Correlation of the Zero-Density Viscosity of Polyatomic Gases[1]

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Correlations are presented for the dilute-gas viscosities of three gases with multipole moments of increasing order: carbon dioxide (quadrupolar), methane (octopolar), and sulfur hexafluoride (hexadecapolar). These are based on high-quality experimental data and are estimated to have an uncertainty of $\pm 0.3\%$ near room temperature, rising to $\pm 1.5\%$ at the extremes of temperature considered (~ 200 to ~ 1000 K). A comparison of these correlations with the two-parameter corresponding-states correlation developed by Kestin and co-workers for monatomic systems indicates systematic deviations, particularly at low temperatures. Model calculations designed to investigate the influence of a quadrupole term in the intermolecular pair potential on the viscosity coefficient indicate that these systematic deviations can be ascribed to such long-range multipolar interactions and suggest the basis for a new, more general three-parameter corresponding-states procedure.

KEY WORDS: carbon dioxide; corresponding states; methane; polyatomic gases; quadrupole; sulfur hexafluoride; viscosity.

1. INTRODUCTION

As part of a program of work under the auspices of the International Union of Pure and Applied Chemistry, definitive, wide-ranging correlations of the transport properties of gases are being prepared [1–4]. The starting point for such correlations is always the representation of the property in question in the limit of zero density, and Kestin and his collaborators [2–4] have reported a complete treatment of all the monatomic gases and their mixtures in this limit. This treatment was based upon the use of the

principle of corresponding states refined by the inclusion of information on the intermolecular pair potentials at both small and large separations, where conformality of the potentials breaks down. The advantages of such a treatment are that the extension of the correlation for a gas into a range of states where no direct measurements of the property exist is straightforward.

For polyatomic gases, which are of greater industrial importance, the same facility for the extension of the range of data would be extremely valuable. Unfortunately, it is not possible, as a matter of principle, to render the nonspherically symmetric pair potentials of polyatomic molecules conformal by a choice of just two scaling parameters, as can be done for spherical potentials. Consequently a two-parameter law of corresponding states for the transport properties cannot follow from statistical mechanical considerations. Nevertheless, it has been reported that a good representation of the viscosity of a number of polyatomic gases over a relatively narrow temperature range does conform to such a law [5]. In contrast, when data for the same gases over a wider range of temperature have been examined, the principle of corresponding states has been found to fail [1].

The most obvious feature of the pair potentials of polyatomic gases which distinguish them from those of monatomic systems is the electrostatic interaction arising from permanent multipoles [5]. In this paper we present high-quality representations of the viscosity of carbon dioxide, methane, and sulfur hexafluoride with multipole moments of increasing order. These correlations clearly demonstrate the inadequacy of a two-parameter law of corresponding states. We subsequently describe a number of model calculations carried out to investigate the possibility of retaining the considerable advantages of the principle of corresponding states by the introduction of a third parameter related to the appropriate multipole moment of the gas.

2. THE VISCOSITY CORRELATIONS

The detailed outline of the methodology for the correlation of the low-density viscosity of polyatomic gases can be found elsewhere [1], so we omit it here. It suffices to state that the correlations are based on a carefully selected set of "primary data," established by a critical review of the available literature. For the present study we consider the three polyatomic multipolar gases: carbon dioxide, CO_2—for which the lowest-order multipole moment is a quadrupole; methane, CH_4—for which it is an octopole; and sulfur hexafluoride, SF_6—for which it is a hexadecapole. The sources of experimental data designated primary, together with the temperature

range of the experiments, the method of measurement employed, and the assigned uncertainty, are listed in Table I.

For the purposes of representation, the experimental viscosities are reduced to dimensionless collision integrals $\Omega_{22}^*(T^*)$ using the kinetic theory relationship [5]

$$\eta = \frac{5}{16} \frac{(mkT)^{1/2}}{\pi\sigma^2 \Omega_{22}^*(T^*)} \tag{1}$$

in which higher-order corrections than the first are incorporated in $\Omega_{22}^*(T^*)$. Here, σ represents a length scaling parameter and ε an energy scaling parameter such that

$$T^* = kT/\varepsilon \tag{2}$$

Table I. Primary Experimental Data for the Viscosity of CO_2, CH_4, and SF_6

Reference	Technique[a]	Temperature range (K)	Estimated uncertainty (%)
	Carbon dioxide		
Harris et al. [6]	C	203–310	±1.5–±1.0
Maitland and Smith [7]	C	292–1497	±1.0–±2.0
Bailey [8]	C	344–718	±1.0–±2.0
Kestin et al. [9]	OD	298–973	±0.2–±0.5
Kestin et al. [10]	OD	298–773	±0.2–±0.4
Kestin et al. [11]	OD	296–673	±0.2–±0.4
	Methane		
Clarke and Smith [12]	C	113–374	±1.5–±1.0
Maitland and Smith [13]	C	294–1021	±1.0–±2.0
Dawe et al. [14]	C	294–1050	±1.0–±2.0
Kestin et al. [15]	OD	298–473	±0.2–±0.3
Kestin et al. [10]	OD	298–473	±0.2–±0.3
Kestin et al. [16]	OD	298–468	±0.2–±0.3
Kestin et al. [11]	OD	296–474	±0.2–±0.3
	Sulfurhexafluoride		
Harris et al. [6]	C	218–302	±1.5–±1.0
Dawe et al. [14]	C	293–873	±1.0
Hellemans et al. [17]	OD	298–573	±0.2–±0.3
Kestin et al. [18]	OD	296–477	±0.2–±0.3
Kestin et al. [10]	OD	298–473	±0.2–±0.3
Kestin et al. [11]	OD	269–474	±0.2–±0.3

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

The experimental values of $\Omega^*_{22}(T^*)$ are subsequently fitted by a weighted least-squares procedure to the equation

$$\ln \Omega^*_{22} = \sum_{i=0}^{4} a_i(\ln T^*)^i \tag{3}$$

which has been found to be satisfactory in previous applications [1–3]. The weighting procedure adopted in the fit is identical to that employed earlier [1]. However, extreme care has been taken to ensure that the preponderance of experimental results at room temperature does not unduly bias the fit by including only a subset of these points.

The values of the coefficients, a_i, that secure the optimum representation of the experimental viscosity data through Eqs. (1) and (3) for each of the gases carbon dioxide, methane, and sulfur hexafluoride are contained in Table II. It also includes the values of the scaling factors ε/k and σ selected in the manner described below.

Figures 1–3 display the deviations of the selected primary viscosity data from the optimum correlations for the gases, CO_2, CH_4, and SF_6, respectively. The standard deviations of the fits are included in Table II, but it is worthwhile remarking here that the deviation plots show no systematic trends beyond those invariably observed [1, 4] between the results of Smith and his co-workers and Kestin and his collaborators. Furthermore, no datum departs from the correlation by more than the estimated uncertainty in the former. On this basis it is estimated that the uncertainty of the correlation of the viscosity is no more than $\pm 0.3\%$ near room temperature for any of the three gases. However, the uncertainty rises to as much as $\pm 1.5\%$ at the extremes of the temperature range studied for each gas.

Table II. Coefficients, a_i, Scaling Parameters, ε/k and σ, and
Standard Deviation, σ_{corr}, for Eq. (3)

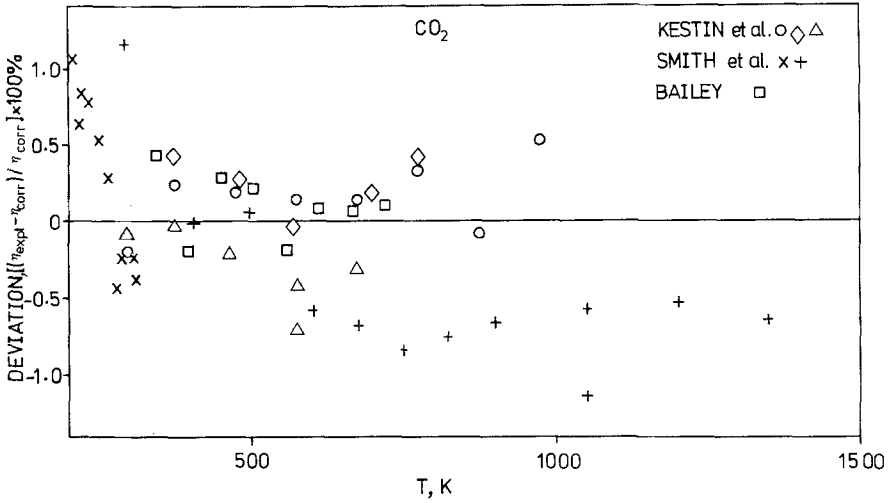|	CO_2	CH_4	SF_6
a_0	0.45885	0.45009	0.42386
a_1	−0.49676	−0.46460	−0.38220
$10a_2$	0.23436	−0.06365	−0.56997
$10a_3$	1.0309	1.0925	0.79345
$10a_4$	−0.33775	−0.32954	−0.11127
ε/k (K)	251.196	163.558	204.510
σ (nm)	0.3751	0.3709	0.5263
$10\,\sigma_{corr}$ (μPa · s)	0.51	0.33	0.34

Fig. 1. Deviation of the primary viscosity data for carbon dioxide from the correlation of Eq. (3) and Table II. X [6]; + [7]; □ [8]; ○ [9]; ◇ [10]; △ [11].
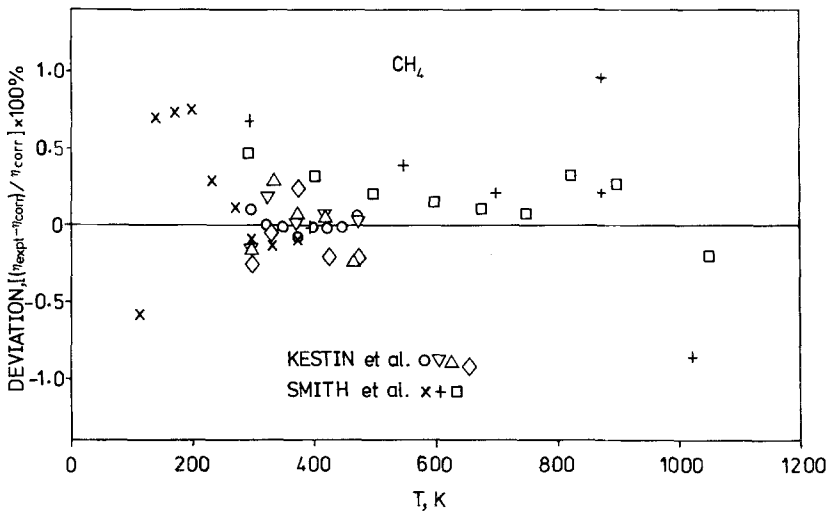

Fig. 2. Deviations of the primary viscosity data for methane from the correlation of Eq. (3) and Table II. X [12]; + [13]; □ [14]; ○ [15]; ◇ [10]; ▽ [16]; △ [11].
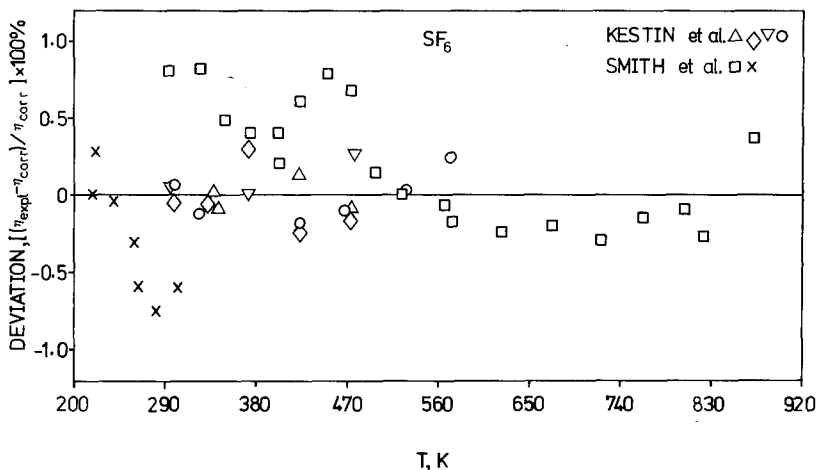
Fig. 3. Deviations of the primary viscosity data for sulfur hexafluoride from the correlation of Eq. (3) and Table II. X [6]; □ [14]; ○ [17]; ▽ [18]; ◇ [10]; △ [11].

3. TWO-PARAMETER CORRESPONDING STATES

If a law of corresponding states characterized by two parameters were valid among the gases studied here, it follows that the collision integral Ω_{22}^* would be a universal function of the reduced temperature, T^* [5]. In order to test this proposition we first attempt to represent the primary data sets for the gases, carbon dioxide, methane, and sulfur hexafluoride, by means of the functional Ω_{22}^* found by Kestin et al. [4] to be universal among the monatomic gases. The pairs of parameters ε/k and σ which secure the optimum representation of this kind are listed in Table II because they are the values employed in the correlation of the previous section.

For later purposes a convenient representation [5] of the result of this process is provided by the behavior of the quantity $\Omega_{22}^* T^{*1/3}$ as a function of $T^{*1/3}$. Figure 4 shows a plot of the group $\Omega_{22}^* T^{*1/3}$ for argon and xenon [4] as well as for the three gases studied here. It can be seen in an intermediate reduced temperature range about $T^* = 1.0$ and $T^* = 10$ that the curves for all gases are very similar. At lower temperatures the differences between the two monatomic gases, themselves among the three polyatomic gases, and between the monatomic gases and the polyatomic gases become more marked. Indeed, at the lowest temperatures, the deviations of the viscosity of SF_6 from the universal correlation amount to 7%. These results imply that no simple two-parameter corresponding-states principle can be used to extend the range of the correlation given here.
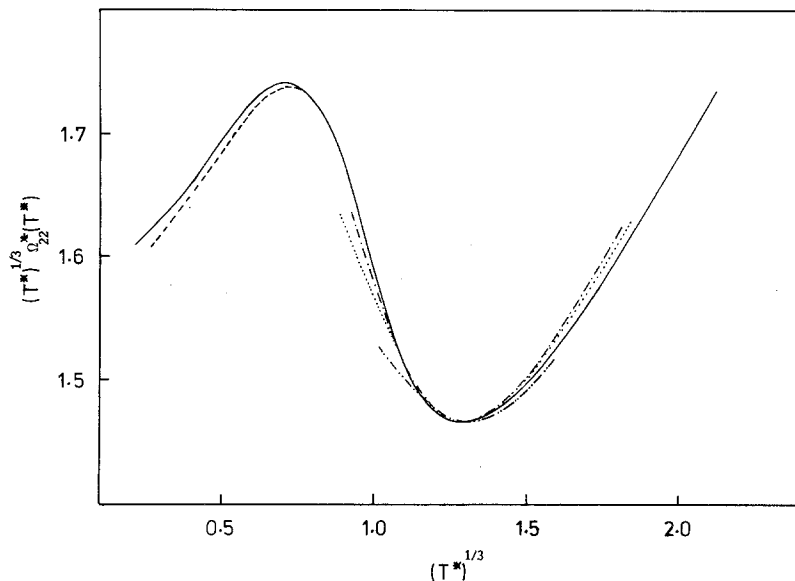
Fig. 4. The low-temperature asymptotic behavior of the functional $\Omega_{22}^*(T^*)$. (——) Ar [3]; (– – –) Xe [3]; (– · – · –) CO_2; (· · · ·) CH_4; (– · · – · · –) SF_6.

The next most simple idea which should be investigated to overcome this difficulty makes use of the proposition that it is the electrostatic, multipolar interactions among the polyatomic gas molecules that are solely responsible for the observed behavior. That is, we propose that the intermolecular pair potential of such gases is a sum of an isotropic contribution, conformal among all gases, together with an anisotropic contribution depending on the order of the multipole moment and its magnitude. In the following section we examine this idea in a preliminary manner with the aid of some model calculations, because for the real system the isotropic part of the potential is still unknown.

4. THE EFFECT OF MULTIPOLE MOMENTS

For these model calculations we employ as the isotropic part of the intermolecular pair potential the Lennard–Jones (12–6) function [5] characterized by the parameters $\tilde{\varepsilon}$ and $\tilde{\sigma}$ that correspond to the well depth of the potential and the separation at the zero crossing, respectively. For the anisotropic electrostatic interaction, we employ here just the term corresponding to the interaction of two permanent point quadrupoles, Θ, in linear molecules [19]

$$U_{\text{quad}} = \frac{2\Theta^2}{4r^5} \zeta(\theta_1, \theta_2, \phi) \tag{4}$$

where the function ζ may be found in Ref. 19. Here θ_1, θ_2, and ϕ define the relative orientation of the molecules.

The total pair potential may then be written in reduced form as

$$\frac{U(r^*)}{\tilde{\varepsilon}} = U^*(r^*) = 4\{r^{*-12} - r^{*-6} - \delta r^{*-5}\} \tag{5}$$

where

$$r^* = r/\tilde{\sigma} \tag{6}$$

and

$$\begin{aligned} \delta &= (3\Theta^2/64\pi\varepsilon_0\tilde{\varepsilon}\tilde{\sigma}^5)\,\zeta(\theta_1, \theta_2, \phi) \\ &= \delta_{\max}\zeta(\theta_1, \theta_2, \phi)/8 \end{aligned} \tag{7}$$

Collision integrals, $\Omega_{22}^*(T^*)$, have been computed for this pair potential model within the Mason–Monchick approximation [20, 21] for five values of the characteristic parameter $\delta_{\max}$ in the range 0.25 to 1.25, which encompasses the tabulated quadrupole moment for CO_2 [22], for which $\delta_{\max} \sim 0.35$.

In order to relate the results of these model calculations to our findings for real gases, we have adopted the following procedure. The collision integrals for the various anisotropic potentials $U(r, \theta_1, \theta_2, \phi)$ were used to generate pseudoexperimental viscosity data for an arbitrary material. Subsequently, we have attempted to represent these pseudoexperimental data by means of the collision integrals of the isotropic potential by the choice of optimum values of just two disposable scaling parameters, ε and σ. This process is therefore entirely analogous to the way in which we treated real experimental data with respect to the universal functional in Section 3.

Figure 5 contains the results of some of our model calculations. The pseudoexperimental data cover the large temperature range $T^* = 0.6$ to 10, and it can be seen that the effect of increasing quadrupole moment is to make the minimum in the plot shallower and wider, in qualitative agreement with the results in Fig. 4 for carbon dioxide, which roughly corresponds to the curve for $\delta_{\max} = 0.35$. This result suggests that the quadrupole component of the pair potential of carbon dioxide is indeed important in determining its viscosity and may well be largely responsible for deviations from a two-parameter correspondence with the functional Ω_{22}^* of the monatomic gases. On this basis it would seem that a rather more general principle of corresponding states involving three parameters, an energy scale, a distance scale, and a suitably reduced multipole moment may prove adequate for the description of the viscosity of the polyatomic gases.
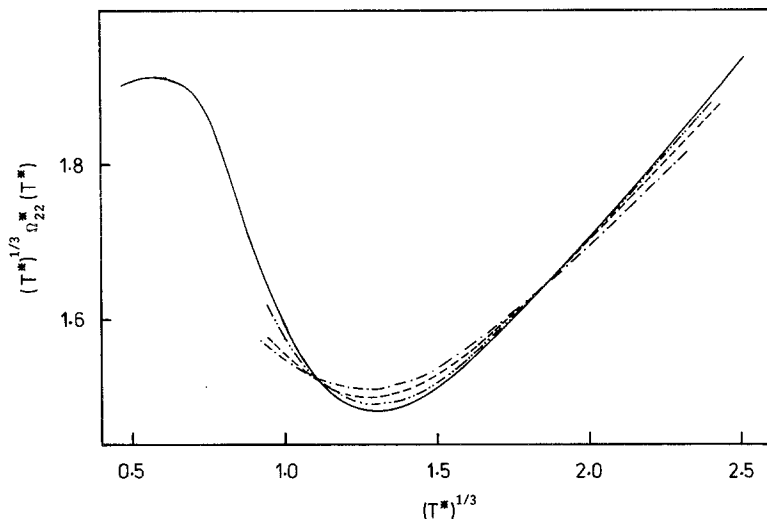
Fig. 5. The group $T^{*1/3}\Omega^*_{22}$ for the quadrupolar potential for various values of δ_{max}.
(———) $\delta_{max} = 0$; (–·—·–·–) $\delta_{max} = 0.35$; (– – – –) $\delta_{max} = 0.75$; (–·—·–) $\delta_{max} = 1.25$.

That such a three-parameter approach is necessary for successful extrapolation of data has been demonstrated by means of the same model calculations. If the pseudoexperimental data over a narrow range of temperature are fitted to the isotropic collision integrals, a close representation can often be achieved. However, if the isotropic collision integral is then used to extrapolate the small range of pseudoexperimental data, pronounced errors can occur at the extremes of the temperature range. Such behavior is entirely analogous to that observed with real experimental data discussed in Section 1, and the results shown in Fig. 5 confirm that it arises from the lack of correspondence of the collision integrals in a two-parameter representation.

ACKNOWLEDGMENTS

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