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The Viscosity of Nitrous Oxide and Tetrafluoromethane in the Limit of Zero Density

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New representations of the viscosity of nitrous oxide and tetrafluoromethane in the limit of zero density are provided. The representation for nitrous oxide extends over the temperature range 180 to 800 K, whereas that for tetrafluoromethane extends from 150 to 1100 K. The behavior of each gas is represented by an independent correlation of the appropriate effective cross section as a function of temperature. The final results are compared with experimental data as well as with representations based on a corresponding-states analysis.

KEY WORDS: effective collision cross section; nitrous oxide; polyatomic gas; tetrafluoromethane; transport properties; viscosity.

1. INTRODUCTION

The transport properties of gases in the limit of zero density provide the essential basis for the representation and prediction of these properties over a wider range of thermodynamic states. The viscosity plays an important role in this context for two reasons. First, it is known from the highly developed kinetic theory [1] that this quantity is practically independent of the existence of internal degrees of freedom and hence is nearly unaffected by inelastic collisions. Second, it has been shown that the knowledge of the viscosity (η_0) and the related effective cross section $\mathfrak{S}(2000)$ forms a basic prerequisite for kinetic theory analyses with respect to a complete set of effective cross sections for a variety of field-free transport properties [2, 3].

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It is the aim of this paper to extend earlier studies on the viscosity of polyatomic gases to nitrous oxide and tetrafluoromethane and to provide the background to a description of the thermal conductivity of these gases. The methodology of our correlations follows exactly that outlined in Ref. 4, which has been used to establish "individual" correlations for

the linear molecules—O_2 [4], N_2 (CO) [4, 5], CO_2 [6], and H_2 [7];
the spherical-top molecules—CH_4 [6], SF_6 [6, 8]; and
the near-linear molecule—C_2H_6 [9].

Here, we extend our studies to another linear molecule (N_2O) and a spherical-top molecule (CF_4).

A similar set of substances has been analyzed using a corresponding-states analysis [10, and references therein]. This complementary method has the advantage of a greater predictive power, but this is achieved at the expense of a modest loss in accuracy.

2. DATA SELECTION

As before, the first step in our analysis is the division of the entire set of published viscosity data into the categories of primary and secondary

Table I. Primary Experimental Data for the Viscosity of Nitrous Oxide and Tetrafluoromethane

Reference	Technique[a]	Temperature range (K)	Ascribed uncertainty (%)
	Nitrous oxide		
Kestin *et al.* [12]	OD	300–473	0.2–0.3
Kestin *et al.* [13]	OD	298–473	0.2–0.3
Harris *et al.* [14]	C	197–276	1.3–1.0
Clifford *et al.* [15]	C	372–773	1.5
Johnston *et al.* [16]	OD	185–300	3.0–2.0
	Tetrafluoromethane		
Hellemans *et al.* [17]	OD	298–873	0.2–0.5
Kestin *et al.* [18]	OD	296–477	0.2–0.3
Kestin *et al.* [19]	OD	296–673	0.2–0.4
Kestin *et al.* [20]	OD	298–668	0.2–0.4
Abe *et al.* [21]	OD	333–468	0.2–0.4
Dawe *et al.* [22]	C	293–873	0.5–1.0
Maitland *et al.* [23]	C	300–1100	0.5–1.1
Gough *et al.* [24]	C	150–320	1.5–0.7

[a] OD, oscillating disk; C, capillary.

data [4, 6, 7, 11]. Table I lists those data selected for inclusion in the primary data set [12–24] which comprise those employed for the development of the representation. The table includes an annotation of the experimental technique employed and our estimate of the uncertainty assigned to the data. With just two exceptions, the primary data for the viscosity of the two gases originate in two laboratories, that of Kestin and his collaborators [12, 13, 17–21] and that of Smith and his collaborators [14, 22–24]. For the instruments employed by both of these laboratories, there exist complete working equations, and the measurements on a wide range of other systems have proved mutually consistent and consistent with independent results derived from known intermolecular potentials [1]. The measurements of Clifford *et al.* [15] are based on the same technique as employed by Smith and his co-workers and enjoy a similar level of confidence. For N_2O, one other set of measurements, of poorer accuracy, performed by Johnston and McCloskey [16] have been included in the primary data set because, for other gases, their results are consistent with accepted values of proven reliability. In each case, the estimate of error assigned to the data has been made on the basis of the original authors' claims modified in the light of experience for other gases or repeated measurements of the same gas.

For N_2O the data of Raw *et al.* [25, 26] obtained with a capillary viscometer have been placed in the category of secondary data because their results, in common with many prior to 1970, show large systematic differences from accepted results for a number of gases. Similar comments apply to the data of Fisher [27], Trautz and Ruf [28], and Uchiyama [29]. For CF_4 the only data in addition to those listed in Table I are those reported by McCoubrey and Singh [30], which are considered to be in the category of secondary data because their results for other gases are all burdened with systematic errors.

3. METHODOLOGY

3.1. Primary Correlation

The viscosity of a pure gas in the limit of zero density may be written in the form

$$\eta_0 = \frac{kT}{\langle v_0 \rangle} \frac{1}{\mathfrak{S}(2000)} f_\eta \tag{1}$$

where

$$\langle v_0 \rangle = 4 \left(\frac{kT}{\pi m} \right)^{1/2} \tag{2}$$

$\mathfrak{S}(2000)$ is the effective cross section that includes all the information about binary molecular collisions, m is the molecular mass, and f_η is the temperature-dependent correction factor that accounts for higher-order terms of the kinetic theory [1]. The correction factor deviates by less than 1% from unity. In line with our previous work [4–9] it is convenient to rewrite Eq. (1) as[3]

$$\eta_0 = \frac{kT}{\langle v_0 \rangle} \frac{1}{\mathfrak{S}_\eta(2000)} \tag{3}$$

where $\mathfrak{S}_\eta(2000)$ incorporates the higher-order correction term. In a more practical form, this can be written

$$\eta_0 = \frac{0.021357(TM)^{1/2}}{\sigma^2 \mathfrak{S}_\eta^*(2000)} \tag{4}$$

where η_0 is in units of μPa · s, the scaling parameter for σ is in nm, M is the relative molecular mass, and $\mathfrak{S}_\eta^*(2000)$ is a reduced form of $\mathfrak{S}_\eta(2000)$ given by

$$\mathfrak{S}^*(2000) = \mathfrak{S}_\eta(2000)/\pi\sigma^2 \tag{5}$$

In developing the correlation of the experimental data for each gas, experimental values of $\mathfrak{S}_\eta(2000)$ are derived from each data source and then the complete set subject to a fit to the functional form

$$\ln \mathfrak{S}_\eta^*(2000) = \sum_{i=0}^{4} a_i (\ln T^*)^i \tag{6}$$

as a function of reduced temperature

$$T^* = kT/\varepsilon \tag{7}$$

in which ε is an energy-scaling parameter. In such a fit the parameters σ and ε are arbitrary but have been chosen for consistency to the those originating from a corresponding-states analysis of the viscosity [10]. In the same fitting procedure, the choice of the statistical weight of each datum is not arbitrary but has been determined by our estimate of the uncertainty in each point as described earlier [4].

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[3] In some papers collision integrals, e.g., Ω_η, are used in place of $\mathfrak{S}_\eta(2000)$. The two are related by the equation $\Omega_\eta = \frac{5}{4}\mathfrak{S}_\eta(2000)$. The values of the fundamental constants used to formulate Eq. (4) have been taken from a recent compilation [31].

4. RESULTS

4.1. Nitrous Oxide

The viscosity of nitrous oxide is represented by Eqs. (4)–(7) with the aid of the coefficients and parameters listed in Table II in the temperature range $180 \leqslant T \leqslant 800$ K. Figure 1 contains a plot of the deviations of the primary data from this representation, which indicates broad agreement except for one isolated point at the lowest temperature reported by Johnston and McCloskey [16] and the high-temperature measurements of Clifford *et al.* [15]. While both of these sets of data are consistent with the present representation within our estimate of their uncertainty, the nature of the deviations does indicate that at the extremes of temperature, it is prudent to be cautious in assigning an uncertainty bound to the representation. For this reason, we assign an uncertainty to the representation of $\pm 0.5\%$ in the temperature range $300 \leqslant T \leqslant 475$ K but increase it to $\pm 1.5\%$ at the temperature limits.

In the interests of brevity, for both N_2O and CF_4, we do not show comparisons with secondary data because such comparisons can be found elsewhere [10, 15] and the discrepancies lie far outside of the range of Figs. 1 and 2.

4.2. Tetrafluoromethane

The viscosity of tetrafluoromethane is represented by Eqs. (4)–(7) with the aid of the coefficients and parameters listed in Table II over the tem-

Table II. Coefficients and Parameters for the Representation of the Functionals for the Viscosity of Nitrous Oxide and Tetrafluoromethane

	$\mathfrak{S}^*_\eta(2000)$	
	Nitrous oxide, $180 \leqslant T \leqslant 800$ K	Tetrafluoromethane, $150 \leqslant T \leqslant 1100$ K
a_0	0.2451718	0.2157348
a_1	−0.5231444	−0.4072572
a_2	−0.1061631	−0.1202826
a_3	0.4694115	0.1894549
a_4	−0.2475927	−0.0508102
ε/k (K)	255.06	164.44
σ (nm)	0.3741	0.4543
M	44.0128	88.005

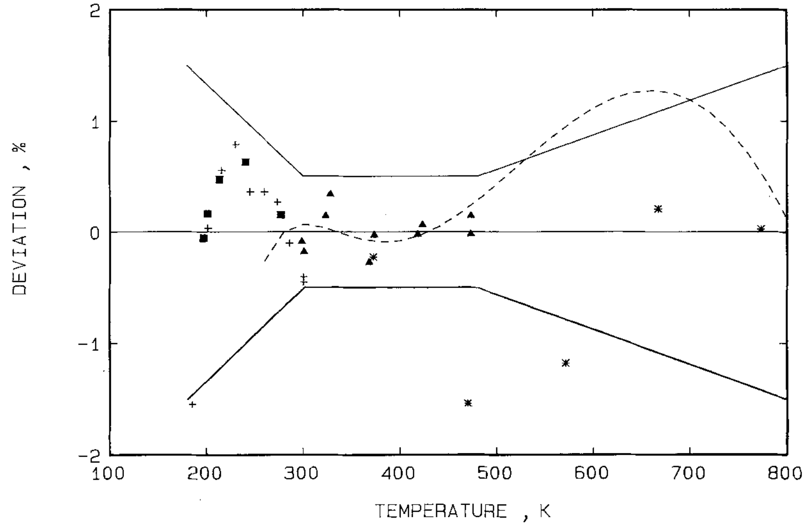

Fig. 1. Deviations of primary data for N_2O from the present correlation. The error estimates are indicated by solid lines. (▲) Kestin *et al.* [12, 13]. (■) Smith *et al.* [14]. (*) Clifford *et al.* [15]. (+) Johnston *et al.* [16]. (---) Universal correlation [10].

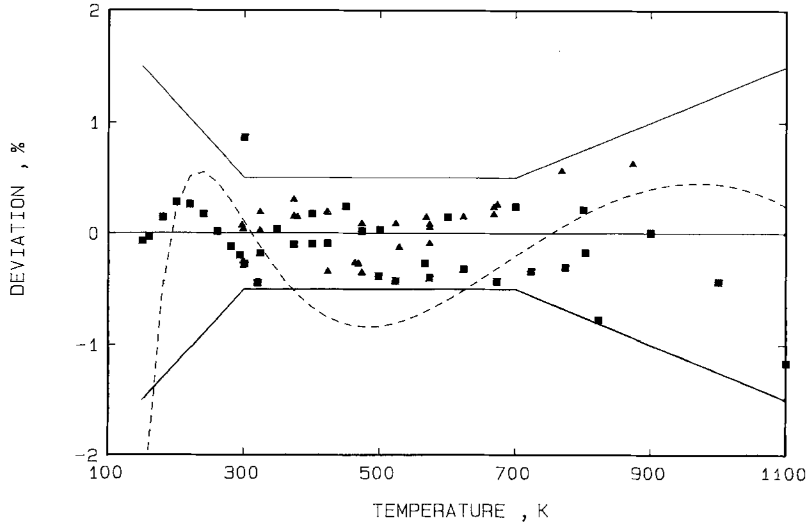

Fig. 2. Deviations of primary data for CF_4 from the present correlation. The error estimates are indicated by solid lines. (▲) Kestin *et al.* [17–21]. (■) Smith *et al.* [22–24]. (----) Universal correlation [10].

Table III. The Viscosity of Nitrous Oxide and Tetrafluoromethane at Selected Temperatures

Temperature (K)	Viscosity (10^{-6} Pa · s)	
	N_2O	CF_4
150	—	9.24
200	10.00	12.02
300	14.95	17.47
400	19.83	22.33
500	24.10	26.59
600	27.93	30.37
700	31.60	33.79
800	35.44	36.98
900	—	40.02
1000	—	42.98
1100	—	45.92

perature range $150 \leqslant T \leqslant 1100$ K. A plot of the deviations of the primary data for this representation is given in Fig. 2. There is again good agreement with all of the data although the accord diminishes at the extremes of temperature. It is estimated that the uncertainty associated with the present representation may be as much as $\pm 0.5\%$ in the temperature range $300 \leqslant T \leqslant 700$ K rising to $\pm 1.5\%$ at either extreme of the entire temperature range of experimental data.

Table III contains a brief listing of the viscosity of nitrous oxide and tetrafluoromethane at selected temperatures to enable users to check their coding of the present correlations.

5. DISCUSSION

An alternative means of describing the viscosity of gases in the limit of zero density makes use of the principle of corresponding states [1, 5, 10]. The attraction of this formulation is that in its simplest, two-parameter form, it makes possible the extension of experimental data available over a small temperature range to a wider range. However, for reduced temperatures, $T^* < 1.0$ or $T^* > 10$, more complicated forms are necessary to represent the experimental data [10] even for systems that are as simple as the monatomic gases. At the same time, the advantages of the two-parameter principle of corresponding states are offset by the modest loss of accuracy resulting from the requirement that $\mathfrak{S}_\eta^*(2000)$ be the same function of reduced temperature for all gases.

It is therefore interesting to assess the loss of accuracy incurred in this way, and to this end, Figs. 1 and 2 include a comparison with the representation of the viscosity of N_2O and CF_4 secured by a two-parameter corresponding states correlation [10, 32]. The comparison is confined to the reduced temperature range $1.0 < T^* < 10$ for which the two-parameter principle is expected to be valid.

In both cases, over most of the temperature range, the universal representation is consistent with the present results with the uncertainty ascribed to the latter. However, it is noteworthy that the behavior at low temperatures given by the corresponding-states representation is markedly different from that obtained here, although the magnitude of the discrepancy is not large. This particular behavior is analogous to that found for other gases [5, 8] and demonstrates that extrapolation of the corresponding-states representation to low temperature may lead to substantial errors. The extrapolation to higher temperatures seems more secure. The former behavior is most likely a result of the substantial difference in the reduced form of the long-range potentials of the two molecules studied here.

6. CONCLUSIONS

Correlations for the viscosity of nitrous oxide and tetrafluoromethane have been presented. These results provide the basis for a detailed analysis of several other transport properties and of related effective cross-sections for the same gases. For nitrous oxide the representation extends over the temperature range $180 \leqslant T \leqslant 800$ K and for tetrafluoromethane over the temperature range $150 \leqslant T \leqslant 1100$ K.

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REFERENCES

1. G. C. Maitland, M. Rigby, E. B. Smith, and W. A. Wakeham, *Intermolecular Forces: Their Origin and Determination* (Clarendon, Oxford, 1987).
2. J. Millat, V. Vesovic, and W. A. Wakeham, *Int. J. Thermophys.* **10**:805 (1989).

3. J. Millat and W. A. Wakeham, *Int. J. Thermophys.* **10**:983 (1989).
4. W. A. Cole and W. A. Wakeham, *J. Phys. Chem. Ref. Data* **14**:209 (1985).
5. E. Vogel, T. Strehlow, J. Millat, and W. A. Wakeham, *Z. Phys. Chem. Leipzig* **270**:1145 (1989).
6. R. D. Trengove and W. A. Wakeham, *J. Phys. Chem. Ref. Data* **16**:175 (1987); G. A. Olchowy, J. V. Sengers, V. Vesovic, W. A. Wakeham, J. T. R. Watson, and J. Millat, *J. Phys. Chem. Ref. Data* **19**:763 (1990).
7. M. J. Assael, S. Mixafendi, and W. A. Wakeham, *J. Phys. Chem. Ref. Data* **15**(4):1315 (1986).
8. T. Strehlow and E. Vogel, *Physica A* **161**:101 (1989).
9. J. Millat, V. Vesovic, and W. A. Wakeham, *J. Phys. Chem. Ref. Data* (in press).
10. A. Boushehri, J. Bzowski, J. Kestin, and E. A. Mason, *J. Phys. Chem. Ref. Data* **16**:445 (1987); Erratum, *J. Phys. Chem. Ref. Data* **17**:255 (1988).
11. H. J. M. Hanley, M. Klein, P. E. Liley, S. C. Saxena, G. Thodos, and H. J. White, *J. Heat Transfer* **93**:479 (1971).
12. J. Kestin and W. A. Wakeham, *Ber. Bunsenges. Phys. Chem.* **83**:573 (1979).
13. J. Kestin and W. A. Wakeham, *Ber. Bunsenges. Phys. Chem.* **86**:948 (1982).
14. E. J. Harris, G. C. Hope, D. W. Gough, and E. B. Smith, *J. Chem. Soc. Faraday Trans. I* **75**:997 (1981).
15. A. A. Clifford, P. Gray, and A. C. Scott, *J. Chem. Soc. Faraday Trans. I* **77**:997 (1981).
16. H. L. Johnson and K. E. McCloskey, *J. Phys. Chem.* **44**:1038 (1940).
17. J. M. Hellemans, J. Kestin, and S. T. Ro, *Physica* **65**:376 (1973).
18. J. Kestin, H. E. Khalifa, and W. A. Wakeham, *J. Chem. Phys.* **65**:5786 (1976).
19. J. Kestin, H. E. Khalifa, S. T. Ro, and W. A. Wakeham, *Physica* **88A**:242 (1977).
20. J. Kestin, H. E. Khalifa, and W. A. Wakeham, *J. Chem. Phys.* **67**:4254 (1977).
21. Y. Abe, J. Kestin, H. E. Khalifa, and W. A. Wakeham, *Ber. Bunsenges. Phys. Chem.* **83**:271 (1979).
22. R. A. Dawe, G. C. Maitland, M. Rigby, and E. B. Smith, *Trans. Faraday Soc.* **66**:1955 (1970).
23. G. C. Maitland and E. B. Smith, *J. Chem. Soc. Faraday Trans. I* **70**:1191 (1974).
24. D. W. Gough, G. P. Matthews, and E. B. Smith, *J. Chem. Soc. Faraday Trans. I* **72**:645 (1976).
25. C. J. G. Raw and C. P. Ellis, *J. Chem. Phys.* **28**:1198 (1958).
26. C. P. Ellis and C. J. G. Raw, *J. Chem. Phys.* **30**:574 (1959).
27. W. Fisher, *Phys. Rev.* **28**:73 (1909).
28. M. Trautz and F. Ruf, *Ann. Phys.* **20**:127 (1934).
29. H. Uchiyama, *Chem. Eng. Jpn.* **19**:342 (1965).
30. J. C. McCoubrey and N. M. Singh, *Trans. Faraday Soc.* **53**:877 (1957).
31. CODATA Bulletin, No. 63 (1986).
32. E. Bich, J. Millat, and E. Vogel, *Wiss. Z. WPU Rostock M-N-Reihe* **36**:5 (1987) (Publ. 1989).