

Computed values of rotational collision number and diffusion coefficients for oxygen

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Abstract. Recent experimental data on thermal conductivity and viscosity are used to calculate values of rotational collision numbers and diffusion coefficients for oxygen in the temperature range 400–1600 K.

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1. Introduction

A knowledge of rotational collision number Z_{rot} is essential for calculating transport properties of polyatomic gases (Mason and Monchick 1962; Saxena *et al* 1964). Experimental values of the number have therefore been obtained using thermal transpiration and ultrasonic absorption techniques (Annis and Malinauskas 1971; Carnevale *et al* 1967; Healy and Storvick 1969; Mason 1963; Malinauskas *et al* 1970; Tao *et al* 1972, Tip *et al* 1967). Such data (figure 1) for oxygen however, show considerable disagreement and thus, it is not possible to establish the values in an unambiguous manner (Tao *et al* 1972). Further, the values of Z_{rot} not being experimentally available above 700 K, have to be theoretically determined at such temperatures.

This paper, therefore, presents a procedure to determine reliable values of Z_{rot} with the help of the recent experimental data on thermal conductivity (k) and viscosity (μ) for oxygen and hence for computing the self diffusion coefficients (D) of the gas within the framework of the present kinetic theory expressions.

2. Theoretical expressions

The thermal conductivity of a polyatomic gas may be expressed as (Hirschfelder *et al* 1967)

$$k = k^0 f \quad (1)$$

where k^0 is the frozen part of k and f is the Eucken type correction factor accounting

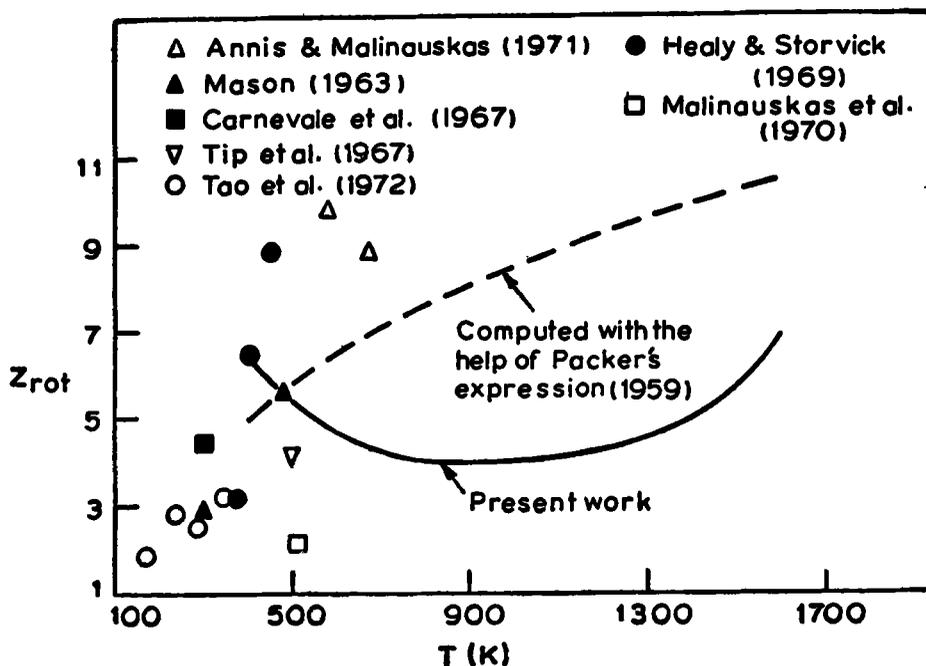


Figure 1. Z_{rot} of O_2 as a function of temperature. The dashed line is "computed with the help of Parker's expression (1959)".

for the transport of energy by internal modes of the molecule. k^0 is in turn related to μ and D through the expressions

$$\mu \text{ (g cm}^{-1} \text{ s}^{-1}\text{)} = \frac{4M}{15R} k^0 \quad (2)$$

$$D \text{ (cm}^2 \text{ s}^{-1}\text{)} = \frac{A^* T k^0}{0.31668 p} \quad (3)$$

where k^0 is expressed in $W \text{ cm}^{-1} \text{ K}^{-1}$, A^* is the ratio of collision integrals, p is the gas pressure in atmospheres, R is the gas constant, M is the molecular weight and T is the temperature of the gas in kelvins.

Several expressions have been suggested for the correction factor f . Assuming equilibrium between the translational and internal modes, Hirschfelder (1967) has shown that f may be represented by

$$f_H = 0.115 + \frac{0.354\gamma}{\gamma-1} \quad (4)$$

where γ is the ratio of the specific heats of the gas. A more rigorous expression due to Mason and Monchick (1962) derived by taking into account the translational and internal energy exchange may be written for a linearized case in the form:

$$f_{MM} = (4/15R) (f_{tr} C_{v_{tr}} + f_{int} C_{v_{int}}) \quad (5)$$

where

$$f_{\text{tr}} = \frac{3}{2} \left[1 - \frac{5}{6} \left(1 - \frac{2}{5} \frac{\rho D_{\text{int}}}{\mu} \right) \frac{C_{v_{\text{int}}}}{R} \frac{4}{\pi Z_{\text{rot}}} \right] \quad (6)$$

$$f_{\text{int}} = \frac{\rho D_{\text{int}}}{\mu} \left[1 + \frac{5}{\pi} \left(1 - \frac{2}{5} \frac{\rho D_{\text{int}}}{\mu} \right) \frac{4}{Z_{\text{rot}}} \right] \quad (7)$$

and $C_{v_{\text{tr}}}$ and $C_{v_{\text{int}}}$ are respectively the contributions of translational and internal energy to the total specific heat at constant volume C_v ; D_{int} is the internal energy diffusion coefficient and ρ is the density of the gas.

Again, with intuitive arguments, Saxena *et al* (1964) have suggested the following expression for f .

$$f_s = f_H - \left(\frac{5}{2} - \frac{\rho D_{\text{int}}}{\mu} \right) \frac{C_{v_{\text{int}}}}{C_v Z_{\text{rot}}}. \quad (8)$$

These expressions being quite different in form lead to thermal conductivity values in appreciable disagreement with each other. But on comparing the results with experimental data, the more consistent of the three expressions for f can be decided upon. It has thus been observed (Jain and Pandya 1978; Jain and Saxena 1977) that the recent experimental data (Jain and Saxena 1977) on oxygen are best represented by the expression due to Saxena *et al* (1964). In this case, the average absolute and maximum deviations (4.7% and 6.7% respectively) are seen to be much less than those found in other cases.

The discrepancies between theoretical and experimental results may be due to inadequacies of either the polyatomic theories themselves or the parameters used for calculating f . Except for Z_{rot} , the factors occurring in (4), (5) and (8) are more or less well established; reliable values of Z_{rot} are, therefore, needed for accurately computing transport properties of the gas, comparing them with the experimental data and hence deciding about the adequacy or otherwise of the theoretical expressions.

3. Computation of Z_{rot}

The procedure for computation of Z_{rot} is as follows. Using (2) and the viscosity data, k^0 is first of all calculated at various temperatures. The correction factor, f is derived from (1) by employing the k data. Z_{rot} is then found from (8).

The thermal conductivity of oxygen has been recently measured by Jain and Saxena (1977) in the temperature range 400–1600 K with an estimated accuracy of about 2%. The viscosity of the gas has also been recently determined by Matthews *et al* (1976) in the temperature range 120–1620 K with an accuracy of about 1%. These data (table 1) can be utilized for computing the values of Z_{rot} as outlined above.

For these calculations, however, it was assumed in (8) that $D_{\text{int}} = D$ and the dimensionless group of properties, $\rho D/\mu$ was taken to be 1.2 A^* , where A^* , the ratio of

Table 1. Transport coefficients of O₂

<i>T</i> (K)	<i>k</i> (m Wm ⁻¹ K ⁻¹)	<i>μ</i> (g cm ⁻¹ s ⁻¹)	<i>D</i> (cm ² s ⁻¹)
400	33.6	261.1	0.354
600	46.3	348.9	0.714
800	58.0	423.5	1.162
1000	69.3	490.7	1.689
1200	80.3	553.0	2.290
1400	91.5	611.6	2.962
1600	103.2	667.2	3.699

Table 2. Computed values of Z_{rot} of O₂ as a function of temperature

<i>T</i> (K)	Z _{rot}
400	6.6
600	4.7
800	4.1
1000	4.1
1200	4.4
1400	5.1
1600	6.9

collision integrals was estimated on the basis of the recent *m*-6-8 potential (Hanley and Klein 1972) (with the parameters: *m*=10, *γ*=1, *σ*=3.437 Å and *ε*/*k*=113.0 K). Finally, *C*_{*v*int} was estimated from the relation:

$$\frac{C_{v_{\text{int}}}}{R} = \frac{C_p}{R} - 2.5 \quad (9)$$

where the values of *C_p* were taken from Svehla (1962).

4. Results and discussions

The computed values of Z_{rot} (table 2) are seen first to decrease with increasing temperature up to 1000 K before increasing again, the values at 400 K and 1600 K being nearly equal (figure 1). This trend is quite different from that observed in the case of Z_{rot} values calculated earlier (Jain and Saxena 1977) with the help of Parker's (1959) expression. In the latter case Z_{rot} increases monotonically with temperature and reaches a maximum value of 10.5 at 1600 K.

It may be added that the values of Z_{rot} calculated by employing the parameters of the recent Smith-Thakkar potential (ST PO₂I) (Thakkar and Smith 1975), were found to be almost the same as those discussed above.

5. Computation of D

With the help of the k^0 values determined as above, those of D can be evaluated using (3). The values computed at one atmosphere are given in table 1 in the temperature range 400–1600K. No comparison of these D values is possible for lack of experimental data.

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