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The Third Virial Coefficient for Non-Polar Gases

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The third virial coefficient for non-polar gases has been calculated with great accuracy by means of punched-card techniques. The Lennard-Jones potential, with inverse twelfth-power repulsion and inverse sixth-power attraction, was used in the calculations. Excellent agreement between our computations and those of Kihara was obtained at very high temperatures; in the moderate temperature region our calculations agree moderately well with those of Montroll and Mayer and those of de Boer and Michels. A comparison with experimental data indicates fairly good agreement for the approximately spherical molecules argon, methane, and nitrogen. In other cases there are discrepancies suggesting deviations from the form of the interaction energy which we assumed. There is considerable difficulty in obtaining accurate third virial coefficients from the equation of state data. A method is suggested whereby the third virial coefficients for mixtures of gases may be estimated. The functions which are tabulated should be particularly useful for extrapolating the equation of state to very high temperatures, where no experimental data are available. The zero-pressure derivative of the Joule-Thomson coefficient with respect to pressure provides additional means for comparing our tabulated functions with experimental data, and the deviations are consistent with those discovered by comparison of the third virial coefficients themselves.

A. CALCULATION OF THE THIRD VIRIAL COEFFICIENT FOR PURE GASES

THE third virial coefficient, $C(T)$, is the temperature-dependent coefficient of the V^{-2} term in the expansion of the compressibility:

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

By statistical mechanics[1] or the kinetic theory of gases[2] it is possible to show how $C(T)$ depends upon the intermolecular potential energy, $E(r)$. For our calculations we have used the Lennard-Jones potential:

$$E(r) = 4\epsilon[(r_0/r)^{12} - (r_0/r)^6] \quad (2)$$

in which ϵ is the maximum energy of attraction and r_0 is that value of the intermolecular separation, r, for which $E(r) = 0$. These parameters may be obtained from experimental second virial or transport coefficient data (see reference 4). A substantial justification for the use of Eq. (2) is the excellent agreement which is obtained between experimental values of the transport coefficients and those calculated no the basis of the Lennard-Jones potential.[3-8]

There have been in the past three evaluations of the third virial coefficient for the Lennard-Jones potential; the results of these calculations, as well as our own, are pictured in Fig. 1. de Boer and Michels,[2] using their expression for the third virial coefficient derived from the pair distribution function, performed a very careful graphical integration over that temperature range

where experimental data were available,—i.e., from $\tau = 1$ to $\tau = 4$ (τ is the reduced temperature obtained by dividing the temperature in °K by ϵ/k). Montroll and Mayer[9] performed a numerical integration over approximately the same range, using a form of the integral which involves rapidly oscillating integrands and does not seem to us to be particularly adaptable for numerical integration. Although the integrals used by de Boer and Michels can be shown to be mathe-
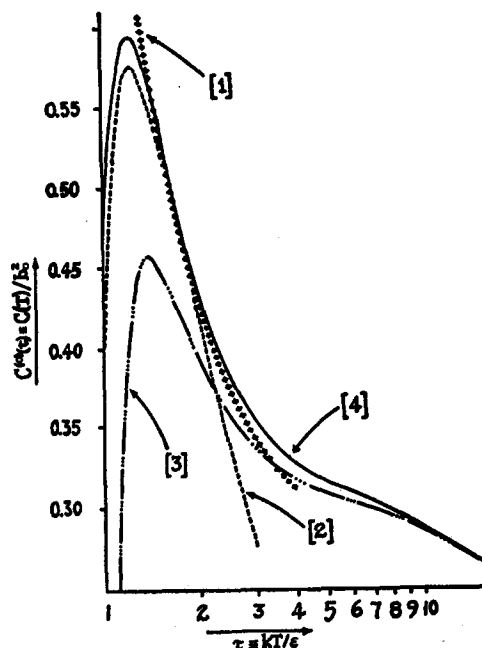

FIG. 1. Comparison of calculated curves of the third virial coefficient. (1) Calculation of de Boer and Michels from pair distribution function; (2) calculation of Montroll and Mayer from statistical mechanics; (3) calculation of Kihara using series expansion technique; and (4) punched-card calculations described in this work. Curves (3) and (4) agree almost exactly above $\tau = 10$.

[1] J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley and Sons, Inc., New York, 1940).
[2] J. de Boer and A. Michels, Physica 6, 97 (1939).
[3] Hirschfelder, Bird, and Spotz, J. Chem. Phys. 16, 968 (1948).
[4] Hirschfelder, Bird, and Spotz, Chem. Rev. 44, 205 (1949).
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[6] E. R. S. Winter, Trans. Faraday Soc. 46, 81 (1950).
[7] M. Kotani, Proc. Phys. Math. Soc. Japan, 24, 76 (1942).
[8] T. Kihara and M. Kotani, Proc. Phys. Math. Soc. Japan 25, 602 (1944).
[9] E. W. Montroll and J. E. Mayer, J. Chem. Phys. 9, 626 (1941).

TABLE I. A tabulation of the third virial coefficient and its derivatives for the Lennard-Jones potential.

$$\tau = kT/\epsilon \qquad b_0 = (2/3)\pi N r_0^3$$
$$C(T) = b_0^2 C^{(0)}(\tau)$$
$$C^{(1)}(\tau) = \tau[dC^{(0)}/d\tau] \quad C^{(2)}(\tau) = \tau^2[d^2C^{(0)}/d\tau^2]$$

(Note: Values of $C^{(0)}$ which are marked with an asterisk * were calculated by punched-card methods; intermediate values were obtained by interpolation. $C^{(1)}$ and $C^{(2)}$ were obtained by differentiation of the interpolating functions.)

τ	$C^{(0)}(\tau)$	$C^{(1)}(\tau)$	$C^{(2)}(\tau)$
0.70	−3.37664*	28.68	−220
0.75	−1.79197	18.05	−140
0.80	−0.84953	11.60	−92.1
0.85	−0.27657	7.561	−62.1
0.90	+0.07650	4.953	−42.7
0.95	0.29509	3.234	−29.8
1.00	0.42966*	2.078	−21.0
1.05	0.51080	1.292	−14.9
1.10	0.55762	0.7507	−10.6
1.15	0.58223	0.3760	−7.52
1.20	0.59240*	+0.1159	−5.29
1.25	0.59326	−0.0646	−3.66
1.30	0.58815	−0.1889	−2.46
1.35	0.57933	−0.2731	−1.57
1.40	0.56831*	−0.3288	−0.910
1.45	0.55611	−0.3641	−0.420
1.50	0.54339	−0.3845	−0.050
1.55	0.53059	−0.3943	+0.224
1.60	0.51803*	−0.3963	0.427
1.65	0.50587	−0.3929	0.572
1.70	0.49425	−0.3858	0.680
1.75	0.48320	−0.3759	0.755
1.80	0.47277	−0.3643	0.806
1.85	0.46296	−0.3516	0.837
1.90	0.45376	−0.3382	0.854
1.95	0.44515	−0.3245	0.859
2.00	0.43710*	−0.3109	0.856
2.10	0.42260	−0.2840	0.830
2.20	0.40999	−0.2588	0.794
2.30	0.39900	−0.2355	0.749
2.40	0.38943	−0.2142	0.700
2.50	0.38108*	−0.1950	0.651
2.60	0.37378	−0.1777	0.602
2.70	0.36737	−0.1621	0.557
2.80	0.36173	−0.1482	0.514
2.90	0.35675	−0.1358	0.473

TABLE I.—*Continued*.

τ	$C^{(0)}(\tau)$	$C^{(1)}(\tau)$	$C^{(2)}(\tau)$
3.00	0.35234*	−0.1247	0.439
3.10	0.34842	−0.1148	0.400
3.20	0.34491	−0.1060	0.369
3.30	0.34177	−0.09826	0.340
3.40	0.33894	−0.09133	0.313
3.50	0.33638	−0.08510	0.288
3.60	0.33407	−0.07963	0.266
3.70	0.33196	−0.07462	0.246
3.80	0.33002	−0.07024	0.277
3.90	0.32825	−0.06634	0.210
4.00	0.32662*	−0.06286	0.194
4.10	0.32510	−0.05989	0.183
4.20	0.32369	−0.05709	0.169
4.30	0.32238	−0.05458	0.156
4.40	0.32115	−0.05237	0.145
4.50	0.32000	−0.05040	0.134
4.60	0.31891	−0.04865	0.125
4.70	0.31788	−0.04712	0.116
4.80	0.31690	−0.04579	0.108
4.90	0.31596	−0.04461	0.100
5.0	0.31508*	−0.04359	0.0934
6.0	0.30771*	−0.03893	0.0449
7.0	0.30166	−0.03989	0.0258
8.0	0.29618*	−0.04231	0.0192
9.0	0.29103	−0.04529	0.0183
10.0	0.28610*	−0.04825	0.0199
20.0	0.24643*	−0.06437	0.0502
30.0	0.21954	−0.06753	0.0654
40.0	0.20012	−0.06714	0.0717
50.0	0.18529*	−0.06566	0.0742
60.0	0.17347	−0.06388	0.0750
70.0	0.16376	−0.06203	0.0748
80.0	0.15560	−0.06025	0.0741
90.0	0.14860	−0.05857	0.0732
100.0	0.14251*	−0.05700	0.0722
200.0	0.10679	−0.04599	0.0619
300.0	0.08943	−0.03970	0.0547
400.0	0.07862*	−0.03551	0.0496

matically equivalent,[10,11] their numerical results are somewhat different. A third calculation was performed by Kihara,[12] who employed a very clever series expansion technique, somewhat analogous to the method used by Lennard-Jones in his integration of the second virial coefficient; this interesting approach was called to our attention as the present work was being concluded. Kihara shows how the third virial coefficient may be written in the form:

$$C(T) = r_0^6 \sum_{j=0}^{\infty} K_j \tau^{-(j+1)/2}. \qquad (3)$$

The K_j are complicated double integrals which are

[10] R. B. Bird, Ph.D. thesis, University of Wisconsin (1950).
[11] R. B. Bird and E. L. Spotz, University of Wisconsin CM-599, Project NOrd 9938 (10 May 1950).
[12] T. Kihara, J. Phys. Soc. Japan, **3**, 265 (1948).

temperature-independent; however, for j-values beyond about $j=12$, the integrals admit analytic evaluation. Between $\tau=1$ and $\tau=4$, Kihara's results are not in agreement with the other calculations; this disagreement is probably due to the fact that the K_j were not evaluated with a high degree of accuracy. In the high temperature region (from $\tau=10$ to $\tau=100$), Kihara's equation gives values for $C(T)$ which agree almost perfectly with our punched-card calculations.

From statistical mechanics[1] it can be shown that the third virial coefficient, for gases composed of monotomic molecules with spherical potential fields, is given by the integral:

$$C(T) = -(1/3V) \int \cdots \int f_{12}f_{23}f_{31}d\omega_1 d\omega_2 d\omega_3 \qquad (4)$$

in which $f_{ij} = [\exp(-E(r_{ij})/kT) - 1]$, the r_{ij} represent the intermolecular distances in a cluster of three colliding molecules, and the $d\omega_i$ are the cartesian coordinates of the ith molecule. In the derivation of this ex-

pression the force between any two molecules is assumed to be independent of the location of the third molecule in the cluster. For the purpose of punched-card calculations, it was found convenient to transform the integral in Eq. (6) into the form:

$$C(T)/b_0^2 = C^{(0)}(\tau) = 18M(\tau) - 6[L(\tau)]^3 \qquad (5)$$

in which

$$b_0 = \tfrac{2}{3}\pi N r_0^3; \quad \tau = kT/\epsilon \qquad (6)$$

$$M(\tau) = \int_0^\infty \int_0^\infty g(\tau, z_1)g(\tau, z_2)Q[\tau, (z_1+z_2)]dz_1dz_2 \qquad (7)$$

$$Q(\tau, w) = \int_w^\infty g(\tau, z)dz \qquad (8)$$

$$L(\tau) = Q(\tau, 0) = \int_0^\infty g(\tau, z)dz \qquad (9)$$

$$g(\tau, z) = z[\exp(-E(z)/kT) - 1]. \qquad (10)$$

The integration variables, z_i, are the intermolecular distances expressed in units of r_0. The integration of $L(\tau)$ can be accomplished analytically:

$$L(\tau) = \sum_{j=0}^\infty (12j!)^{-1}\Gamma[(3j-1)/6](4/\tau)^{(3j+1)/6}. \qquad (11)$$

The summation converges quite rapidly, particularly at high temperatures, and can be evaluated by punched-card methods in several steps. No integration of the M-integral in closed form was discovered; hence, standard numerical cubature techniques were employed, the integrand being evaluated essentially at 10,000 points on the z_1z_2-plane for 17 values of the reduced temperature. The occurrence only of the functions g and Q and their symmetrical appearance in the M-integral made the form of the third virial coefficient given in Eq. (5) particularly well-suited for numerical integration by punched-card methods; in this work, IBM's 602-A (Calculating Punch) and auxiliary equipment were used. Details of the calculations have been given elsewhere.[10, 11]

In Table I are presented our values of the third virial coefficient and its temperature derivatives for over seventy values of the reduced temperature, τ, from $\tau = 0.7$ to $\tau = 400$. The functions tabulated are $C^{(0)}$, $C^{(1)}$, and $C^{(2)}$; $C^{(0)}$ was defined in Eq. (5), and $C^{(1)}$ and $C^{(2)}$ are defined by:

$$C^{(j)}(\tau) = \tau^j [d^j C^{(0)}/d\tau^j] \quad j = 1, 2. \qquad (12)$$

The mechanical accuracy of the $C^{(j)}$-functions is approximately: $C^{(0)}$, 1 part in 5000; $C^{(1)}$, 1 part in 1000; and $C^{(2)}$, 1 part in 500. The seventeen values of $C^{(0)}$ which were calculated by punched-card methods are marked with asterisks in Table I. The intermediate values of $C^{(0)}$ were obtained by interpolation. The

tables of $C^{(1)}$ and $C^{(2)}$ were then prepared by differentiating the interpolating functions.

B. COMPARISON OF CALCULATED AND EXPERIMENTAL THIRD VIRIAL COEFFICIENTS

A comparison of the calculated third virial coefficients with the experimental values of Michels and coworkers is given in Table II and summarized graphically in Fig. 2. The "experimental values" of $C(T)$ listed in Table II are obtained in the following manner: one fits the experimental values of pV/RT with a power series in $(1/V)$ like that shown in Eq. (1), using, however, only a finite number of terms in the curve fit; the coefficient of the $(1/V^2)$-term is then assumed to be the third virial coefficient. Different values of $C(T)$ are of course obtained when polynomials of different degrees are used to represent the compressibility; the degrees of the polynomial curve fits for the various gases are indicated in Table II.

Because of the sensitivity of the third virial coefficient to the assumed form of the potential, discrepancies between calculated and experimental results were expected. Fairly satisfactory agreement was found for the approximately spherical molecules argon, methane, and nitrogen; the calculated values of $C(T)$ for the cylindrical molecules carbon dioxide, ethylene, and ethane are in marked disagreement with the experimental values; also, for the light gases hydrogen, deuterium, and helium distinct discrepancies are observed. We shall now discuss more fully the gases studied, in decreasing order of goodness of agreement.

(a) Argon, Methane, and Nitrogen (Fairly Good Agreement)

For these gases reasonably satisfactory agreement between calculated and experimental results can be re-
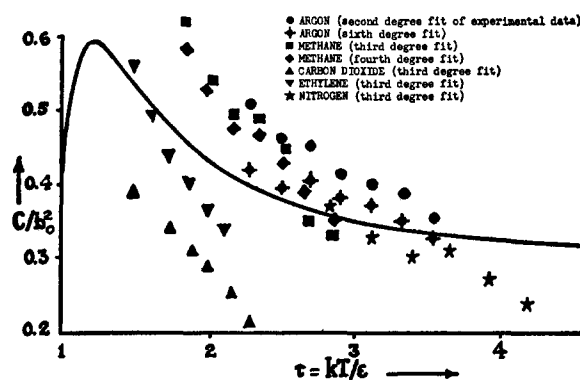

FIG. 2. Comparison of experimental third virial coefficients with values calculated from the Lennard-Jones potential. Reduced third virial coefficients are plotted against reduced temperatures, the basis for the reduction being the force constants, r_0 and ϵ/k, derived from experimental second virial coefficients. The solid curve represents the function $C^{(0)}(\tau)$ tabulated in Table I. The experimental points are represented by the symbols as shown in the legend on the figure. Not shown are the experimental points for ethane (which are large and negative) and those for hydrogen, deuterium and helium (which are available only for very high values of the reduced temperature).

TABLE II. Comparison of calculated and experimental second and third virial coefficients. The force constants used were obtained from experimental second virial coefficients. The number in parenthesis following B_{exp} and C_{exp} indicates the degree of the polynomial which was used to fit the experimental data. The units of the various quantities concerned are: $r_0(\text{A})$, $\epsilon/k(°\text{K})$, $b_0(\text{cm}^3/\text{mole})$, $B(T)(\text{cm}^3/\text{mole})$, and $C(T)(\text{cm}^6/\text{mole}^2)$.

Gas (Force Consts.)	$T(°\text{C}) \rightarrow$	0	25	50	75	100	125	150
Argon[a]	$B_{exp}(2)$	−21.45	−15.75	−11.24	−7.25	−4.00	−1.18	1.38
	$B_{exp}(6)$	−21.12	−15.48	−11.05	−7.14	−3.89	−1.08	1.42
$r_0 = 3.405$	B_{calc}	−21.49	−15.93	−11.16	−7.28	−3.98	−1.14	1.31
$b_0 = 49.804$								
$\epsilon/k = 119.75$	$C_{exp}(2)$	1270	1160	1130	1040	1000	970	880
	$C_{exp}(6)$	1050	990	1020	960	920	880	830
	C_{calc}	990	950	910	880	860	850	830
Methane[b]	$B_{exp}(3)$	−54.1	−43.4	−34.7	−27.9	−21.7	−16.1	−11.5
	$B_{exp}(4)$	−53.9	−43.3	−34.6	−27.7	−21.6	−16.4	−11.6
$r_0 = 3.817$	B_{calc}	−53.9	−43.4	−34.7	−27.5	−21.3	−16.1	−11.6
$b_0 = 70.16$								
$\epsilon/k = 148.2$	$C_{exp}(3)$	3050	2620	2430	2410	2230	1750	1660
	$C_{exp}(4)$	2870	2620	2370	2340	2140	2000	1770
	C_{calc}	2290	2140	2030	1940	1870	1810	1770
Nitrogen[a, d]	$B_{exp}(3)$	−10.3	−4.71	−0.28	3.20	6.56	9.45	12.3
	B_{calc}	−10.1	−4.71	−0.27	3.42	6.56	9.25	11.6
$r_0 = 3.698$								
$b_0 = 63.78$	$C_{exp}(3)$	1540	1320	1220	1260	1080	960	690
$\epsilon/k = 95.05$	C_{calc}	1460	1410	1380	1350	1330	1317	1300
Carbon dioxide[e, f]	$B_{exp}(3)$	−151.2	−123.6	−103.5	−86.7	−73.7	−62.2	−52.2
	B_{calc}	−147.3	−123.4	−104.1	−87.5	−74.1	−62.2	−52.1
$r_0 = 4.486$								
$b_0 = 113.9$	$C_{exp}(3)$	5610	4930	4930	4430	4150	3620	3050
$\epsilon/k = 189$	C_{calc}	7230	6790	6390	6020	5730	5470	5260
Ethylene[g]	$B_{exp}(3)$		−140.6	−118.1	−99.9	−85.1	−72.6	−62.1
	B_{calc}		−139.3	−118.1	−100.3	−85.4	−72.6	−61.7
$r_0 = 4.507$								
$b_0 = 115.5$	$C_{exp}(3)$		7640	6740	6000	5470	4990	4670
$\epsilon/k = 199.2$	C_{calc}		7260	6840	6450	6120	5830	5600
Hydrogen[*h]	$B_{exp}(2)$†	13.7	13.8	14.2	14.8	14.7	14.9	15.1
	$B_{exp}(2)$‡	13.8	14.1	14.6	14.9	15.2	15.4	15.6
$r_0 = 2.92$	$B_{exp}(3)$	13.5	13.6	13.9	14.1	14.5	14.3	14.5
$b_0 = 31.409$	B_{calc}**	13.6	14.2	14.7	15.1	15.3	15.4	15.5
$\epsilon/k = 36.77$								

ported. The experimental $C(T)$ values for argon and methane are somewhat higher than the calculated ones, while those for nitrogen are somewhat lower. For all three gases, the experimental points seem to exhibit a somewhat steeper slope than the calculated curve. This is also consistent with the disagreements between calculated and experimental Joule-Thomson coefficients, as will be discussed presently. This discrepancy is probably due to the incorrectness of the assumed form for the potential. If the experimental data were sufficiently accurate we could use the discrepancy as a function of the temperature to determine the correct shape of the potential. However, in the present case only qualitative conclusions can be formulated.[*, 13]

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* Kihara, see reference 12, has suggested that perhaps the potential function should have a slightly steeper repulsive region and that the "soup-bowl" part of the function (i.e., that portion of the curve representing negative potential energy of interaction) should be a little wider. He arrived at this conclusion because the experimental $C(T)$ curves seem to resemble more the shape of the $C(T)$ curve which one obtains for a square-well potential (reference 13)—which has an infinitely steep repulsion and a very wide "soup-bowl."

(b) Carbon Dioxide, Ethylene, and Ethane (Poor Agreement for Ellipsoidal Molecules)

Even in the second virial coefficient (which is relatively insensitive to the form of the potential), the ellipsoidal nature of molecules is evident, for the curvature of the observed $B(T)$ curve is somewhat different from that of the theoretical one (which is based on spherical molecules). Corner[14] has shown that the curvature of the theoretical curve may be made more nearly like the experimental one by using the Lennard-Jones potential, but essentially taking into account the fact that the force constants must be functions of the orientations of the pairs of colliding molecules. Thus, force constants obtained by fitting the experimental second virial data with the values of $B(T)$ obtained from the Lennard-Jones potential are really "average" force

However, the square-well potential is so far from reality that it is difficult to evaluate the strength of this argument.

13 T. Kihara, Nippon Sugaku-Buturigakukaisi 17, 11 (1943) (In Japanese).
14 J. Corner, Proc. Roy. Soc. A192, 275 (1948).

Table II.—*Continued*

Gas (Force Consts.)	$T(°C)\rightarrow$	0	25	50	75	100	125	150
	$C_{exp}(2)$†	(420)	(660)	(690)	(530)	(710)	(690)	(760)
	$C_{exp}(2)$‡	420	410	400	390	380	370	350
	$C_{exp}(3)$	(920)	(1160)	(1110)	(1420)	(960)	(1500)	(1410)
	C_{calc}**	300	290	290	290	280	280	280
Deuterium*ⁱ	$B_{exp}(2)$†	13.0	13.5	13.8	14.2	14.4	14.8	14.8
	$B_{exp}(2)$‡	13.2	13.8	14.2	14.7	14.9	15.1	15.4
$r_0=$ 2.92	$B_{exp}(3)$	13.0	13.2	12.9	13.2	13.6	13.9	14.2
$b_0=31.409$	B_{calc}**	13.0	13.7	14.2	14.6	14.9	15.0	15.2
$\epsilon/k=36.77$								
	$C_{exp}(2)$†	(710)	(780)	(800)	(820)	(830)	(850)	(870)
	$C_{exp}(2)$‡	390	390	380	370	360	360	350
	$C_{exp}(3)$	(2250)	(950)	(2140)	(2340)	(1900)	(1820)	(1730)
	C_{calc}**	300	290	290	290	280	280	280
Helium*ᵏ	$B_{exp}(3)$	11.9	11.7	11.6	11.4	11.3	11.2	11.1
	B_{calc}**	11.6	11.6	11.5	11.4	11.3	11.3	11.2
$r_0=$ 2.56								
$b_0=21.165$	$C_{exp}(3)$	76	72	72	95	91	94	110
$\epsilon/k=10.16$	C_{calc}**	102	99	97	94	93	90	89
Ethaneᵐ	$B_{exp}(2)$	−200	−135	−126				
	B_{calc}	−161	−138	−118				
$r_0=$ 3.954								
$b_0=$ 78	$C_{exp}(2)$	−37300	−72100	−30900				
$\epsilon/k=243$	C_{calc}	+3464	+3607	+3546				

* Force constants given by de Boer and Michels, Physica **5**, 945 (1938); these constants were obtained by taking into account quantum effects.
** Quantum effects were taken into account in the calculation of B but *not* for the calculation of C.
† Quadratic fit good in range from 9–31 amagat density units.
‡ Quadratic fit good in range from 9–132 amagat density units, probably the best fit for purposes of comparison with the calculated results.
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ᶜ Michels, Wouters, and de Boer, Physica, **1**, 587 (1934).
ᵈ Michels, Wouters, and de Boer, Physica **3**, 585 (1936).
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ᵏ A. Michels and H. Wouters, Physica **8**, 923 (1941).
ᵐ A. Michels and G. W. Nederbragt, Physica **6**, 656 (1939).

constants—averaged in the sense of two body collisions. Similarly fitting the experimental $C(T)$ values with the functions in Table I would give a set of "average" force constants—averaged in the sense of three-body collisions (we shall call these r_{0c} and ϵ_c/k). There is no reason why the two sets of average force constants should be the same. Figure 2 shows a comparison between calculated and experimental third virial coefficients based on the force constants, ϵ/k and r_0, determined from the experimental second virial coefficients. A simple translation of the experimental points upward and to the left would bring them into substantial agreement with the theoretical curve. This indicates that the ellipsoidal molecules at high pressures behave as though r_0 were slightly smaller and ϵ/k were slightly larger. Or, in other words, the third virial coefficient integral emphasizes three-molecule collisions in which the molecules are lined up with their long axes more or less parallel.

This tendency towards alignment has previously been discussed by Hirschfelder *et al.*,[15] who have pointed out that such a phenomenon explains why b_0 is anomalously large for ellipsoidal molecules. For many non-

polar, spherical molecules, $b_0 \doteq 0.68 V_c$[16,17] (V_c is the critical volume in the same units as b_0). For ellipsoidal molecules, however, the b_0 values obtained from second virial coefficient data are considerably larger than $0.68 V_c$; this is explainable, since in the critical state the ellipsoidal molecules are packed together like cigars while in the dilute gas the molecules sweep out spherical cavities the diameters of which correspond to the length of the long axis of the molecule.

Consequently in order to use Table I for making the second pressure correction to the equation of state for gases composed of ellipsoidal molecules, the set of force constants, r_{0c}, and ϵ_c/k should be employed. The values of these force constants (along with the values of the

TABLE III. Force constants from second and third virial coefficients for ellipsoidal molecules.

Gas	b_0/V_c	Force constants from second virial coefficients		Force constants from third virial coefficients	
		r_0	ϵ/k	r_{0c}	ϵ_c/k
Carbon dioxide	1.25	4.486	189	4.11	221
Ethylene	0.92	4.507	199.2	4.30	211

[15] Hirschfelder, McClure, Curtiss, and Osborne, NDRC Report No. A-116 (November 22, 1942).

[16] Buehler, Wentorf, Hirschfelder, and Curtiss, University of Wisconsin CM-565, Project NOrd 9938 (3 February 1950).
[17] J. E. Lennard-Jones and A. F. Devonshire, Proc. Roy. Soc. **A165**, 1 (1938).

TABLE IV. Tabulation of the function, $A(\tau)$, for estimating third virial coefficients for gaseous mixtures.

$$(C_{ijk})_{L.J.} = (C_{ijk})_{S.W.} A(\tau_{ij}) A(\tau_{jk}) A(\tau_{ik})$$

τ	$A(\tau)$	τ	$A(\tau)$
1.00	0.71099	3.50	0.86275
1.05	0.74603	3.60	0.86259
1.10	0.76746	3.70	0.86233
1.15	0.78196	3.80	0.86198
1.20	0.79246	3.90	0.86157
1.25	0.80047	4.00	0.86109
1.30	0.80684	4.10	0.86055
1.35	0.81206	4.20	0.85996
1.40	0.81649	4.30	0.85931
1.45	0.82032	4.40	0.85863
1.50	0.82369	4.50	0.85792
1.55	0.82671	4.60	0.85717
1.60	0.82947	4.70	0.85640
1.65	0.83199	4.80	0.85560
1.70	0.83432	4.90	0.85478
1.75	0.83648	5.00	0.85394
1.80	0.83851	6.00	0.84502
1.85	0.84041	7.00	0.83580
1.90	0.84219	8.00	0.82692
1.95	0.84388	9.00	0.81857
2.00	0.84545	10.0	0.81075
2.10	0.84834	20.00	0.75449
2.20	0.85091	30.0	0.71957
2.30	0.85315	40.0	0.69443
2.40	0.85510	50.0	0.67488
2.50	0.85678	60.0	0.65893
2.60	0.85823	70.0	0.64549
2.70	0.85944	80.0	0.63391
2.80	0.86043	90.0	0.62374
2.90	0.86123	100.0	0.61468
3.00	0.86185	200.0	0.55663
3.10	0.86231	300.0	0.52415
3.20	0.86261	400.0	0.50186
3.30	0.86278		
3.40	0.86283		

ratio b_0/V_c) for several ellipsoidal molecules are given in Table III. While these choices of force constants (r_{0c} and ϵ_c/k) are by no means unique, these values would probably be more proper for extrapolation to high temperatures than those obtained from the second virial coefficient.

It is interesting to note the negative values of the third virial coefficient of ethane as given in Table II. No other experimental data is known to the authors which substantiate the negative region of the theoretical $C(T)$ curve. The values for ethane correspond to third virial force constants which differ from the second virial ones in the same manner as in the case of CO_2 and other cigar-shaped molecules. Unfortunately there are not enough experimental data to determine r_{0c} and ϵ_c/k for ethane.

(c) Hydrogen, Deuterium, and Helium (Poor Agreement)

For these molecules it is known from the direct quantum-mechanical calculation of the interaction potential, that the energy of repulsion does not increase as rapidly with decreasing separation as would be indicated by our inverse twelfth power.[18-20] Furthermore, the quantum correction to the third virial coefficients may not be negligible for the temperature range under consideration. On these accounts the poor agreement with out calculations is not surprising.

In the case of hydrogen and deuterium there was considerable difficulty in obtaining the third virial coefficients from the raw experimental data. Different methods of fitting the experimental values led to values of $C(T)$ differing by several hundred percent. On this account the difference between the third virial coefficients of H_2 and D_2 cannot be used to determine the quantum corrections quantitatively; however, the third virial coefficient values for D_2 would seem to be roughly 10 percent smaller than for H_2 at 0°C and about equal to 150°C.

It is difficult to interpret the comparison for helium given in Table II. The experimental third virial coefficients have a distinct upward trend, while the calculated $C(T)$ values are monotone decreasing; the two sets of values are of very nearly the same order of magnitude. The unusually high values of the experimental third virial coefficients in the third-degree polynomial fit for the four highest temperatures may be related to the fact that the corresponding experimental fourth virial coefficients (as given by the series fit) are given as negative. According to Mayer[1] and Harrison[21] the fourth virial coefficient must be positive in this temperature region; the curve-fitting which produces a negative fourth virial coefficient would tend to distort the third virial coefficient values. Similar behavior has been noted in connection with the curve-fitting of the data for other gases.

C. THE THIRD VIRIAL COEFFICIENT FOR MIXTURES OF GASES

For a mixture of f components, the third virial coefficient is given by:[22]

$$C(T)_{\text{mixture}} = \sum_{u=1}^{f} \sum_{v=1}^{f} \sum_{w=1}^{f} C_{uvw}(T) x_u x_v x_w \qquad (13)$$

in which x_u is the mol fraction of the uth component. The functions $C_{uvw}(T)$ are third virial coefficients calculated on the basis of clusters of three colliding molecules, 1, 2, 3, of chemical species u, v, w respectively. The separation between molecules 1 and 2 is r_{12} and the potential energy of interaction between them is $E^{uv}(r_{12})$, the superscript "uv" indicating that the potential energy depends upon the chemical species of the molecules 1 and 2. Then if we define f_{12}^{uv} by the relation:

$$f_{12}^{uv} = \{\exp[-E^{uv}(r_{12})/kT] - 1\} \qquad (14)$$

[18] J. C. Slater, Phys. Rev. 32, 349 (1928).
[19] G. Gentile, Zeits. f. Physik 63, 795 (1930).
[20] J. de Boer, Physica 9, 363 (1942).
[21] S. C. F. Harrison, doctoral dissertation, Johns Hopkins University (1938).
[22] J. E. Mayer, J. Phys. Chem. 43, 71 (1939).

we can write, analogously to Eq. (4):

$$C_{uvw} = -(1/3V) \int \cdots \int f_{12}{}^{uv} f_{23}{}^{vw} f_{31}{}^{wu} d\omega_1 d\omega_2 d\omega_3. \quad (15)$$

The functions C_{uvw} are the same for any permutations of the indices and $C_{uuu}(T)$ is the third virial coefficient for the pure uth component.

Kihara[13] has shown that the functions C_{uvw} may be evaluated in closed analytical form for a three-constant "square-well" potential of the form:

$$
\begin{aligned}
E^{uv}(r_{12}) &= \infty && \text{for} && r_{12} < r_0{}^{uv} \\
E^{uv}(r_{12}) &= -d^{uv} && \text{for} && r_0{}^{uv} < r_{12} < R^{uv} r_0{}^{uv} \quad (16) \\
E^{uv}(r_{12}) &= 0 && \text{for} && R^{uv} r_0{}^{uv} < r_{12}
\end{aligned}
$$

in which the superscripts indicate force constants, d, r_0, and R, characteristic of the interaction between molecules of the uth and vth species. Using this potential energy function, C_{uvw} can be expressed by:

$$
\begin{aligned}
3C_{uvw} = I(0) &- [I(1.1)\Delta_{uv} + I(1.2)\Delta_{uw} + I(1.3)\Delta_{vw}] \\
&+ [I(2.1)\Delta_{uv}\Delta_{uw} + I(2.2)\Delta_{uv}\Delta_{vw} + I(2.3)\Delta_{uw}\Delta_{vw}] \\
&- [I(3)\Delta_{uv}\Delta_{uw}\Delta_{vw}] \quad (17)
\end{aligned}
$$

in which

$$\Delta_{uv} \doteq (\exp(d^{uv}/kT) - 1) \quad (18)$$

and

$$I(0) = W(r_0{}^{uv}, r_0{}^{uw}, r_0{}^{vw})$$

$$I(1.1) = W(R^{uv} r_0{}^{uv}, r_0{}^{uw}, r_0{}^{vw}) - I(0)$$

$$I(1.2) = W(r_0{}^{uv}, R^{uw} r_0{}^{uw}, r_0{}^{vw}) - I(0)$$

$$I(1.3) = W(r_0{}^{uv}, r_0{}^{uw}, R^{vw} r_0{}^{vw}) - I(0)$$

$$I(2.1) = W(R^{uv} r_0{}^{uv}, R^{uw} r_0{}^{uw}, r_0{}^{vw})$$
$$- [I(0) + I(1.1) + I(1.2)]$$

$$I(2.2) = W(R^{uv} r_0{}^{uv}, r_0{}^{uw}, R^{vw} r_0{}^{vw})$$
$$- [I(0) + I(1.1) + I(1.3)]$$

$$I(2.3) = W(r_0{}^{uv}, R^{uw} r_0{}^{uw}, R^{vw} r_0{}^{vw})$$
$$- [I(0) + I(1.2) + I(1.3)]$$

$$I(3) = W(R^{uv} r^{uv}, R^{uw} r^{uw}, R^{vw} r^{vw})$$

$$- \left[I(0) + \sum_{k=1}^{3} I(1, k) + \sum_{k=1}^{3} I(2, k) \right]. \quad (19)$$

The function, $W(a, b, c)$, which occurs in the formulas for the I's, is:

$$
W(a, b, c) = (\pi^2/18) \left[
\begin{aligned}
&a^6 + b^6 + c^6 + 18a^2 b^2 c^2 \\
&\qquad + 16(b^3 c^3 + c^3 a^3 + a^3 b^3) \\
&- 9\{ a^4(b^2 + c^2) + b^4(c^2 + a^2) \\
&\qquad\qquad + c^4(a^2 + b^2) \}
\end{aligned}
\right]
$$

when

$$a \leqslant b + c \quad (20)$$

$$W(a, b, c) = (16\pi^2/9) b^3 c^3 \quad \text{when} \quad a \geqslant b + c.$$

It would be very difficult to calculate exactly the C_{uvw} for the Lennard-Jones potential; however, they may be estimated, if we make use of the above results for the square-well potential. It is first necessary to modify the square-well potential so that it will contain only the two arbitrary parameters, $r_0{}^{uv}$ and ϵ^{uv}, which appear in the Lennard-Jones potential. This may be accomplished by letting $R^{uv} = 1.8$ and $d^{uv} = 0.56\epsilon^{uv}$; for this particular choice of constants, the second virial coefficients calculated on the basis of this two-constant square-well potential agrees over a remarkably wide temperature range with that calculated on the basis of the Lennard-Jones potential.[†,10,11,13,23]

Let us now define a function, $A(\tau)$, such that its cube is the ratio of $C(T)$ for a pure gas (the uth component) calculated for the Lennard-Jones potential to $C(T)$ calculated for the two-constant square-well potential:

$$(C_{uuu}(T))_{\text{L.J.}} = (C_{uuu}(T))_{\text{s.w.}} (A(\tau_u))^3 \quad (21)$$

in which τ_u is the reduced temperature for the uth component. As a result of the above discussion, it
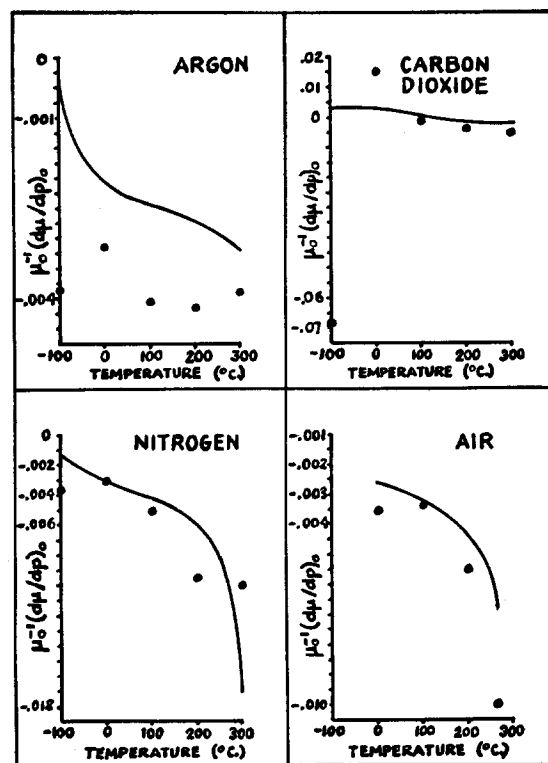

FIG. 3. Comparison of zero-pressure derivatives of the experimental Joule-Thomson versus pressure curves with calculated results. The solid lines represent the values of $\mu_0{}^{-1}(d\mu/dp)_0$ calculated from Eq. (23); the dots represent the corresponding experimental quantities.

† The second virial coefficient for a square-well potential is, (see reference 18),

$$B(T) = b_0[1 - (R^3 - 1)\Delta]$$

where b_0 is expressed in terms of the square-well r_0.

[23] Hirschfelder, Ewell, and Roebuck, J. Chem. Phys. 6, 205 (1938).

would seem fairly reasonable to write then for the "non-diagonal" terms, $(C_{uvw}(T))_{\text{L.J.}}$:

$$(C_{uvw}(T))_{\text{L.J.}} = (C_{uvw}(T))_{\text{S.W.}}(A(\tau_{uv})A(\tau_{uw})A(\tau_{vw})) \quad (22)$$

where the τ_{uv} are reduced temperatures referred to the force constants ϵ^{uv}/k, between pairs of dissimilar molecules; the A-function is slowly-varying in τ and is given in Table IV. The validity of the assumption of Eq. (22) cannot be justified until there are available good experimental data for the equation of state of mixtures of gases which contain reasonably spherical molecules.‡ [24,25] Meanwhile, Eq. (22) should provide a possible method for estimating the high temperature compressibilities for gaseous mixtures.

D. JOULE-THOMSON COEFFICIENTS

Joule-Thomson coefficients (μ) have been accurately measured as functions of pressure and temperature by Roebuck and his co-workers.[26-30] The zero pressure slope of the μ vs. pressure curve (i.e., $(d\mu/dp)_0$) is related to the first temperature derivative of the third virial coefficient in the following manner:

$$\mu_0^{-1}(d\mu/dp)_0 = (b_0/RT)(B^{(1)} - B^{(0)})^{-1}$$
$$\times \begin{bmatrix} C^{(1)} - 2C^{(0)} + 2(B^{(0)})^2 \\ -2B^{(0)}B^{(1)} + \mu_0 B^{(2)} R/b_0 \end{bmatrix}, \quad (23)$$

in which μ_0 is the zero-pressure Joule-Thomson coefficient and the functions $B^{(i)}(\tau)$ are the dimensionless derivatives of the second virial coefficient, defined (analogously to Eq. (12)) as:

$$B^{(0)}(\tau) = B(T)/b_0; \quad B^{(i)}(\tau) = \tau^i[d^i B^{(0)}/d\tau^i]. \quad (24)$$

Tables of the functions $B^{(i)}$ have been presented elsewhere.[10,11]

As an additional check with experiment, $\mu_0^{-1}(d\mu/dp)_0$ values from experiment and from Eq. (23) have been compared. This comparison is exhibited graphically in Fig. 3. For argon, the calculated curve is definitely higher than the experimental points; this corresponds to the fact that in this temperature region $C_{\text{calc}}^{(0)} < C_{\text{exp}}^{(0)}$ and $C_{\text{calc}}^{(1)} > C_{\text{exp}}^{(1)}$ (as can be seen in Fig. 2). The two effects are additive in producing an error in $\mu_0^{-1}(d\mu/dp)_0$. For carbon dioxide and nitrogen, however, $C_{\text{calc}}^{(0)} > C_{\text{exp}}^{(0)}$ and $C_{\text{calc}}^{(1)} > C_{\text{exp}}^{(1)}$, these two effects tend to cancel one another. And, indeed, for these gases the experimental points do not all fall below the calculated curve as they did for argon. It would thus seem that the discrepancies between calculated and experimental Joule-Thomson coefficients are reasonably consistent with the differences between calculated and observed third virial coefficients.

‡ The only data on gaseous mixtures which seemed sufficiently accurate for comparison with theoretical calculations were those on N_2-H_2 mixtures (see reference 19) and those on $CH_4-C_2H_6$ mixtures (see reference 20). However, pure H_2 does not give good agreement with the theory, and in the other mixture, the data for pure C_2H_6 are not sufficiently complete.

[24] R. Wiebe and V. L. Gaddy, J. Am. Chem. Soc. 60, 2300 (1938).
[25] A. Michels and G. W. Nederbragt, Physica 6, 656 (1939).
[26] J. R. Roebuck and H. Osterberg, Phys. Rev. 48, 450 (1935).
[27] J. R. Roebuck and H. Osterberg, Phys. Rev. 46, 785 (1934).
[28] Roebuck, Murrell, and Miller, J. Am. Chem. Soc. 64, 400 (1942).
[29] J. R. Roebuck, Proc. Am. Acad. 60, 537 (1925).
[30] J. R. Roebuck, Proc. Am. Acad. 64, 287 (1930).