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AEC RESEARCH AND DEVELOPMENT REPORT

A METHOD OF USING A POROUS MEDIUM TO DETERMINE
THE COEFFICIENTS OF VISCOSITY
FOR BROMINE TRIFLUORIDE

AUTHOR:

T. W. Selby

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FOR BROMINE TRIFLUORIDE

Author: T. W. Selby

ABSTRACT

Experimental evaluations have been made of a porous-medium method for determining relative coefficients of viscosity for corrosive and non-corrosive gases. The apparatus and operating procedure are described in detail. Measurements of the coefficients of viscosity for argon were made over the temperature range of 35°C. to 200°C. and are given by the equation,

$$\eta, \text{ micropoise} = 22.14 \sqrt{T, ^\circ\text{K.}} - 157.9$$

Measurements of the coefficients of viscosity for bromine trifluoride were made over the temperature range of 130°C. to 200°C. and are given by the equation,

$$\eta, \text{ micropoise} = 21.33 \sqrt{T, ^\circ\text{K.}} - 230.2$$

From these data, the force constants for the Lennard-Jones (6-12) potential for bromine trifluoride were calculated to be,

$$\epsilon/k = 595^\circ\text{K.}$$

$$\sigma = 4.04 \text{ A.}$$

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INTRODUCTION

All substances possess a property which, when flow occurs within the substance, causes forces to arise in such a direction as to oppose the flow. The net effect is a decrease in the rate at which one layer moves with respect to another layer making it necessary to continually apply force in order to maintain flow. This retarding influence is called viscosity; and the coefficient of viscosity is defined (1) as the tangential force, in dynes per square centimeter of layer, exerted between the two parallel layers spaced 1 centimeter apart when the velocity of the moving layers differs by 1 centimeter per second, i.e., for a velocity gradient of unity. As given by Eirick (2) Newton's definition of viscosity is expressed by the equation,

$$f(\tau) = \frac{\tau}{\eta} \quad (1)$$

where,

$$\begin{aligned} f(\tau) &= \text{rate of shear} \\ \tau &= \text{shear stress} \\ \eta &= \text{coefficient of viscosity} \end{aligned}$$

A number of different apparatus may be employed to determine the coefficient of viscosity. In each case, the function $f(\tau)$ and τ must be defined in terms of measurable quantities (absolute determination) or in terms of known and unknown quantities in such a manner that the unknown quantities may be cancelled (relative determination).

Although the role of viscosity in flow through porous media has been recognized for many years, very little has been done to investigate the feasibility of determining coefficients of viscosity from flow through porous materials. Ruppert (3) substituted a porous medium for a capillary in a gas transpiration method. Biles and Putnam (4) suggested that the nonlinearity of flow with average pressure through porous media at high pressures could be accounted for by the change in the coefficient of viscosity with pressure. They calculated coefficients of viscosity for air that would give a linear relationship for a porous Alundum plug up to pressures of 900 pounds per square inch.

The purpose of this work was to develop a porous-medium method to determine relative coefficients of viscosity for both corrosive and non-corrosive gases; and specifically to determine relative coefficients of viscosity for bromine trifluoride. Coefficients of viscosity for argon were also determined to demonstrate the accuracy of this method.

SUMMARY AND CONCLUSIONS

The following statements summarize the results obtained in this work.

- a. The porous-medium method was used to determine relative coefficients of viscosity for a corrosive and a non-corrosive gas.
- b. Coefficients of viscosity for argon were determined over the temperature range of 35°C. to 200°C.
- c. Coefficients of viscosity for bromine trifluoride were determined over the temperature range of 130°C. to 200°C.
- d. Force constants for the Lennard-Jones (6-12) potential were calculated from the experimental data for bromine trifluoride.

Coefficients of viscosity for bromine trifluoride are given by the equation,

$$\eta, \text{ micropoise} = 21.33 \sqrt{T, ^\circ\text{K.}} - 230.2$$

and for argon by the equation,

$$\eta, \text{ micropoise} = 22.14 \sqrt{T, ^\circ\text{K.}} - 157.9$$

For bromine trifluoride, the Lennard-Jones (6-12) potential force constants were calculated to be,

$$\epsilon/k = 595^\circ\text{K.}$$

$$\sigma = 4.04 \text{ \AA.}$$

The porous-medium method can be used to determine relative coefficients of viscosity for both corrosive and noncorrosive gases. The upper temperature limit of this work (200°C.) was by choice and should not be considered a limitation imposed by the method. The method could be extended to higher temperatures by the proper choice of system components. Similarly, the effective coefficients of viscosity of gas mixtures could be determined since the same principles would apply.

THEORY

The porous-medium method, based on the theory of flow through porous materials, is a relative method for determining coefficients of viscosity. The theory of flow through porous materials has been adequately covered. The equations used in this work will be developed from the works of Carman (5), and deBethune (6).

Coefficients of viscosity for gases can be calculated by a theoretical extension of experimental data. These calculations, discussed in detail by Hirschfelder, Curtis, and Bird (7), make use of force constants obtained from the experimental data. The relationships used in determining the force constants for bromine trifluoride will be discussed.

Flow of Gases Through a Porous Medium

In developing a theory for the flow of gases through a porous medium, one can utilize the Poiseuille equation for viscous flow and the Knudsen equation for free molecular flow through a capillary. The Poiseuille equation is,

$$G_p = \frac{\pi r^4 M (P_2^2 - P_1^2)}{16 \eta L R T} \quad (2)$$

and the Knudsen equation is,

$$G_k = \frac{16 r^3 (P_2 - P_1)}{3 L \bar{v}} \quad (3)$$

where,

- G_p = Poiseuille mass flow rate
- G_k = Knudsen mass flow rate
- r = capillary radius
- P_2 = upstream pressure
- P_1 = downstream pressure
- $\bar{v}$ = mean molecular velocity
- L = capillary length
- η = coefficient of viscosity
- R = gas constant
- T = absolute temperature
- M = molecular weight

In calculating the mass flow rate through a capillary, the Knudsen equation holds in the density region where the mean free path is greater than the capillary diameter and the Poiseuille equation holds where the mean free path is less than the capillary diameter.

If a porous medium is considered as analogous to a bundle of capillaries, one would expect the flow through this medium to consist of both Knudsen and Poiseuille flow with a predictable transition region. Carman (5) states that Adzumi first realized that in fine-pored media, the mean free path was comparable to the "capillary" diameter even at atmospheric pressure. This being the case, the transition from Knudsen to Poiseuille flow would be continuous over a considerable pressure range. By combining Knudsen and Poiseuille terms then, one should be able to describe flow through a porous medium. Carman and Arnell (8) showed experimentally that in porous media these flow components are additive.

If one considers a single capillary, the flow over the entire pressure range is given by,

$$Q = \frac{\pi r^4 M (P_2^2 - P_1^2)}{16 \eta L R T} + \frac{16 r^3 (P_2 - P_1)}{3 L \bar{v}} \quad (4)$$

where Q is the total mass flow rate. Then for a porous medium the flow rate would be given by equation (4) multiplied by the total number of pores (capillaries) where r is the average pore radius and L the average pore length.

The analogy ends when one considers the internal structure of a porous medium in which are found all forms of constrictions and voids open to the molecules. These constrictions will alter the direction of flow many times as the molecules traverse the medium. To account for this, geometric factors are introduced into each term of equation (4) giving the result,

$$Q = \frac{\pi r^4 M (P_2^2 - P_1^2) \theta_1}{16 \eta L R T} + \frac{16 r^3 (P_2 - P_1) \theta_2}{3 L \bar{v}} \quad (5)$$

where θ_1 and θ_2 are the geometric factors (5, 6).

At this point it is convenient to define a dimensionless transport parameter, W , related to the transmission probability (9, 10) by,

$$W = \frac{Q \bar{v}}{A (P_2 - P_1)} \quad (6)$$

where A is the sample area. Then,

$$W = \frac{r^4 (P_2 + P_1) \theta_1}{2 \bar{v} \eta L A} + \frac{16 r^3 \theta_2}{3 L A} \quad (7)$$

For a given porous medium this can be rewritten as,

$$W = I + m (P_2 + P_1) \quad (8)$$

where,

$$I = \frac{16r^3\theta_2}{3LA} = \text{constant} \quad (9)$$

and m varies only as $1/\eta\bar{v}$. Hence, if W is measured at various summation pressures $(P_2 + P_1)$ the slope of the line, m , should be determined by the gas used. Therefore,

$$m\eta\bar{v} = \frac{r^4\theta_1}{2LA} = \text{constant} \quad (10)$$

The coefficient of viscosity for gas "a" could then be calculated by the following equation if the coefficient of viscosity of gas "b" is known and m_a , $\bar{v}_a$, m_b , and $\bar{v}_b$ are determined.

$$\eta_a = \eta_b \left(\frac{m_b \bar{v}_b}{m_a \bar{v}_a} \right) \quad (11)$$

Since $\bar{v} = (8RT/\pi M)^{1/2}$, equation (11) reduces to,

$$\eta_a = \eta_b \left(\frac{m_b}{m_a} \right) \left(\frac{T_b M_a}{T_a M_b} \right)^{1/2} \quad (12)$$

Equation (12) is the basic equation used in this work to determine the relative coefficients of viscosity.

Theoretical Calculations of the Coefficients of Viscosity

In presenting this section of the theory, the work of Hirschfelder, Curtis, and Bird (7) has been heavily relied on. The basic equation, derived from statistical mechanics, is,

$$\eta, \text{ micropoise} = \frac{26.693 \sqrt{MT}}{\sigma^2 \left[\Omega(2,2) \star (T^*) \right]} \quad (13)$$

where,

26.693 = constant of the first approximation
for Sonine expansion coefficients

σ = collision diameter in angstroms

$\Omega^{(2,2)\star}(T^*)$ = reduced collision integral

The reduced collision integral represents an averaging of the collision cross section over all orientations and relative kinetic energies of colliding molecules and is a result of a triple integration of a potential function describing the potential energy of interaction, $\phi(r)$, of the colliding molecules. The form of $\phi(r)$ depends on the model chosen to represent the colliding molecules.

Recently, emphasis has been placed on the Lennard-Jones (6-12) potential (11), given by the equation,

$$\phi(r) = 4 \epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (14)$$

where,

ϵ = minimum value of $\phi(r)$

r = intermolecular separation of the
colliding molecules.

This potential function is shown in figure 1. The model is one of induced-dipole-induced-dipole interaction. The electron configuration at any instant produces an instantaneous dipole in the molecule. This dipole induces dipoles in surrounding molecules. The effect of this induced-dipole-induced-dipole is to produce the attractive-repulsive forces. These forces are more important at lower temperatures.

The quantity $\left(\frac{\sigma}{r} \right)^{12}$ represents the repulsive forces. The exponent agrees with theoretical considerations and molecular beam scattering measurements, both of which indicate that the exponents for most gases lie between about 6 and 15. The quantity $-\left(\frac{\sigma}{r} \right)^6$ represents the attractive forces. The exponent is the first in the series (r^{-6} , r^{-8} , r^{-10} , ...) for the attractive forces between molecules. The reduced collision integrals for the Lennard-Jones (6-12) potential are tabulated by Hirschfelder, Curtis, and Bird (7) as a function of kT/ϵ where k is the Boltzman constant.

LENNARD-JONES (6-12) POTENTIAL

FIGURE 1

Force Constants From Experimental Data

The values of σ and ϵ may be determined from experimental viscosity measurements (7) at two temperatures, T_1 and T_2 . One first defines a quantity k_η by,

$$k_\eta = \left(\frac{\eta_2}{\eta_1} \right) \left(\frac{T_1}{T_2} \right)^{1/2} \quad (15)$$

where,

η_2 = experimental coefficient of viscosity at T_2
 η_1 = experimental coefficient of viscosity at T_1

By utilizing equation (13), k_η is also given by,

$$k_\eta = \left[\frac{\Omega^{(2,2)\star}(T_1^*)}{\Omega^{(2,2)\star}(T_2^*)} \right] \left[\frac{f_\eta^{(3)}(T_2^*)}{f_\eta^{(3)}(T_1^*)} \right] \quad (16)$$

where $T_i^* = kT_i/\epsilon$, and $f_\eta^{(3)}(T_i^*)$ is a very slowly varying function of T^* differing only slightly from unity⁺.

The value of ϵ/k is determined by trial and error from equation (16). As a first approximation to ϵ/k ,

$$\epsilon/k = 1.18 T_b$$

where T_b is the boiling point temperature. Different values of ϵ/k are then chosen until the value of k_η of equation (16) agrees with that of equation (15). Once the value of ϵ/k has been determined, the collision diameter is determined from,

$$\sigma^2 = \frac{26.693 \sqrt{MT} \left[f_\eta^{(3)}(T_i^*) \right]}{\left[\eta(T_i), \text{ micropoise} \right] \left[\Omega^{(2,2)\star}(T_i^*) \right]} \quad (17)$$

⁺Values for this function are tabulated on page 1130 of reference (7) as a function of T^* .

where T_i is either T_1 or T_2 . Slightly different sets of parameters are obtained from different choices of T_1 and T_2 since the Lennard-Jones (6-12) potential is an empirical function and does not give an exact description of the dependence of the intermolecular force on the separation between the molecules.

These equations were used to calculate the values of ϵ/k and σ for the Lennard-Jones (6-12) potential from the experimental data obtained for bromine trifluoride.

EXPERIMENTAL METHODS

An experimental system was assembled with which to obtain relative coefficients of viscosity for corrosive and noncorrosive gases at various temperatures. This was done by determining, for a porous medium, the W versus summation-pressure relationship of each gas at each temperature. A schematic diagram and a photograph of the system are shown in figures 2 and 3, respectively.

Experimental System

The experimental system consists of eight main functional sections. These sections, or their functions, are; test gases, the porous medium, porous-medium holder, vacuum facilities, pressure measurement and control, temperature measurement and control, flow measurement, and calibration facilities. Each will be discussed separately. The system was constructed of parts and materials that were conveniently at hand. In many instances other materials or equipment would probably have worked as well. Therefore, functional aspects are discussed here in detail only if there is unusual application of these parts and equipment.

Test Gases. Nitrogen, argon, and bromine trifluoride were selected due to availability, general properties, and the accurate knowledge of the coefficients of viscosity for nitrogen and argon over the temperature range to be studied. For nitrogen and argon, standard-cylinder gas was used throughout this work. The bromine trifluoride was contained in 1-pound lecture bottles. Fluorine was used to pretreat the metal surfaces because of the corrosive properties of bromine trifluoride (12).

Porous Medium. The porous medium, a disc made of nickel powder, was compacted at 40,000 pounds per square inch pressure and sintered for 10 minutes at 600°C. The diameter and thickness, set by considering system limitations on flow measurements and the flow-determining properties of the porous medium, were 2.64 and 0.025 centimeters, respectively. The mercury intrusion average pore radius was 0.0001 centimeter.

Porous-Medium Holder. A cross section of the porous-medium holder is shown in figure 4. The holder was made from Monel. Since external and internal sealing (around the porous medium) were required, three ring-shaped Teflon gaskets were used in obtaining a seal. The positioning of these gaskets around the sample is shown in the figure. The area of

SCHEMATIC DIAGRAM OF THE VISCOSITY SYSTEM

FIGURE 2

PHOTOGRAPH OF THE VISCOSITY SYSTEM

FIGURE 3

CROSS-SECTION OF THE POROUS-MEDIUM HOLDER

FIGURE 4

the porous medium exposed to the test gas, determined by the size of the hole openings in the two outside gaskets, was approximately 2.84 square centimeters. The holder was equipped with gas inlet and outlet lines, high-side and low-side pressure-measurement lines, and thermocouple connections.

Vacuum Facilities. It was desired to operate below atmospheric pressure; therefore, vacuum pumping had to be obtained for both corrosive and noncorrosive gases. This was done by connecting a freeze-out trap, a chemical trap, and a Stokes' vacuum pump (modified for use with corrosive gases) in series with the flow outlet from the system. The vacuum pump was vented to the atmosphere. Valving was installed to bypass the freeze-out trap and the chemical trap when noncorrosive gases were tested. The freeze-out trap was maintained at -78°C . by a dry ice-trichloroethylene slush. The small amount of bromine trifluoride not frozen out after a test run was reacted with alumina in the chemical trap when the system was evacuated. The reaction products of the chemical trap were removed by continuous pumping.

Pressure Measurement and Control. Three model 206RF Taylor pneumatic pressure transmitters were used for pressure measurements. These were located in the right side of the heated compartment and maintained at 65°C . during argon and nitrogen testing and at 135°C . during bromine trifluoride, argon, and nitrogen testing. The latter temperature was required to prevent condensation of bromine trifluoride in the transmitter input lines. The high-side and differential pressure transmitters and the pressure-rise flowmeter had to be carefully calibrated at each of the two temperatures. The output pressures from the three transmitters were read on three well-type manometers.

High-side and low-side pressures were controlled by using Superior HGP valves with diaphragm air operators. A pressure regulator was used to set the reference pressure on one side of the diaphragm. The output from the pressure transmitter was connected to the other side of the diaphragm to complete the control loop.

Temperature Measurement and Control. Although fourteen thermocouples were used in the experimental system, only three were used to determine temperatures involved in taking data. The other eleven were incorporated with a Model 1130IP-10 Brown recorder and were used only to monitor temperature levels. The three thermocouples used to determine gas or porous-medium temperatures were introduced directly into the gas streams. The thermocouples were made from iron-constantan wire.

Two of the three thermocouples used in measuring gas and porous-medium temperatures were calibrated. The third thermocouple was used to determine the temperature of the pressure-rise volume and any temperature bias from published calibration data was incorporated in that calibration. A thermocouple reference junction, immersed in dibutyl phthalate in a small glass tube, was placed in an ice-water bath. A standard cell and a Minneapolis-Honeywell null indicator were used along with a Leeds and Northrup K-2 potentiometer to measure the thermocouple output.

Two Yellow Springs Model 63RA temperature controllers were used to govern the temperatures. One controller maintained the transmitter compartment at constant temperature while the other was used to control the porous-medium temperature. The transmitter compartment was heated but did not require "tight" control. A fan was placed in this compartment to prevent cold spots from developing. The sample compartment was baffled and equipped with two fans in order to obtain precise control of the sample temperature.

Flow Measurement. Flow measurements were made by measuring the elapsed time required for a flow to effect a set pressure increase in a calibrated volume. The pressure increase was measured with a pressure transmitter having an input range of 0 to 2.5 centimeters of mercury absolute. Photocells were used to set the pressure change and were fastened permanently to the pressure-rise manometer. The photocells in turn activated a Model PE3B Farmer Electric relay system which started and stopped a counter. Elapsed time measurements were made with a Model 480 Potter crystal-controlled counter. The accuracy of the counter (1×10^{-5} seconds) was determined in previous work (13) by comparison with signals broadcast by the National Bureau of Standards over Radio Station WWV, Beltsville, Maryland. Elapsed-time measurements were not considered a source of significant error in determining flows because of the high accuracy of the counter.

Calibrations. Pressure calibrations were made using U-tube manometers incorporated in the system. The thermocouples were calibrated with a platinum resistance thermometer and a precisely controlled temperature bath. The orifice used to calibrate the pressure-rise flowmeter was calibrated with a gravimetric primary standard (14).

Operational Procedures

This section is divided into three parts which deal with the operation of the experimental system and the procedures employed to obtain the experimental data. The purely mechanical details of operating this system will not be discussed. Because of the corrosive properties of bromine trifluoride, a leak-tight system had to be maintained at all times. Daily checks were made to assure that no leaks had developed. The system was always operated below atmospheric pressure while using bromine trifluoride.

The first part of this section will deal with the sample and system preparation. The second part describes the system operation. Data reduction is discussed in the final part.

Sample and System Preparation. During the initial testing with argon and nitrogen, no special treatment of the internal surfaces of the system was necessary. The surfaces at this time were probably covered with an oxide film. Bromine trifluoride, however, will not only cause wood and paper to burst into flame, but can react vigorously with bare metal or metal oxides (12). For this reason, all metal surfaces exposed to this gas

were pretreated with fluorine. This was done as follows (15): a mixture of approximately 20 percent fluorine and 80 percent nitrogen was introduced into the system with the porous sample in place. The high-side pressure transmitter output manometer was observed for approximately one-half hour to determine the progress of the fluorine consumption. When only a slight pressure change was observed, the system was maintained at these conditions for approximately four hours. The system was then evacuated and 100 percent fluorine was introduced into the system and remained for four hours. After diluting the fluorine with nitrogen, the system was evacuated and again treated with 100 percent fluorine for 16 hours. All system and sample pretreatment was carried out with the transmitter compartment at 65°C. and the sample compartment at approximately 145°C.

After this pretreatment, minimum exposure to the atmosphere was permitted. When long-term exposure was necessary, the system was again treated with 100 percent fluorine for four hours prior to operation.

System Operation. A total of 29 tests was made on the porous-medium sample. Each test required approximately seven hours to complete. The first 20 tests were made on argon and nitrogen at five temperatures (35°C., 70°C., 120°C., 155°C., and 200°C.). The remaining nine tests were made on nitrogen, bromine trifluoride, and argon at three temperatures (130°C., 170°C., and 200°C.). During operation, the electrical components operated continuously with the exception of the temperature recorder. This was used only to indicate the temperature level when changing temperatures and was not used during actual operation. Prior to any test, the system was evacuated and leak checked at a pressure less than 0.015 centimeter of mercury absolute as determined by a General Electric thermocouple vacuum gauge. Usually five to seven points were taken to establish a W versus summation-pressure curve. These were spaced along the summation-pressure curve at approximately equal increments. System start-up and a typical data point will be described to illustrate how the system was operated and how the data were obtained.

Assume the system is leak tight and at a constant pressure of less than 0.015 centimeter of mercury absolute. Assume also that the system compartments are at the desired temperature and the temperature controllers are maintaining these temperatures. The gas to be tested is introduced into the manifold. The high-side pressure control valve and the differential pressure control valve are then set to obtain a summation pressure in the desired range. As soon as the pressure transmitters stabilize, the vacuum block valve is closed. This starts a pressure build-up in the pressure-rise volume which activates the pressure-rise transmitter. When the mercury column of the pressure-rise output manometer breaks the light beam of the lower photocell, the counter is started by the relay system. When the mercury column breaks the light beam of the upper photocell, the counter is stopped by the relay system and the elapsed time recorded. When the mercury column is approximately half-way between the photocells, the temperature in the pressure-rise volume is measured with the potentiometer and null point indicator; the sample high-side pressure and differential pressure manometers are also read.

After the mercury column is past the upper photocell, the vacuum block valve is opened, and the pressure-rise volume evacuated until the mercury column is below the lower photocell assembly. The counter is reset and the vacuum block valve is again closed. This procedure is repeated until flow equilibrium is attained throughout the entire system. This is indicated by obtaining two consecutive elapsed-time measurements at essentially constant pressure conditions. These two elapsed-time measurements generally agree within 0.1 percent or less. At this time, the sample temperature is measured. The final values for the volume temperature, high-side pressure transmitter, differential pressure transmitter, and elapsed time, along with the sample temperature, are used to calculate W and the summation pressure.

Data Reduction. The experimental data were converted into terms of W and summation pressure using the pressure-rise flowmeter calibration, pressure transmitter calibrations, and the theoretical equations developed earlier. To avoid computational errors, a computer program was written and these calculations were made using an IBM 7090 electronic computer. Examples of test data are given in the appendix.

RESULTS

A summary of the 29 tests is presented in table I in terms of the slope, m , and the intercept, I , of the W versus summation pressure relationship. The individual coefficients of viscosity determined from these tests are presented in table II along with the average values at each test temperature.

Coefficients of Viscosity for Argon

Figure 5 shows the comparison between the argon viscosity data obtained in this work and the data reported by Kestin and Whitelaw (16). The coefficients of viscosity determined in this work are about one percent lower than these published data. The temperature relationship is given by the following equation,

$$\eta, \text{ micropoise} = 22.14 \sqrt{T, ^\circ K.} - 157.9$$

The confidence limits are $\pm 0.09^*$ for the value of 22.14 and $\pm 1.9^*$ for the value of 157.9.

*95 percent confidence level.

TABLE I
SUMMARY OF THE EXPERIMENTAL TESTS

Test Number	Nitrogen*		Argon*		Bromine Trifluoride*	
	slope, m, cm. Hg ⁻¹	Intercept, I, 10 ⁻⁴	slope, m, cm. Hg ⁻¹	Intercept, I, 10 ⁻⁴	slope, m, cm. Hg ⁻¹	Intercept, I, 10 ⁻⁴
1	0.11635	6.806	0.11029	6.794		
2	0.09947	6.737	0.09312	6.780		
3	0.09976	6.692	0.09248	6.725		
4	0.07728	6.309	0.07217	6.289		
5	0.07786	6.322	0.07241	6.317		
6	0.07015	6.348	0.06471	6.382		
7	0.06990	6.378	0.06470	6.347		
8	0.06101	6.415	0.05556	6.427		
9	0.06123	6.453	0.05678	6.396		
10	0.06065	6.410	0.05603	6.408		
11	0.06112	6.340	0.05633	6.360		
12	0.06843	6.363	0.06367	6.331		
13	0.06808	6.374	0.06336	6.373		
14	0.07454	6.358	0.06896	6.376		
15	0.07430	6.382	0.06868	6.397		
16	0.08729	6.327	0.08213	6.290		
17	0.08743	6.297	0.08156	6.312		
18	0.09651	6.200	0.09199	6.132		
19	0.09824	6.135	0.09203	6.178		
20	0.09885	6.109	0.09304	6.138		
21	0.04735	4.903			0.11460	4.913
22	0.04750	5.046	0.04374	5.124	0.11301	5.156
23	0.04720	4.904			0.11415	4.960
24	0.05508	5.061	0.05158	5.091	0.13710	5.041

SUMMARY OF THE EXPERIMENTAL TESTS (CONT.)

Test Number	Nitrogen*		Argon*		Bromine Trifluoride*	
	slope, m, cm. Hg ⁻¹	Intercept, I, 10 ⁻⁴	slope, m, cm. Hg ⁻¹	Intercept, I, 10 ⁻⁴	slope, m, cm. Hg ⁻¹	Intercept, I, 10 ⁻⁴
25	0.05483	5.061	0.05112	5.071	0.13727	5.091
26	0.05444	5.056	0.05080	5.079	0.13558	5.086
27	0.04361	4.927	0.04041	4.965	0.10340	4.940
28	0.04415	4.931	0.04078	4.984	0.10394	4.963
29	0.04379	4.965	0.04067	5.026	0.10413	4.989

*For a 6-point curve, the precision at the 95 percent C.L. is ± 0.00039 for m and $\pm 0.0302 \times 10^{-4}$ for I.

TABLE II
SUMMARY OF THE EXPERIMENTAL COEFFICIENTS OF VISCOSITY

Test Number	Test Temperature, °C.	η , micropoise			
		Argon		Bromine Trifluoride	
		Individual	Average	Individual	Average
1	35	229.4			
18	35	228.1			
19	35	232.1			
20	35	231.1	230.2		
2	70	252.3			
3	70	254.8			
16	70	251.1			
17	70	253.2	252.8		
4	120	279.9			
5	120	281.1			
14	120	282.6			
15	120	282.8	281.6		
24	130	284.3		198.0	
25	130	285.6		196.9	
26	130	285.3	285.1	197.9	197.9
6	155	301.5			
7	155	300.4			
12	155	298.9			
13	155	298.8	299.9		
21	170			218.1	
22	170	309.5		221.8	
23	170		309.5	218.2	219.4
8	200	328.2			
9	200	322.3			
10	200	323.5			
11	200	324.3			
27	200	323.6		233.4	
28	200	322.5		235.0	
29	200	321.8	323.7	232.7	233.7

COEFFICIENTS OF VISCOSITY FOR ARGON OVER THE
TEMPERATURE RANGE OF 300°K . to 470°K .

FIGURE 5

Coefficients of Viscosity and Force Constants for Bromine Trifluoride

Figure 6 shows the viscosity coefficients obtained in this work for bromine trifluoride. The temperature relationship is given by the following equation,

$$\eta, \text{ micropoise} = 21.33 \sqrt{T, ^\circ\text{K.}} - 230.2$$

and the confidence limits at the 95 percent confidence level are ± 0.61 for the value 21.33 and ± 12.8 for the value 230.2. The force constants calculated for the Lennard-Jones (6-12) potential are,

$$\epsilon/k = 595^\circ\text{K.}$$

$$\sigma = 4.04 \text{ \AA.}$$

Sources of Error

The principal sources of experimental error in this experiment were the measurements of high-side and differential pressure, flow rate, and temperature. A summary of the error estimates for these sources, in terms of the standard deviation at the 95 percent confidence level, is given in table III.

TABLE III
SUMMARY OF EXPERIMENTAL ERROR

<u>Source of Error</u>	<u>Transmitter Compartment Temperature, $^\circ\text{C.}$</u>	<u>Error*</u>
High-Side Pressure	65	$\pm 0.06 \text{ cm. Hg}$
	135	$\pm 0.14 \text{ cm. Hg}$
Differential Pressure	65	$\pm 0.021 \text{ cm. Hg}$
	135	$\pm 0.044 \text{ cm. Hg}$
Flow Rate	65-135	$\pm 0.000019 \text{ moles per minute}$
Temperature	---	$\pm 0.25 \text{ degree}$

*95 percent confidence level.

COEFFICIENTS OF VISCOSITY FOR BROMINE TRIFLUORIDE
OVER THE TEMPERATURE RANGE OF 400°K. to 470°K.

FIGURE 6

Additionally, the purity of the test gases could affect the values obtained. A mass spectrometer showed the purity of the nitrogen as 99.2 percent and the purity of the argon as 99.9 percent. The bromine trifluoride was obtained from the Matheson Company and had a guaranteed minimum purity of 98 percent. Attempts made to verify the purity with the mass spectrometer were unsuccessful because of the reactive nature of the compound. However, the existence of bromine trifluoride as a liquid at room temperature (boiling point approximately $126^{\circ}\text{C}.$) permitted the elimination of any remaining gaseous impurities. The container was flashed several times and then continuously pumped for about four hours by the corrosive gas vacuum system prior to testing. Although the exact amount of impurities could not be determined, their effect was thought to be small.

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BIBLIOGRAPHY

- (1) Glasstone, S., Textbook of Physical Chemistry, D. Van Nostrand Co., New York, N. Y., 1943, p. 272.
- (2) Eirick, F. R., Rheology, Academic Press, Inc., New York, N. Y., 1956, Vol. I, p. 32.
- (3) Ruppert, W., "The Viscosity of Gases, Its Determination and Significance in Flow Measurements," Die Messtechnik, 11, 237 (1932).
- (4) Biles, M. B., and Putnam, J. A., Use of a Consolidated Porous Medium for Measurement of Flow Rate and Viscosity of Gases at Elevated Pressures and Temperatures, University of California, Berkeley, California, 1952 (NACA TN 2783).
- (5) Carman, P. C., Flow of Gases Through Porous Media, Academic Press Inc., New York, N. Y., 1956.
- (6) de Bethune, A. J., The Intrinsic Geometrical and Flow Properties of Powder Packs, (Part 1), Boston College, Chestnut Hill, Mass., 1953.
- (7) Hirschfelder, J. O., Curtis, C. F., and Bird, R. B., Molecular Theory of Gases and Liquids, John Wiley and Sons, Inc., New York, N. Y., 1954.
- (8) Carman, P. C. and Arnell, J. C., "Surface Area Measurements of Fine Powders Using Modified Permeability Equations," Can. J. Research, 26A, 129 (1948).
- (9) Clausing, P., "The Flowing of Very Dilute Gases Through Tubes of Any Length," Ann. Physik, 12, 961 (1932).
- (10) Berman, A. S., and Lund, L. M., "Deviations from Classical Kinetic Theory in the Low Pressure Transport of Gases Through Porous Media," Proceedings of the Second International Conference, United Nations Peaceful Uses of Atomic Energy, 4, 359 (1958).
- (11) Svehla, R. A., Estimated Viscosities and Thermal Conductivities of Gases at High Temperatures, Lewis Research Center, Cleveland, Ohio, 1962 (NASA TR R-132).
- (12) Oliver, G. D., and Grisard, J. W., "Thermal Data, Vapor Pressure And Entropy of Bromine Trifluoride," J. Am. Chem. Soc., 74, 2705 (1952).
- (13) Evans, E. C., and Ray, G. W., Gas Mass Flow Measurements Accurate to One-Tenth Per Cent, Union Carbide Nuclear Company, Oak Ridge Gaseous Diffusion Plant, September 6, 1962 (K-1543).

- (14) Collins, W. T., and Selby, T. W., A Gravimetric Gas Flow Standard-Part II. Performance and Evaluation, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, April 15, 1966 (K-1632, Part II).
- (15) Smith, D. F., "Hydrogen Fluoride Polymer Spectrum, Hexamer and Tetramer," J. Chem. Phys., 28, 1040 (1958).
- (16) Kestin, J., and Whitelaw, J. H., A Relative Determination of the Viscosity of Several Gases by the Oscillating Disk Method, Brown University, Providence, Rhode Island, 1962 (BRN-2-P).

APPENDIX

EXAMPLES OF THE EXPERIMENTAL DATA

Examples of the W versus summation-pressure data for nitrogen, argon, and bromine trifluoride are given in tables IV, V, and VI. These data are test 29. Calculated pressures are given rather than the transmitter output readings. The same format is used for each of these tables. The test number, gas, and temperature are given in the table title. Columns one and two give the high-side and differential pressures, respectively. Column three gives the individual values of the transport parameter W; the corresponding summation pressures are given in column four.

TABLE IV

TEST 29. W VERSUS SUMMATION-PRESSURE DATA
FOR NITROGEN AT 200°C.

High-Side Pressure, cm. Hg abs.	Differential Pressure, cm. Hg	10^4 W	Summation Pressure, cm. Hg abs.
29.19	4.705	7.322	53.68
20.77	4.627	6.593	36.91
13.77	4.539	5.961	22.99
36.08	4.769	7.912	67.39
45.80	4.835	8.762	86.76

TABLE V

TEST 29. W VERSUS SUMMATION-PRESSURE DATA
FOR ARGON AT 200°C.

<u>High-Side Pressure, cm. Hg abs.</u>	<u>Differential Pressure, cm. Hg</u>	<u>10⁴ W</u>	<u>Summation Pressure, cm. Hg abs.</u>
20.53	4.641	6.503	36.41
36.76	4.776	7.822	68.75
46.16	4.842	8.577	87.49
29.87	4.723	7.282	55.01
13.81	4.556	5.959	23.07

TABLE VI

TEST 29. W VERSUS SUMMATION-PRESSURE DATA
FOR BROMINE TRIFLUORIDE AT 200°C.

<u>High-Side Pressure, cm. Hg abs.</u>	<u>Differential Pressure, cm. Hg</u>	<u>10⁴ W</u>	<u>Summation Pressure, cm. Hg abs.</u>
13.16	4.560	7.232	21.76
36.99	4.779	12.199	69.20
45.33	4.836	13.905	85.82
29.43	4.722	10.631	54.14
20.67	4.646	8.798	36.69
27.76	4.715	10.312	50.80
20.39	4.651	8.768	36.13