

Transport Properties of Polyatomic Gases¹

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The paper reviews the current status of the study of the transport properties of polyatomic gases. The experimental techniques which have a proven record of accurate measurement of the viscosity, diffusion coefficient, and thermal conductivity are identified and the extent of available data is briefly discussed. Attention is concentrated upon the measurement of the thermal conductivity since it has proved to be the most difficult property to measure accurately and yet is of the greatest significance in industrial heat-transfer processes. The theoretical description of the transport properties of polyatomic gases is also considered, and the results of the first exact evaluation of the interaction viscosity of a model atom-rigid rotor system are reported. A comparison with the results of approximate, but simpler, calculation schemes reveals a good agreement at sufficiently high temperatures. In contrast, for the thermal conductivity, the same approximation schemes lead to a substantial difference between the calculated values and the experimental observation, even when the approximations are used to evaluate just one parameter. An empirical method of calculation of the same parameter is shown to lead to substantially improved predictions of the thermal conductivity.

KEY WORDS: intermolecular potentials; kinetic theory; polyatomic gases; thermal conductivity; transport properties; viscosity.

1. INTRODUCTION

The transport properties of gases possess two attributes which have encouraged their study over more than a century. On the one hand, these macroscopic properties are the consequences of collisional events on a microscopic scale and are, therefore, related to the forces between the

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molecules in the gas [1]. On the other hand, numerical values of the same properties are required for the design of process plant equipment, and in many cases, the accuracy of the values employed has significant economic consequences for plant construction and operation [2]. At the outset of the study of transport properties, the motivation was exclusively that of understanding the forces between molecules and their relationship to macroscopic properties. More recently, the emphasis has shifted to industrial needs for transport-property data as a response to increasing pressure for relevance in studies of thermophysical properties. However, there is now a fresh realization that it is impossible to satisfy the demands of industry for transport-property data based upon a program of measurements alone, because of the wide variety of conditions and materials encountered in practice. Furthermore, the entirely empirical approach to the prediction of the transport properties of fluids has become less attractive as the requirement for improved accuracy has grown. The consequence of these developments has been the fusion of the two motivations for the study of transport properties in coherent research programs. These programs concentrate upon the acquisition of a body of experimental data of a high accuracy over a modest range of conditions, its interpretation with the aid of fundamental statistical mechanical theory, and the application of the theory to the generation of a greater body of data.

The latter approach has reached its zenith in the work of J. Kestin and E. A. Mason, with their collaborators, on the extended corresponding states correlation of the dilute gas properties of the noble gases [3, 4]. However, the facts that polyatomic gases lack spherical symmetry and possess internal energy makes the problem of representing the properties of such systems more difficult, and, at present we are only a small way along the path towards the ideal representation. In this paper, guided by the experience gained with monatomic gases, the progress made with polyatomic species is reviewed, the problems that need to be addressed are identified, and suggestions for the directions of future effort are offered.

2. GENERAL FEATURES OF POLYATOMIC GASES

A partial list of the nonequilibrium properties of a gas is given in Table I, where the increased number of properties for a polyatomic gas is contrasted with that for a monatomic system. In the present paper we consider in detail the "traditional" transport coefficients of the gas referring to the other properties (such as those revealed in the presence of a magnetic field [1, 5]) only when they are necessary for a discussion of the primary subject matter. However, it is worthy of note here that the additional trans-

Table I. A Partial List of the Accessible Nonequilibrium Macroscopic Properties of a Dilute Gas

Property	Existence for		Direct measurement
	Monatomic	Polyatomic	
Shear viscosity, η	Yes	Yes	Yes
Thermal conductivity, λ	Yes	Yes	Yes
Diffusion coefficient, D	Yes	Yes	Yes
Bulk viscosity, κ	No	Yes	No, via ζ_{int}
Collision number, ζ_{int}	No	Yes	Yes
Internal-energy diffusion coefficient, D_{int}	No	Yes	No, via $\eta, \lambda, \zeta_{\text{int}}, c_{\text{int}}$
Thermal-conductivity tensor in magnetic field, $\lambda_{\parallel}, \lambda, \lambda_{\text{tr}}$	No	Yes	Yes
Viscosity tensor in a magnetic field, $\eta_0^+, \eta_1^+, \eta_2^+, \eta_1^-, \eta_2^-$	No	Yes	Yes

port properties for polyatomic gases owe their existence to the nonspherical nature of the intermolecular pair potential and that therefore, in principle, they provide specific probes of this aspect of the interaction. Thus, whereas the characterization of a nonspherical pair potential requires more information than for a spherical potential, there seems to be a number of possible sources of this extra information.

3. EXPERIMENTAL STUDIES

Beside the fact that polyatomic molecules are less thermally stable than monatomic species, there is essentially no difference between measurements of the transport coefficients of the two types of gases or gas mixtures. However, the lack of stability, exacerbated by the catalytic effects of some materials, means that the upper temperature limit for which accurate measurements are possible is frequently quite low. Furthermore, because of the low volatility of many polyatomic systems, the lowest temperature for practical studies is often quite high. Nevertheless, the complete range of techniques which have been employed to study the viscosity, thermal conductivity, diffusion coefficient, and thermal diffusion factor are immediately applicable to studies of polyatomic systems. At the same time, experience dictates that the technique selected should be of proven accuracy in order that the inevitable degradation which accompanies the

theoretically based extrapolation of the original data should not lead to unacceptably large uncertainties.

3.1. Viscosity

In the case of viscosity, there are only two types of instruments which may be classified as primary instruments, leading to results with an uncertainty of no more than $\pm 1\%$. The first is the group of oscillating-body viscometers developed by Kestin and his collaborators, of which the oscillating-disk instrument is the most familiar example [6]. The second is the capillary viscometer developed as a relative device by Smith and his co-workers [7] and the group at Los Alamos [8].

The oscillating-disk viscometer is characterized by a high precision and accuracy in measurement. This is because an exact working equation for the analysis of results is available and because all measurements of the characteristics of the oscillation are reduced to measurements of length and time. However, the instrument has not been employed for temperatures in excess of 1000 K owing to the degradation in the elastic properties of the suspension strand of the disk. In addition, no measurements of a high accuracy have been carried out with such instruments below room temperature. The long exposure of the gas to the high temperatures may also lead to significant decomposition for some substances unless the instrument is constructed entirely of quartz as in one recent design [9].

In contrast to the complexity of the oscillating-disk viscometer [6], the capillary viscometer employed by Smith and his collaborators is relatively simple to construct [7]. Again a complete working equation plus a set of corrections exists for this viscometer, and when employed in a relative manner the measurements required are reduced to that of time. Generally speaking, capillary viscometers yield results of a slightly inferior precision compared to those from oscillating-disk instruments but the short time which the gas spends in the working region of the viscometer allows much higher temperatures to be studied for polyatomic fluids. Furthermore, the instrument has been operated at cryogenic temperatures.

Taken together, these two type of instruments have provided a substantial body of high-quality data for the viscosity of polyatomic gases and gas mixtures. Figure 1 summarizes the accurate results which have been obtained thus far. It can be seen that the substantial gaps in the data which exist are for low-volatility organic compounds of higher molecular weight than butane around room temperature and for all except the simplest molecules at high and low temperatures. There is therefore evidently a need for further measurements to provide the missing information, although currently neither of the instruments discussed above is in operation.

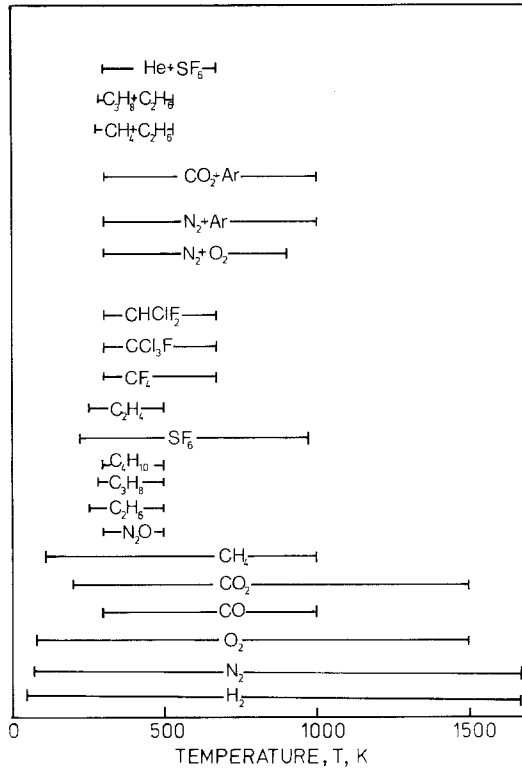


Fig. 1. A summary of the accurate viscosity data available for polyatomic gases.

3.2. Diffusion Coefficients

The diffusion coefficient of a binary gas mixture undoubtedly provides the most direct probe of the unlike interaction between molecular species of all the transport coefficients [1]. However, even in the case of monatomic species, there have been only a few measurements of a high quality, and only two sets have encompassed a significant temperature range [10, 11]. The essential reasons for this paucity of data are the time-consuming nature of the measurements and the need for careful thermostating of any diffusion cell. The preferred technique of measurement seems to be a refined two-bulb cell method and Dunlop and his collaborators in Adelaide [12] are now beginning to produce results for polyatomic systems over a range of temperature without loss of their high accuracy ($\pm 0.1\%$). The future of diffusion coefficient measurements is therefore encouraging, although the

time and effort required to achieve these high-quality results should not be underestimated.

3.3. The Thermal Diffusion Factor

Although it has long been recognized that thermal diffusion is the transport property most sensitive to the intermolecular pair potential, it has only occasionally proved to be possible to make measurements of a high accuracy over a range of temperatures [13], despite many attempts. The property itself is of little direct significance industrially, except in isotope separation, and so there is little incentive to pursue its measurement.

3.4. Thermal Conductivity

Together with the viscosity, the thermal conductivity is the most important transport property for industrial purposes since it enters the design of any equipment involving heat transfer. However, the measurement of this property has lagged far behind that for the viscosity and many of the available data are in substantial error. In the case of the monatomic gases, the lack of data is not serious because the thermal conductivity of such systems can be evaluated from the viscosity essentially directly [1]. However, in the case of polyatomic gases this route is not available so that the need for accurate measurements is reinforced. Furthermore, the fact that the thermal conductivity of polyatomic gases is not simply related to the viscosity means that the two properties yield complementary information about interactions in the gases rather than the identical information characteristic of monatomic gases.

In the last decade a considerable effort has been expended to improve the techniques for the measurement of the thermal conductivity of gases. Notwithstanding the existence of a small set of measurements made with steady-state techniques [14, 15], the modern version of the transient hot-wire method has emerged as the preferred technique for a wide range of conditions [16]. The principle of operations of this instrument is rather simple, and an essentially exact theory of it is available. Furthermore, following the development of solid-state devices, the measurement process itself became quite straightforward [17]. However, most of the development was completed around 1978, when it was demonstrated that an accuracy of $\pm 0.3\%$ was possible with the instrument [16, 18]. This result is confirmed in Fig. 2, which shows a plot of the experimental values of the reduced Eucken factor,

$$Eu = \frac{15R \eta_{ij}}{8M \lambda_{ij} f(T)} \left(\frac{M_i + M_j}{M_i M_j} \right) \quad (1)$$

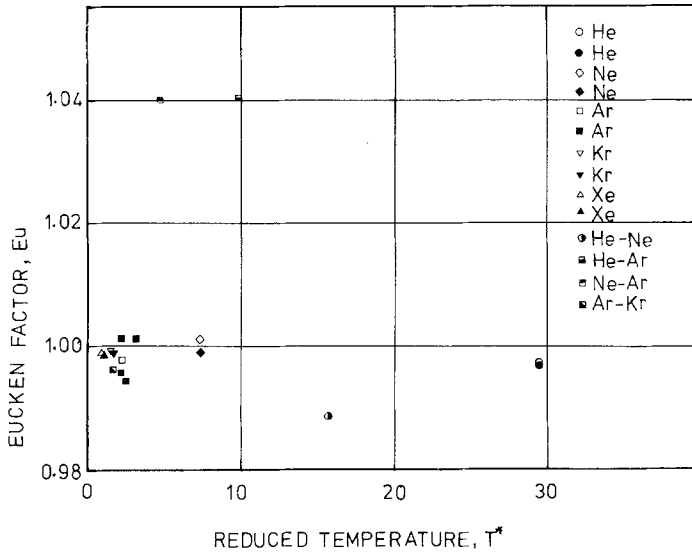


Fig. 2. The reduced Eucken factor for the monatomic gases and their mixtures.

for the monatomic gases and some of their mixtures, which according to the kinetic theory, should be identically unity. Only for the mixtures, for which the uncertainty in the interaction quantities η_{ij} and λ_{ij} derived from mixture property measurements is quite large, is the deviation from unity greater than the estimated uncertainty in the direct property measurements. Since 1975 almost all measurements with the same high accuracy have been confined to room temperature because of practical difficulties discussed in detail elsewhere together with their resolution [19]. Here, it suffices to record that we are only now in a position, after 15 years of work, to begin routine, high-precision measurements of the thermal conductivity of polyatomic gases over a wide range of temperatures.

4. KINETIC THEORY

The additional features of polyatomic gases referred to earlier have necessitated the development of a kinetic theory beyond that provided by Boltzmann, Chapman, and Enskog for monatomic gases [1, 5]. In fact, there exist three kinetic theories for polyatomic gases: the classical theory of Taxman [20], the semiclassical theory of Wang Chang and Uhlenbeck [21], and the quantum mechanical theory of Waldmann and Snider [22, 23]. The most commonly employed for the usual transport coefficients

is the semiclassical theory because its results are rather simpler than those of the full quantum theory. Although this theory cannot account for all the behavior of real polyatomic gases, specifically the Senftleben-Beenakker effects [5], it can be corrected using the results of quantum theory to provide a useful set of equations for the viscosity, thermal conductivity, and diffusion coefficient of such systems [1].

The collision dynamics of polyatomic gas molecules are considerably more complicated than those for monatomic species. The complications are such that the exact evaluation of any of the transport coefficients of a polyatomic gas for an assumed pair potential has so far proved beyond the capabilities of even the fastest digital computers. If we consider just the viscosity of a pure polyatomic gas the Wang Chang and Uhlenbeck kinetic theory leads to the result that to a first-order approximation,

$$[\eta]_1 = \frac{kT}{\langle V \rangle_0} \frac{1}{\Xi(2000)} \quad (2)$$

where $\Xi(2000)$ is an effective cross section.

The essential dynamical information about the system is contained in a quantity $\sigma_{ij}^{kl}(g, \chi, \psi)$, which is the differential scattering cross section for a pair of molecules in quantum states i and j initially, which end up in states k and l . The evaluation of $\Xi(2000)$ requires the summation of σ_{ij}^{kl} over all quantum states and its integration over g , the relative speed of the two molecules initially, as well as χ and ψ , the polar angles, defining the resulting trajectory. It is the evaluation of σ_{ij}^{kl} which has proved the stumbling block to direct and exact calculation of transport properties, and there seems no immediate prospect that the difficulty will be overcome. Progress will therefore rely on the development of approximate methods of evaluating the differential scattering cross section and the transport coefficients. The most widely used of the existing approximation schemes for transport properties is that proposed ad hoc by Mason and Monchick [24, 25] and subsequently justified by means of the infinite-order sudden approximation of scattering theory [26]. In this approximation, the viscosity is given by

$$[\eta]_1 = \frac{5}{16} \frac{(mkT)^{1/2}}{\langle \bar{\Omega}^{(2,2)}(\boldsymbol{\omega}, T) \rangle} \quad (3)$$

where $\bar{\Omega}^{(2,2)}(\boldsymbol{\omega}, T)$ is the familiar collision integral of monatomic gas kinetic theory [1] for elastic collisions at a fixed relative $\boldsymbol{\omega}$ of the two molecules, and the angle brackets indicate an equally weighted average over all orientations. This result means that the evaluation of the viscosity is only

slightly more time-consuming for polyatomic gases than for monatomic gases. However, the accuracy of the resulting equation has been unknown.

In order to establish the accuracy of the approximation, exact calculations of the viscosity and diffusion coefficient have just been completed [27] for a model of the system helium–nitrogen [28], which is the most complicated that can be attempted on the fastest computers currently available. The calculations employ a close-coupled evaluation of the scattering cross section [1]. The results are contained in Table II for a number of temperatures, where they are compared with the results of classical calculations of the same quantities for the same potential model and values deduced by applying the Mason–Monchick approximation. At the lowest temperatures for which the calculations have presently been analyzed, there is a discrepancy of as much as 8% between the close-coupled result for the diffusion coefficient and that obtained from the Mason–Monchick approximation. As the temperature is increased the differences between the Mason–Monchick results and the others decrease but remain significant. For the interaction viscosity the agreement between the Mason–Monchick approximation results and the more exact calculations is always better and often good enough for most purposes. The implication of these results is that whereas the Mason–Monchick approximation may be adequate for viscosity, it is certainly not sufficiently accurate for diffusion coefficients or, presumably, for quantities more sensitive to inelasticity.

Table II. A Comparison of the Evaluation of the Transport Coefficients of the He–N₂ Interaction by Various Methods^a

<i>T</i> (K)	Viscosity η_{12} ($\mu\text{Pa} \cdot \text{s}$)			Diffusion coefficient $10^5 D_{12}$ ($\text{m}^2 \cdot \text{s}^{-1}$)		
	CC	MM	CT	CC	MM	CT
70	5.463	5.280	—	0.610	0.570	—
77.3	5.881	5.716	5.770	0.727	0.684	0.718
90	6.580	6.429	—	0.947	0.892	—
100	7.09	6.959	6.99	1.135	1.078	1.126
110	7.58	7.456	—	1.337	1.273	—
120	8.06	7.947	—	1.550	1.481	—
130	8.51	8.422	—	—	—	—
140	8.95	8.870	—	—	—	—
150	9.38	9.312	9.31	—	—	—

^a CC, Close-coupled calculation; MM, Mason–Monchick approximation; CT, classical trajectory calculation.

A second indirect test of the Mason–Monchick approximation is afforded by the limited set of accurate thermal-conductivity data for polyatomic gases in conjunction with viscosities for the same systems. The Wang Chang–Uhlenbeck kinetic theory leads to the following relationship between the viscosity and the thermal conductivity of a polyatomic gas, suitably corrected for the effects of spin polarization [1],

$$\frac{[\lambda]_1}{[\eta]_1} = \frac{5k}{2m} \left(\frac{3}{2} - A \right) + \frac{k\rho D_{\text{int}}}{[\eta]_1} \left(\frac{c_{\text{int}}}{k} \right) (1 - \delta) \quad (4)$$

where

$$A = \left(\frac{2c_{\text{int}}}{k\pi\zeta_{\text{int}}} \right) \left[\frac{5}{2} - \frac{\rho D_{\text{int}}}{[\eta]_1} \right] \left[1 + \frac{2}{\pi\zeta_{\text{int}}} \left(\frac{5c_{\text{int}}}{3k} + \frac{\rho D_{\text{int}}}{[\eta]_1} \right) \right]^{-1} \quad (5)$$

and

$$\delta = \frac{5}{3} \left[1 + \frac{[\lambda_{\text{tr}}]_1}{[\lambda_{\text{int}}]_1} \right] \left(\frac{\Delta\lambda_{\parallel}}{\lambda} \right)_{\text{sat}} \quad (6)$$

In these expressions c_{int} is the internal heat capacity of the gas per molecule, ζ_{int} is the internal-energy collision number, $(\Delta\lambda_{\parallel}/\lambda)_{\text{sat}}$ is the relative change in the thermal conductivity of a gas parallel to an applied magnetic field at saturation, and D_{int} is the so-called diffusion coefficient of internal energy [1]—essentially a further transport coefficient of polyatomic gases (Table I).

For many gases all of the quantities which enter on the right-hand side of Eq. (4) are obtainable from independent experiment with the exception of D_{int} . Consequently, we can assess the validity of the Mason–Monchick approximation by using it to evaluate D_{int} and, subsequently, a predicted value of $[\lambda]_1/[\eta]_1$ for each gas. For this purpose we use the result that within the Mason–Monchick approximation

$$\frac{\rho D_{\text{int}}}{[\eta]_1} = \frac{\rho[D]_1}{[\eta]_1} = \frac{6}{5} A^* \quad (7)$$

where D is the self-diffusion coefficient of the gas and A^* a calculable ratio of collision integrals [1]. The value of $[\lambda]_1/[\eta]_1$ calculated on this basis is compared with the experimental ratio λ/η in Fig. 3. It can be seen that for some gases, specifically those in which inelastic collisions are rare, such as hydrogen and methane, the agreement is good. In contrast, for other systems such as ethane, ethylene, and nitrogen, the discrepancy amounts to as much as 15%.

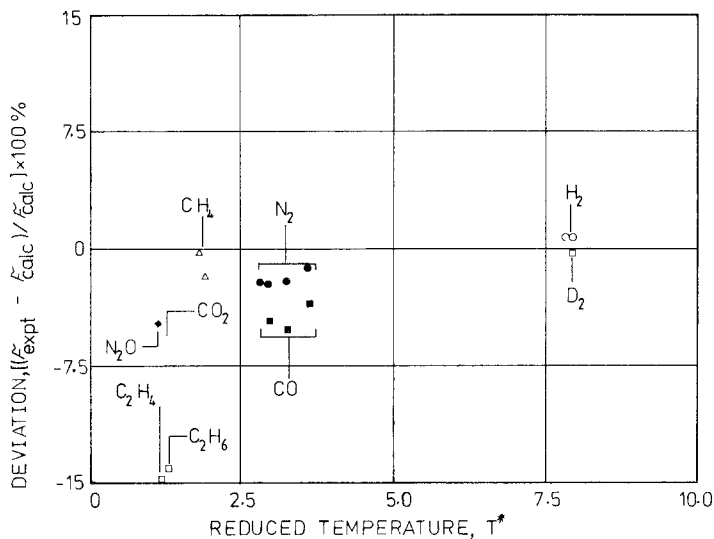


Fig. 3. A comparison between experimental values of the ratio $\mathcal{F} = [\lambda]_1/[\eta]_1$ and those calculated on the basis of the Mason-Monchick approximation.

The immediate conclusion from this comparison, that the Mason-Monchick approximation is inappropriate for the evaluation of D_{int} , must be tempered by consideration of other sources of the discrepancy [27, 29]. Some of these possibilities have been considered and discounted [27], and when taken together with independent theoretical evidence [30], it seems the inescapable conclusion is that either the Mason-Monchick approximation is inadequate for the evaluation of the thermal conductivity of polyatomic gases or there is a fundamental and important omission in the semiclassical kinetic theory for gases in which inelastic collisions are commonplace. Similar conclusions follow from an estimation of the thermal conductivity of mixtures involving at least one polyatomic component. Whether it be a failure in the kinetic theory or the invalidity of the Mason-Monchick approximation that is responsible for these discrepancies for pure gases and mixtures, their existence is a source of concern from the fundamental point of view. Furthermore, their magnitude is a source of concern from the viewpoint of providing accurate property values for systems of industrial interest.

Future fundamental work must aim at a more suitable approximation for the evaluation of D_{int} than the Mason-Monchick form. It is to assist in the development of such new approximations that we have performed the set of exact transport-property calculations referred to earlier since the

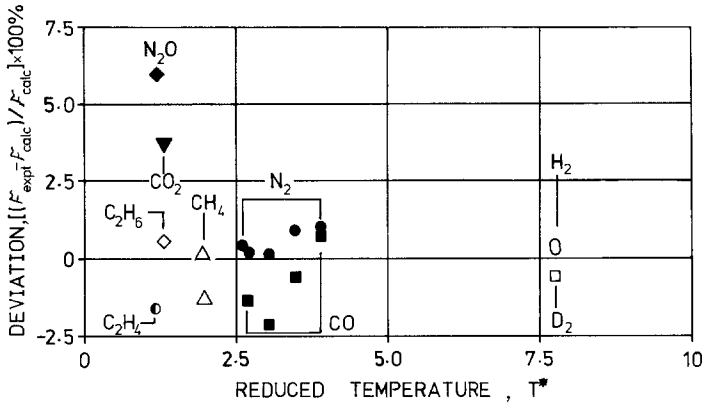


Fig. 4. A comparison between experimental values of the ratio $\mathcal{F} = [\lambda]_1/[\eta]_1$ and those calculated with a correlation for D_{int}/D .

results provide a unique benchmark against which approximate procedures can be tested. From the practical point of view a more pragmatic approach must be adopted. Accordingly, Maitland et al. [31] have proposed that D_{int} be treated as an empirically determined quantity and correlated it as a function of ζ_{rot} universal among all gases. When this correlation for D_{int} is employed in place of the Mason–Monchick approximation, the deviations of the calculated values of ratio $[\lambda]_1/[\eta]_1$ from the experimental values are significantly improved as can be seen from Fig. 4, which displays the results for the new calculation.

In view of the small set of results upon which the procedure is based, it would be premature to offer a definite conclusion at this stage. Nevertheless, there is sufficient encouragement in these preliminary results to warrant further investigation as more thermal-conductivity data for polyatomic gases become available. A corollary to this is, of course, the fact that the implementation of this scheme relies on the availability of values of ζ_{rot} over an extended range of temperature. Few data are available at present, but given that ζ_{rot} is itself a functional of the intermolecular pair potential, sensitive to anisotropy, new measurements of this parameter would, in any event, be a worthwhile endeavor.

5. PAIR POTENTIALS AND CORRELATION

There remains the question of whether measurements of the transport properties of polyatomic gases can be used to define any, or all, of the features of the intermolecular pair potential. Preliminary investigations

[32] suggest that the process of inversion, which proved a powerful tool in the analysis of the transport properties of monatomic gases [1], may have a useful role to play in the treatment of polyatomic gases. While these properties may not be sufficient to determine the entire nonspherical pair potential, it seems that they can be used to evaluate well-defined averages over a series of intermolecular configurations [32].

A related issue concerns the extension of the principle of corresponding states developed by Kestin and his collaborators for monatomic species [3, 4] to the representation of transport-property data of polyatomic systems. If the extension were valid it should be possible to represent the functional $\langle \bar{Q}^{(2,2)}(\omega, T) \rangle$ by means of the functional $\Omega_{22}^*(T^*)$ universal among the monatomic gases and two scaling parameters, σ for length and ε for energy, so that

$$\langle \bar{Q}^{(2,2)}(\omega, T) \rangle = \sigma^2 \Omega_{22}^*(T^*) \tag{8}$$

and

$$T^* = kT/\varepsilon$$

We have carried out a critical analysis of the viscosity measurements for three multipolar, polyatomic gases (CO_2 , CH_4 , SF_6) over a wide range of temperature and established correlations for the data in terms of the functional $\Omega_{22}^*(T^*)$, which have an estimated accuracy of $\pm 1.5\%$ [31, 33]. Figure 5 contains a plot of the functional $\Omega_{22}^*(T^*)$ for these three gases,

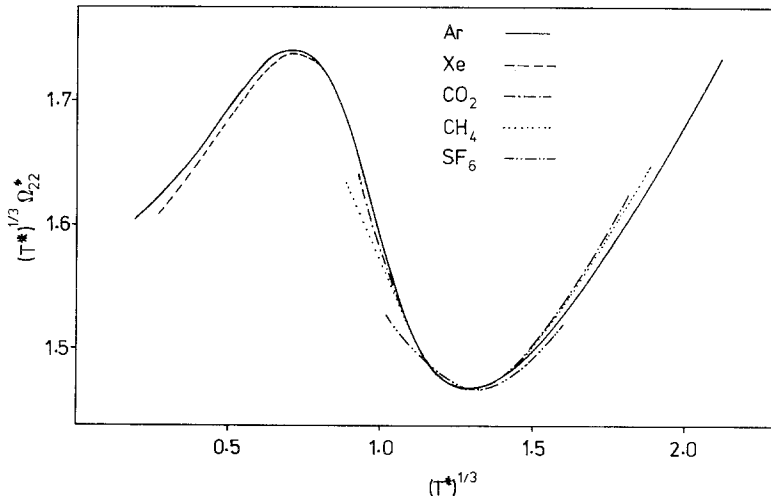


Fig. 5. The functional $\Omega_{22}^*(T^*)$ at low temperatures. (—) Ar [3]; (-----) Xe [3]; (-·-·-·-) CO_2 [31]; (·····) CH_4 [31]; (- - - -) SF_6 [31].

together with those for two of the monatomic gases in the form of $\Omega_{22}^* T^{*\frac{1}{3}}$ vs $T^{*\frac{1}{3}}$. It can be seen that whereas there is a degree of universality among all the systems over a limited range of temperatures, the curves for the different gases diverge at low temperatures and the differences become much larger than those observed between the various monatomic gases. This result implies that there are significant differences between the pair potentials for polyatomic and those for monatomic gases of which account must be taken in representing experimental data.

6. CONCLUSIONS

The paper has set out briefly the current position with regard to the measurement, interpretation, and correlation of the transport properties of dilute polyatomic gases. In every case there remains a large amount of work to be performed to obtain the level of knowledge characteristic of the monatomic gases; as a guideline, it has been possible to define those areas which need attention before further progress is possible. Perhaps the greatest need and that which seems most likely to be fulfilled in the near-future is that for accurate measurements of the thermal conductivity of gases over a wider range of temperature.

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