

MOLECULAR DIAMETER DATA FROM THERMO MOLECULAR FLOW EXPERIMENTS. II

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ABSTRACT

The theory presented in the preceding paper¹ has been applied to the thermo molecular flow measurements published earlier by different authors. The different results are compared and the comparison is extended with molecular diameters from other types of experiments.

INTRODUCTION

Thermo molecular flow (TMF) forces occur when a temperature gradient exists along a vessel in which a sample is located surrounded by a gas at low pressure, see Fig. 1. Usually these forces are measured by means of a balance from which the sample is suspended. In previous papers^{1,2} such TMF measurements were reported together with a theoretical treatment in which the experimental results were related to data concerning the diameters of the molecules of the ambient gas. TMF forces were examined earlier by different authors who had other aims than contributing to the knowledge of molecular diameters. In the present paper their measurements³⁻⁵ will be reanalysed in order to obtain additional molecular diameter data⁶⁻⁸.

THEORY

The treatment presented in the preceding paper¹ is based upon the fact that TMF forces when plotted as a function of pressure show a maximum, the value of which is used for the calculation of the molecular diameter. In some of the papers

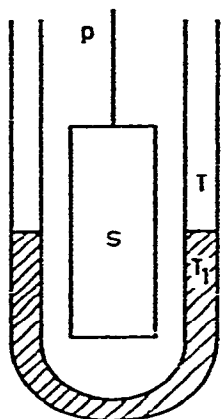


Fig. 1. Scheme of a TMF experiment. The vertical force, being a function of the gas pressure p , acts on the sample due to the difference between the temperatures T_1 and T .

from which we are going to compare the TMF data, the value for the maximum force has not been reported, the measurements having been restricted to the two slopes towards the maximum. In order to cope with this difficulty in the present paper, the existing theory is extended to make it possible to draw conclusions about molecular diameter data from the two slopes.

In the preceding paper the following expression for the TMF force F is given

$$F = f(\lambda, r_s, r_v, T_1, T) r_s r_v \frac{C}{R^2 \lambda} \left(1 - \sqrt{\frac{T_1}{T}} \right) \quad (1)$$

where λ is the mean free path of the gas molecules,
the function $f(\lambda, r_s, r_v, T_1, T)$ —in the following abbreviated to $f(\lambda)$ —is independent of the nature of the gas,
 r_s and r_v are the radii of sample and vessel respectively,
 T_1 and T characterise the temperature difference along the vessel,
 $2R$ is the molecular diameter of the gas and
 C is related to the gas pressure p by means of

$$\lambda = \frac{C}{R^2 p} \quad (2)$$

When the maximum force F_m occurs at the gas pressure p_m and at the mean free path λ_m , it follows from eqn (1) that

$$\frac{F}{F_m} = \frac{f(\lambda)}{f(\lambda_m)} \cdot \frac{\lambda_m}{\lambda} \quad (3)$$

In this relation $f(\lambda)$ is independent of the nature of the gas and so the relation between F/F_m and λ_m/λ ($= p/p_m$) can be represented by means of one simple picture for

different gases, see Fig. 2. The two slopes of the maximum show linear parts in the double logarithmic plot, this is supported by theory^{9,10}. Extrapolation of these two linear parts yields as intersection the point B in Fig. 2, the location of which we will represent by λ_m/λ_i and F_i/F_m . As the curve in Fig. 2 is under equal experimental conditions independent of the nature of the gas, λ_i and F_i will also be independent of it.

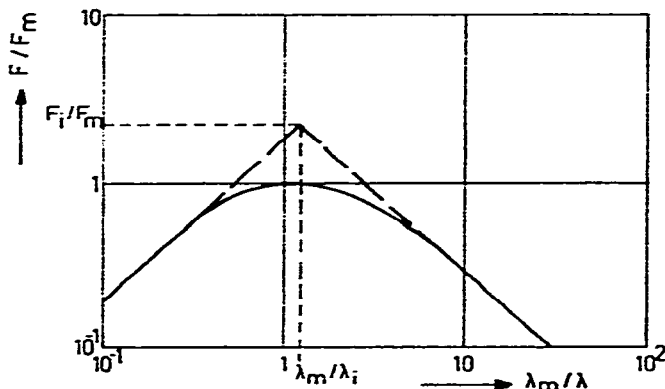


Fig. 2. The relation between F/F_m and λ_m/λ (double logarithmic) for illustration of the procedure being followed (see text) to obtain molecular diameter data from TMF experiments.

This enables us when comparing two gases A and B to use the relation

$$\frac{F_{iA}}{F_{iB}} = \frac{F_{mA}}{F_{mB}} \quad (4)$$

Using the relation

$$\frac{F_{mA}}{F_{mB}} = \left(\frac{R_B}{R_A}\right)^2 \quad (5)$$

from the preceding paper¹, we then obtain for the two molecular diameters

$$\frac{F_{iA}}{F_{iB}} = \left(\frac{R_B}{R_A}\right)^2 \quad (6)$$

Molecular diameters from TMF data

In Table 1 the values of the molecular diameters as calculated with the aid of eqn (5) or (6) from the work of various investigators^{1,3-5} are given.

As a reference gas N_2 was used. When the series contained no measurements on N_2 , we took the O_2 measurements as reference and used the relation

$$\frac{F_{mO_2}}{F_{mN_2}} = \left(\frac{R_{N_2}}{R_{O_2}}\right)^2 = (1.036)^2 \quad (7)$$

The value in the RHS is obtained upon averaging of the values 1.042, 1.028 and 1.038 originating from heat conductivity, viscosity and isotherm data⁸, respectively. In case this procedure is applied, the symbol * is added to the resulting data in Table 1.

TABLE 1

MOLECULAR DIAMETER DATA FROM TMF MEASUREMENTS AS CALCULATED WITH THE AID OF EQN (5) OR (6)

<i>Ref.</i>	<i>Gas</i>	F_m	F_1	$F_m(\text{gas})/F_m(\text{N}_2)$	$R_{\text{gas}}/R_{\text{N}_2}$
3	N ₂	3.27		1	1
	Ar	3.75		1.1435	0.94
	Kr	2.46		0.751	1.16
	He	7.75		2.36	0.65
	H ₂	7.36		2.246	0.67
4	O ₂		3.09		
	He		8.56	2.97*	0.58*
	H ₂		5.13	1.78*	0.75*
1	N ₂	8.5		1	1
	He	17		2.0	0.71
	CO ₂	6.8		0.80	1.12
5	O ₂	0.93			
	Ne	1.83		2.127*	0.69*

* Calculated with the aid of eqns (6) and (7).

TABLE 2

COMPARISON OF MOLECULAR DIAMETER DATA FROM TMF MEASUREMENTS WITH DATA FROM OTHER TYPES OF EXPERIMENTS

<i>Gas</i>	$R_{\text{gas}}/R_{\text{N}_2}$						
	<i>TMF</i>	<i>Ref.</i>	<i>Isotherms</i> ⁸	<i>Viscosity</i>	<i>Ref.</i>	<i>Heat conductivity</i> ⁸	<i>Mean free path</i> ⁶
H ₂	0.67	3	0.74	0.84	7	0.66	0.73
	0.75	4		0.76	8		
He	0.71	1	0.84	0.64	7	0.65	0.58
	0.65	3		0.60	8		
	0.56	4					
Ne	0.69	5		0.70	7		0.69
Ar	0.94	3	0.93	0.96	7	0.81	0.97
				0.91	8		
Kr	1.16	3	1.17	1.13	7	0.89	
CO ₂	1.12	1	1.03	1.22	7	0.96	1.23
				1.06	8		

COMPARISON

Molecular diameter data exist originating from several types of experiments. They are closely related to mean free path data which through the kinetic theory of gases follow from viscosity and heat conductivity measurements. Besides the molecular diameters can be obtained from the molecular volumes as measured by means of gas isotherms.

In Table 2 the collection of diameter data from TMF measurements is compared with the data from the other types of experiments. The data are in satisfactory agreement, discrepancies are neither regular nor systematic.

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