quantities as association quotients and the different hydration numbers of the many solute species, including $CaSO_4^0$, Ca^{2+}, and SO_4^{2-}, at the high formal ionic strengths. Therefore, it does not appear to be possible at this time to correlate by mass-action models the solubilities and association behavior in the many different systems of electrolyte solutions, although excellent correlations of this type are obtained within each system; a Harned's rule approach also provides a correlation, but with greater complexity.

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RECEIVED for review July 22, 1971. Accepted November 2, 1971. Research sponsored by the U.S. Atomic Energy Commission under contract with the Union Carbide Corp. and performed at Oak Ridge National Laboratory, Oak Ridge, Tenn. 37830. Presented before the Division of Physical Chemistry at the 162nd National Meeting of the American Chemical Society, Washington, D.C., September 12–17, 1971.

Second and Third Virial Coefficients for System Tetrafluoromethane–Sulfur Hexafluoride

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The Burnett method was employed to study the volumetric behavior of the tetrafluoromethane–sulfur hexafluoride system from —1.5–150°C at pressures up to 27 atm. The data were analyzed by the method of least squares to determine the second and third virial coefficients of the Leiden equation of state. Mixture virial coefficients are presented as functions of composition at each experimental temperature. Also derived are the pure component and interaction second and third virial coefficients. The De Rocco spherical-shell intermolecular potential energy function was used to fit the pure component second virial coefficient data. An extension of this model to the interaction second virial coefficient for two molecules of different sizes is presented and adequately represents the experimental results of this work.

The detailed *P-V-T* studies of many gases and several mixtures which should exhibit nearly angular independence in their molecular interactions have been described in the literature (*4, 7, 14*). Few of these studies report mixture third virial coefficients, and fewer still report interaction third virial coefficients (*23*).

The present investigation aimed to determine the mixture second and third virial coefficients and the interaction second and third virial coefficients for a binary mixture of quasi-spherical molecules using the Burnett method (*3*). This method is particularly advantageous for the study of gas mixtures (*16, 24*) and requires only repetitive measurements of pressure and temperature.

The tetrafluoromethane-sulfur hexafluoride system was chosen for study because the hard shell and spherical symmetry characteristics of both species make this pair of exceptional interest for the theoretical phase of virial coefficient studies. In addition, the fact that the molecular structure of both compounds consists of a central atom surrounded by fluorine atoms may help to provide insight into the central core–peripheral atom relationship in treatments of fluid mixtures, as well as the nature of the fluorine–fluorine interaction in mixtures of fluorocarbons with the hexafluorides of Group Six.

EXPERIMENTAL

The sulfur hexafluoride was supplied by Air Products and Chemicals, Inc. The analytical report received with the sample showed 50 ppm tetrafluoromethane and less than 3 ppm oxygen, 3 ppm argon, 10 ppm nitrogen, and 34 ppm water. Subsequent mass spectrometric analysis showed that the sample had a minimum purity of 99.99% by volume. The tetrafluoromethane sample was donated by E. I. du Pont de Nemours and Co. The impurities of this material were reduced to less than 0.05% by alternate freezing, melting, and distillation in vacuo.

The volumetric behavior of the system was measured at −1.5°, 35°, 50.4°, 75°, 100°, and 150°C at various compositions, including the pure components at each temperature. The pressure range was from 1–27 atm. Pressures above 18 atm were measured with a Ruska Instrument Corp. deadweight pressure gauge. Lower pressures were measured with a Texas Instruments fused quartz Bourdon gauge. The precision of this arrangement ranged from about two parts in 100,000 at the highest pressure to about one part in 10,000 at the lowest pressure measured. In general, it is believed that systematic errors in pressure were less than 0.015% of the pressure.

The temperature level of the system was established by

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means of a platinum resistance thermometer immersed in the constant-temperature oil bath containing the Burnett apparatus. A pair of Chromel-constantan thermocouples indicated the temperature differences between the platinum thermometer and the two chambers of the Burnett apparatus. The total uncertainty in the absolute temperature determined by this system was approximately three parts in 100,000. Temperatures reported are on the International Temperature Scale of 1948.

Further details of the pressure and temperature measuring system appear elsewhere (*27*).

BURNETT METHOD

The Burnett apparatus used has been previously described (*3, 12, 28*). The basic apparatus consists of a measuring chamber and an expansion chamber, the volumes of which are independent of pressure over the range studied in this work. Both chambers are maintained at the same constant temperature. The measuring chamber is filled initially with gas "A" to some density ρ_A, and the pressure P_A and absolute temperature T_A are measured. The compressibility behavior of gas "A" must be known. The second gas "B" is then added to the measuring chamber and the contents are allowed to mix. The measuring chamber is thus filled to some unknown density ρ_0 with gas of unknown composition Y_A. The initial temperature T_0 and pressure P_0 are measured. It was found that either CF_4 or SF_6 could be used equally well as the initial gas.

The density of the gas in the measuring chamber is then decremented to the fraction $1/N$ of its initial value by expansion into the previously evacuated expansion chamber. The apparatus constant, N, is defined as the ratio of the system volume after expansion to that before the expansion and is independent of pressure. When thermal equilibrium is restored, the expansion valve is again closed and another pressure P_1 and perhaps slightly different temperature T_1 is measured. The contents of the expansion chamber are then discarded and the process is repeated. In this manner, a series of nearly isothermal pressures is obtained: $P_0, P_1, \ldots, P_r, \ldots, P_f$. The final pressure P_f is generally the lowest pressure that can be measured within a predetermined accuracy. A typical run consisted of between seven and nine expansions.

As shown by Silberberg et al. (*28*), the series of decremented densities may be related to the measured pressures and temperatures through the Leiden form of the virial expansion as

$$P_r/RT_r = \rho_r + B\rho_r^2 + C\rho_r^3 + \ldots \qquad (1)$$

where

$$\rho_r = \rho_0 N^{-r} \qquad (2)$$

and $B, C, \ldots$ are the second, third, etc., virial coefficients.

The best values of ρ_0, N, B, C, etc., are taken to be those values found by the Gauss method of least-squares estimation of nonlinear parameters (*1, 30*) as applied to this problem (*27*). The composition is then determined as (*24*):

$$Y_A = \frac{\rho_A}{\rho_0} = \frac{P_A}{\rho_0 Z_A R T_A} \qquad (3)$$

where Z_A is the previously determined or otherwise known compressibility factor ($Z = P/\rho RT$) of the pure gas "A" at pressure P_A and temperature T_A.

For this study, truncation of the virial series, Equation 1, after the third term, was made on the basis of examination of the largest contribution of the next term in the series, $D\rho_r^4$, where D was estimated from the fourth virial coefficient of a Lennard-Jones "6–12" potential (*2*), as suggested by Sengers (*18*). This contribution to P_0/RT_0 was generally found to be less than one part in 10,000, and the relative significance of the fourth term decreased by a factor of four for each observed P_r/RT_r thereafter. It was also found that the overall standard error (S.E.) criterion

$$\text{S.E.} = \left[\frac{1}{m-n}\Sigma\left(\frac{P_r}{RT_r} - \frac{\hat{P}_r}{RT_r}\right)^2\right]^{1/2} \qquad (4)$$

was generally smaller when the series was terminated with the third virial term than when the fourth was included. The individual values of N determined from each run in this manner were then averaged, and this average value used as a fixed parameter in refitting Equation 1 to the experimental data.

SECOND VIRIAL COEFFICIENTS

The values of the second virial coefficients of the pure gases and mixtures determined from the experimental data as indicated are shown as "Obs. B_M" in Table I and plotted in Figure 1. The standard errors shown in Table I are the con-

Table I. Second and Third Virial Coefficients for Mixtures of Tetrafluoromethane and Sulfur Hexafluoride

Mol frac, CF_4	Obs. B_M ± S.E., cm³/g-mol	Smoothed B_M, cm³/g-mol	(C_M ± S.E.) × 10^{-2}, (cm³/g-mol)²
−1.5°C			
1.0000	−112.33 ± 0.09	−112.99	76.2 ± 0.2
0.8970	−131.29 ± 0.71	−130.20	86.0 ± 1.7
0.7869	−150.84 ± 0.87	−150.58	96.4 ± 1.7
0.5562	−194.23 ± 1.69	−197.82	126.0 ± 5.8
0.3925	−235.30 ± 0.70	−235.72	135.4 ± 1.3
0.1797	−288.47 ± 0.29	−290.39	168.2 ± 1.5
0.0000	−339.26 ± 0.60	−340.98	189.7 ± 2.1
0.0000	−339.19 ± 0.53	−340.98	183.9 ± 1.5
0.0000	−339.10 ± 0.63	−340.98	185.7 ± 1.7
30°C			
0.0000	−266.06 ± 0.11	−266.40	193.4 ± 0.1
35°C			
1.0000	−81.82 ± 0.71	−81.18	68.8 ± 0.9
0.9408	−88.91 ± 0.23	−88.71	67.3 ± 0.3
0.6475	−131.65 ± 0.21	−131.39	92.9 ± 0.3
0.3453	−184.62 ± 0.14	−184.52	133.7 ± 0.2
0.2712	−200.02 ± 0.27	−198.95	136.4 ± 0.5
0.0000	−255.84 ± 0.10	−256.56	191.5 ± 0.3
50.4°C			
1.0000	−70.95 ± 0.21	−70.61	54.3 ± 1.0
1.0000	−70.61 ± 0.40	−70.61	55.3 ± 1.0
0.7956	−96.15 ± 0.65	−95.53	61.4 ± 1.5
0.5889	−124.44 ± 0.63	−124.65	80.2 ± 1.4
0.3580	−162.86 ± 0.76	−161.77	111.3 ± 1.9
0.1896	−189.97 ± 0.57	−192.02	153.9 ± 2.2
0.0000	−230.88 ± 0.43	−229.18	177.0 ± 2.0
0.0000	−229.54 ± 0.55	−229.18	178.8 ± 1.1
75°C			
1.0000	−56.18 ± 0.69	−56.16	40.6 ± 1.6
1.0000	−57.38 ± 0.50	−56.16	42.6 ± 1.9
0.7980	−77.22 ± 0.87	−77.28	52.1 ± 2.0
0.5820	−104.04 ± 0.59	−103.44	60.7 ± 1.5
0.3649	−135.01 ± 0.85	−133.41	96.0 ± 2.5
0.1908	−161.10 ± 0.46	−160.16	118.3 ± 1.4
0.0000	−193.46 ± 0.57	−192.26	153.3 ± 1.8
0.0000	−195.50 ± 0.63	−192.26	154.6 ± 4.3
100°C			
1.0000	−44.77 ± 0.76	−44.48	46.7 ± 2.1
1.0000	−44.50 ± 0.69	−44.48	45.1 ± 1.8
0.8077	−61.71 ± 0.80	−61.50	48.1 ± 2.0
0.5896	−85.61 ± 0.35	−84.01	57.6 ± 2.0
0.4459	−102.66 ± 0.47	−100.62	64.5 ± 2.5
0.1880	−136.16 ± 0.74	−134.06	96.0 ± 2.9
0.0000	−163.08 ± 0.48	−161.35	120.4 ± 2.1
0.0000	−163.86 ± 0.59	−161.35	122.1 ± 3.0
150°C			
1.0000	−23.39 ± 0.62	−24.66	43.9 ± 0.9
0.8336	−37.64 ± 1.44	−35.85	11.1 ± 6.5
0.5800	−54.21 ± 2.44	−55.73	36.2 ± 6.8
0.3049	−80.28 ± 0.35	−81.13	81.1 ± 0.7
0.0755	−105.20 ± 0.74	−105.32	95.4 ± 1.4

Table II. Tetrafluoromethane, Sulfur Hexafluoride, and Interaction Second Virial Coefficients[a]

Temp, K	$B_{CF_4-CF_4}$ ± S.E.	$B_{SF_6-SF_6}$ ± S.E.	$B_{CF_4-SF_6}$ ± S.E.
271.61	−112.36 ± 0.13	−338.92 ± 0.44	−193.24 ± 1.26
308.12	−81.22 ± 0.56	−255.87 ± 0.23	−144.56 ± 0.66
323.55	−70.93 ± 0.41	−230.00 ± 0.72	−125.42 ± 1.93
348.10	−56.93 ± 0.55	−194.29 ± 0.54	−104.14 ± 1.27
373.15	−44.48 ± 0.30	−163.41 ± 0.23	−88.08 ± 0.42
423.15	−23.71 ± 0.89	−113.61 ± 1.53	−55.00 ± 2.22

[a] Second virial coefficients in cm³/g-mol.

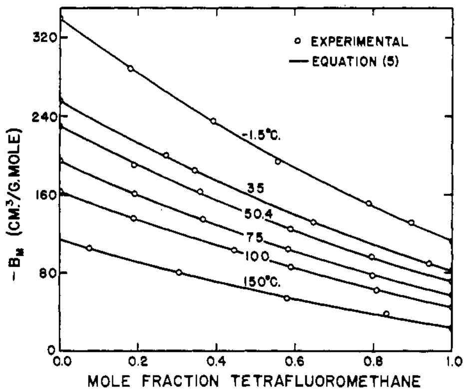


Figure 1. Second virial coefficients of tetrafluoromethane–sulfur hexafluoride system

ventional estimates found from the variance-covariance matrix and overall standard error of the least-squares fit (*1, 30*). Such standard errors are an indication of the precision of a given run but do not give a measure of the systematic errors that may occur. These systematic errors are felt to arise from the following sources listed in order of decreasing importance: (1) uncertainty in the apparatus constant N, used as a fixed parameter, (2) systematic errors in the pressure P_r, (3) the truncation of the infinite virial series after the third term, (4) systematic errors in the temperature T_r, and (5) impurities present in the sulfur hexafluoride and carbon tetrafluoride. Consideration of the magnitude of each source of systematic error (*27*) showed that the last three uncertainties were insignificant in comparison with the first two. The systematic error in the values of B_M from these combined effects is estimated (*27*) to be no greater than 2.40 cm³ mol⁻¹.

The Lennard-Jones and Cook equation (*17*)

$$B_M = B_{11}y_1^2 + 2\,B_{12}Y_1Y_2 + B_{22}Y_2^2 \tag{5}$$

was used to obtain the pure component (B_{11} and B_{22}) and interaction (B_{12}) second virial coefficients from the observed second virial coefficients of the mixtures at each temperature. In the least-squares analysis used, the residuals ($B_M - \hat{B}_M$) were weighted with the reciprocals of the standard error (S.E.) of B_M shown in Table I. The resulting least-squares estimates of B_{11}, B_{12}, and B_{22} are shown with their standard errors in Table II. The pure component second virial coefficients shown in this table can be seen to agree quite well with those found from the individual pure component runs shown in Table I as "Obs B_M." The maximum uncertainty in composition as determined from Equation 3 is estimated to be no greater than 0.001. The systematic errors for the pure component second virial coefficients in Table II are estimated not to exceed 2.40 cm³ mol⁻¹, and those for the interaction second virials not to exceed 2.80 cm³ mol⁻¹. Maximum uncertainties in $B_{11}(CF_4)$, $B_{22}(SF_6)$ and B_{12} (CF_4-SF_6) are estimated to be 2.70, 2.80, and 3.70 cm³ mol⁻¹, respectively.

In Tables III and IV, a comparison is made of the second virial coefficient data for CF_4 and SF_6 obtained in this work with those found by other investigators. Since the data of the various investigators were frequently reported at slightly different temperatures, it was necessary to adjust some of the data to common temperatures using the first derivative dB/dT. These adjustments were made for both CF_4 and SF_6 by fitting the Lennard-Jones "6–12" potential energy function to all the experimental second virial coefficient data for each gas.

In general, there is good agreement among the CF_4 data reported by the various investigators shown in Table III. The largest discrepancy (2.29 cm³ mol⁻¹) exists at 423.15K between the data of this work and that of MacCormack and Schneider (*19*) but is less than the estimated maximum uncertainty of this work. For SF_6 in Table IV, however, there is considerably more disagreement among the values reported. Discrepancies between the data of this work and of other investigators are commonly as great as twice the estimated maximum uncertainty of the former. The value reported by MacCormack and Schneider (*19*) at 323.55K appears to be considerably in error.

No interaction second virial coefficient data for the tetrafluoromethane–sulfur hexafluoride system have been previously reported. Consequently, no comparison is possible for this case.

CORRELATION OF SECOND VIRIAL COEFFICIENT DATA

The spherical-shell intermolecular potential function described by De Rocco and Hoover has been used previously (*5*) to correlate pure component second virial coefficients. The model is based on the assumption that spherically symmetric molecules exhibit a force field that may be characterized by Lennard-Jones interaction sites uniformly distributed on a sphere of diameter d. This diameter d is (*5, 6, 21*) closely approximated by the diameter of a sphere circumscribing the interatomic distances between the peripheral atoms and the central atom of the molecule.

The spherical shell potential model can easily be extended to the case of two spherical molecules of different diameters d_1 and d_2 which is of interest in the study of gas mixtures. The resulting equation, derived in the Appendix, is

$$B_{12}(T) = b_0B_{12}^*(r_0^*,\ T^*,\ d^*) \tag{6}$$

where

$$B_{12}^*(r_0^*,\ T^*,\ d^*) = 3\int_0^\infty (1 - e^{-U^*/T^*})r^{*2}dr^* \tag{7}$$

$$U^* = \frac{U(r^*,\ d^*)}{\epsilon} = \frac{(3\,r_0^*P_0^{*(4)} + P_0^{*(3)})P^{*(9)} - (9\,r_0^*P_0^{*(10)} + P_0^{*(9)})P^{*(3)}}{(9\,P_0^{*(10)}P_0^{*(3)} - 3\,P_0^{*(9)}P_0^{*(4)})r^*} \tag{8}$$

$$P^{*(n)} = \left(r^* + \frac{1+d^*}{2}\right)^{-n} - \left(r^* + \frac{1-d^*}{2}\right)^{-n} - \left(r^* - \frac{1-d^*}{2}\right)^{-n} + \left(r^* - \frac{1+d^*}{2}\right)^{-n} \tag{9}$$

$$P_0^{*(n)} = P^{*(n)}(r_0^*,\ d^*) \tag{10}$$

$$b_0 = \frac{2}{3}\,\pi\tilde{N}d_1^3 \tag{11}$$

$$r^* = r/d_1 \tag{12}$$

Table III. Comparison of Second Virial Coefficients of Tetrafluoromethane with Other Investigations[a]

Temp, K	This work	Douslin et al. (*8*)	MacCormack, Schneider (*19*)	McManamey (*22*)	Kalfoglou, Miller (*14*)
271.61	−112.36	−112.60	112.60	—	—
308.21	−81.22	—	—	—	—
323.55	−70.93	−70.66	−70.66	−72.66	—
348.10	−56.93	−55.67	—	−56.07	—
373.15	−44.48	−43.50	−43.10	−43.90	−43.54
423.15	−23.71	−24.40	−26.00	—	—

[a] Second virial coefficients in cm^3/g-mol. Values adjusted to same temperature using slope of least-squares curve fitted to all data.

Table IV. Comparison of Second Virial Coefficients of Sulfur Hexafluoride with Other Investigations[a]

Temp, K	This work	Clegg et al. (*4*)	Hamann et al. (*10*)	Hamann et al. (*11*)	MacCormack, Schneider (*19*)
271.61	−338.92	—	—	—	−338.00
303.19	−266.06	—	—	−274.86	—
308.21	−255.87	−259.68	—	—	—
323.55	−230.00	−230.90	—	−237.06	−217.56
348.10	−194.29	−191.10	−185.2	−195.5	—
373.15	−163.41	−167.2	−163.0	−162.8	−159.2
423.15	−113.61	—	—	−119.2	−118.6

[a] Second virial coefficients in cm^3/g-mol. Values adjusted to same temperature using slope of least-squares curve fitted to all data.

$$r_0^* = r_0/d_1 \qquad (13)$$

$$T^* = kT/\epsilon \qquad (14)$$

$$d^* = d_2/d_1 \qquad (15)$$

When the core diameters, d_1 and d_2, are regarded as fixed geometrical characteristics and not as free parameters, this potential function becomes a two-parameter model. Also it should be noted that Equations 6–12 reduce to the equations presented by De Rocco and Hoover (*5*) when molecules "1" and "2" are identical in size ($d^* = 1$) and to the Lennard-Jones "6–12" potential for $d^* = 0$.

Since De Rocco and Hoover (*5*) had reported for both CF_4 and SF_6 strikingly good agreement between the shell diameters determined as free parameters from experimental second virial coefficient data and those found from X-ray diffraction data, it was considered that the modified model for shells of different diameters would be of interest in correlating interaction second virial coefficients from mixtures of these two molecules. When we used the Marquardt algorithm (*20*) to minimize the sum of the squares of the deviations between observed and calculated values of $B(T)$, the optimum values of ϵ/k and r_0 for the spherical-shell potential energy function were found for both the pure component and the interaction second virial coefficient data obtained in this work. A complete discussion of the technique, which required both numerical integration and differentiation, is presented elsewhere (*27*). The values of d_1 and d_2 used were twice the C—F and S—F interatomic distances, respectively, as determined from X-ray diffraction data (*9*). They were $d_{CF_4} = 2.646$ Å and $d_{SF_6} = 3.160$ Å. The optimum values of ϵ/k and r_0 appear in Table V.

For comparison, the spherical-shell parameters ϵ/k and r_0 were also determined from a similar least-squares analysis of the tetrafluoromethane second virial coefficient data reported here together with those reported by other investigators (*8, 14, 19, 22*) at temperatures as high as 500°C. The values were $\epsilon/k = 310.2 \pm 3.3$K and $r_0 = 4.592 \pm 0.024$ Å, which differ from those obtained from the data of this work alone by approximately 1.5%. The parameters found from a similar analysis of all available sulfur hexafluoride data (*4, 10, 11, 19*), which extend over a temperature range of −1.5–250°C, where $\epsilon/k = 425.0 \pm 30.5$K and $r_0 = 5.327 \pm 0.166$ Å, which differ from those found from the data of this work alone by less than 1%.

Because of its general interest and application, parameters for the Lennard-Jones "6–12" potential energy function were also calculated from the data of this work alone and are presented in Table VI. As the standard errors of the regressions indicate, the Lennard-Jones "6–12" function gave a better representation of the CF_4 data, whereas the De Rocco spherical-shell function was superior for SF_6 data. For the interaction second virial coefficients, the De Rocco function was slightly superior. However, both functions represented the experimental data essentially within the limits of the estimated maximum uncertainties. Furthermore, as Klein and Hanley (*15*) have shown, in the limited temperature range of these experimental data, no significant comparison can be made of the abilities of intermolecular potential energy functions to represent second virial coefficient data.

To develop second virial coefficients smooth with respect to both temperature and composition, values of the pure component and interaction second virial coefficients were calculated from the spherical-shell model using the parameters in Table V. These temperature-smoothed values were then used to calculate from Equation 5 smoothed values of B_M at each tempera-

Table V. Parameters of De Rocco Spherical-Shell Potential Energy Function

Molecular pair	S.E.R.	$\epsilon/k \pm$ S.E., K	$r_0 \pm$ S.E., Å
CF_4–CF_4	0.78	314.8 ± 8.5	4.556 ± 0.058
SF_6–SF_6	1.66	423.4 ± 41.7	5.326 ± 0.228
CF_4–SF_6	1.73	376.4 ± 30.0	4.848 ± 0.171

$d_{CF_4} = 2.646$ Å; $d_{SF_6} = 3.160$ Å. S.E.R. = Standard error, regression, cm^3/g-mol. S.E. = Standard error, parameter

Table VI. Parameters of Lennard-Jones "6–12" Potential Energy Function

Molecular pair	S.E.R.	$\epsilon/k \pm$ S.E., K	$\sigma \pm$ S.E., Å
CF_4–CF_4	0.38	148.7 ± 0.5	4.838 ± 0.016
SF_6–SF_6	1.95	182.0 ± 2.1	6.031 ± 0.053
CF_4–SF_6	1.93	165.1 ± 2.5	5.354 ± 0.066

S.E.R. = Standard error of regression, cm^3/g-mol. S.E. = Standard error of parameter.

ture studied. The mixture second virial coefficients so obtained are shown in Table I. Changes in B_M as a result of this smoothing can be seen to be small but nonetheless generally exceed the standard errors of the original values, "Obs. B_M."

THIRD VIRIAL COEFFICIENTS

Mixture third virial coefficients C_M were first obtained simultaneously with ρ_0 and B_M by fitting Equation 1 to the observed P_r/RT_r as described previously. When plotted as functions of temperature and composition, these original least-squares estimates scattered quite badly. However, the scatter of these values could be reduced considerably by refitting Equation 1 to the observed P_r/RT_r, using as fixed parameters both N and the values of "Smoothed B_M" shown in Table I. The mixture third virial coefficients obtained in this manner are presented with their standard errors from the regression in Table I and are graphed in Figure 2.

The data of Table I were then used to obtain the pure component and interaction third virial coefficients at each temperature from the equation

$$C_M = C_{111}Y_1^3 + 3\,C_{112}Y_1^2Y_2 + 3\,C_{122}Y_1Y_2^2 + C_{222}Y_2^3 \quad (16)$$

As with the second virial coefficients, each residual of the third virial coefficient was weighted with the reciprocal of the standard error shown in Table I. The resulting values for each temperature are shown in Table VII along with their standard errors from the regression.

All the curves of Figure 2, with the exception of that at 150°C, are calculated from Equation 16 using the least-squares values of the third virial coefficients in Table VII. The data at 150°C scattered so badly that meaningful results could not be obtained from a least-squares analysis; hence the curve drawn is based on values of the pure component and interaction third virial coefficients obtained by extrapolation of the lower temperature data (Figures 3–5).

Systematic errors in the mixture third virial coefficients shown in Table I and in the pure component and interaction third virial coefficients shown in Table VII result from the same sources cited previously, plus an additional error introduced through the use of smoothed spherical-shell second virial coefficients as fixed parameters. In the unlikely event that all such systematic errors were to act in the same direction, there

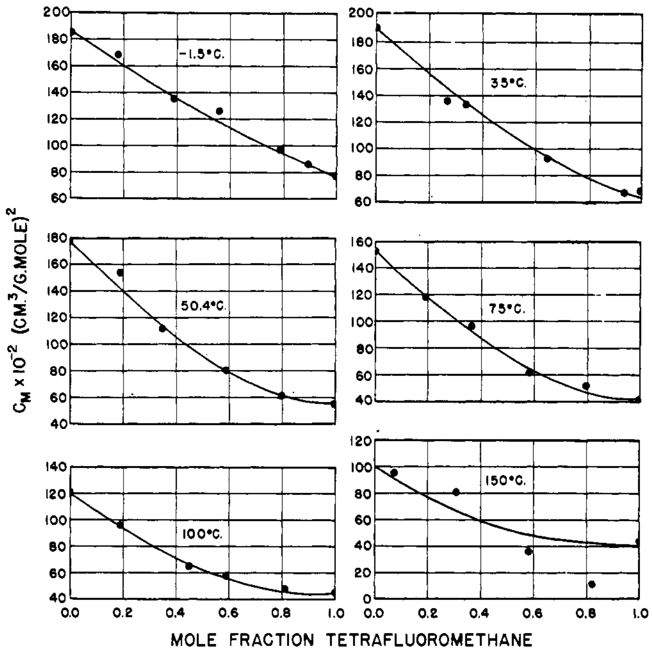


Figure 2. Third virial coefficients of tetrafluoromethane–sulfur hexafluoride system

● Experimental
— Equation (16)

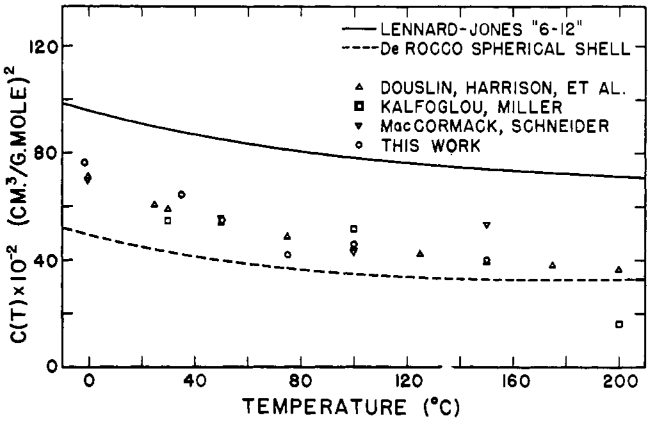


Figure 3. Temperature dependence of third virial coefficients of tetrafluoromethane

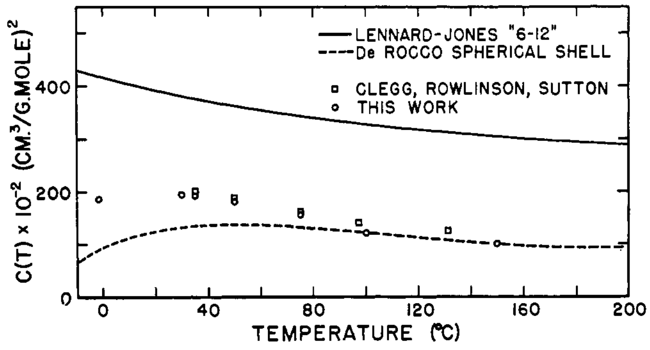


Figure 4. Temperature dependence of third virial coefficients of sulfur hexafluoride

Table VII. Tetrafluoromethane, Sulfur Hexafluoride, and Interaction Third Virial Coefficients[a]

Temp, K	($C_{CF_4-CF_4-CF_4}$) × 10^{-2}, exptl ± S.E.	($C_{SF_6-SF_6-SF_6}$) × 10^{-2}, exptl ± S.E.	($C_{CF_4-CF_4-SF_6}$) 10^{-2} exptl ± S.E.	($C_{CF_4-SF_6-SF_6}$) 10^{-2} exptl ± S.E.
271.61	76.2 ± 0.4	186.4 ± 1.9	102.6 ± 7.8	145.3 ± 6.9
308.21	64.4 ± 5.0	191.2 ± 3.6	82.1 ± 13.7	128.1 ± 10.0
323.55	55.0 ± 2.4	178.7 ± 2.3	46.4 ± 9.3	124.4 ± 10.6
348.10	41.9 ± 2.4	153.8 ± 3.3	42.2 ± 8.7	87.7 ± 8.9
373.15	45.8 ± 1.0	121.2 ± 1.3	44.9 ± 4.1	66.7 ± 5.0
423.15	40[b]	100[b]	40[b]	55[b]

[a] Third virial coefficients in (cm^3/g-mol)^2. S.E. = Standard error of the virial coefficient. [b] Estimated by extrapolation.

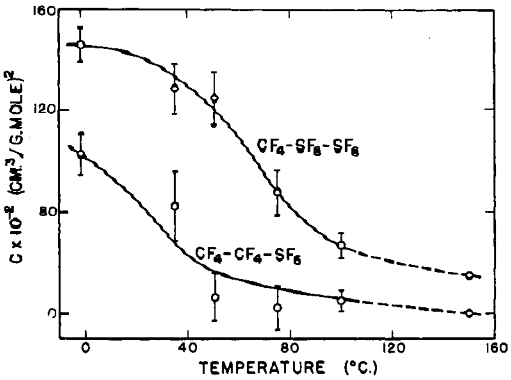


Figure 5. Interaction third virial coefficients of tetrafluoromethane—sulfur hexafluoride system

would result a maximum uncertainty of 4000 cm^6 mol^{-2} in the values of the third virial coefficients.

In Figures 3 and 4, a comparison is made of the third virial coefficients for CF_4 and SF_6 obtained in this work with those found by other investigators. In general, for CF_4 there is good agreement between the four sets of measurements shown, with the exceptions of the 150°C value reported by MacCormack and Schneider (*19*) and the 200°C value reported by Kalfoglou and Miller (*14*). The good agreement of the data of this work with the very precise values reported by Douslin and co-workers (*8*) indicates that the actual systematic errors in the third virial coefficients of this work are likely much less than the previously stated maximum error. The sulfur hexafluoride third virial coefficients were found to be in very good agreement with those reported by Clegg et al. (*4*), as shown in Figure 4. The only other values of C_{SF_6} reported at the time of this study were those of MacCormack and Schneider (*19*), which vary so irregularly with temperature as to cast grave doubts regarding their reliability.

In Figure 5, there are presented the temperature dependencies of the interaction third virial coefficients $C_{CF_4-CF_4-SF_6}$, and $C_{CF_4-SF_6-SF_6}$ determined in this work. The vertical bars through the data points indicate the standard errors given in Table VII. The interaction third virial coefficients are essentially smooth with respect to temperature within these limits.

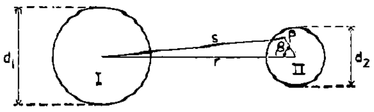
Figures 3 and 4 show the theoretical additive third virial coefficients (C_{add}) for the De Rocco spherical shell and Lennard-Jones "6–12" potentials. These curves were prepared from the parameters summarized in Tables V and VI and the tabulations for additive third virial coefficients of Storvick et al. (*29*) and Sherwood and Prausnitz (*26*). The Lennard-Jones "6–12" potential clearly predicts additive third virial coefficients too great at all temperatures in the 0–200°C range. When nonadditivity corrections are made for both long-range dispersive (*26*) and short-range repulsive (*25*) forces, the departure of theory from experiment increases. On the other hand, the De Rocco potential function predicts additive third virial coefficients not greatly in error in the higher temperatures of this range, where the nonadditivity corrections should be least. Unfortunately, it is not yet possible to make reliable corrections for nonadditivity to the third virial coefficient for the De Rocco potential, but Storvick et al. (*29*) have indicated that the net effect of such corrections will likely be in the direction of improved agreement with the experimental data shown here.

ACKNOWLEDGMENTS

The authors thank the E. I. du Pont de Nemours & Co. for providing the tetrafluoromethane used in this investigation. Also, the contribution of research equipment by Gulf Oil Corp. is gratefully acknowledged.

APPENDIX

Consider two spherical molecules, denoted by I and II, of diameters d_1 and d_2, respectively, in the coordinate system shown below.



As shown by Hoover (*13*), the potential of point P with respect to I is

$$U(P, d_1, s) = \frac{1}{sd_1(2-n)}\left[\left(s + \frac{d_1}{2}\right)^{2-n} - \left(s - \frac{d_1}{2}\right)^{2-n}\right] \quad (17)$$

Integrating $U(P, d_1, s)$ over the surface of II, gives us

$$U(d_1, d_2, r) = \frac{1}{2}\int_0^{\pi} U(P, d_1, s) \sin\beta \, d\beta =$$

$$\frac{1}{2(2-n)}\int_0^{\pi} \frac{1}{sd_1}\left[\left(s + \frac{d_1}{2}\right)^{2-n} - \left(s - \frac{d_1}{2}\right)^{2-n}\right] \sin\beta \, d\beta \quad (18)$$

Using the law of cosines, we get

$$s^2 = \left(\frac{d_2}{2}\right)^2 + r^2 - rd_2 \cos\beta \quad (19)$$

and, noting that

$$ds = \frac{rd_2 \sin\beta \, d\beta}{2\, s} \quad (20)$$

a change of variable can be made in order to integrate with respect to s. The integral then becomes

$$U(d_1, d_2, r) = \frac{1}{2(2-n)}\int_{r-\frac{d_2}{2}}^{r+\frac{d_2}{2}} \frac{2\, s}{sd_1rd_2}\left[\left(s + \frac{d_1}{2}\right)^{2-n} - \left(s - \frac{d_1}{2}\right)^{2-n}\right] ds \quad (21)$$

$$= \frac{1}{(3-n)(2-n)d_1d_2r}\left[\left(r + \frac{d_1 + d_2}{2}\right)^{3-n} - \left(r + \frac{d_1 - d_2}{2}\right)^{3-n} - \left(r - \frac{d_1 - d_2}{2}\right)^{3-n} + \left(r - \frac{d_1 + d_2}{2}\right)^{3-n}\right] \quad (22)$$

which, for $d_1 = d_2$, reduces to the result of De Rocco and Hoover (*5*).

Define the following reduced quantities:

$$r^* \equiv r/d_1 \quad (23)$$

$$r_0^* \equiv r_0/d_1 \quad (24)$$

$$d^* \equiv d_2/d_1 \quad (25)$$

$$P^{*(n)} \equiv P^{*(n)}(r^*, d^*) \equiv \left(r^* + \frac{1+d^*}{2}\right)^{-n} - \left(r^* + \frac{1-d^*}{2}\right)^{-n} - \left(r^* - \frac{1-d^*}{2}\right)^{-n} + \left(r^* - \frac{1+d^*}{2}\right)^{-n} \quad (26)$$

$$P_0^{*(n)} \equiv P^{*(n)}(r_0^*, d^*) \quad (27)$$

When we combine the cases for $n = 12$ and $n = 6$, Equation 22 may then be written in reduced form as

$$U(r^*, d^*) = a\frac{P^{*(9)}}{r^*} - b\frac{P^{*(3)}}{r^*} \quad (28)$$

The constants a and b may be evaluated from the conditions at the energy minimum, $dU/dr^* = 0$ and $U = -\epsilon$ at $r^* = r_0^*$.

Equation 28 can then be written as

$$U^* = \frac{U(r^*, d^*)}{\epsilon} =$$

$$\frac{(3\, r_0^* P_0^{*(4)} + P_0^{*(3)})P^{*(9)} - (9\, r_0^* P_0^{*(10)} + P_0^{*(9)})P^{*(3)}}{(9\, P_0^{*(10)} P_0^{*(3)} - 3\, P_0^{*(9)} P_0^{*(4)})r^*} \quad (29)$$

which has the same form as that given by Hoover (*5*) for molecules of one size only.

The second virial coefficient for this case of two differently sized molecules may then be expressed as

$$B_{12}(T) = b_0 B_{12}^*(r_0^*, d^*, T^*) \quad (30)$$

where

$$b_0 = \frac{2}{3}\pi \tilde{N} d_1^3 \quad (31)$$

$$T^* = kT/\epsilon \quad (32)$$

$$B_{12}^*(r_0^*, d^*, T^*) = 3\int_0^\infty (1 - e^{-U^*/T^*})r^{*2}dr^* \quad (33)$$

NOMENCLATURE

B = second virial coefficient, Leiden equation
b_0 = spherical-shell molecular volume, $^2/_3(\pi \tilde{N} d_1^3)$
C = third virial coefficient, Leiden equation
D = fourth virial coefficient, Leiden equation
d = spherical-shell diameter
k = Boltzmann constant
m = number of experimental observations
N = Burnett apparatus constant
$\tilde{N}$ = Avogadro's number
n = number of adjustable parameters, or integral exponent in potential energy function
P = absolute pressure
R = universal gas constant
r = intermolecular separation
r_0 = intermolecular separation at the minimum of the potential function
T = absolute temperature, K = °C + 273.15
Y = mole fraction
Z = compressibility factor, $P/\rho RT$
ϵ = depth of the potential well
ρ = molar density

SUBSCRIPTS

A = initial component in measuring chamber
f = state after the final expansion
M = mixture
r = state after the rth expansion
0 = state before the first expansion
1 = refers to CF_4
2 = refers to SF_6

SYMBOLS

$\hat{}$ = calculated (least-squares) value
$*$ = reduced quantity

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RECEIVED for review July 26, 1971. Accepted November 19, 1971. The National Science Foundation furnished partial support for this work.