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Virial Coefficients and Critical Properties of Perfluorohexanes

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Compressibility measurements of the gas phase are reported for the compounds n-C_6F_{14}, 2-$CF_3C_5F_{11}$, 3-$CF_3C_5F_{11}$, 2,3-$(CF_3)_2C_4F_8$, and cyclo C_6F_{12}. The measurements range from 1 to 18 atm. pressure and from 80° to 180°C. Second and third virial coefficients and critical properties have been calculated and are reported.

In order that various intermolecular potential energy functions might be studied for large nonpolar molecules, compressibility measurements have been made for five perfluorohexanes. From these measurements the second and third virial coefficients have been calculated and the vapor pressures and critical properties obtained. Measurements on four of these compounds have been made by Cecil (*1*) in the low temperature range. Garner and McCoubrey (*2*) have reported measurements on n-C_6F_{14}.

APPARATUS

A recent review (*3*) describes numerous types of compressibility apparatus and discusses the limitations and accuracy of each apparatus. The apparatus selected for this work was based upon the designs of Kay and Rambosek (*4*) and Connolly and Kandalic (*5*). This design was adopted because with the proper auxiliary equipment a high degree of accuracy could be attained with only a small amount of sample.

The measurements were made by confining the sample in a calibrated glass piezometer over mercury, maintaining a constant temperature around the piezometer by boiling liquid at constant pressure in a vapor jacket, and then measuring the pressure exerted by the sample with a manometer or dead weight pressure gauge. The compressibility data were obtained as isotherms, and the virial coefficients could be calculated directly.

The apparatus is shown schematically in Figure 1. The main components are a glass piezometer (a), vapor jacket (b), mercury reservoir (c), mercury-oil interface detector (d), dead weight gauge (e), and manometer (f). Auxiliary apparatus included a compressed gas source, vacuum system, manostat, thermocouples, potentiometer, mercury level indicator, magnetic stirring device, and cathetometer.

The piezometer was constructed of 3 mm. I.D. precision bore borosilicate glass capillary tubing of 3 mm. wall thickness. It was 70 cm. in length and was connected to a ¼ in. stainless steel tubing system by a compression block (g). Gasketing between the piezometer and compression block was accomplished by the use of viton 0 rings.

The piezometer was surrounded by a vapor jacket (b) which could be sealed to the compression block (g) with 0 ring gaskets. The vapor jacket was 20 mm. I.D. glass tubing, surrounded with an evacuated jacket. The interior of the vacuum jacket was silvered except for a 1 cm. strip along the length of the jacket for observation of the piezometer. The vapor jacket could be removed without disturbing the piezometer connection. A boiling flask (h) was attached to the vapor jacket. A ground glass joint (i) at the top of the vapor jacket allowed for the connection of a condenser, thermocouples, and pressure control line. The pressure control line was connected through a Cartesian manostat to a vacuum system.

The mercury reservoir was constructed of stainless steel and had a volume of approximately 1 liter and could be opened to the piezometer. It was connected so that either vacuum or pressure could be exerted on the surface of the mercury in the reservoir.

The mercury-oil interface detector was a stainless steel cylinder and had a volume of approximately 1 liter and a cross-sectional area of 75 sq. cm. Three tungsten wires were inserted in the detector, each one connected in series with an indicating lamp. The middle detector was used as the reference to which the interface was adjusted for all measurements. The other two indicators served as safety devices. The interface detector was connected to the deadweight tester directly and could be opened to the piezometer.

The deadweight tester (e) was a commercial type. It was designed for a pressure range of 5 to 500 lb./sq.in. gauge and contained weights so that determinations could be made at 5 lb./sq. in. intervals.

The two open end manometer tubes (f) could be connected to the piezometer. One manometer was constructed of

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Table 1. Second and Third Virial Coefficients of n-C_6F_{14}

Temperature, °K.	B, cc./g.-mole	C, (liter/g.-mole)^2
341.10	−1,612	
351.85	−1,484	
374.78	−1,209	
395.56	−1,051	0.25
415.48	−920	0.23
432.68	−818	0.21
451.55	−725	0.20

Table 2. Second and Third Virial Coefficients of 2-$CF_3C_5F_{11}$

Temperature, °K.	B, cc./g.-mole	C, (liter/g.-mole)^2
333.23	−1,837	
351.65	−1,412	
370.65	−1,179	
417.39	−882	0.20
433.13	−794	0.18
441.70	−756	0.18
454.63	−691	0.17

3 mm. I.D. capillary glass tubing and the other of 10 mm. I.D. glass tubing. Both manometers were connected to the vacuum system so they could be used as absolute manometers or opened to atmospheric pressure.

Two copper-constantan thermocouples were used for the temperature measurements. Reference junctions for the thermocouples were placed in a stirred bath of crushed ice. A potentiometer was used for the measurement of the thermocouple electromotive force.

A glass vacuum system was used for the preparation of samples. The vacuum system could be opened to the piezometer to allow evacuation and transfer of sample to the piezometer and degassing of the mercury in the reservoir. Stirring was accomplished with a 2 mm. steel ball located in the sample space within the piezometer and driven by a magnet.

CALIBRATION OF APPARATUS

It was necessary to calibrate the piezometer tube for volume, the thermocouples for temperature, and the deadweight gauge for pressure. The calibration of the piezometer was carried out by filling it with mercury, adjusting the vapor bath to 40°C., and withdrawing small volumes of mercury from the heated portion of the tube through a specially designed compression block. After each withdrawal, the distance between the mercury meniscus and a reference mark on the piezometer was measured with a cathetometer. The density of the mercury used in this work was checked by using previously calibrated pycnometers and found to be 15.5331 g./cc. at 25.02°C. Three calibrations runs were made, and all agreed to within 0.1% except for small volumes of less than 0.35 cc. which were reproduced to within 0.4%.

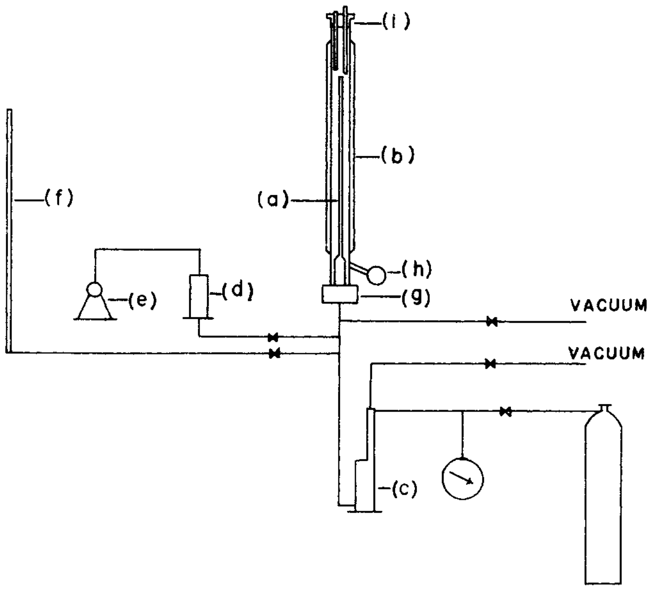

Fig. 1. Compressibility apparatus.

The thermocouples were calibrated at the ice point, steam point, and boiling point of napthalene. The resulting calibration equation was checked against vapor pressure measurements of 2,2,4-trimethylpentane. Agreement was better than 0.05°C.

The cross-sectional area of the deadweight gauge piston and the mass of the weights were determined. The accuracy of measurements with the deadweight gauge is limited by the accuracy to which the piston area is known. For this work the piston area was determined to within 0.05%.

EXPERIMENTAL PROCEDURE

The sample was degassed in the vacuum system and transferred to a precision bore capillary tube used to obtain an estimate of sample size to be charged to the piezometer. Experimental runs were made at 20°C. intervals from 60°C. to the critical temperature. The pressure range was from 1 atm. to saturation pressure up to the critical pressure. The details of the sample preparation and experimental procedure are given elsewhere (*6*).

MATERIALS

The fluorocarbons used in this work were prepared from hydrogen free compounds. They were purified by preparative scale gas chromatography. Chromatographic analysis of the samples indicated that no impurities were present. Vapor pressures of these materials have been reported from this laboratory (*10*).

CALCULATIONS

The volume calculated from the calibration at 40°C. was corrected for the thermal expansion of the piezometer. The deadweight pressure was corrected for the vapor pressure of mercury in the piezometer, capillary effects, the mercury and oil heads, barometric pressure, and the local gravitational constant. The oil and mercury heads were measured with a cathetometer. Handbook (*8*) values were used for the density and vapor pressure of mercury. The oil density was determined with pycnometers in a thermostated bath. Capillary corrections were determined from the observed menicus height and handbook tables. Pressures less than 2 atm. were measured by mercury columns. These measurements were corrected for the heated and ambient heads of mercury, vapor pressure of mercury, and atmospheric pressure. The probable error in the PV data is less than 0.1% for pressures up to 2 atm. and 0.05% for the higher pressures. The raw compressibility data are given in reference *6*.

VIRIAL COEFFICIENTS

The virial equation of state in terms of the density series

TABLE 3. SECOND AND THIRD VIRIAL COEFFICIENTS OF 3-$CF_3C_5F_{11}$

Temperature, °K.	B, cc./g.-mole	C, (liter/g.-mole)^2
351.45	−1,443	
376.72	−1,113	
394.73	−1,003	
417.05	−883	0.19
432.99	−795	0.18
450.49	−715	0.17

can be written as

$$PV = nRT + n^2RTBV^{-1} + n^3RTCV^{-2} + \dots \quad (1)$$

The virial equation in terms of the pressure series was found to have too much curvature to allow a realistic fit of the experimental data. Virial coefficients for each isotherm were obtained by fitting the data to an equation of the form

$$PV = \alpha + \beta V^{-1} + \gamma V^{-2} \dots \quad (2)$$

with a step-by-step multiple regression analysis computer program. For isotherms above 400°K., only the first-order terms were found to be significant.

The constants in Equation (2) reproduced the data to within experimental error. The sample mass and virial coefficients were calculated from these constants by comparing coefficients in Equations (1) and (2) as

$$n = \alpha/RT \quad (3)$$

$$B = \beta/n^2RT \quad (4)$$

$$C = \gamma/n^3RT \quad (5)$$

The virial coefficients are given in Tables 1 through 5. Except for the lowest isotherm, values were obtained for the sample mass from Equation (3) that agreed to within 0.1% for the different temperatures. The low temperature isotherm gave a sample mass of 0.5 to 0.6% higher than the rest of the isotherms. The standard error of the coefficients obtained in the fit of Equation (2) was within the experimental accuracy. Since the second and third virial coefficient involve the first and second derivatives of the compressibility data and a loss of accuracy of approximately an order of magnitude is associated with each differentiation, the probable accuracy of second virial coefficients is 1% for all values above 350°C. and 5% for the low temperature values. The decreased accuracy in the low temperature isotherms resulted from the fact that only a few experimental points could be determined before condensation occurred. The probable error in third virial coefficients is 10%.

Cecil (*1*) has measured low temperature virial coefficients for all the compounds reported in this work except the perfluorocyclohexane, and his results are given in the appendix. His measurements were made in a different apparatus at temperatures less than 350°K. Agreement for perfluoro-*n*-hexane and perfluoro-2-methylpentane is good. The agreement for the perfluoro-3-methylpentane and perfluoro 2,3-dimethyl butane is inconclusive. Garner and McCoubrey (2) have measured the second virial coefficients for perfluoro-*n*-hexane and report larger virial coefficients than were obtained in this work. They state that their sample was known to be only 99% pure perfluorocarbon material and that they did not determine the percentage of isomers present.

TABLE 4. SECOND AND THIRD VIRIAL COEFFICIENTS OF 2,3-$(CF_3)_2\ C_4F_8$

Temperature, °K.	B, cc./g.-mole	C, (liter/g.-mole)^2
351.21	−1,372	
374.63	−1,130	
394.65	−1,012	
414.62	−906	0.19
433.22	−786	0.16
450.36	−702	0.14

TABLE 5. SECOND AND THIRD VIRIAL COEFFICIENTS OF CYCLO C_6F_{12}

Temperature, °K.	B, cc./g.-mole	C, (liter/g.-mole)^2
350.32	−1,152	
378.36	−941	
395.00	−851	0.15
410.81	−770	0.15
433.17	−669	0.13
451.01	−599	0.12

CRITICAL PROPERTIES

The critical pressure, temperature, and volume were determined for the perfluoro-*n*-hexane, the perfluoro-2-methylpentane, and the perfluoro-2,3-dimethylbutane. The critical pressure and temperature were determined for the perfluoro-3-methylpentane. These were calculated by utilizing the data obtained from experimental isotherms in the range of the critical points. Except for the 3-$CF_3C_5F_{11}$ and 2,3-$(CF_3)_2C_4F_8$, isotherms were obtained above the critical point and at approximately 1-deg. intervals close to the critical temperature isotherm. These isotherms located the critical temperature to within a degree. The critical pressure was then determined from the vapor pressure curve by using this approximate critical temperature. For all the compounds except 3-$CF_3C_5F_{11}$, the orthobaric densities were determined, the rectilinear diameter was plotted vs. temperature, and the critical volume obtained for the approximate critical temperature. This volume was plotted on the P-V plot at the critical temperature. If the corresponding pressure differed from that obtained from the vapor pressure curve, a new temperature was assumed and the iteration carried out until a consistent set of critical properties were obtained. The experimental orthobaric densities are given in Table 6. These values were obtained from the

TABLE 6. ORTHOBARIC DENSITIES OF PERFLUORO HEXANES

Compound	Temperature, °K.	ρL, g./cc.	ρV, g./cc.
n-C_6F_{14}	395.56	1.322	0.082
	415.48	1.207	0.136
	432.68	1.065	0.360
	447.56	0.858	0.360
2-$CF_3C_5F_{11}$	441.70	1.024	0.253
	447.54	0.953	0.302
	449.41	0.926	0.331
	451.11	0.896	0.368
3-$CF_3C_5F_{11}$	448.56	—	0.302
	449.78	—	0.315
2,3-$(CF_3)_2C_4F_8$	433.22	1.200	0.169
	450.36	1.068	0.264
	451.76	1.048	0.275
	452.79	1.044	0.284

TABLE 7. CRITICAL PROPERTIES AND ACENTRIC FACTORS OF PERFLUOROHEXANE

Compound	P_c, atm.	T_c, °K.	V_c, cc.	Z_c	ω
n-C_6F_{14}	18.1	451	555	0.271	0.483
2-$CF_3C_5F_{11}$	18.0	453	550	0.267	0.466
3-$CF_3C_5F_{11}$	16.7	450	—	—	0.475
2,3-$(CF_3)_2C_4F_8$	18.5	463	525	0.256	0.400

experimental isotherms and are reported only for the higher temperatures. During the measurement of the low temperature isotherms, condensation occurred at such a large volume that during the following compression of the sample to liquid phase, liquid was trapped between the mercury and piezometer wall and the mass as previously determined could not be used.

Since experimental isotherms were not obtained above the critical temperature for the 2,3-$(CF_3)_2C_4F_8$, extrapolation of the rectilinear diameter was uncretain, and the same confidence can not be placed in the critical constants obtained for this compound as in the values for the *n*-C_6F_{11} and 2-$CF_3C_5F_{11}$. There were not sufficient liquid densities obtained to allow a determination of critical volume for the 3-$CF_3C_5F_{11}$. The critical point of the cyclo-C_6F_{12} was beyond the design pressure and temperature of the apparatus.

The critical properties are given in Table 7. Also listed in Table 7 are values for the acentric factor and the critical compressibility factor. Dunlap and co-workers (9) have reported values of 16 atm. and 447.7°K. for the critical pressure and temperature of *n*-C_6F_{14}. Dunlap used sealed tubes to determine the critical temperature and extrapolated the vapor pressure data from 1 atm. to find the critical pressure. This extrapolation resulted in an uncertain critical pressure.

The critical properties given in Table 7 are the first reported that have been obtained by compressibility measurements in the critical region. These measurements can be improved by making a more precise measurement of the saturated liquid densities close to the critical point.

CONCLUSION

The small difference that exists between the virial coefficients of the isomers make it difficult to generalize as to the effect of molecular structure on the intermolecular interaction, except to say that there is little effect of structural changes. However, the magnitude of both the second and third virial coefficient is observed to decrease when the molecular structure is altered by increasing the number of groups (for example CF_3, C_2F_5) at a point of branching, or/and by decreasing the size of these groups. This would suggest that the fluorine atoms are more exposed in the normal structure and become more shielded in the isomer structures. However, the vapor pressure at a given temperature also decreases with branching of structure in the above sense, which would suggest more exposure of fluorine atoms to intermolecular interaction as the isomers become more compact in structure. A discussion of intermolecular potential energy functions follows in a second paper.

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NOTATION

B = second virial coefficient in the density series virial equation
C = third virial coefficient in the density series virial equation
n = number of moles
P = pressure
P_c = critical pressure
R = gas constant
T = absolute temperature
T_c = critical temperature
V = total volume
V_c = critical molar volume
Z_c = critical compressibility factor

Greek Letters

α = constant defined in Equation (2)
β = constant defined in Equation (2)
γ = constant defined in Equation (2)
ρ = density
ω = acentric factor; negative logarithm, in base 10, of ten times the reduced vapor pressure at a reduced temperature of 0.7

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APPENDIX: SECOND VIRIAL COEFFICIENTS OF FOUR PERFLUOROHEXANES DETERMINED BY CECIL (1)

n-C_6F_{14}

T, °K.	$-B$, cc./mole
303.2	2,320
323.5	1,922
341.1	1,571
351.3	1,528

2-$CF_3C_5F_{11}$

T, °K.	$-B$, cc./mole
303.8	2,142
304.0	2,098
322.5	1,813
334.8	1,601
341.3	1,500
352.0	1,444

3-$CF_3C_5F_{11}$

T, °K.	$-B$, cc./mole
303.9	1,700
321.0	1,716
323.2	1,642
332.0	1,438
342.0	1,434
350.4	1,364

2,3-$(CF_3)_2C_4F_8$

T, °K.	$-B$, cc./mole
303.6	2,670
323.1	1,610
335.4	1,582
345.3	1,391