J. Chem. Eng. Data 1993, 38, 139–140

Second Virial Coefficients for Fluoromethanes and Their Binary Mixtures with Helium and Argon

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Using an accurate method which has been described in detail previously, second virial coefficients of methane, fluoromethane, difluoromethane, trifluoromethane, and tetrafluoromethane and their binary mixtures with helium and argon have been measured at 290, 300, and 310 K.

Introduction

In a recent publication (*1*) we described an apparatus and methods (*1*) for measuring the three second virial coefficients which characterize the molecular interactions in a binary gas mixture. It is suggested that this paper be read in conjunction with that work. These methods essentially involve use of a Texas Instruments (TI) quartz spiral gauge to accurately measure pressure changes when gases are mixed or expanded at constant temperature in a cell which consists of two identical volumes. Details were given which greatly improve the techniques we used on previous occasions (*2–6*). The purpose of this paper is to report second virial coefficients for fluoromethanes and their mixtures with helium and argon which have been measured with the same apparatus.

Theory

(a) Pure Gases. The virial equation of state may be written as

$$PV/nRT = 1 + B'P + C'P^2 + \dots \qquad (1)$$

where P is the pressure, V the volume, T the temperature, R the gas constant, n the number of moles of gas, and B' and C' the second and third virial coefficients, respectively. If two gases, a reference gas and one of interest, are individually expanded from the same initial pressure P_i and volume V_1 to the same final volume $V_2 = 2V_1$, then the second virial coefficient of interest is related (*1*) to the virial coefficients of the reference gas by the relation

$$B' = (P - P_r) + B_r'\,(P_rP - P_iP_r) + C'\,(PP_i^2 - P_rP^2)/A \qquad (2a)$$

$$A = (PP_r - PP_i) \qquad (2b)$$

where P_r and P are the final pressures of the reference gas and the gas of interest, respectively, and C_r' for the reference gas nitrogen has been taken as zero. Calculations show that the third term containing C' is negligible at pressures lower than two atmospheres.

(b) Gas Mixtures. As explained in detail in several previous publications (*1–6*) it is possible to measure the excess second virial coefficient, $\mathcal{E}$, for binary gas mixtures in the present apparatus:

$$\mathcal{E} \equiv B_{12} - (1/2)(B_{11} + B_{22}) \qquad (3)$$

Table I. Purities of Gaseous Components (mol %)

He	99.99	CH_2F_2	99.1
Ar	99.9	CHF_3	98.0
CH_4	99.99	CF_4	99.9
CH_3F	99.0		

Table II. Second Virial Coefficients for Pure Gases ($cm^3{\cdot}mol^{-1}$)[a]

	290 K	300 K	310 K	ref
He	(11.7)	(11.6)	(11.6)	10
Ar	(−18.0)	(−15.6)	(−14.0)	10
CH_4	−47.0 (−46.0)	−44.0 (−42.0)	−38.7 (−38.0)	10
CH_3F	−220.2 (−224)	−201.9 (−206)	−180.7 (−189)	11
CH_2F_2	−315.7 (−346)	−292.5 (−318)	−264.5 (−293)	12
CHF_3	−205.0 (−198)	−188.3 (−183)	−172.2 (−170)	13
CF_4	−98.0 (−95)	−89.4 (−86)	−82.7 (−79)	14

[a] The data in parentheses are literature values. The experimental CH_4 values were taken from ref 1. The data taken from ref 10 are the recommended values.

where B_{12}, which characterizes the unlike interactions, can be obtained from the relation (*7, 8*)

$$\mathcal{E} = (2RT\Delta P/P_i^2)(1 + (B_{11} + B_{22})P_i/RT) - (P_i(B_{11} - B_{22})^2/2RT)(1 + 2(B_{11} + B_{22})P_i/RT) \qquad (4)$$

where ΔP is the pressure change on mixing two gases at *identical* initial pressures, P_i, and volumes, V_i, and the B_{11} and B_{22} are *volume* second virial coefficients for the heavy and light components, respectively. If third virial coefficients are available for the pure components, a very small correction may be applied to the above expression for $\mathcal{E}$ to obtain a slightly better value. The cross term coefficient is obtained from eq 3 and the B_{11} and B_{22} values which have been reported in Table II.

Excess molar enthalpies, H^E, may also be obtained (*9*) from values of ϵ and their temperature derivatives at low pressures:

$$H^E = 2x_1x_2P\,(\mathcal{E} - T(d\mathcal{E}/dT)) \qquad (5)$$

where x_1 and x_2 are the mole fractions of the two components.

Experimental Section

Using the present apparatus, second virial coefficients have been measured for the pure fluoromethanes at 290, 300, and 310 K: the purities of the gases given by the manufacturer are listed in Table I. The results are listed in Table II and compared, where possible, with corresponding data extracted from the literature. We estimate the experimental errors in each value to be less than 1.5 $cm^3{\cdot}mol^{-1}$.

Excess virial coefficients were measured for methane and the fluoromethanes in binary systems with helium and argon, and interaction virial coefficients, B_{12}, were calculated using

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0021-9568/93/1738-0139$04.00/0

Table III. Excess Second Virial Coefficients, $\mathcal{E}$, and Corresponding Interaction Coefficients for Systems Containing Methane or a Fluoromethane[a]

T (K)	$\mathcal{E}$ (cm^3·mol^{-1})	B_{12} (cm^3·mol^{-1})	$\mathcal{E}$ (cm^3·mol^{-1})	B_{12} (cm^3·mol^{-1})
	He + CH_4		Ar + CH_4	
290	42.5	24.9	4.6	-27.9
300	39.3	23.1	5.0	-24.8
310	35.9	22.4	5.2	-21.2
	He + CH_3F		Ar + CH_3F	
290	129.5	25.2	78.6	-40.5
300	120.9	25.8	73.1	-35.6
310	111.8	27.3	68.4	-29.0
	He + CH_2F_2		Ar + CH_2F_2	
290*	181.9	30.0	126.5	-40.4
300*	170.4	29.9	116.6	-37.4
310*	158.5	32.0	106.6	-32.8
	He + CHF_3		Ar + CHF_3	
290	123.8	27.2	62.8	-43.3
300	116.8	28.5	63.3	-38.6
310	109.2	28.9	59.1	-34.0
	He + CF_4		Ar + CF_4	
290	71.6	28.5	20.0	-38.0
300	68.6	29.7	19.6	-32.9
310	65.1	29.6	19.2	-29.1

[a] In calculating the B_{12} values from eqs 3 and 4, our values of the pure components in Table II were used. All experiments were performed at approximately 152.0 kPa, except those designated with an asterisk which were performed at 96.0 kPa.

eq 3 and the B_{11} and B_{22} values in Table II; the experimental values of $\mathcal{E}$ and B_{12} are listed in Table III. We estimate the errors in the $\mathcal{E}$ values to be less than 1.0 cm^3·mol^{-1}; the errors in the values of B_{12} are larger because of the errors in B_{11} and B_{22}. We have reported previously (*4, 6*) data for CH_4 and CF_4 in mixtures with He and Ar; we believe the results in Table III are the most accurate even though the differences are rather small.

Table IV. Excess Molar Enthalpies of Mixing, H^E, at 300 K for Equimolar Mixtures

	H^E (J·mol^{-1})				
	CH_4	CH_3F	CH_2F_2	CHF_3	CF_4
P (kPa)	152.0	152.0	96.3	152.0	152.0
He	10.5	59.4	50.8	51.7	20.0
Ar	-1.1	34.8	40.5	30.8	24.0

Excess molar enthalpies of mixing were calculated using eq 5 and the data in Table III; we estimate the errors in each value of H^E to be approximately ±2 J·mol^{-1}.

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Received for review July 20, 1992. Accepted September 4, 1992. This research was supported in part by a grant from the Australian Research Council.