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MOLECULAR DIAMETER DATA FROM THERMO MOLECULAR FLOW EXPERIMENTS

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ABSTRACT

Based on the theory of thermo molecular flow forces at low gas pressures, an equation is evaluated which relates the thermo molecular flow effect at high gas pressures to the molecular diameters of the gas molecules. Our experimental results are compared with molecular diameters from other types of experiment.

INTRODUCTION

In the last decades much attention has been paid to Thermo Molecular Flow (TMF) effects. This was because these effects were among the most serious factors limiting the reliability of weighing at low pressures[1,2]. Theoretical treatments have been shown to give a satisfactory explanation of experimental data concerning TMF effects[3,4], which once understood, have led to suggestions of practical applications[5,6].

In the present paper a discussion is given to show how TMF experiments can contribute to the determination of specific data for gases, *i.e.* the molecular diameter.

Forces due to TMF effects are strongly pressure dependent and show a maximum at pressures where the mean free path of gas molecules is of the order of the dimensions of the experimental system. Separate theoretical treatments have been given for TMF effects at the two slopes of the maximum[3,4]. Neither of these two treatments however covers the pressure region in the immediate vicinity of the maximum. In the present paper a treatment is given where the diameter of gas molecules will be shown to be related to the height of that maximum.

THEORY

The theoretical results for the low pressure region[3,6] will be the basis of our treatment. These results were obtained for a system with a cylindrical sample and vessel; such a system has also been used for our experiments described later on in this paper, see Fig. 1. A beam-type balance inside a vacuum chamber is shown. The cylindrical sample S, radius r_s, is coaxially suspended in a cylindrical vessel with radius r_v; r_s and r_v are chosen such that $r_v - r_s \ll r_s$ implying that the gas between sample and vessel can be considered as a gas between two parallel plates. At the position of the sample a temperature jump from T to T_1 exists along the vessel. When operating at low gas pressures (Knudsen conditions) this temperature jump gives rise to both normal and longitudinal Knudsen forces which in combination give us the TMF effect measured with the balance. When the mean free path λ of the gas molecules satisfies $\lambda \gg r_v - r_s$ the TMF effect, F_k, can be written as[6]

$$F_k = r_s r_v p \left(1 - \sqrt{\frac{T_1}{T}}\right) \tag{1}$$

where p is the gas pressure. This equation shows that at low pressures the TMF effect increases linearly with the gas pressure. At higher pressures, near the maximum, where λ becomes of the order of $r_v - r_s$, eqn (1) is no longer valid. To cope with this pressure region we introduce a factor $f(\lambda)$. This factor is determined by the ratios between λ and the geometrical dimensions (*e.g.* r_v and r_s) and is taken to be independent of the nature of the gas. For a given system we can therefore write for the TMF effect

$$F = f(\lambda) F_k = f(\lambda) \cdot r_s r_v p \left(1 - \sqrt{\frac{T_1}{T}}\right). \tag{2}$$

$f(\lambda)$ equals unity for low gas pressures but when λ becomes of the order of the geometrical dimensions of the system it will decrease with increasing gas pressure to become zero at high pressures where the TMF effect disappears. At intermediate pressures the force F therefore shows a maximum F_m (at a pressure p_m) the magnitude of which, as mentioned above, will be used for the determination of molecular diameters.

As F_m and p_m are determined by $(\delta F/\delta p)_{p_m} = 0$ eqn (2) yields

$$\left(\frac{\partial f(\lambda)}{\partial \lambda}\right)_{\lambda_m} \cdot \left(\frac{\partial \lambda}{\partial p}\right)_{p_m} p_m + f(\lambda_m) = 0 \tag{3}$$

where λ_m is the value of λ at the pressure p_m. Consider the relation between λ and p

$$\lambda = \frac{C}{R^2 p} \tag{4}$$

where $2R$ is the collision diameter of the gas molecules and C is purely a function of temperature and independent of the nature of the gas. Substituting eqn (4) in eqn (3) gives

$$\left(\frac{\partial f(\lambda)}{\partial \lambda}\right)_{\lambda_m} \cdot \frac{C}{R^2 p_m} = f(\lambda_m) \tag{5}$$

which simplifies to

$$\left(\frac{\partial f(\lambda)}{\partial \lambda}\right)_{\lambda_m} = \frac{f(\lambda_m)}{\lambda_m}. \tag{6}$$

From eqn (6) we see that λ_m is independent of the nature of the gas. Substituting eqns (4) and (6) in eqn (2) we obtain for F_m

$$F_m = \frac{C}{R^2}\left(\frac{\partial f(\lambda)}{\partial \lambda}\right)_{\lambda_m} r_s r_v \left(1 - \sqrt{\frac{T_1}{T}}\right). \tag{7}$$

As R is the only parameter in eqn (7) to be dependent upon the nature of the gas, we may, when comparing two gases A and B under the same experimental conditions, use

$$\frac{F_{m_A}}{F_{m_B}} = \left(\frac{R_B}{R_A}\right)^2. \tag{8}$$

Equation (8) will be used as the basis of the calculation of the ratio R_B/R_A from the maxima of TMF effects for different gases.

EXPERIMENTS AND RESULTS

The apparatus with which the experiments were carried out is shown in Fig. 1. A closed glass cylinder, $r_s = 1.7$ cm, was used, as a sample and was suspended from a Sartorius vacuum microbalance (type 4104, after Gast) into a glass vessel. This vessel was surrounded by two water jackets. The temperatures of the jackets were controlled by means of circulating thermostats. The jackets were arranged such that the temper-

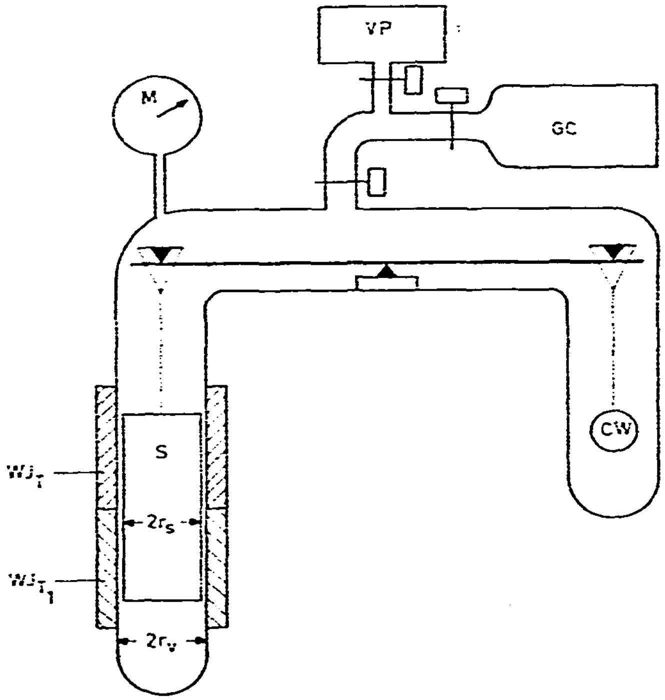

Fig. 1. The apparatus used. S, sample; CW, counterweight; WJ, water jacket; M, manometer; VP, vacuum pump; GC, gas container.

ature jump from T to T_1 occurred at the middle of the sample. T was chosen equal to the room temperature. The measurements were carried out with N_2, He and CO_2 as gases. After filling the vacuum chamber with a certain gas, the pressure of this gas was decreased and the TMF force F was measured as a function of pressure. The maximum values F_m of this force as found for different gases are shown in Table 1. From the data in Table 1 the ratios of the molecular diameters were calculated with the help of eqn (8).

TABLE 1

Gas	*F_m (dyne)*	*F_m (gas)/F_m (N_2)*	*R_{gas}/R_{N_2}*			
			Present paper	*Literature*[7]		
				Viscosity	*Isotherms*	*Heat conductivity*
N_2	8.5	1	1	1	1	1
He	17	2.0	0.71	0.60	0.84	0.65
CO_2	6.8	0.80	1.12	1.06	1.03	0.96

The accuracy of the measurements was not limited by the force measurements which were reliable up to 10^{-3} dynes. The geometrical conditions were not affected when changing from one gas to another, so the remaining source of error originates from the temperature control of T and T_1. T and T_1 differing by 70°C in the experiments described, the resultant inaccuracy in the TMF forces may well amount to some 5%.

In Table 1 our results are compared with data from ref. 7 which were obtained from other experiments, *viz.* measurements of viscosity, of isotherms and of heat conductivity. To make comparison possible, the literature data are also presented as a ratio of molecular diameters with nitrogen as a reference gas.

The differences between the data obtained from different experiments do not appear either regular or systematic. However, they could partly be ascribed to the different roles the accomodation and scattering coefficients play in the different types of experiment.

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