Second Virial Coefficients from Tabulated *P-V-T* Data

Results for $CClF_3$, CCl_2F_2, CCl_3F, and $B(OCH_3)_3$

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Values of the second virial coefficient derived from tabulated *P-V-T* data are reported here for methyl borate, $B(OCH_3)_3$; chlorotrifluoromethane, $CClF_3$; dichlorodifluoromethane, CCl_2F_2; and trichlorofluoromethane, CCl_3F. The method of calculation is illustrated with the methyl borate data.

THE UNIQUE relationship between the second virial coefficient and the potential energy of two-body interactions in the gas phase has made it a particularly useful tool in the understanding of physical properties from a fundamental point of view. In a study exploring possible relationships between potential function parameters and molecular structure, data for many structurally simple materials were sought, to be analyzed by a newly developed technique (*10*). However, some of the simplest materials—among them three fluorocarbon refrigerants, $CClF_3$, CCl_2F_2, and CCl_3F, and methyl borate—were initially absent from this compilation.

Although second virial coefficients were not to be found for the compounds, sources of tabulated *P-V-T* data were available with no attempt by the original investigators to derive virial coefficients from them.

DATA REDUCTION AND RESULTS

Upon rearrangement, the virial equation of state

$$Z = PV/RT = 1 + B(T)/V + C(T)/V^2 + \ldots\ldots \quad (1)$$

takes on the form

$$(Z-1)V = B(T) + C(T)/V + \ldots\ldots \quad (2)$$

A plot of Equation 2 as $(Z-1)V$ *vs.* $1/V$ becomes linear at low densities, with intercept $B(T)$ the second virial coefficient, and limiting slope $C(T)$ the third. The basic data reduction scheme follows for the raw data of methyl borate.

The compressibility of methyl borate was measured by Griskey *et al.* (*7*) at four temperatures between 225° and 300° C. over a pressure range of 30 to 200 atm. Virial coefficients were later determined from these data by Fok *et al.* (*5*). Unfortunately, their primary interest was the calculation of potential function parameters, and the second virial coefficients were reported only in the form of a small graph with reduced coordinates B^* and T^*.

In the present study, the second virial coefficients were redetermined from a fit of $(Z-1)V$ *vs.* $1/V$, using a linear regression routine (Figure 1). Data beyond 4.8 gram moles per liter were not included because of the significant curvature due to the influence of higher order virial coefficients at high densities. Also omitted, for statistical considerations, are the point at 6.37 gram moles per liter on the 225° C. isotherm, the point at 1.12 gram moles per liter on the 250° C. isotherm, and the points at 2.75 and 2.84 gram moles per liter on the 300° C. isotherm. The intercepts evaluated by fitting straight lines through the remaining points by the method of least squares appear as second virial coefficients (Table I). Percentage errors at the 95% confidence interval ranged from ±1% at 375° C. to ±5% at 300° C.

Also shown in Table I are similar results for the three halogenated methanes calculated from industrial publications (*1, 3, 4*) by the above technique. The same method of reducing the raw data to the form $(Z-1)V$ *vs.* $1/V$, plotting it, and fitting straight lines through the remaining good points by computer was followed here also. For the three halogenated materials, the fitting procedure resulted everywhere in smaller percentage errors than for methyl borate. More weight should be given to the data points for $CClF_3$ at 288.71° K. and above, and for CCl_2F_2 at 333.15° K. and above. Below these points, pressures of 5 atm. and below (where errors in the absolute pressure measurements become increasingly important) must be treated to stay below the saturation pressure at a given temperature. To avoid tabular values at such pressures

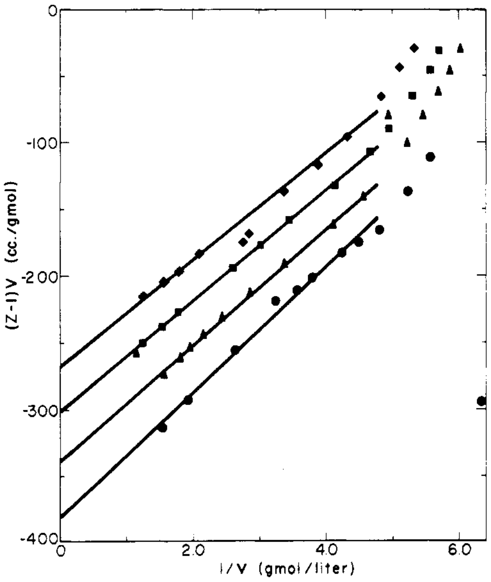

Figure 1. Methyl borate

$(Z-1)V$ *vs.* $1/V$

Data of Griskey *et al.* (*7*)

● 225° C.
▲ 250° C.
■ 275° C.
● 300° C.

—— Least squares line, calculated this work

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Table I. Calculated Second Virial Coefficients

Temp., °K.	*B*, Cc./G. Mole	Temp., °K.	*B*, Cc./G. Mole
$B(OCH_3)_3$		CCl_2F_2	
498.15	−380.7	477.59	−158.5
523.15	−338.8	466.48	−167.9
548.15	−301.3	455.37	−178.6
573.15	−267.3	444.26	−189.3
$CClF_3$		433.15	−200.9
		422.04	−213.4
533.15	−40.3	410.93	−227.0
522.04	−47.4	399.82	−242.0
510.93	−51.5	388.71	−258.3
499.82	−54.6	377.59	−276.3
488.71	−59.3	366.48	−295.8
477.59	−64.8	355.37	−317.7
466.48	−71.2	344.26	−342.3
455.37	−78.0	333.15	−370.3
444.26	−84.4	322.04	−401.8
433.15	−90.4	310.93	−437.9
422.04	−96.2	299.82	−479.3
410.93	−104.0	288.71	−527.3
399.82	−112.2	277.59	−583.7
388.71	−121.3	266.48	−648.7
377.59	−129.3	255.37	−725.0
366.48	−139.8	CCl_3F	
355.37	−152.0		
344.26	−162.6	477.59	−267.2
333.15	−171.0	472.04	−277.3
322.04	−183.5	466.48	−287.1
310.93	−202.8	460.93	−297.6
299.82	−219.8	455.37	−308.3
288.71	−238.6	449.82	−319.4
277.59	−261.2	444.26	−330.5
266.48	−288.2	438.71	−341.9
255.37	−321.3	433.15	−353.9
244.26	−355.1	427.59	−366.0
233.15	−393.8	422.04	−378.5
		416.48	−390.8
		410.93	−403.7
		405.37	−417.5

only values of the virial coefficient at the highest temperatures given in the data source have been calculated.

The final data are plotted in Figure 2 along with the analogous calculation made by Hirschfelder *et al.* (*9*) many years earlier. Results of both investigations are in excellent agreement for CCl_3F, deriving ultimately from the same source of P-V-T measurements. Newer tables were available for CCl_2F_2, and Hirschfelder's results, although apparently calculated correctly, are somewhat in error because of the original data. He states, "Of the Freons, CCl_2F_2—Freon 12—is the least accurate, since the temperature measurements were uncertain to 1°." The broken line on the graph is the extrapolation of the higher temperature values using the Lennard-Jones parameters which best reproduce the data at the upper temperatures and seems to fit in better with the other two materials. It comes closer to the triangles, but they still appear to be too low in magnitude. However, the new results appear to be consistent with one another and with the second virial coefficients of tetrafluoromethane (*2, 8, 11*) and carbon tetrachloride (*6, 12*) (not shown).

When used as inputs to the governing thermodynamic relationships, the second virial coefficient data reported here allow calculations for all of the materials of properties whose origins can be traced to vapor phase nonideality, and it is hoped that they will be of value for this purpose. Their significance in terms of the intermolecular potential is discussed elsewhere (*10*).

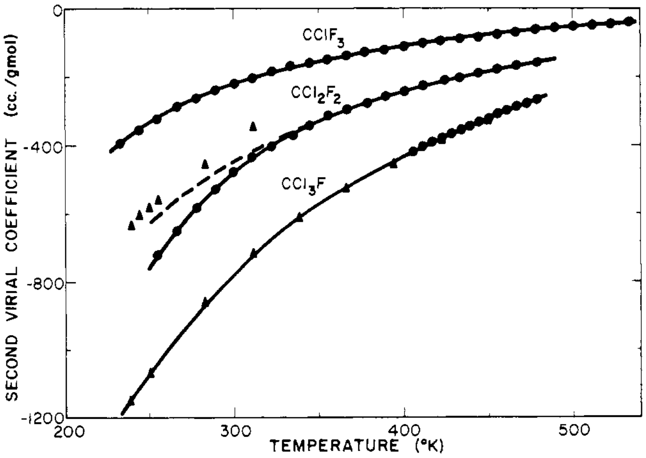

Figure 2. Second virial coefficient vs. temperature

$CClF_3$, CCl_2F_2, and CCl_3F

● This work, using tabulated data of (*1, 3, 4*)

▲ Hirschfelder *et al.* (*9*)

—— Best fit lines, this work

----- Extrapolation of high temperature data

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