PHYSICAL REVIEW A VOLUME 36, NUMBER 8 OCTOBER 15, 1987

Second viscosity and thermal-conductivity virial coefficients of gases: Extension to low reduced temperature

James C. Rainwater and Daniel G. Friend
Thermophysics Division, National Bureau of Standards, Boulder, Colorado 80303
(Received 13 April 1987)

A recent theory of the initial density dependences of both viscosity and thermal conductivity has been extended to include lower reduced temperatures. New data on the second viscosity virial coefficients of some organic vapors are found to be in substantial agreement with the theory even at the lowest temperatures. We present in tabular form the numerical values for both transport virial coefficients in the reduced temperature range $0.5 \leq T^* \leq 100$ and include values for the constituent two-monomer, three-monomer, and monomer-dimer contributions. A brief discussion of the theoretical approach and calculational methods is also given.

I. INTRODUCTION

We have recently developed a microscopically based theoretical model for the second transport virial coefficients of gases.[1,2] The second viscosity virial coefficient B_η is defined by

$$\eta = \eta_0(1 + B_\eta \rho + \cdots) , \tag{1}$$

where η is the viscosity, η_0 is the dilute gas or Chapman-Enskog limit of η, and ρ is the number density. The second thermal conductivity virial coefficient B_λ, where λ is thermal conductivity, is defined similarly. We demonstrated that, for a Lennard-Jones 12-6 potential, our model agrees well for both transport virial coefficients with experimental results in the region $T^* \geq 1$, where $T^* = k_B T/\varepsilon$, k_B is Boltzmann's constant, and ε is the intermolecular potential energy parameter.

More recently, Vogel, Bich, and Nimz[3] have determined B_η from their measurements of the viscosity of benzene and methanol vapors at $T^* < 1$. These data show that B_η becomes negative and rapidly decreases with decreasing temperature. They discuss our model in some detail and show graphically that our previous results, if extrapolated, would agree qualitatively with their data. However, they also emphasize that, in the absence of numerical values for B_η according to our model for $T^* < 1$, a quantitative comparison cannot be made.

Since our numerical results for B_η and B_λ were presented only in graphical form in Ref. 2, it is difficult at present for experimentalists to make quantitative comparisons with our model. This problem was noted in Refs. 4 and 5, as well as for the low reduced temperature measurements of Ref. 3. In order to facilitate such comparisons in the future, we present in this report a table of numerical results for the reduced transport virial coefficients as functions of T^*. Included in the table are new numerical calculations with the Lennard-Jones 12-6 potential for $0.5 \leq T^* \leq 0.9$. We also compare our model with the new viscosity data of Vogel *et al.*,[3] and find that the theoretical transport virial coefficients, as calculated with the Lennard-Jones potential, agree with experiment well within the limits that can be expected for polyatomic gases.

II. SUMMARY OF THEORY

We reduce the second transport virial coefficients according to $B_\eta^* = B_\eta/\sigma^3$ and $B_\lambda^* = B_\lambda/\sigma^3$ where σ is the intermolecular potential distance parameter, and subdivide the coefficients as

$$B_\eta^* = B_\eta^{(2)*} + B_\eta^{(3)*} + B_\eta^{(M-D)*} , \tag{2}$$

and similarly for B_λ^*. The terms in Eq. (2) represent a two-monomer contribution, a three-monomer contribution, obeying $B_\eta^{(3)*} = B_\lambda^{(3)*}$ in our model, and the monomer-dimer contribution.

The two-body terms were first derived by Snider and Curtiss.[6] Our primary theoretical contribution has been to revise these terms to ensure that integrations are performed only over free two-body phase space,[1] in part because bound and metastable contributions are expected to be included in $B_\mu^{(M-D)*}$, $\mu = \eta$ or λ.

Calculation of $B_\mu^{(2)*}$ involves two types of integrals. The first are similar to the $\Omega^{(l,s)*}$ integrals in the Chapman-Enskog theory of dilute gas transport properties.[7] However, in addition to integration over the energy and the impact parameter of a binary collision, these terms require a path integral over the interparticle distance along the collision trajectory.[1,8] The second are much simpler two-dimensional integrals to obtain the free part of the pressure second virial coefficient B and its temperature derivatives according to two different conventions, which are described in detail in Ref. 1.

Expressions for $B_\eta^{(2)*}$ and $B_\lambda^{(2)*}$ are given by Eqs. (88) and (89), respectively, of Ref. 1. These quantities are easily calculated algebraically with input from Tables I and II of Ref. 1, but, for convenience in comparisons with experimental work, their values are listed in Table I of this paper.

TABLE I. Second transport virial coefficients and their subdivisions according to Eq. (2).

T^*	$B_\eta^{(2)*}$	$B_\lambda^{(2)*}$	$B_\eta^{(M-D)*}$	$B_\lambda^{(M-D)*}$	$B_{\eta,\lambda}^{(3)*}$	B_η^*	B_λ^*
0.5	−3.148	−0.624	3.8093	34.411	−22.54	−21.88	11.25
0.6	−1.954	0.170	2.5181	20.917	−10.15	−9.586	10.94
0.7	−1.152	0.691	1.8530	14.307	−5.281	−4.580	9.716
0.8	−0.6035	1.038	1.4292	10.515	−3.023	−2.197	8.530
0.9	−0.1988	1.286	1.1847	8.169	−1.857	−0.871	7.598
1.0	0.0820	1.4519	1.0060	6.5755	−1.213	−0.125	6.814
1.2	0.4670	1.6674	0.7694	4.6043	−0.6191	0.617	5.653
1.5	0.7515	1.8032	0.5930	3.1008	−0.3642	0.980	4.540
2.0	0.9457	1.8634	0.4175	1.9332	−0.3519	1.011	3.445
3.0	1.0211	1.8224	0.2520	1.0350	−0.5018	0.771	2.356
4.0	1.0107	1.7559	0.1718	0.6715	−0.6109	0.572	1.817
5.0	0.9834	1.6941	0.1264	0.4814	−0.6801	0.430	1.495
8.0	0.8992	1.5606	0.0650	0.2408	−0.7736	0.191	1.028
30.0	0.6821	1.1909	0.0091	0.0338	−0.7782	−0.087	0.447
100.0	0.5149	0.9106	0.0015	0.0056	−0.6523	−0.136	0.264

The three-body terms were first derived by Hoffman and Curtiss,[9,10] and are unchanged in our model. They require an integral similar to the two-body terms described above, except that included in the integrand is the function $y_1(r)$, defined by

$$y(r)=g(r)e^{\phi(r)/k_BT}=1+\rho y_1(r)+O(\rho^2) \ , \tag{3}$$

where $\phi(r)$ is the potential and $g(r)$ is the radial distribution function. Calculation of $y_1(r)$ requires a separate two-dimensional numerical integration.[10,11]

Table I lists our numerical results for $B_\eta^{(3)*}=B_\lambda^{(3)*}$. The entries for $0.5\le T^*\le 0.9$ are new and make possible the comparison with the recent data of Vogel *et al.*[3] Hoffman and Curtiss,[10] and later Bennett and Curtiss,[12] have published results for five of the higher temperatures.

The monomer-dimer terms are due to Stogryn and Hirschfelder.[13–15] They depend on the free part of B according to a third convention[1] and the $\Omega^{(2,2)*}$ integrals of Chapman-Enskog theory.[7] The approximation is made that the effective monomer-dimer potential is also a Lennard-Jones 12-6, but with different length and energy scales.[14] Hence, there are two parameters, a ratio of length scales δ (monomer-dimer to monomer-monomer) and a similar ratio of energy scales θ. We have found[2] that agreement with both the viscosity and thermal conductivity data is optimized by the choice $\delta=1.02$, $\theta=1.15$. The numerical results with this choice for $B_\eta^{(M-D)*}$ and $B_\lambda^{(M-D)*}$ are listed in Table I.

The idea of restricting the two-body contribution to free two-body phase space, and then adding to the Snider-Curtiss and Hoffman-Curtiss terms the monomer-dimer contributions of Stogryn and Hirschfelder, was first proposed by Kuznetsov.[16] We have shown,[1] however, that Kuznetsov's replacement of certain terms in $B_\eta^{(2)*}$ by the free part of B as defined by Stogryn and Hirschfelder is not justified. Furthermore, although Kuznetsov did not examine thermal conductivity, we have shown[2] that B_λ, as predicted from Kuznetsov's hypotheses, would disagree with experiment at moderately low T^*.

III. NUMERICAL METHODS

We have put forth considerable effort to develop efficient and reliable computer codes for numerical evaluation of the generalized collision integrals appearing in $B_\eta^{(2)*}$, $B_\lambda^{(2)*}$, and $B_\eta^{(3)*}$. These codes are modeled after the dilute gas collision integral program of O'Hara and Smith,[17] which we have considerably extended to accommodate potentials with multiple extrema.[18] The quadrature used is due to Clenshaw and Curtis,[19] and its advantages over other quadratures, including a built-in error estimate, have been explained in detail elsewhere.[17,18]

The other important feature of the O'Hara-Smith program is its careful analysis of singularities in the integrals due to orbiting collisions, classical turning points, and infinite limits of integration. At no point in the computation are these singular regions excluded from the integration volume. Rather, transformations of the integration variables are made to remove or to suppress the singularities. These techniques have been carried over to the generalized collision integrals for the transport virial coefficients.

Techniques for calculating the two-body collision integrals and the subdivisions of B have been described previously.[1] The three-body collision integral has been calculated similarly, with additional features to include $y_1(r)$. We again used Clenshaw-Curtis quadrature to evaluate the integral expression for $y_1(r)$ and fit the function to a finite Chebyshev series,[17] since considerable computer time is saved when performing the collision integral by determining $y_1(r)$ from a fit. The polynomial fits and the analytic expressions[11] for small and large r were explicitly incorporated into the collision integral.

The numerical results may be checked in two ways, first by comparison with previous results and second by internal consistency checks. As for the former, two-body collision integrals were first evaluated numerically for the Lennard-Jones 12-6 potentials by Curtiss, McElroy, and Hoffman.[8] These authors used Gaussian and Gauss-Mehler quadratures, which, unlike Clenshaw-Curtis quadratures, do not possess an error estimate. Also, they specifically excluded sections of the integration volume near the singularities. For these reasons, we believe our numerical techniques are more reliable than theirs. In general, agreement between equivalent integrals[8,12,20] is better than 2%, with detailed numerical comparisons given in Tables V and VI of Ref. 1. Of course the final values of $B_\eta^{(2)*}$ and $B_\lambda^{(2)*}$ of Refs. 8, 12, and 20 differ substantially from ours (as given in Table I), differing in sign and order of magnitude for $B_\lambda^{(2)*}$ at the lowest temperature, because of our (self-consistent) treatment of the free portion of phase space in all expressions for collision integrals and pressure virial coefficients.

Three-body terms were first numerically evaluated by Hoffman and Curtiss,[10] and later by Bennett and Curtiss,[12] using similar methods at five reduced temperatures with $1 \leq T^* \leq 100$. As in our calculations, fits to $y_1(r)$ were used in the collision integrals, but these fits included substantially fewer terms than ours and disagreed in the $r \rightarrow 0$ and $r \rightarrow \infty$ limits.[11] Despite these differences, agreement between the results of Table I and those in Refs. 10 and 12 is better than 1% for these five temperatures.

Kuznetsov[16] has reported results at five additional temperatures above $T^*=1$, which disagree substantially with our values. For example, after correcting for differing reduction schemes, the difference is 47% at $T^*=1.5$. Because Kuznetsov does not indicate a source for these numbers, in contradistinction to the other values reported in Ref. 16, we feel that these disagreements do not cast doubt on the accuracy of our methods.

There are several internal consistency checks for our integration methods. For the two-body terms, rigorous relations have been derived[1,21] among the various definitions of the bound part of B. Also, identities have been found relating differences of certain two-body collision integrals and the various definitions of the free part of B and its temperature derivatives. Numerically, these relations are obeyed for $0.5 \leq T^* \leq 100$ within the accuracy input of the integration.[1,21]

For the three-body collision integrals, we have shown[22] that removal of $y_1(r)$ from the integrand yields a result proportional to the (tabulated[23]) $\Omega^{(2,2)*}$ integral. Also, five identities[11] involving integrals of $y_1(r)$, and the second and third pressure virial coefficients or their temperature derivatives, were checked by using numerical integration of the polynomial fits of $y_1(r)$ and tabulated values of virial coefficients.[7,23] In all cases, these internal checks were satisfactory.

IV. COMPARISON WITH EXPERIMENT

Figure 1 shows B_η^* and its two-body, three-body, and monomer-dimer parts as a function of reduced temperature. Also displayed are the data for benzene and methanol of Vogel *et al.*[3] and B_η^* according to the modified Enskog theory (MET) (Ref. 24) for the Lennard-Jones 12-6 potential.

The reduced temperature range can be divided into three regions. At high temperatures, $T^* \geq 10$, the monomer-dimer term is negligible because the population of dimers becomes very small. $B_\eta^{(2)*}$ and $B_\eta^{(3)*}$ are nearly equal in magnitude but are opposite in sign, so the full B_η^* is quite small. For $T^* \geq 20$, B_η^* is negative, in agreement with experimental data on helium[25] and our earlier conclusions for the inverse twelfth potential,[22] to which the Lennard-Jones 12-6 reduces in the high-temperature limit. Since, at these temperatures, the distinction between the free and full part of B is negligible, these results essentially coincide with those of Hoffman and Curtiss.[9,10]

At intermediate temperature, $1.5 \leq T^* \leq 10$, both the monomer-dimer contribution and the full contribution are much larger and increase smoothly with decreasing temperature. It is within this range that most experimental data have been reported.[2] While the turning points of both B_η^* and $\eta_0 B_\eta$ are located in this region, they are not easily observed because of the flatness of the curve and the large experimental uncertainties involved.

At low temperature, $T^* \leq 1.5$, both the two-body and three-body contributions rapidly decrease with decreasing temperature, whereas the monomer-dimer term increases at a lower rate. Hence, the full B_η^* goes negative and decreases rapidly with decreasing temperature, as shown.

The methanol data in Fig. 1 were reduced with the Lennard-Jones parameters $\sigma=0.3359$ nm and $\varepsilon/k_B=649.0$ K as reported by Vogel *et al.*[3] For benzene, Ref. 3 does not present an independently determined set of parameters, so we have adopted the values

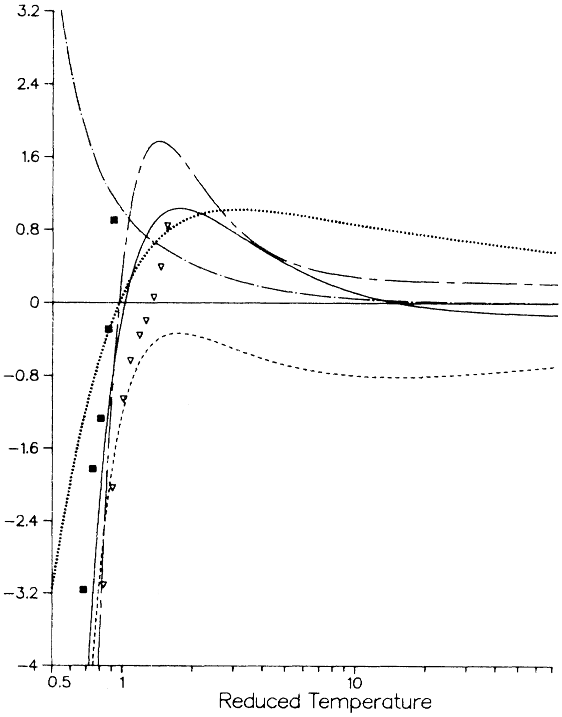

FIG. 1. Plots of the second viscosity virial coefficient B_η^*. ——, full theory; · · · ·, two-body contribution; — — —, three-monomer contribution; —·—·—·, monomer-dimer contribution; ————, modified Enskog theory; ■, data for methanol;[3] ∇, data for benzene.[3] Three additional points for methanol are outside the range of the figure; see Table II.

TABLE II. B^*_η for methanol below $T^*=0.65$. Data are from Ref. 3. For the last two columns, two-point linear extrapolation or interpolation from tabulated points was used.

T,K	T^*	B^*_η, Expt.	B^*_η, Theory	B^*_η, MET
323.15	0.498	−36.1	−22.1	−48.3
363.15	0.560	−12.5	−14.6	−31.4
403.15	0.621	−5.52	−8.52	−17.9

$\sigma=0.5455$ nm and $\varepsilon/k_B=401.2$ K, from Mourits and Rummens.[26] Our model curve passes between the experimental curves of benzene and methanol, and displays the same negative values and abrupt decrease with decreasing temperature. It is emphasized that the Lennard-Jones 12-6 potential is approximate even for monatomic gases, but is a particularly oversimplified potential for polyatomic molecules such as those of methanol or benzene. In view of this considerations, the agreement of Fig. 1 is as good as can be expected.

The MET (Ref. 24) is an *ad hoc* variant of Enskog's hard-sphere theory. It does not incorporate collision dynamics of particles interacting with realistic potentials. Rather, it starts with the Enskog theory based on hard-sphere collision dynamics, and adds the *ad hoc* replacement of a thermodynamic property (the thermal pressure) by that of a model fluid with a realistic potential, or the experimental fluid. Therefore, the MET is not microscopically based in the same sense that our model is.

In Fig. 1 the MET results for B^*_η are also shown, where the second and third pressure virial coefficients, required as input, are the theoretical values calculated from the Lennard-Jones 12-6 potential. The MET also shows negative rapidly decreasing results for B^*_η, although our model is generally closer to the data. For the three methanol points outside the range of Fig. 1 ($T^*<0.65$ and $B^*_\eta<-5.0$), Table II indicates that two are in much better agreement with our model than with the MET, whereas deviations for the third and lowest are about equal. The MET generally overestimates B^*_η in the intermediate temperature range and incorrectly predicts a positive result in the high-temperature limit, as we have shown for the inverse twelfth potential.[22] At low temperature, the MET predicts a decreasing thermal conductivity virial coefficient with decreasing temperature. This contrasts with our model and the available experimental evidence.[2]

V. DISCUSSION

Vogel *et al.*[3] include a thoughtful and informative critique of theories for density corrections to transport properties in general, and our model in particular. We are mostly in agreement both with their endorsements and caveats concerning our work. To their discussion we would like to add only a few further comments.

First, while ours is a microscopically based theory, we do not claim that it is strictly rigorous. The treatment of monomers and dimers is intuitively reasonable but clearly *ad hoc*. Ideally, we should start from a fundamentally derived set of coupled kinetic equations for reacting monomers and dimers along the lines of a formal theory such as that by Lowry and Snider.[27] Also, the three-body terms follow the approximation of Hoffman and Curtiss,[9,10] suggested first by Enskog's hard sphere theory,[7] that only binary collisions occur but the collision rate is changed by the presence of a third particle. A more rigorous theory would probably require integrals over true three-body collisions.

Therefore, the two parameters δ and θ, as optimized for our model, may not be the most physically meaningful choices. Stogryn and Hirschfelder,[14,15] using an approximate scheme for angular averaging, derived the values $\delta=1.16$ and $\theta=1.32$. Vogel *et al.*[3] correctly point out that $B_\eta^{(M-D)*}$ is extremely sensitive to simultaneous increases or decreases in δ and θ and that experimental evidence[28] suggests that $B_\eta^{(M-D)*}<0$. However, there is evidence that θ can be increased and δ decreased, or vice versa, such that $B_\eta^{(M-D)*}$ and $B_\lambda^{(M-D)*}$ remain essentially the same[29] so that our model in effect has one degree of freedom rather than two. Stogryn and Hirschfelder[15] used $\delta=1.04$ instead of their derived 1.16 to fit experimental data. Kim and Ross,[29] using a completely different formalism, chose the values $\delta=1.02$ and $\theta=1.23$.

Kuznetsov[16] used the derived values of Stogryn and Hirschfelder. However, as we have stated, his procedure is inconsistent with the phase-space structure of the second virial coefficient and the two-body collision integrals, as well as with low-temperature thermal conductivity data. In summary, there is ample precedent in the literature for treating δ and θ as adjustable parameters, and substantial disagreement over their optimal values.

In order to ascertain the best values of δ and θ to approximate monomer-dimer potentials realistically, further work is necessary. A more rigorous theory that includes explicit monomer and dimer kinetic equations and true three-body collisions could lead to a solution. Further experimental work, analogous to that of Ref. 28, which measures viscosity as a function of the degree of dimerization, would assist this effort, as would an explicit spectroscopic investigation of monomer-dimer potential functions and their spherical approximations. Regardless, our modification of the Snider-Curtiss-Hoffman and Stogryn-Hirschfelder theories has yielded a model which agrees well with density corrections to viscosity and thermal conductivity, and, at present, is the only theoretical model that can predict such density corrections over the complete experimental temperature range with reasonable confidence.

We hope that the numerical values in Table I will assist in making comparisons between experimental measurements of transport virial coefficients and the present theory. Such comparisons must be based on Lennard-Jones potential parameters, preferably derived from low-density viscosity data using the standard methods[7] and the reduction scheme of Eqs. (1) and (2). Experimental measurements of both viscosity and thermal conductivity along isotherms with a sufficient number of low-density points to resolve both slope and zero density limit would be useful in order to refine the theory further. Additional results for gases with spherical and nearly spherical constituents over the broadest possible temperature ranges and with accuracies better than 0.2% for viscosity and 0.5% for thermal conductivity are most important. The substantial agreement between the new low-temperature viscosity points of Ref. 3 and the theory increases our confidence in its utility for the prediction and correlation of transport virial coefficients.

---

[1] J. C. Rainwater, J. Chem. Phys. **81**, 495 (1984).

[2] D. G. Friend and J. C. Rainwater, Chem. Phys. Lett. **107**, 590 (1984).

[3] E. Vogel, E. Bich, and R. Nimz, Physica **139A**, 188 (1986).

[4] U. V. Mardolcar, C. A. Nieto de Castro, and W. A. Wakeham, Int. J. Thermophys. **7**, 259 (1986).

[5] M. Ross, R. Szczepanski, R. D. Trengove, and W. A. Wakeham, presented at the American Institute of Chemical Engineers Winter Meeting, Miami, 1986; M. Mustafa, M. Ross, R. D. Trengove, W. A. Wakeham, and M. Zalaf, Physica **141A**, 233 (1987).

[6] R. F. Snider and C. F. Curtiss, Phys. Fluids **1**, 122 (1958); **3**, 903 (1960).

[7] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954).

[8] C. F. Curtiss, M. B. McElroy, and D. K. Hoffman, Int. J. Eng. Sci. **3**, 269 (1965).

[9] D. K. Hoffman and C. F. Curtiss, Phys. Fluids **7**, 1887 (1964); **8**, 667 (1965).

[10] D. K. Hoffman and C. F. Curtiss, Phys. Fluids **8**, 890 (1965).

[11] D. G. Friend, J. Chem. Phys. **79**, 4553 (1983).

[12] D. E. Bennett and C. F. Curtiss, J. Chem. Phys. **51**, 2811 (1969).

[13] D. E. Stogryn and J. O. Hirschfelder, J. Chem. Phys. **31**, 1531 (1959).

[14] D. E. Stogryn and J. O. Hirschfelder, J. Chem. Phys. **31**, 1545 (1959).

[15] D. E. Stogryn and J. O. Hirschfelder, J. Chem. Phys. **33**, 942 (1960).

[16] V. M. Kuznetsov, High Temp. Res. **16**, 1005 (1979).

[17] H. O'Hara and F. J. Smith, J. Comput. Phys. **5**, 328 (1970).

[18] J. C. Rainwater, P. M. Holland, and L. Biolsi, J. Chem. Phys. **77**, 434 (1982).

[19] C. W. Clenshaw and A. R. Curtis, Numer. Mater. **2**, 197 (1960).

[20] R. D. Olmsted and C. F. Curtiss, J. Chem. Phys. **63**, 1966 (1975).

[21] D. G. Friend, J. Chem. Phys. **82**, 967 (1985).

[22] J. C. Rainwater, J. Chem. Phys. **74**, 4130 (1981).

[23] M. Klein, H. J. M. Hanley, F. J. Smith, and P. Holland, *Tables of Collision Integrals and Second Virial Coefficients for the (m,6,8) Intermolecular Potential Function,* Natl. Bur. Stand. (U.S.) Monogr. No. 47, Natl. Stand. Ref. Data System (U.S. GPO, Washington, D.C., 1974).

[24] H. J. M. Hanley, R. D. McCarty, and E. G. D. Cohen, Physica **60**, 322 (1972).

[25] J. Kestin and W. Leidenfrost, Physica **25**, 1033 (1959); G. P. Flynn, R. V. Hanks, N. A. Lemaire, and J. Ross, J. Chem. Phys. **38**, 154 (1963).

[26] F. M. Mourits and F. H. A. Rummens, Can. J. Chem. **55**, 3007 (1977).

[27] J. T. Lowry and R. F. Snider, J. Chem. Phys. **61**, 2320 (1974).

[28] D. L. Timrot, M. A. Serednitskaya and S. A. Traktueva, Teplofiz. Vys. Temp. **7**, 885 (1969).

[29] S. K. Kim and J. Ross, J. Chem. Phys. **42**, 263 (1965).