

The Third Virial Coefficient of Ethane

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THE product pV/RT for a gas is frequently expressed by the power series

$$pV/RT = 1 + B(T)/V + C(T)/V^2 + \dots, \quad (1)$$

$$pV/RT = 1 + B'(T)p + C'(T)p^2 + \dots, \quad (2)$$

$B(T)$, $C(T)$, ... are customarily called the second, third, ... virial coefficients, and they are related to $B'(T)$, $C'(T)$, ... by the formulas

$$B(T) = B'(T)RT, \quad C(T) = [B'(T)^2 + C'(T)]R^2T^2, \dots \quad (3)$$

Bird, Spatz, and Hirschfelder¹ have calculated the third virial coefficient $C(T)$ for gases whose molecules interact according to a Lennard-Jones 12, 6 potential, and they have compared their theoretical figures with the experimental third virial coefficients for a number of gases. Among these experimental data were some values of $C(T)$ for ethane which Bird, Spatz, and Hirschfelder derived from the compressibility measurements of Michels and Nederbragt.² They were $C(273.16) = -37,300$, $C(298.16) = -72,100$, $C(323.16) = -30,900$ cm⁶ mole⁻². Both in their negative sign and in their large magnitude, these figures are in contrast to all the other experimental data and are in conflict with the theory of $C(T)$. We believe that they were based on a faulty analysis of the experimental results.

It would appear that, for ethane, Bird, Spatz, and Hirschfelder fitted pV/RT , by the method of least squares, with Eq. (2) (ending the series at $C'(T)p^2$) and then used the conversion (3) to find $C(T)$. We have applied this procedure to the same experimental data and found that it gives $C(T)$ in good agreement with

the figures quoted above. But at the same time we observed that the quadratic in p is a very bad fit of the experimental results when there are more than three points. The disagreement is much greater than the experimental inaccuracy and means that insufficient terms have been used and that the coefficients are therefore highly suspect. Fitting a limited pressure series for pV/RT is, in general, an unreliable way of calculating the virial coefficients unless the reduced temperature is high.

On the other hand, we have found that the expansion of pV/RT in powers of density [Eq. (1)] gives an excellent fit of Michels and Nederbragt's data, even when it stops at the term $C(T)/V^2$. The two expansions are compared in Table I. The coefficients in the

TABLE I. Experimental and fitted values of $1 - pV/RT$ for ethane at 25°C.

p (atmos)	0	10	20	30	40
Experimental ($1 - pV/RT$)	0	0.0809	0.1737	0.2882	0.4695
Quadratic in p ($1 - pV/RT$)	0	0.0705	0.1712	0.3020	0.4630
Quadratic in $1/V$ ($1 - pV/RT$)	0	0.0807	0.1736	0.2884	0.4695

density formula are $B(273.16) = -223$, $B(298.16) = -187$, $B(323.16) = -157$ cm³ mole⁻¹; $C(273.16) = +11,710$, $C(298.16) = +11,070$, $C(323.16) = +9660$ cm⁶ mole⁻². Both the second and third virial coefficients differ markedly from the values listed by Bird, Spatz, and Hirschfelder and both are in much better agreement with theory.

Further information on $C(T)$ for ethane is found in the measurements of Reamer, Olds, Sage, and Lacey.³ From an analysis of their compressibility factors as functions of the density we have derived the values given in Table II.

TABLE II. $C(T)$ for ethane from the measurements of Reamer, Olds, Sage, and Lacey.

$T^\circ\text{K}$	310.94	344.27	377.60	410.94	444.27	477.60	510.94
$C(T)$ (cm ⁶ mole ⁻²)	+9100	+8300	+7400	+6600	+6000	+5400	+4700

Finally, it is interesting to compare the two new sets of $C(T)$ with the theoretical third virial coefficients of Bird, Spatz, and Hirschfelder. This is done in the reduced plot of Fig. 1. The parameters b_0 and ϵ , associated with the intermolecular potential, were derived from some second virial coefficients which we had previously calculated⁴ from the results of Reamer, Olds, Sage, and Lacey. They are $b_0 = 123.8$ cm³ mole⁻¹, $\epsilon/k = 217.5^\circ\text{K}$. It is seen that ethane shows as good agreement as most gases with the theoretical plot and that the trend in the experimental points parallels the trend in the third virial coefficient of ethylene.¹

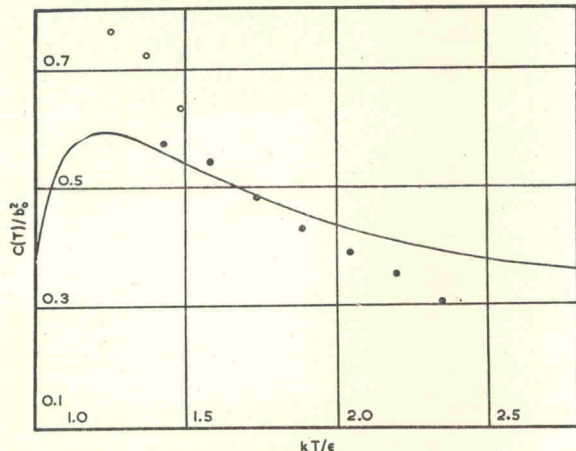


FIG. 1. The reduced third virial coefficient of ethane. The circles represent the data of Michels and Nederbragt; the dots are calculated from the results of Reamer, Olds, Sage, and Lacey. The curve is the theoretical one derived by Bird, Spatz, and Hirschfelder.

¹ Bird, Spatz, and Hirschfelder, *J. Chem. Phys.* **18**, 1395 (1950).

² A. Michels and G. W. Nederbragt, *Physica* **6**, 656 (1939).

³ Reamer, Olds, Sage, and Lacey, *Ind. Eng. Chem.* **36**, 956 (1944).

⁴ S. D. Hamann and W. J. McManamey (to be published).