Determination of the Second Virial Coefficients of Six Fluorochloromethanes by a Gas Balance Method in the Range 40° to 130° C.

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The second virial coefficients of $CClF_3$, CCl_2F_2, CCl_3F, CHF_3, $CHClF_2$, and $CHCl_2F$ were determined in the temperature range 40° to 130° C. The method consisted of using a gas balance modified for magnetic weighing, in conjunction with a reference gas, CF_4. Pressures of the test gas, P_x, and that of the reference gas, P_r, were determined under conditions of identical temperature and density, at different settings of the balance. The second virial coefficients were calculated from plots of P_x/P_r against P_x. The force constants, ε/k and σ, were then calculated from the values of the second virial coefficients.

FOR GASES under low pressures—e.g., below 2 atm.—the compressibility factor may be expressed by

$$\frac{PV}{RT} = Z = 1 + B'P + \cdots \qquad (1)$$

where B', the second virial coefficient, is in units of reciprocal pressure (*1*). The compressibility factor may also be expressed by

$$\frac{PV}{RT} = Z = 1 + \frac{B}{V} + \cdots \qquad (2)$$

Here, B is in units of volume per mole. B is related to B' by the relationship $B = B'RT$, or B (cc./mole) $=$ B' (1/mm.) (6.2363×10^4) T. The prime will now be deleted, since it will be clear in what units B is expressed.

The method used in this investigation for the determination of the second virial coefficient $B(T)$ is essentially the method of limiting pressures used originally by Cawood and Patterson (*2*) in determining the molecular weights of a number of gases.

Let the test and reference gases be denoted by the subscripts x and r, respectively. Since the pressure of the gas in the gas density balance is adjusted so as to obtain conditions of equal density, $\rho_x = \rho_r$, then from Equation 1, $PV = (m/M)\ RT(1 + BP)$, or the density $\rho = (PM/RT)\ (1 + BP)^{-1}$, and the condition of equal density becomes

$$\left(\frac{P_xM_x}{T_x}\right)\left(\frac{1}{1 + B_xP_x}\right) = \left(\frac{P_rM_r}{T_r}\right)\left(\frac{1}{1 + B_rP_r}\right)$$

Solving for P_x/P_r, one obtains

$$\frac{P_x}{P_r} = \left(\frac{T_x}{T_r}\right)\left(\frac{M_r}{M_x}\right) + P_x\left[\left(\frac{T_x}{T_r}\right)\left(\frac{M_r}{M_x}\right) B_x - B_r\right]$$

At constant temperature, the above equation becomes

$$\frac{P_x}{P_r} = \left(\frac{M_r}{M_x}\right) + P_x\left[\left(\frac{M_r}{M_x}\right) B_x - B_r\right] \qquad (3)$$

Hence, a plot of P_x/P_r *vs.* P_x should be a straight line whose slope is given by $(M_x/M_r)B_x - B_r$ and its intercept by (M_r/M_x). If $B_r(T)$ is known, then $B_x(T)$ may be calculated. An example of such a plot is given in Figure 1.

Carbon tetrafluoride was chosen as the reference gas because its $B(T)$ values have been determined accurately by a number of investigators in the temperature range of this study. A summary of these results appears in Table I. The reference $B(T)$ values of Table II were interpolated from the values given in Table I, relying more on the values of MacCormack and Schneider (*9*), since they appear to be more accurate. Another reason for the choice of carbon tetrafluoride is that, since its molecular weight is in the range of the molecular weights of the gases used in this study, the pressure ratios P_x/P_r would not be very large or very small. This minimizes any change in the volume of the float with change in pressure of the gas inside the balance.

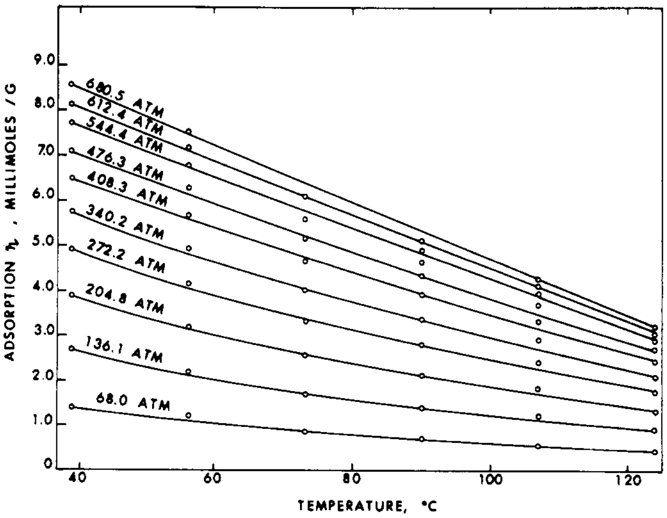

Figure 1. Plot of P_{CClF_3}/P_{CF_4} *vs.* P_{CClF_3} at 130.00° C.

Intercept $=$ 0.84245

Slope $= -2.81 \times 10^{-6} \frac{1}{\text{mm.}}$

Table I. Second Virial Coefficients of Carbon Tetrafluoride

Temp.		B, Cm.^{3}/Mole		
° C.	° K.	Ref. (*3*)	Ref. (*9*)	Ref. (*6*)
0	273.16	−111.00	−111.0	
25	298.16	−88.30		
30	303.16	−84.40		
50	323.16	−70.40	−70.4	−72.4
75	348.16	−55.70		−56.1
100	373.16	−43.50	−43.1	−43.9
125	398.16	−33.20		−30.1 −31.1
150	423.16	−24.40	−26.0	
175	448.16	−16.80		
200	473.16	−10.10		
225	498.16	−4.25		

Table II. Values of $B(T)$ for CF_4, Used as Reference in This Study
(Interpolated from Table I)

Temp.		
° C.	° K.	B, Cm.^{3}/Mole
40.01	313.17	−77.0
70.28	343.44	−58.2
100.00	373.16	−43.3
130.00	403.16	−31.8

EXPERIMENTAL

The gas balance (Figure 2) used in this investigation was of the type originally developed by Edwards (*4*) and tested at the National Bureau of Standards by Smith *et al.* (*10*). It consisted of an aluminum-alloy float supported to the end of a horizontally suspended beam and enclosed in a gas-tight cylindrical case. The balance was modified by mounting a permanent magnet vertically on the beam. A solenoid was mounted inside the balance such that the magnet could swing freely in the annular space of the solenoid. The leads from the solenoid, as well as the leads from the copper-constantan thermocouple, were passed through gas-tight glands in the face of the balance. A constant voltage current, 60 ma. maximum, when passed through the solenoid, afforded a method of changing the range of the balance without opening it.

The balance was enclosed in a constant-temperature air bath heated by two elements mounted on the sides, and was shielded from direct heating by two asbestos boards. The current through the heaters was controlled by a proportional temperature controller with a thermistor sensing device. The temperature of the bath could be controlled to better than ±0.03° C., while the temperature of the gas sample inside the balance was believed to be better than ±0.01° C. This was due to the large mass of the balance itself, which tended to maintain a uniform temperature, and also to frequent stirring of the gas before and after each reading. The stirring was done by interrupting the current to the solenoid momentarily, causing the float to start swinging.

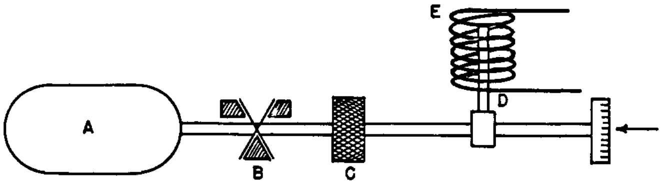

Figure 2. Gas balance

A. Float
B. Phosphor-bronze springs
C. Counterweight
D. Permanent magnet
E. Solenoid

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The temperature of the gas sample within the balance was measured by means of a copper constantan thermocouple passing through the face of the balance, and insulated from it by means of two gas-tight Teflon glands. The thermocouple was connected to a precision potentiometer and was standardized in the temperature range from 35° to 135° C. against mercury-in-glass thermometers certified by the N.B.S.

Pressure measurements were made by means of a mercury-in-glass U-tube manometer (19-mm. i.d.) connected directly to the balance. The manometer was read by means of a precision cathetometer, having a glass scale of low coefficient of expansion. For pressures above atmospheric, the other leg of the manometer was opened to the atmosphere and the atmospheric pressure read in a similar way on an adjacent barometer. The cathetometer scale was compared with a standard scale certified by the N.B.S. The error was of the order of 0.005 mm. for a 60-cm. length of the cathetometer scale. This is less than 0.1 of the experimental error in the pressure determination, and hence no corrections to the cathetometer scale readings were made.

The balance was exacuated by means of a vacuum pump connected to the balance through a trap. The trap had a standard taper outlet, to which a sampling flask could be attached for collecting samples for mass spectroscopic analysis.

The gaseous samples used in this study were obtained from the Freon Division of du Pont de Nemours and from Matheson. The purity ranged between 97 and 99.9%. Mass spectroscopic analysis showed that most of the impurities consisted of oxygen, nitrogen, carbon dioxide, and water vapor. Gas density measurements are sensitive to impurities, hence all samples used were distilled three times under their own vapor pressure in an all-glass system. The "heavy" and "light" fractions, each about 15% of the original sample, were discarded. During distillation, the samples were stirred continuously by means of a magnetic device. The purification process proved effective, as the results from mass spectroscopic analyses showed that water vapor and carbon dioxide were almost completely absent, although in a few instances traces of nitrogen or oxygen were left.

One test of the purity of the gases is the value of the intercept of the plot of Equation 3 (Figure 1). These values (Table III) show that the maximum error between the theoretical values of the ratio of the molecular weights and the experimental values was in all cases less than 1%.

Preliminary preparation prior to each run consisted of evacuating the whole system, including the balance and the traps, for at least 12 hours. All the traps and connecting lines were then flamed to remove any gas adhering to the inside of the walls. The system was filled to about 100 mm. of Hg with the gas to be used, and then the whole system was evacuated and flamed again. This was repeated a second time prior to the actual distillation of the sample.

After loading the balance, the temperature controller

Table III. Comparison of Theoretical and Experimental Values of the Intercept of the Plots of Equation 3

			Temp., ° C.				
Compound	Mol. Wt.[a]	Theoretical, M_r/M_x	40.01	70.28	100.00	130.00	Maximum Error, %
			Experimental, M_r/M_x				
$CClF_3$	104.47	0.8424	0.8430	0.8427	. . .	0.8424	0.07
CCl_2F_2	120.92	0.7278	0.7267	0.7261	0.7292	0.7274	0.23
CCl_3F	137.38	0.6406	. . .	0.6452	0.6448	0.6423	0.71
CHF_3	70.02	1.2569	1.2578	1.2564	1.2570	1.2574	0.25
$CHClF_2$	86.48	1.0177	1.0166	1.0148	1.0209	1.0174	0.28
$CHCl_2F$	102.93	0.8551	0.8590	0.8524	0.8607	0.8568	0.65

[a] Molecular weight of the reference compound, CF_4, is 88.01.

was set to the desired temperature and the system left overnight to reach equilibrium.

In taking measurements, the solenoid current was first set at 60 ma. The pressure inside the balance was then adjusted to the equilibrium pressure corresponding to this current setting.

When the pressure was reduced to a new equilibrium at a lower current setting, the temperature of the gas in the balance dropped approximately a degree. Thermal equilibrium was re-established by allowing the balance to stand for about an hour before taking any further readings. This change of temperature also affected the resistance of the solenoid, and hence the magnitude of the current. When thermal equilibrium was re-established, the current was checked and readjusted.

A set of three readings of the pressure was then made. One or two other sets of three readings were made after readjusting the pressure to the balance zero point. Hence, a total of six or nine pressure readings were obtained for each solenoid current setting.

The solenoid current was then adjusted to a new value, usually 5 or 10 ma. lower than the previous setting, and the above procedure repeated.

The apparatus was tested before any actual data were taken. Tests were made on sulfur hexafluoride, using carbon tetrafluoride as a reference gas. SF_6 was chosen because its $B(T)$ values were determined accurately by MacCormack and Schneider (*9*) in the same kind of apparatus they used for determining the values of $B(T)$ for CF_4. Two tests were conducted at 70° and 100° C., and in both cases the results were in close agreement with the published values, as shown in Table IV. Hence, it was assumed that the equipment was functioning properly.

RESULTS

In calculating the pressure, the difference in height of the mercury columns in the manometer was corrected for the meniscus height, using the data of Gould and Vickers (*5*). Corrections for the temperature of mercury and for standard gravity were also made. When the pressure inside the balance was above atmospheric, the manometer was opened to the atmosphere and the barometric pressure was read. The total pressure was then added up. This was corrected to the temperature of the isotherm when the temperature of the balance was not identical with that of the isotherm. The six or nine corrected pressure readings made at each solenoid current setting were then averaged. A plot of (P_x/P_r) *vs.* P_x was made, as shown in Figure 1. The intercept and the slope, determined by the method of least squares, were used in calculating the values of B_x by Equation 3. The results are given in Table V and plotted in Figure 3.

The parameters, ε/k and σ, where ε is the depth of the potential well and σ is the collision diameter, were calculated as outlined by Hirschfelder *et al.* (*7*). For the molecules $CClF_3$, CCl_2F_2, and CCl_3F, the dipole moments are small enough (< 0.6 debye) to justify the use of an angle-independent potential, and the Lennard-Jones 12–6 potential was used. For the molecules CHF_3, $CHClF_2$, and $CHCl_2F$, the dipole moments are sufficiently large (> 1.3 debye) to require an angle-dependent potential. The parameters ε/k and σ were calculated using the Stockmayer potential. The values of these parameters are also given in Table V.

Table IV. Comparison of Experimental and Literature Values of the Second Virial Coefficient of Sulfur Hexafluoride

Temp., ° C.	MacCormack and Schneider (*9*)	This Study
70.28	−189.8 (interpolated)	−193.5
100.00	−159.2	−161.0

DISCUSSION

Values of the second virial coefficient in the temperature range covered by this study were previously known for only one of the six halogen-substituted methanes. Table VI gives the values of $B(T)$ for $CHCl_2F$ reported in Hirschfelder *et al.* (*7*).

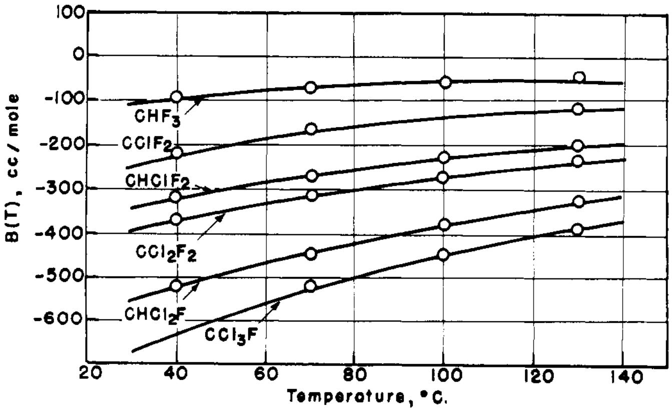

Figure 3. Second virial coefficient *B(T)* as a function of temperature

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Table V. Second Virial Coefficients of the Six Halogen-Substituted Methanes and the Intermolecular Potential Parameters, ε/k and σ

Compound	Temp., ° C. 40.01	70.28	100.00	130.00	ε/k, ° K.	σ, A.
	B(T), Cc./Mole					
$CClF_3$	−220.9	−168.1	−142 (estim.)	−121.5	225	4.90
CCl_2F_2	−372.4	−319.1	−279.4	−237.1	289	5.20
CCl_3F	−628 (estim.)	−525.9	−454.6	−394.7	343	5.41
CHF_3	−94.4	−72.5	−60.3	−50.2	197	4.26
$CHClF_2$	−323.5	−275.0	−236.1	−204.2	274	4.52
$CHCl_2F$	−526.2	−451.5	−388.3	−332.7	385	4.88

Table VI. Comparison of B(T) Values of $CHCl_2F$, Cc./Mole

Temp., ° K.	Ref. (8)	Interpolated from Ref. (8)	This Study
239	−766		
250	−734		
283	−616		
311	−528		
313		−524	−526.2
339	−446		
343		−449	−451.5
366	−403		
373		−390	−388.3
394	−354		
403		−335	−332.7
422	−310		
450	−271		

The $B(T)$ values of $CClF_3$ at 100° C. and of CCl_3F at 40° C. have been estimated from the values for other isotherms, since the corresponding pressure measurements were found later to be in error, probably because of leakage of the system.

Table III shows that the percentage error of the ratio of the molecular weights tends to increase with molecular weight of the compound investigated. This probably is due to the greater difficulty in purifying the less volatile compounds.

NOMENCLATURE

$B, B(T), B', B'(T)$ = second virial coefficient
k = Boltzmann constant
M = molecular weight
m = mass
P = pressure
R = gas constant
T = temperature, ° K.
V = volume; also molar volume in Equations 1 and 2
Z = compressibility factor
ε = depth of the intermolecular potential
ρ = density
σ = collision diameter given by the intermolecular potential

Subscripts

r = reference gas, CF_4, in this study
x = test gas

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RECEIVED for review May 22, 1968. Accepted May 12, 1969.