30–32*).

The sum of squares, S, is written as

$$S \equiv \sum_{i=1}^{N} \{W_{y_i}R_{y_i}^2 + W_{x_i}R_{x_i}^2\} = \sum_{i=1}^{N} d_i^2 = S_y + S_x \tag{5}$$

and the residuals and weights are given as

$$R_{y_i} \equiv Y_i - y_i$$

$$R_{x_i} \equiv X_i - x_i \tag{6}$$

$$W_{y_i} \equiv \sigma_{y_i}^{-2}$$

$$W_{x_i} \equiv \sigma_{x_i}^{-2}$$

The variances of the measurement error, $\sigma_{y_i}^2$ and $\sigma_{x_i}^2$, were assumed to be either directly measurable or calculable from a knowledge of the experimental conditions. It was also assumed that the measurement errors are independent of one another.

For testing the residuals, a composite residual, eq 7, was used

$$d_i \equiv \text{sign}\,(R_{y_i})\{W_{y_i}R_{y_i}^2 + W_{x_i}R_{x_i}^2\}^{1/2} \tag{7}$$

Examination of the standardized residuals, d_i, was done to detect possible systematic error (bias) in the data arising from a poor model choice. Systematic error in the data can also be detected by examining the standardized residuals. Draper and Smith (*11*) have presented a statistical test based on measured values of the number of negative residuals, n_1, the number of positive residuals, n_2, and the number of runs, u (successive residuals of the same sign), to calculate the probability, Pr, of randomness of the residuals.

Because of bias in nonlinear estimation, a corrected sum of squares, M, was defined as:

$$M \equiv \sum_{i=1}^{N} (d_i - \bar{d})^2 \equiv S - \bar{d}^2N \tag{8}$$

where $\bar{d}$ is the average value of the d_i's. The mean of M is $f(\equiv N - n)$ and the variance and standard deviation of M are $2f$ and $(2f)^{1/2}$, respectively. If the measurements are independent and systematic error is not present, the fact that for a given model and data set the resulting value of M does not equal f indicates that all the σ_{y_i}'s and σ_{x_i}'s were under (over) estimated.

The standard deviation of the residuals also plays an important role in the discrimination between various models. The standard deviation, a measure of the absolute magnitude of the residuals, was defined as:

$$s_d = [M/(f - 1)]^{1/2} \tag{9}$$

The root-mean-square (rms) value of the d_i's was calculated as:

$$d_{rms} \equiv \left(\frac{1}{N}\sum_{i=1}^{N} d_i^2\right)^{1/2} \tag{10}$$

and is nearly equal to s_d when $\bar{d} \simeq 0$ and $M \simeq S$.

Generalized Least Squares. Generalized least squares allow simultaneous weighting of the independent and dependent variables to be done in order that a set of parameters be determined from a given data set and model. A recent solution of Britt (*8*) of the generalized least-squares problem for nonlinear, implicit models was used in this study to fit the unsmoothed experimental pressure–volume data to the nine isothermal com-

Table III. Comparison of Ordinary and Generalized Nonlinear Least-Squares Fitting of the UTE and the BE_2 to Experimental PVT Data for OMCTS and CCl_4

	Case I $[\sigma_V = 1; \sigma_P = 0]$		Case II $[\sigma_V = 0; \sigma_P = 1]$		Case III $[\sigma_V = f(t,P,x); \sigma_P = 0]$		Case IV $[\sigma_V = 0; \sigma_P = f(P)]$		Case V $[\sigma_V = 1; \sigma_P = 1]$		Case VI $[\sigma_V = f(t,P,x); \sigma_P = f(P)]$	
	UTE	BE_2	UTE	BE_2	UTE	BE_2	UTE	BE_2	UTE	BE_2	UTE	BE
					OMCTS t = 39.99 °C (N = 28; z_{max} = 0.09)							
$\hat{K}_0 \pm \hat{\sigma}$	5868 ± 31	5711 ± 55	5899 ± 32	5711 ± 64	5859 ± 30	5711 ± 54	5775 ± 22	5770 ± 62	5868 ± 31	5711 ± 55	5786 ± 23	5721 ± 50
$\hat{K}_0' \pm \hat{\sigma}$	10.74 ± 0.21	14.35 ± 1.16	10.53 ± 0.20	14.34 ± 1.23	10.81 ± 0.21	14.35 ± 1.17	11.24 ± 0.27	11.42 ± 2.11	10.74 ± 0.21	14.35 ± 1.16	11.20 ± 0.20	13.43 ± 1.57
$\hat{\psi} \pm \hat{\sigma}$	—	−205 ± 66	—	−204 ± 67	—	−205 ± 68	—	−20 ± 123	—	−205 ± 66	—	−141 ± 96
S	1.06×10^{-6}	0.745×10^{-6}	76.0	53.2	126.0	90.1	93.0	92.8	10.6×10^{-7}	7.45×10^{-7}	29.9	27.4
M	1.04×10^{-6}	0.744×10^{-6}	74.1	53.2	124.5	90.0	90.8	90.7	10.4×10^{-7}	7.44×10^{-7}	29.3	26.9
s_d	2.04×10^{-4}	1.76×10^{-4}	1.722	1.488	2.231	1.936	1.906	1.944	2.04×10^{-4}	1.76×10^{-4}	1.083	1.059
d_{rms}	1.94×10^{-4}	1.63×10^{-4}	1.647	1.378	2.121	1.794	1.822	1.821	1.94×10^{-4}	1.63×10^{-4}	1.033	0.990
S_V/S	1.0	1.0	0.0	0.0	1.0	1.0	0.0	0.0	>0.999	>0.999	0.558	0.640
$n_1/n_2/u$	17/11/17	14/14/19	16/12/17	14/14/19	16/12/15	14/14/19	11/17/13	11/17/13	17/11/17	14/14/19	12/16/13	12/16/15
Pr, %	90	96	86	96	62	96	73	73	90	96	63	62
					OMCTS t = 140.02 °C (N = 72; z_{max} = 0.94)							
$\hat{K}_0 \pm \hat{\sigma}$	2237 ± 4	2252 ± 11	2231 ± 6	2294 ± 29	2237 ± 3	2240 ± 7	2230 ± 3	2241 ± 6	2237 ± 4	2252 ± 11	2231 ± 3	2239 ± 5
$\hat{K}_0' \pm \hat{\sigma}$	10.60 ± 0.02	10.14 ± 0.17	10.62 ± 0.02	9.54 ± 0.34	10.60 ± 0.01	10.37 ± 0.13	10.62 ± 0.01	10.16 ± 0.11	10.60 ± 0.02	10.14 ± 0.17	10.62 ± 0.01	10.24 ± 0.11
$\hat{\psi} \pm \hat{\sigma}$	—	5 ± 3	—	16 ± 6	—	0.5 ± 3	—	6 ± 2	—	5 ± 3	—	4 ± 2
S	5.35×10^{-6}	5.63×10^{-6}	964.4	959.0	232.9	245.4	83.7	87.4	5.35×10^{-6}	5.62×10^{-6}	46.3	48.4
M	5.35×10^{-6}	5.62×10^{-6}	963.6	957.6	232.6	245.2	83.6	87.3	5.35×10^{-6}	5.62×10^{-6}	46.3	48.3
s_d	2.79×10^{-4}	2.88×10^{-4}	3.737	3.753	1.836	1.899	1.100	1.133	2.79×10^{-4}	2.88×10^{-4}	0.819	0.843
d_{rms}	2.73×10^{-4}	2.80×10^{-4}	3.660	3.650	1.799	1.846	1.078	1.102	2.73×10^{-4}	2.80×10^{-4}	0.802	0.820
S_V/S	1.0	1.0	0.0	0.0	1.0	1.0	0.0	0.0	>0.999	>0.999	0.368	0.369
$n_1/n_2/u$	38/34/38	39/33/40	32/40/42	39/33/36	39/33/40	39/33/38	30/42/42	36/36/38	38/34/38	39/33/40	32/40/42	35/37/40
Pr, %	65	82	92	95	82	66	94	64	65	82	92	80
					CCl_4 t = 0.00 °C (N = 26; z_{max} = 0.04)							
$\hat{K}_0 \pm \hat{\sigma}$	11 021 ± 75	10 804 ± 145	11 041 ± 73	10 814 ± 149	11 016 ± 75	10 803 ± 145	10 804 ± 63	10 751 ± 173	11 021 ± 75	10 804 ± 145	10 857 ± 65	10 696 ± 122
$\hat{K}_0' \pm \hat{\sigma}$	10.01 ± 0.49	14.67 ± 2.81	9.86 ± 0.47	14.44 ± 2.74	10.04 ± 0.50	14.69 ± 2.84	11.30 ± 0.89	13.19 ± 5.78	10.01 ± 0.49	14.67 ± 2.81	10.98 ± 0.50	15.89 ± 3.26
$\hat{\psi} \pm \hat{\sigma}$	—	−408 ± 249	—	−388 ± 235	—	−411 ± 253	—	−196 ± 572	—	−408 ± 249	—	−483 ± 325
S	5.14×10^{-7}	4.56×10^{-7}	82.8	73.2	58.5	52.1	182.5	181.6	5.14×10^{-7}	4.56×10^{-7}	21.9	19.8
M	5.09×10^{-7}	4.56×10^{-7}	81.9	73.2	58.0	52.1	180.3	179.1	5.09×10^{-7}	4.56×10^{-7}	21.7	19.6
s_d	1.49×10^{-4}	1.44×10^{-4}	1.887	1.824	1.588	1.539	2.800	2.854	1.49×10^{-4}	1.44×10^{-4}	0.972	0.943
d_{rms}	1.41×10^{-4}	1.32×10^{-4}	1.785	1.678	1.500	1.415	2.649	2.643	1.41×10^{-4}	1.32×10^{-4}	0.918	0.873
S_V/S	1.0	1.0	0.0	0.0	1.0	1.0	0.0	0.0	>0.999	>0.999	0.681	0.737
$n_1/n_2/u$	17/9/9	15/11/12	17/9/9	15/11/12	17/9/9	15/11/12	11/15/9	11/15/9	17/9/9	15/11/12	13/13/7	14/12/11
Pr, %	15	63	15	63	15	63	9	9	15	62	<1	33
					CCl_4 t = 140.02 °C (N = 80; z_{max} = 1.07)							
$\hat{K}_0 \pm \hat{\sigma}$	3126 ± 4	3146 ± 13	3112 ± 8	3188 ± 35	3129 ± 4	3129 ± 10	3109 ± 7	3110 ± 13	3126 ± 5	3146 ± 13	3114 ± 6	3107 ± 10
$\hat{K}_0' \pm \hat{\sigma}$	9.53 ± 0.01	9.31 ± 0.12	9.56 ± 0.02	8.93 ± 0.27	9.52 ± 0.01	9.50 ± 0.11	9.57 ± 0.02	9.54 ± 0.12	9.53 ± 0.01	9.31 ± 0.12	9.56 ± 0.01	9.62 ± 0.10
$\hat{\psi} \pm \hat{\sigma}$	—	−5 ± 2	—	1 ± 4	—	−9 ± 2	—	−8 ± 2	—	−5 ± 2	—	−10 ± 2
S	5.79×10^{-6}	5.49×10^{-6}	2794.9	2567.0	306.5	303.9	321.5	316.0	5.79×10^{-6}	5.48×10^{-6}	107.4	104.9
M	5.79×10^{-6}	5.47×10^{-6}	2788.3	2564.6	305.0	302.6	321.1	315.6	5.79×10^{-6}	5.47×10^{-6}	107.3	104.9
s_d	2.74×10^{-4}	2.68×10^{-4}	6.018	5.809	1.990	1.995	2.042	2.038	2.74×10^{-4}	2.68×10^{-4}	1.181	1.175
d_{rms}	2.69×10^{-4}	2.62×10^{-4}	5.911	5.665	1.957	1.949	2.005	1.987	2.69×10^{-4}	2.62×10^{-4}	1.159	1.145
S_V/S	1.0	1.0	0.0	0.0	1.0	1.0	0.0	0.0	>0.999	>0.999	0.520	0.523
$n_1/n_2/u$	31/49/54	31/49/56	30/50/46	41/39/47	32/48/56	32/48/56	28/52/42	28/52/42	31/49/54	31/49/56	30/50/46	28/52/50
Pr, %	99	99	97	93	99	99	90	90	99	99	97	99

Table IV. Results for Generalized (Case VI) Nonlinear Least-Squares Fitting of Nine Compressibility Equations to Experimental PVT Data for CCl_4 (t = 79.99° and t = 100.00 °C)

	$n = 2$				$n = 3$				
	UTE	ME_1	BE_1	LSME	ME_2	BE_2	3SE	3DGE	QSME
	CCl_4, t = 79.99 °C (N = 65; $z_{max} \simeq 0.39$)								
$\hat{K}_0 \pm \hat{\sigma}$	5797 ± 15	5902 ± 21	5536 ± 25	6356 ± 50	5746 ± 21	5710 ± 23	5799 ± 32	5718 ± 24	5850 ± 26
$\hat{K}_0' \pm \hat{\sigma}$	9.88 ± 0.04	9.13 ± 0.05	12.60 ± 0.11	6.69 ± 0.07	10.08 ± 0.10	10.68 ± 0.19	7.99 ± 0.33	10.44 ± 0.22	8.71 ± 0.09
$\hat{\psi} \pm \hat{\sigma}$	—	—	—	—	−8 ± 0.8	−29 ± 5	131 ± 10	−16 ± 6	23 ± 0.3
S	107.4	224.0	218.9	1620.9	90.0	80.2	129.2	82.8	172.7
M	106.8	219.9	217.8	1535.2	90.0	80.2	129.1	82.8	172.5
s_d	1.312	1.883	1.874	4.976	1.215	1.147	1.455	1.165	1.682
d_{rms}	1.286	1.856	1.835	4.993	1.177	1.111	1.410	1.129	1.630
S_v/S	0.592	0.614	0.541	0.637	0.547	0.560	0.488	0.553	0.517
$n_1/n_2/u$	28/37/27	28/37/17	36/29/16	36/29/7	28/37/30	30/35/36	28/37/24	30/35/36	26/39/14
Pr, %	17	<1	0	0	54	79	3	79	<1
	CCl_4, t = 100.00 °C (N = 69; $z_{max} \simeq 0.56$)								
$K_0 \pm \sigma$	4726 ± 10	4851 ± 19	4425 ± 28	5383 ± 53	4691 ± 14	4655 ± 15	4794 ± 28	4670 ± 16	4824 ± 23
$K_0' \pm \sigma$	9.93 ± 0.02	9.03 ± 0.04	13.37 ± 0.14	6.27 ± 0.07	9.98 ± 0.07	10.59 ± 0.13	6.24 ± 0.31	10.17 ± 0.15	8.30 ± 0.07
$\hat{\psi} \pm \hat{\sigma}$	—	—	—	—	−6 ± 0.4	−23 ± 3	198 ± 8	−3 ± 4	24 ± 0.3
S	95.8	338.9	499.6	3556.4	76.2	63.8	182.5	67.5	278.6
M	95.8	336.0	496.0	3407.9	75.6	63.2	180.1	66.8	278.5
s_d	1.205	2.256	2.741	7.186	1.078	0.986	1.665	1.014	2.070
d_{rms}	1.178	2.216	2.691	7.179	1.051	0.961	1.626	0.989	2.010
S_v/S	0.545	0.590	0.527	0.616	0.488	0.494	0.424	0.484	0.500
$n_1/n_2/u$	27/42/27	31/38/21	34/35/6	37/32/5	28/41/30	31/38/42	28/41/22	27/42/36	27/42/10
Pr, %	10	<1	0	0	34	96	<1	75	0

pressibility equations in Table II to obtain estimates for the parameter and variance values.

Six cases were studied to determine the effect of weighting both the pressure and relative volume variables. These six cases correspond to: case I $\sigma_v = 1$, $\sigma_p \simeq 0$; case II $\sigma_v \simeq 0$, $\sigma_p = 1$; case III $\sigma_v = f(T,P,x)$, $\sigma_p \simeq 0$; case IV $\sigma_v \simeq 0$, $\sigma_p = f(P)$; case V $\sigma_v = 1$, $\sigma_p = 1$; case VI $\sigma_v = f(T,P,x)$, $\sigma_p = f(P)$. Cases I and II correspond to ordinary unweighted least squares, cases III and IV to ordinary weighted least squares, and cases V and VI to generalized least squares.

Since the relative volume is an indirectly measured quantity being a function of $\Delta L_B(T,P)$, $A(T,P)$, $\rho(T,P_0)$, and W_{vc}, it was necessary to estimate $\sigma_v^2 = f(T,P,x)$ using the propagation of error formula.

The estimated precision in the pressure measurement is pressure dependent. The two Heise gauges, 0–1500 psi and 0–50 000 psi, have an estimated precision of ±0.1% of full scale (*19*). The variance of the pressure as measured by the two Heise gauges is summarized as:

$$\sigma_p^2 = 0.104\,18 \text{ atm}^2 \quad 1 \leq P \leq 103.07 \text{ atm}$$

$$\sigma_p^2 = 11.5756 \text{ atm}^2 \quad 103.07 < P \leq 3403.28 \text{ atm}$$

Comparison of Ordinary and Generalized Least-Squares Fitting. In order to compare ordinary and generalized least-squares fitting of the pressure–relative volume data, six weighting cases were examined for four isotherms: OMCTS, t = 39.99 °C and t = 140.02 °C, and CCl_4, t = 0.00 °C and t = 140.02 °C. The two compressibility equations used in the comparison, the UTE and the BE_2, were chosen as representative, and later shown to be the "best", of the two- and three-parameter equations available.

Table III summarizes the results of the comparison. It should be cautioned that direct comparison between cases of the values for S, M, s_d, and d_{rms} is not possible because of differences in the weighting.

The widest disparity among the six cases for $\hat{K}_0$, $\hat{K}_0'$, and $\hat{\psi}$ for cases I through V are usually within one or two standard deviations of $\hat{K}_0$, $\hat{K}_0'$, and $\hat{\psi}$ from case VI for both the UTE and the BE_2. The low z_{max} region for the BE_2 is also characterized by large estimates of $\hat{\sigma}$ for $\hat{K}_0$, $\hat{K}_0'$, and $\hat{\psi}$. In nearly all instances $\hat{\sigma}$ for $\hat{K}_0$ and $\hat{K}_0'$ from the UTE is smaller than $\hat{\sigma}$ for $\hat{K}_0$ and $\hat{K}_0'$ from the BE_2. As z_{max} increases, the difference between the values of $\hat{\sigma}$ for the two equations decreases.

The values of s_d reflect the magnitude of the least-squares residuals. For case I ($\sigma_v = 1$; $\sigma_p \simeq 0$), the value of s_d for the relative volume residuals is on the order of 2×10^{-4}. For case II ($\sigma_v \simeq 0$; $\sigma_p = 1$), the pressure residuals are on the order of 4 atm. Case III ($\sigma_v = f(T,P,x)$; $\sigma_p \simeq 0$) and case IV ($\sigma_v \simeq 0$; $\sigma_p = f(P)$) correspond to ordinary least-squares fitting with one variable, either the relative volume or pressure, weighted. If only one of the variables were error corrupted and $\sigma_v = f(T,P,x)$ or $\sigma_p = f(P)$ represented the correct weighting, then s_d should be very close to unity. Examination of cases III and IV shows, however, s_d values considerably larger than unity indicating that not all of the error can be attributed to a single variable, and that a generalized least-squares procedure is necessary.

Case V ($\sigma_v = 1$; $\sigma_p = 1$) shows the results for equal weighting of the relative volume and the pressure, a situation not generally encountered. The magnitude of the relative volume is on the order of 0.8–1.0, and the pressures range from atmospheric to several kiloatmospheres. The relative significance of error in the pressure is then much smaller than error in the relative volume. As verified by a comparison of cases I and V, the fitting is effectively done with $\sigma_v = 1$ and $\sigma_p = 0$.

For case VI if σ_v and σ_p are correctly chosen and the model is "correct", then $s_d \simeq 1$ and $M \simeq N - n$ as previously noted. For the four isotherms in Table III, s_d is in the range of 0.819–

Table V. Summary of Results for Generalized (Case VI) Nonlinear Least-Squares Fitting of the UTE and BE_2 to Experimental PVT Data for CCl_4 OMCTS, and Three Binary Mixtures

System	T (°C)	P_0 (atm)	$\rho(P_0, T)$ g cm^{-3}	$\hat{K}_0 \pm \hat{\sigma}$ (atm) UTE	BE_2	$\hat{K}_0' \pm \hat{\sigma}$ UTE	BE_2	$\hat{\psi} \pm \hat{\sigma}$ UTE	BE_2
OMCTS	39.99	1	0.933 219	5786 ± 23	5721 ± 50	11.20 ± 0.20	13.43 ± 1.57	—	−141 ± 96
MW = 296.622	59.99	1	0.910 130	4887 ± 16	4791 ± 18	11.06 ± 0.07	13.40 ± 0.38	—	−104 ± 16
g mol^{-1}	79.99	1	0.886 728	4146 ± 12	4100 ± 18	10.83 ± 0.04	11.61 ± 0.28	—	−31 ± 9
	100.00	1	0.862 914	3469 ± 7	3440 ± 11	10.77 ± 0.03	11.20 ± 0.17	—	−17 ± 5
	120.01	1	0.838 447	2764 ± 6	2725 ± 7	10.84 ± 0.02	11.46 ± 0.12	—	−20 ± 3
	140.02	1	0.813 200	2231 ± 3	2239 ± 5	10.62 ± 0.01	10.24 ± 0.11	—	4 ± 2
CCl_4(1) +	39.99	1	0.991 646	5966 ± 21	5932 ± 39	10.53 ± 0.13	11.57 ± 1.03	—	−62 ± 53
OMCTS(2),	59.99	1	0.966 986	5088 ± 14	5080 ± 22	10.47 ± 0.06	10.62 ± 0.39	—	−14 ± 14
x_1 = 0.2491$_4$	79.99	1	0.941 924	4319 ± 9	4339 ± 13	10.40 ± 0.03	9.95 ± 0.20	—	6 ± 6
MW = 261.045 g mol^{-1}	100.00	1	0.916 271	3591 ± 7	3604 ± 11	10.47 ± 0.02	10.13 ± 0.17	—	2 ± 4
CCl_4(1) +	39.99	1	1.082 005	6319 ± 19	6350 ± 30	10.29 ± 0.09	9.52 ± 0.56	—	24 ± 23
OMCTS(2),	59.99	1	1.054 918	5345 ± 12	5329 ± 19	10.41 ± 0.04	10.64 ± 0.26	—	−16 ± 8
x_1 = 0.5012	79.99	1	1.027 247	4544 ± 8	4552 ± 13	10.24 ± 0.03	10.05 ± 0.26	—	−2 ± 5
MW = 225.046 g mol^{-1}	100.00	6.78	1.0005	3755 ± 8	3740 ± 12	10.49 ± 0.02	10.59 ± 0.15	—	−9 ± 4
CCl_4(1) +	39.99	1	1.232 934	6855 ± 18	6849 ± 28	10.14 ± 0.07	10.22 ± 0.39	—	−13 ± 25
OMCTS(2),	59.99	1	1.201 900	5914 ± 14	5941 ± 21	10.04 ± 0.04	9.61 ± 0.23	—	5 ± 7
x_1 = 0.7492	79.99	1	1.170 221	4951 ± 9	4960 ± 14	10.03 ± 0.02	9.85 ± 0.15	—	−3 ± 4
MW = 189.624 g mol^{-1}	100.00	8.69	1.139 2	4086 ± 7	4101 ± 12	10.19 ± 0.02	9.89 ± 0.15	—	0 ± 3
CCl_4	0.00	1	1.632 704	10857 ± 65	10696 ± 122	10.98 ± 0.50	15.89 ± 3.26	—	−483 ± 325
MW = 153.823	19,99	1	1.594 066	9287 ± 39	9110 ± 50	10.20 ± 0.16	13.32 ± 0.71	—	−181 ± 40
g mol^{-1}	39.99	1	1.554 960	8092 ± 16	8034 ± 24	9.61 ± 0.05	10.26 ± 0.23	—	−33 ± 8
	59.99	1	1.515 305	6939 ± 20	6900 ± 34	9.80 ± 0.05	10.16 ± 0.29	—	−19 ± 9
	79.99	10.46	1.476 9	5797 ± 15	5710 ± 23	9.88 ± 0.04	10.68 ± 0.19	—	−29 ± 5
	100.00	7.67	1.434 5	4726 ± 10	4655 ± 15	9.93 ± 0.02	10.59 ± 0.13	—	−23 ± 3
	120.01	7.87	1.391 9	3951 ± 3	3996 ± 13	9.75 ± 0.02	9.22 ± 0.12	—	3 ± 2
	140.02	11.68	1.347 9	3114 ± 6	3107 ± 10	9.56 ± 0.01	9.62 ± 0.10	—	−10 ± 2

1.181. The s_d(UTE) was greater than $s_d(BE_2)$ for three of the four isotherms for all six cases.

Results for Case VI Weighting. The isothermal pressure–relative volume data for the two pure components and three binary mixtures were fit to the nine compressibility equations in Table II assuming both the pressure and relative volume to be error corrupted. The results for two isotherms for CCl_4 (t = 79.99 and t = 100.00 °C) are shown in Table IV. A complete Table IV for all 26 isotherms is available in the microfilm edition; see paragraph at end of paper regarding supplementary material. The results shown in Table IV are representative of all systems tested. The results of case VI weighting for all 26 isotherms using the UTE and the BE_2 are summarized in Table V.

In the low pressure region the values of $\hat{\sigma}$ for $\hat{K}_0$ evaluated from the two-parameter equations were approximately one-half of the corresponding value of $\hat{\sigma}$ for $\hat{K}_0$ evaluated from the three-parameter equations for those equations where systematic error associated with a wrong model choice was limited. Similar behavior was noted for $\hat{\sigma}$ evaluated for $\hat{K}_0'$ in the low z_{max}(= $p_{max}/\hat{K}_0$) region. As z_{max} increased, the estimates of $\hat{\sigma}$ for $\hat{K}_0$ from the two- and three-parameter equations became essentially the same whereas $\hat{\sigma}$ for $\hat{K}_0'$ evaluated from the two-parameter equations remained considerably smaller than $\hat{\sigma}$ for $\hat{K}_0'$ from the three-parameter equations.

In the low z_{max} region the values of $\hat{K}_0$ evaluated from the two-parameter equations were more than one or two standard deviations larger than the corresponding value of $\hat{K}_0$ from the three-parameter equations. As z_{max} increased, the values of $\hat{K}_0$ for the two-parameter equations showing the least systematic error were within one or two standard deviations of the value of $\hat{K}_0$ from the three-parameter equations. In most instances $\hat{K}_0'$ from the two- and three-parameter equations were not within one or two standard deviations of one another. However, $\hat{K}_0'$ for n = 2 in most cases was smaller than $\hat{K}_0'$ for n = 3. The estimates of $\hat{\sigma}$ for $\hat{\psi}$ were usually quite large, especially in the low z area. In some cases even the sign of $\hat{\psi}$ is uncertain.

For even the lowest pressure range it became evident that the LSME was an inadequate model for the pressure–relative volume data. As the maximum pressures increased, the performance of the LSME rapidly deteriorated. For example for OMCTS at t = 140.02 °C ($z_{max} \simeq$ 0.94) the LSME had s_d = 11.940 (M = 9836.4, N = 72) indicating strong systematic error associated with a wrong model choice. The QSME, 3SE, BE_1, and the ME_1 also showed strong systematic error as the values of z_{max} increased. The QSME was the only equation for which convergence was not achieved at the higher temperatures and pressures. Convergence could be obtained if error was assumed in either the pressure or relative volume but not both.

The results of case VI weighting for the nine equations and 26 isotherms verify several points concluded by previous investigators and are in direct opposition to some others. As Macdonald and Powell noted (*32*), discrimination among various compressibility equations, with the possible exception of the LSME, is difficult at levels below z = 0.1 when the error in the relative volume is on the order of 2 × 10^{-4} as it is in this study. The region below z = 0.1 for this study is characterized mainly by large estimates of $\hat{\sigma}$ for $\hat{K}_0$, $\hat{K}_0'$, and $\hat{\psi}$ and in general a coalescing of the results for the nine equations. As z increased, discrimination among the equations became easier.

In general the UTE was superior to the ME_1 in terms of s_d and Pr. This result is in conflict with conclusions reached by Macdonald (*31*), who found the UTE generally inferior in his analysis of data for water and mercury. Hayward's claim that two-parameter compressibility equations cannot be expected to represent P–V data over pressure ranges greater than 1 katm (*18*) was refuted by the generally good performance of the UTE. Even the QSME, a three-parameter equation claimed by Hayward (*18*) as adequately representing the P–V region above 1 katm for water, was inferior to the UTE and in most cases to the ME_1. In

Table VI. Calculated Excess Volumes as a Function of Temperature and Pressure for the CCl_4(1) + OMCTS(2) Binary System

Pressure (atm)	$V^E(T,P,x)$ ($\pm\sigma V^E$) ($cm^3\ mol^{-1}$) x_1 0.249 14	x_1 = 0.501 24	x_1 = 0.749 19
	t = 39.99 °C		
1	−0.06	−0.12	−0.01
100	−0.07 (±0.05)	−0.09 (±0.04)	0.02 (±0.04)
200	−0.11 (±0.05)	−0.12 (±0.04)	0.02 (±0.04)
300	−0.15 (±0.05)	−0.16 (±0.04)	0.01 (±0.04)
400	−0.18 (±0.05)	−0.18 (±0.04)	0.01 (±0.04)
500	−0.19 (±0.06)	−0.18 (±0.05)	0.01 (±0.05)
	t = 59.99 °C		
1	−0.05	−0.10	0.00
100	−0.01 (±0.05)	−0.07 (±0.04)	0.08 (±0.04)
200	−0.07 (±0.05)	−0.90 (±0.04)	0.08 (±0.04)
300	−0.14 (±0.05)	−0.13 (±0.04)	0.06 (±0.04)
400	−0.20 (±0.05)	−0.17 (±0.04)	0.04 (±0.04)
500	−0.24 (±0.06)	−0.19 (±0.05)	0.03 (±0.05)
600	−0.27 (±0.06)	−0.21 (±0.05)	0.02 (±0.05)
700	−0.28 (±0.07)	−0.21 (±0.06)	0.01 (±0.07)
800	−0.28 (±0.07)	−0.21 (±0.06)	0.01 (±0.06)
900	−0.26 (±0.08)	−0.20 (±0.07)	0.01 (±0.07)
1000	−0.24 (±0.08)	−0.18 (±0.07)	0.02 (±0.07)
	t = 79.99 °C		
100	0.06 (±0.05)	0.03 (±0.04)	0.10 (±0.04)
200	0.02 (±0.05)	0.03 (±0.04)	0.12 (±0.04)
300	−0.03 (±0.05)	0.00 (±0.04)	0.12 (±0.04)
400	−0.09 (±0.05)	−0.03 (±0.04)	0.10 (±0.04)
500	−0.14 (±0.06)	−0.07 (±0.05)	0.08 (±0.05)
600	−0.18 (±0.06)	−0.10 (±0.05)	0.06 (±0.05)
700	−0.21 (±0.07)	−0.13 (±0.06)	0.04 (±0.06)
800	−0.23 (±0.07)	−0.16 (±0.06)	0.02 (±0.06)
900	−0.25 (±0.08)	−0.18 (±0.07)	0.01 (±0.07)
1000	−0.26 (±0.08)	−0.19 (±0.07)	−0.01 (±0.07)
1100	−0.27 (±0.08)	−0.21 (±0.07)	−0.02 (±0.07)
1200	−0.27 (±0.08)	−0.22 (±0.07)	−0.02 (±0.07)
1300	−0.27 (±0.09)	−0.23 (±0.08)	−0.03 (±0.08)
1400	−0.27 (±0.09)	−0.23 (±0.08)	−0.03 (±0.08)
	t = 100.00 °C		
100	0.10 (±0.05)	0.01 (±0.04)	0.17 (±0.04)
200	0.07 (±0.05)	−0.03 (±0.04)	0.15 (±0.04)
300	0.02 (±0.05)	−0.07 (±0.04)	0.12 (±0.04)
400	−0.03 (±0.05)	−0.10 (±0.04)	0.09 (±0.04)
500	−0.08 (±0.06)	−0.12 (±0.05)	0.06 (±0.05)
600	−0.12 (±0.06)	−0.14 (±0.05)	0.03 (±0.05)
700	−0.15 (±0.07)	−0.16 (±0.06)	0.01 (±0.06)
800	−0.17 (±0.07)	−0.17 (±0.06)	−0.01 (±0.06)
900	−0.19 (±0.08)	−0.18 (±0.07)	−0.02 (±0.07)
1000	−0.21 (±0.08)	−0.19 (±0.07)	−0.03 (±0.07)
1100	−0.22 (±0.08)	−0.19 (±0.07)	−0.04 (±0.07)
1200	−0.23 (±0.08)	−0.20 (±0.07)	−0.05 (±0.07)
1300	−0.23 (±0.09)	−0.20 (±0.09)	−0.05 (±0.09)
1400	−0.24 (±0.09)	−0.20 (±0.09)	−0.06 (±0.09)
1500	−0.24 (±0.09)	−0.20 (±0.09)	−0.06 (±0.09)
1600	−0.24 (±0.09)	−0.20 (±0.09)	−0.06 (±0.09)

addition the LSME was not "unquestionably superior" as Hayward concludes from his study of the Kell and Whalley P–V data for water (*26*).

Although the relative importance of bias cannot be directly assessed (*6*), it should be noted that unless the model is applicable, the various parameter values and standard deviation estimates must be discounted as biased. The fact that s_d is very nearly unity for the majority of the isotherms fitted to the UTE and the BE_2 should add confidence to the parameter and standard deviation estimates.

While no one equation best represented the pressure–relative volume data for all 26 isotherms, it is concluded that in terms of overall s_d and Pr values, the UTE was the "best" two-parameter equation and the BE_2 was the "best" three-parameter equation of the equations studied. The performance of the BE_2 was generally superior to that of the UTE.

Experimental Excess Volumes. The excess volume at any temperature, pressure, and composition is defined by eq 11 as

$$V^E(T,P,x) = V_m(T,P,x) - x_1 V_1(T,P) - x_2 V_2(T,P) \qquad (11)$$

where V_m is the molar volume of the mixture, and x_1 and x_2 are the mole fractions of components 1 and 2 in the binary mixture. The molar volumes of the three binary mixtures and the two pure components are calculated from the relative volumes obtained by iteration from the BE_2 using the isothermal parameters from the case VI weighting as reported in Table V, the molecular weight, and the density at pressure P_0.

The experimental excess volumes for the CCl_4(1) + OMCTS(2) binary mixture presented in Table VI were calculated in 100 atm increments for pressures up to the maximum pressures encountered for the OMCTS isotherms. The uncertainty in the calculated excess volumes was computed using the propogation of error formula and estimates of the uncertainty in V_m, V_1, V_2, x_1, and x_2.

Temperature and Composition Dependence of the Compressibility Equation Parameters. The temperature and composition dependence of the UTE and the BE_2 compressibility equation parameters were assumed to be of the form

$$\begin{aligned} K_0(t) &= \sum_{i=1}^{3} A_i(t + 273.15)^{i-1} \\ K_0'(t) &= \sum_{i=4}^{6} A_i(t + 273.15)^{i-4} \qquad (12) \\ \psi(t) &= \sum_{i=7}^{9} A_i(t + 273.15)^{i-7} \end{aligned}$$

$$\begin{aligned} K_0(x_1) &= \sum_{i=1}^{3} A_i x_i^{\,i-1} \\ K_0'(x_1) &= \sum_{i=4}^{6} A_i x_i^{\,i-4} \qquad (12a) \\ \psi(x_1) &= \sum_{i=7}^{9} A_i x_1^{\,i-7} \end{aligned}$$

Initial attempts to determine the A_i parameters in eq 12 and 12a using the UTE and the BE_2 were unsuccessful for the five systems and the generalized nonlinear least-squares procedure. Pressure, relative volume, and temperature or composition were the weighted variables. Nonconvergence was caused by singularities in the matrix solution of the problem. As an alternative, the values of $\hat{K}_0$, $\hat{K}_0'$, and $\hat{\psi}$ from the case VI isothermal fit were correlated with temperature or composition. The generalized least-squares procedure was used with the corresponding value of $\hat{\sigma}$ from the isothermal fit serving as the weighting for the compressibility equation parameter.

The results of the temperature and composition correlation for UTE and BE_2 parameters are presented in Tables VII and VIII. Figure 1 illustrates the temperature dependence of the bulk modulus, $\hat{K}_0$, as obtained from the isothermal case VI weighting of the P–V data and the BE_2. Figure 2 presents the dependence of $\hat{K}_0$ on the mole fraction and the volume fraction. To within the experimental uncertainty, $\hat{K}_0$ is a linear function of the volume fraction.

Comparison of Results with Literature Data

PVT Data. There are four sources of liquid phase PVT data for CCl_4 in the literature (*7, 15, 22, 45*); however, in only one case are experimental data and not compressibility equation parameters reported. Gibson and Loeffler present temperature

Table VII. Temperature Correlation of the UTE and BE_2 Compressibility Equation Parameters

	OMCTS (N = 319) UTE	OMCTS (N = 319) BE_2	x_1 = 0.249 14 (N = 192) UTE	x_1 = 0.249 14 (N = 192) BE_2	x_1 = 0.501 24 (N = 210) UTE	x_1 = 0.501 24 (N = 210) BE_2	x_1 = 0.749 29 (N = 225) UTE	x_1 = 0.749 29 (N = 225) BE_2	CCl_4 (N = 467) UTE	CCl_4 (N = 467) BE_2
$K_0(t)$:										
A_1	0.285 599 × 10^{5}	0.295 499 × 10^{5}	0.279 530 × 10^{5}	0.240 559 × 10^{5}	0.302 668 × 10^{5}	0.304 096 × 10^{5}	0.289 879 × 10^{5}	0.279 369 × 10^{5}	0.405 086 × 10^{5}	0.398 134 × 10^{5}
A_2	−0.100 975 × 10^{3}	−0.107 627 × 10^{3}	−0.961 479 × 10^{2}	−0.743 393 × 10^{2}	−0.105 337 × 10^{3}	−0.105 766 × 10^{2}	−0.909 484 × 10^{2}	−0.849 027 × 10^{2}	−0.144 434 × 10^{3}	−0.141 957 × 10^{3}
A_3	0.901 411 × 10^{-1}	0.100 451 × 10^{0}	0.827 126 × 10^{-1}	0.523 494 × 10^{-1}	0.919 151 × 10^{-1}	0.919 582 × 10^{-1}	0.648 720 × 10^{-1}	0.563 121 × 10^{-1}	0.130 567 × 10^{0}	0.128 685 × 10^{0}
$K_0'(t)$:										
A_4	0.653 392 × 10^{1}	0.612 597 × 10^{1}	0.246 303 × 10^{2}	0.123 308 × 10^{3}	0.378 086 × 10^{2}	0.384 897 × 10^{2}	0.305 857 × 10^{2}	0.370 985 × 10^{2}	−0.355 757 × 10^{1}	0.102 870 × 10^{2}
A_5	0.267 792 × 10^{-1}	0.573 873 × 10^{-1}	−0.810 010 × 10^{-1}	−0.631 656 × 10^{0}	−0.160 632 × 10^{0}	−0.169 247 × 10^{0}	−0.120 479 × 10^{0}	−0.157 296 × 10^{0}	0.756 205 × 10^{-1}	0.131 116 × 10^{-1}
A_6	−0.408 269 × 10^{-4}	−0.114 023 × 10^{-3}	0.115 357 × 10^{-3}	0.879 881 × 10^{-3}	0.234 211 × 10^{-3}	0.252 794 × 10^{-3}	0.176 379 × 10^{-3}	0.226 277 × 10^{-3}	−0.106 175 × 10^{-3}	−0.365 592 × 10^{4}
$\psi(t)$:										
A_7	—	−0.548 999 × 10^{3}	—	−0.383 872 × 10^{4}	—	0.144 274 × 10^{3}	—	0.584 903 × 10^{2}	—	−0.807 091 × 10^{3}
A_8	—	0.197 480 × 10^{1}	—	0.213 556 × 10^{2}	—	0.865 899 × 10^{0}	—	−0.375 407 × 10^{0}	—	0.394 669 × 10^{1}
A_9	—	−0.155 032 × 10^{-2}	—	−0.296 556 × 10^{-1}	—	−0.134 050 × 10^{-2}	—	0.583 409 × 10^{-3}	—	−0.486 678 × 10^{-2}
s_d:										
Case III	2.919	3.004	2.405	2.499	2.287	2.275	2.445	2.438	3.306	3.242
Case IV	1.803	1.854	1.572	1.585	1.556	1.567	1.621	1.602	3.308	3.078
Case VI	3.452	3.531	2.873	2.960	2.766	2.763	2.935	2.917	4.686	4.470
S_V/S:										
Case III	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Case IV	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Case VI	0.735	0.726	0.701	0.714	0.684	0.678	0.694	0.698	0.509	0.535
$n_1/n_2/u$	128/191/124	140/179/104	94/98/102	94/98/95	100/110/104	102/108/105	113/112/106	119/106/108	204/263/120	187/280/120
Pr, %	<1	0	79	83	86	95	35	54	0	0

Table VIII. Composition Correlation of the UTE and the BE_2 Compressibility Equation Parameters

	t = 39.99 °C (N = 192) UTE	t = 39.99 °C (N = 192) BE_2	t = 59.99 °C (N = 259) UTE	t = 59.99 °C (N = 259) BE_2	t = 79.99 °C (N = 287) UTE	t = 79.99 °C (N = 287) BE_2	t = 100.00 °C (N = 317) UTE	t = 100.00 °C (N = 317) BE_2
$K_0(x_1)$:								
A_1	0.584 913 × 10^{4}	0.580 459 × 10^{4}	0.493 771 × 10^{4}	0.482 202 × 10^{4}	0.420 516 × 10^{4}	0.415 660 × 10^{4}	0.349 442 × 10^{4}	0.346 200 × 10^{4}
A_2	−0.555 267 × 10^{3}	−0.346 164 × 10^{3}	−0.277 003 × 10^{3}	0.147 286 × 10^{3}	−0.179 701 × 10^{3}	0.146 613 × 10^{3}	−0.139 307 × 10^{3}	0.619 251 × 10^{2}
A_3	0.275 796 × 10^{4}	0.253 766 × 10^{4}	0.221 306 × 10^{4}	0.186 106 × 10^{4}	0.168 270 × 10^{4}	0.132 781 × 10^{4}	0.132 662 × 10^{4}	0.110 347 × 10^{4}
$K_0'(x_1)$:								
A_4	0.109 475 × 10^{2}	0.130 150 × 10^{2}	0.109 610 × 10^{2}	0.132 055 × 10^{2}	0.107 740 × 10^{2}	0.113 804 × 10^{2}	0.107 211 × 10^{2}	0.111 254 × 10^{2}
A_5	−0.930 933 × 10^{0}	−0.869 352 × 10^{1}	−0.135 943 × 10^{1}	−0.882 713 × 10^{1}	−0.137 535 × 10^{1}	−0.562 375 × 10^{1}	−0.486 608 × 10^{0}	−0.341 556 × 10^{1}
A_6	−0.389 382 × 10^{0}	0.598 366 × 10^{1}	0.209 795 × 10^{0}	0.571 748 × 10^{1}	0.499 983 × 10^{0}	0.491 161 × 10^{1}	−0.288 348 × 10^{0}	0.280 434 × 10^{1}
$\psi(x_1)$:								
A_7	—	−0.110 744 × 10^{3}	—	−0.941 369 × 10^{2}	—	−0.237 205 × 10^{2}	—	−0.165 432 × 10^{2}
A_8	—	0.361 204 × 10^{3}	—	0.280 462 × 10^{3}	—	0.115 003 × 10^{3}	—	0.757 472 × 10^{2}
A_9	—	−0.284 860 × 10^{3}	—	−0.204 731 × 10^{3}	—	−0.120 223 × 10^{3}	—	−0.807 976 × 10^{2}
s_d:								
Case III	3.937	3.857	4.045	4.149	4.947	4.722	4.178	4.037
Case IV	2.416	2.407	2.679	2.868	3.463	3.342	2.995	2.930
Case VI	4.662	4.547	4.853	5.038	6.038	5.782	5.139	4.988
S_V/S:								
Case III	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Case IV	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Case VI	0.727	0.720	0.699	0.679	0.672	0.667	0.663	0.656
$n_1/n_2/u$	78/114/46	76/116/34	105/154/56	105/154/54	127/160/52	129/158/56	126/191/68	130/187/68
Pr, %	0	0	0	0	0	0	0	0

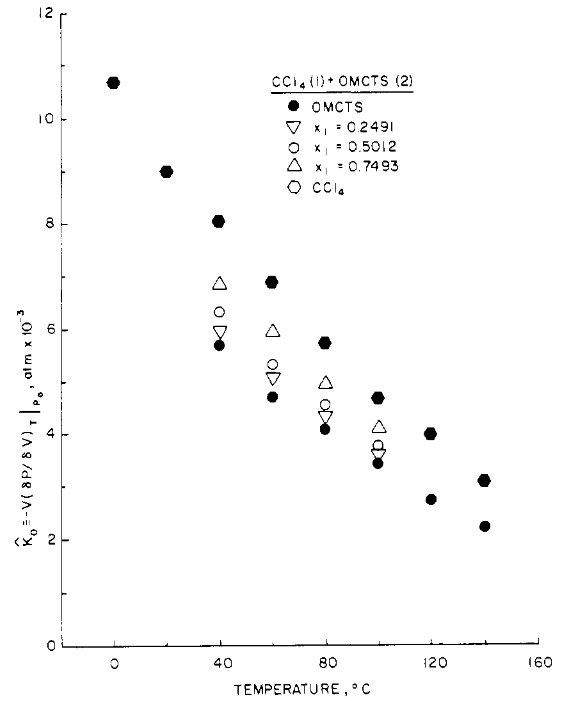

Figure 1. Temperature dependence of $\hat{K}_0$ from the BE_2 for the CCl_4(1) + OMCTS(2) binary system.

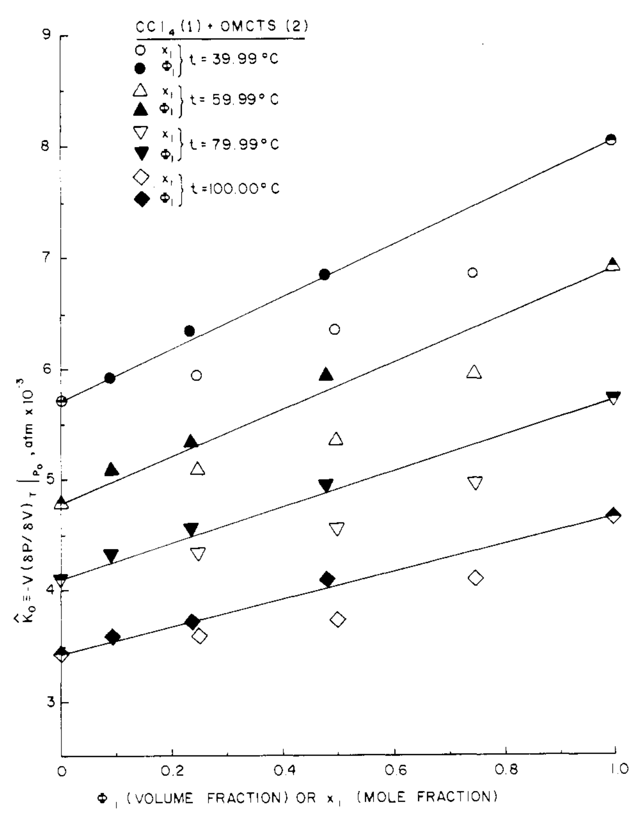

Figure 2. Volume fraction and mole fraction dependence of $\hat{K}_0$ from the BE_2 for the CCl_4(1) + OMCTS(2) binary system.

correlated UTE parameters for temperatures in the range of t = 25–65 °C and pressures to 1 katm (*15*). Schamp et al. present UTE parameters for one temperature, t = 25 °C, and pressures to 900 atm (*45*). Holder and Whalley's CCl_4 PVT data are presented at temperatures of 25.00, 37.50, 50.29, 62.55, and 75.00 °C as a cubic in pressure for pressures to 100 atm (*22*). Bridgman presents five data points at 50 °C and pressures to 1400 atm (*7*). The data of Holder and Whalley, although limited in the pressure range, are the most accurate data with an uncertainty in the relative volume of less than ±0.0001. When compared to the excellent water relative volume data of Kell and Whalley (*26*), the relative volume data of Gibson and Loeffler for water exhibit deviations of up to ±0.001 at the highest pressures. The uncertainty in the relative volume for CCl_4 of Schamp et al. and Bridgman is probably on the same order as the uncertainty in the Gibson and Loeffler data.

Table IX. Comparison of Literature and Experimental[a] Relative Volume Data for CCl_4

t, °C	s_d
Holder and Whalley (*22*) (P_{max} = 100 atm)	
25.00	1.70×10^{-4}
37.50	0.53×10^{-4}
50.29	0.36×10^{-4}
62.55	0.94×10^{-4}
75.00	0.60×10^{-4}
Gibson and Loeffler (*15*) (P_{max} = 1000 atm)	
25.0	5.98×10^{-4}
35.0	5.14×10^{-4}
45.0	3.58×10^{-4}
55.0	1.87×10^{-4}
65.0	0.86×10^{-4}
Schamp et al. (*45*) (P_{max} = 900 atm)	
25.0	7.02×10^{-4}
Bridgman (*7*) (P_{max} = 1400 atm)	
50.0	2.52×10^{-4}

[a] V_{exp} calculated using the BE_2 and temperature correlated parameters.

In order to compare the relative volumes of this study for CCl_4 to the earlier investigations, synthetic data sets were generated for the literature data using reported compressibility equation parameters. Data sets for Gibson and Loeffler and Schamp et al. were generated at 50 atm intervals and at 5 atm intervals for the data of Holder and Whalley.

The results of the comparison are given in Table IX. In all instances the difference between the literature value of the relative volume and the relative volume from this study for CCl_4 was within the combined experimental uncertainty of this study and previous investigators.

Isothermal Bulk Modulus. The isothermal bulk modulus, the reciprocal of the isothermal compressibility, can be obtained either from direct measurement or from PVT data and equation of state parameters. Isothermal values of $\hat{K}_0$ from a fit of the CCl_4 PVT data of this study to the UTE and the BE_2 using case VI weighting has been compared to literature values of K_0 and is illustrated in Figure 3. The literature data includes values of K_0 from both direct measurement and equation of state estimates. The agreement of these data with both $\hat{K}_0$ from the isothermal data and K_0 calculated from the temperature correlation is well within the disparities among the available data (±5%).

Isothermal bulk modulus data for OMCTS are scarce in the literature. Shinoda et al. (*46*) report K_0 for OMCTS at 25.00 °C and atmospheric pressure as 6410 atm. Ewing (*12*) reports a value of K_0 for OMCTS, also at 25.00 °C but extrapolated to zero pressure, as 6446 atm. Values of K_0 extrapolated from the temperature correlated UTE and BE_2 parameters are 6467 and 6390 atm, respectively. This agreement is considered to be very good.

Adiabatic Compressibility. The adiabatic compressibility, β_S, is defined by eq 13 as

$$\beta_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S \tag{13}$$

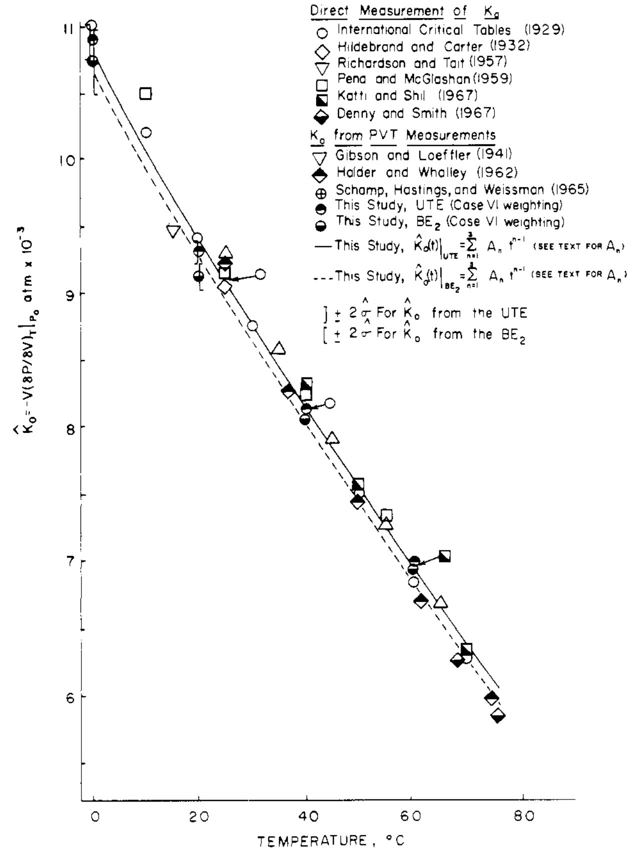

Figure 3. Comparison of literature and experimental values for the isothermal bulk modulus of CCl_4 at atmospheric pressure.

and is related to the isothermal compressibility, $\beta_T [= 1/K = -(1/V)(\partial V/\partial P)_T]$ as

$$\beta_S(T,P) = \beta_T(T,P) - T \cdot V(T,P) \cdot \alpha_p^2(T,P)/C_p(T,P) \quad (14)$$

where α_p is the coefficient of thermal expansion and is defined as

$$\alpha_p = (1/V)(\partial V/\partial T)_P \quad (15)$$

There are two methods by which the adiabatic compressibility of a liquid can be experimentally measured, either by a sudden (adiabatic) compression of the sample or from velocity of sound measurements. If the density, $\rho(T,P)$, and velocity of sound, $U(T,P)$, of the liquid are known as functions of T and P, β_S can be calculated using eq 16

$$\beta_S(P,T) = 1/[\rho(P,T) \cdot U^2(P,T)] \quad (16)$$

Given the heat capacity at atmospheric pressure, $C_p(P_0,T)$, all quantities on the right hand side of eq 14 can be calculated from a compressibility equation and a set of temperature correlated parameters. Available heat capacity data for CCl_4 (*16, 17, 21*) were fit to a second degree polynomial in t to obtain $C_p(P_0,T)$. The form of $C_p(P_0,T)$ is

$$C_p(P_0,T) = 32.38 - 0.1999 \times 10^{-1}(t + 273.15) + 0.5763 \times 10^{-4}(t + 273.15)^2 \text{ (cal mol}^{-1}) \quad (17)$$

The heat capacity at T and P is then calculated as

$$C_p(P,T) = C_p(P_0,T) - T\int_{P_0}^{P}\left(\frac{\partial^2 V}{\partial T^2}\right)_p dP \quad (18)$$

The uncertainty in $\beta_S(P,T)$ calculated using eq 14 and the temperature correlated parameters for the BE_2 is on the order of ±3% (*2*). Figure 4 is a comparison of experimental (literature) data for β_S of CCl_4 at atmospheric pressure against calculations

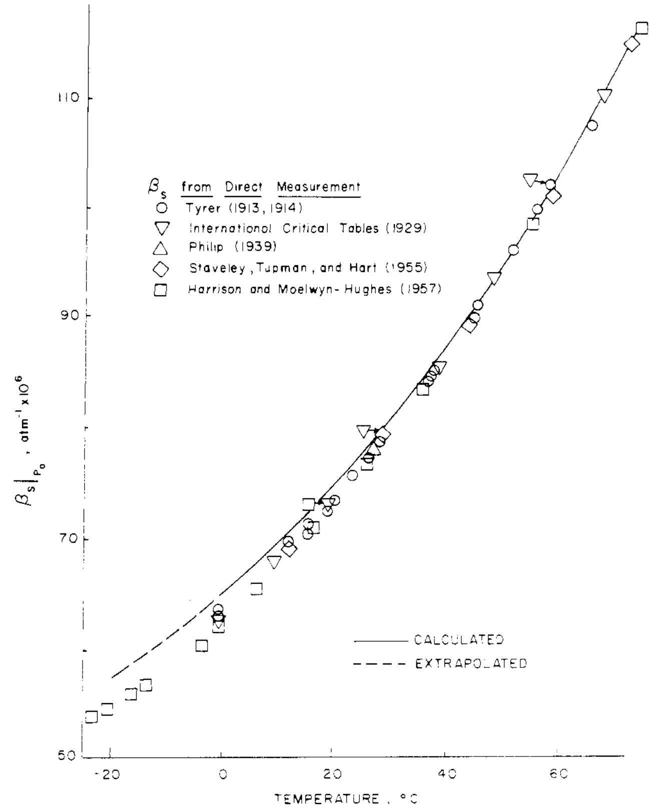

Figure 4. Comparison of literature values of β_S from direct measurement and calculated values for β_S for CCl_4 at atmospheric pressure.

from our results. The necessary properties in eq 14 were evaluated using the temperature correlated parameters in the BE_2 equation. Figure 5 is a comparison of β_S calculated from velocity

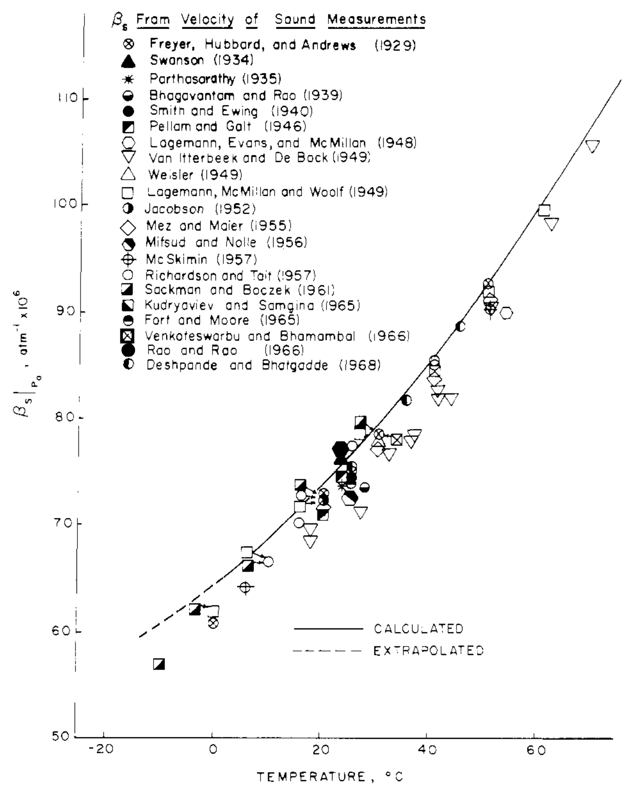

Figure 5. Comparison of literature values of β_S from velocity of sound measurements and calculated values of β_S at atmospheric pressure.

of sound measurements using eq 16 (data points) against calculations from our results as in Figure 3. The region below 0 °C represents an extrapolation of the temperature correlated parameters and is indicated by a dashed line on Figures 4 and 5. Comparisons of experimental with calculated results were also made at pressure to 1000 atm using velocity of sound measurements at these pressures and are illustrated in Figure 6.

Glossary

$A(P,T)$	cross-sectional area of bellows at pressure P and temperature T, cm^2
K	isothermal bulk modulus, $K \equiv -V(\partial P/\partial V)_T$, atm
K_0	isothermal bulk modulus at $p = 0$, atm
K_0'	$(\partial K/\partial P)_T\vert_{p=0}$
K_0''	$(\partial^2K/\partial P^2)_T\vert_{p=0}$, atm^{-1}
$\Delta L_B(P,T)$	temperature and pressure corrected change in bellows length at pressure P and temperature T, cm
M	modified least-squares sum, eq 8
N	number of data points
P	pressure, atm
P_0	reference pressure, atm
Pr	probability of randomness of the least-square residuals
S	least-squares sum of squared residuals, eq 5
T	temperature, K
U	velocity of sound, cm s^{-1}
V_m	molar volume, cm^3 mol^{-1}
V/V_0	relative volume
$\Delta V/V_0$	compression or relative volume change
W	least-squares weighting variable
W_{vc}	vacuum corrected weight, g
d_i	composite residuals, eq 7
$\bar{d}$	sample mean of d_i's
d_{rms}	root-mean-square value of d_i's, eq 10
f	number of degrees of freedom, $N - n$
$k(P,T)$	compression or relative volume change
n	number of parameters
n_1	number of negative residuals
n_2	number of positive residuals
p	reduced pressure, $p \equiv P - P_0$, atm
s_d	standard deviation of least-squares residuals, eq 9
t	temperature, °C
u	successive residuals of the same sign
v	specific volume, cm^3 g^{-1}
x	V_0/V
x_i	mole fraction for component i
z	p/K_0

Greek

ϕ	volume fraction
β_S	adiabatic compressibility, atm^{-1}
β_T	isothermal compressibility, atm^{-1}
γ	$[K_0' - 2\psi]^{1/2}$
$\rho(P,T)$	density at pressure P and temperature T, g cm^{-3}
$\hat{\sigma}$	estimate of standard deviation of a parameter from least-squares fitting
$\sigma_V{}^2$	error variance of the relative volume, atm^2
$\sigma_P{}^2$	error variance of the pressure, atm^2
ψ	K_0K_0''

Superscripts

E	excess
M	mixture property
ˆ	estimate from least-squares fitting

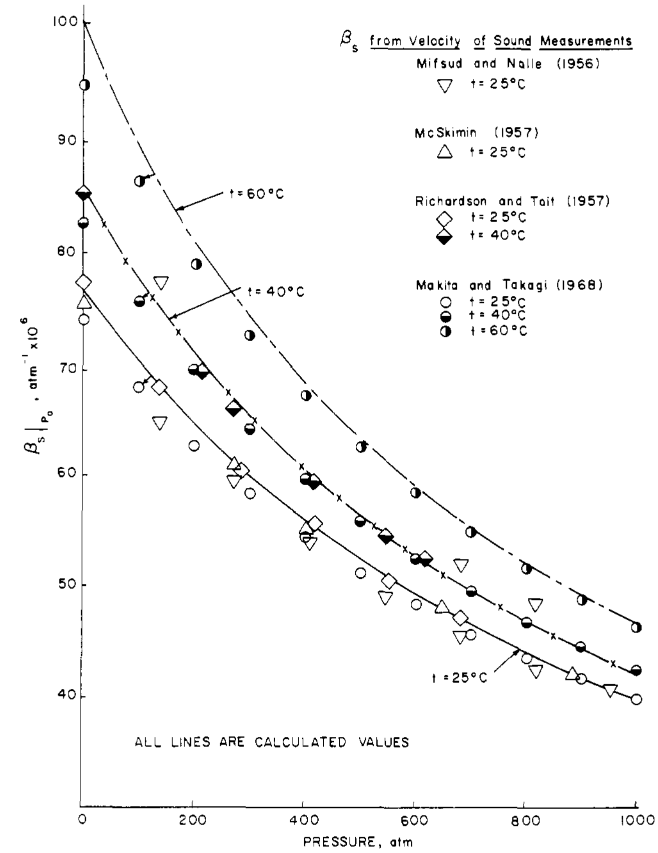

Figure 6. Comparison of literature values of β_S from velocity of sound measurements and calculated values of β_S for CCl_4 at elevated pressures.

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Supplementary Material Available: Experimental PVT data and Table IV (60 pages). Ordering information is given on any current masthead page.

The Densities of Methylcyclohexane–*n*-Heptane Mixtures

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Despite the popularity of the methylcyclohexane–*n*-heptane mixture for testing laboratory fractionating columns, extensive physical property data for the combination are somewhat lacking. The results of this investigation offer some help in this regard by giving correlations of experimentally observed densities as a function of temperature and composition. The empirical equations to which the data were fitted may be employed, along with appropriate cross-plots, for the estimation of density over the entire composition range, and for temperatures up to and including the normal boiling points of the various mixtures.

For many years, the *n*-heptane–methylcyclohexane system has been used for distillation studies. As far back as 1939, Ward (*10*) cited this as an excellent system for testing laboratory fractionating columns. Despite the continued use of this system, extensive measurements of the various physical properties necessary for comparison and correlation have not yet been made. Densities of the pure components have been cited in Egloff (*5, 6*), Driesbach (*3, 4*), Mussche and Verhoeye (*8*), and API Research Project 44 (*1*). Bromiley and Quiggle (*2*) observed mixture densities at 20 °C, and also measured the normal boiling points of various solution compositions.

The present work gives the results of measurements of the densities for the pure components as well as mixtures, and correlates these as a function of temperature and composition of the mixtures. Extrapolation of these data to the boiling point provides requisite data for distillation correlations.

Experimental Section

The methylcyclohexane, practical grade, and the *n*-heptane, reagent grade, used for this work were supplied by Matheson, Coleman and Bell. The former boiled over the range of 100.5–101.5 °C which included the normal boiling point (100.934 °C in ref 1) while the latter boiled between 98 and 99 °C which also included its normal boiling point (98.427 °C in ref 1).

A Robertson pycnometer, with graduated capillary arms (*9*), was used for the density measurements. Pure, deionized water (specific resistance between 400 000 and 450 000 ohms), at 25.0 °C, was used for calibrating the volumes of the pycnometer corresponding to the various graduated markings. All observations were carried out in a water bath, which was maintained to within ±0.1 °C; readings of the capillary heights were facilitated by the use of a cathetometer. Complete calibration details are in ref 7.

The compositions of the pure components and all of the binary mixtures were ascertained refractometrically. For this purpose, a Bausch and Lomb precision refractometer was used, and observations were recorded to within ±0.000 03 units at 25.0 °C, for the sodium D-line. This corresponds to ±0.196% in composition.

Results and Discussion

Densities of pure *n*-heptane and methylcyclohexane were measured from 25 to 80 °C at 5 °C intervals. These observations were compared with the data of Egloff (*5, 6*), Driesbach (*3, 4*), Mussche (*8*), and the API Research Project 44 results (*1*) and are presented in Table I. The largest difference between data of this study and that reported in the literature is 0.26%.

Since the purpose of this work was to supply data for large scale distillation studies, practical and reagent grade materials were used. To verify whether these grades would yield data comparable to that of pure materials, densities of chromatographic quality methylcyclohexane and *n*-heptane at 25 °C were also measured. These density values are compared with other data from this study in Table II. It should be noted that there is less than a 0.012% difference which indicates reliable applicability of the data taken using practical and reagent grade chemicals.

Densities of known composition for five mixtures of the two components were determined under similar conditions. Compositions of the mixtures were checked before and after determinations to be assured that the compositions were unaltered during the heating and cooling processes. These data, along with extrapolations to the boiling point are shown in Table III.