High-Temperature
GAS TRANSPORT

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The three major gas transport properties are diffusion of matter due to a concentration gradient, conduction of heat due to a temperature gradient, and the transport of momentum due to a velocity gradient. These are characterized by coefficients of diffusion, thermal conductivity, and viscosity, which enter into various aspects of basic and applied science. For example, the transport properties are closely related to collisions between molecules, and measurements of the former have added to our knowledge in this area. Many engineering situations involving heat and mass transfer and fluid flow require reliable data on the transport coefficients. Present trends are toward ever-widening extremes of conditions in such uses, particularly higher temperatures in propulsion systems, where there has been a notable lack of useful information on transport properties.

During an intensive APL study of laminar flame structure,[1] accurate molecular diffusion

coefficients were needed for certain binary gas systems up to 2000°K. This need, together with the lack of other transport data at high temperatures, stimulated a search for new methods of measurement. A technique for diffusion that was quite unlike accepted methods was soon developed and has since been adapted to thermal-conductivity measurement. This represents a distinct advance in the field of experimental transport-property measurements. A broad discussion of the new technique and some results of its use are given here.

Classical Methods

Before describing the new approach, let us review the classical methods of measuring the transport coefficients. Thermal conductivity of a gas is determined experimentally by measuring the temperature difference and the thermal flux between two isothermal surfaces. These are usually arranged to form a "cell" of either concentric cylinders or parallel plates. To measure diffusion coefficients, the most common method is to use a tube divided into two parts by a valve.

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[1] R. M. Fristrom and A. A. Westenberg, "Fundamental Processes and Laminar Flame Structure," *APL Technical Digest*, 1, 3, Jan.-Feb. 1962, 10-15.

Difficulties in conventional methods of measuring coefficients of diffusion and thermal conductivity in gases at even moderately high temperatures have led to development of novel techniques. A steady point source of one gas in a laminar flow of a second gas is used for measuring diffusion, while for thermal conductivity a steady line source of heat is necessary.

MEASUREMENTS

by the Source-in-Flow Method

Starting with a different gas in each of the two sections of the tube, the diffusion coefficient is obtained by analyzing the resultant mixtures in the two sections after the valve has been opened for a known time. The viscosity of gases has been measured in several ways, but most high-temperature measurements (500 to 2000°K) have been made by the capillary flow technique. Knowledge of the pressure drop and rate of gas flow through a capillary of known size may be used to obtain the viscosity.

One of the chief problems in operating much above room temperature (especially serious in the first two of these techniques) is the need for very close control of temperature uniformity—particularly spatial uniformity. Since the data of interest are *molecular* transport properties, it is important that the mixing or transfer be done only by molecular motion and not by movements of the gas as a whole, i.e., convection. Temperature gradients tend to set up thermal convection currents which would invalidate the experiments. Therefore, the necessary gradient held in the thermal conductivity cell must be very small.

Another problem with the thermal conductivity cell is in determining the part of the total heat input to the cell that is transferred between the surfaces by gas conduction alone. To do so requires a knowledge and minimization of radiation and end losses. The various forms and dimensions of the cells used usually are the results of compromises dictated by these heat losses and the requirements of the uniformity of temperature, both in distance and time. Further, we need precisely calibrated thermometers for accurate measurements of temperature differences.

In the case of diffusion, another strict limit on use of the diffusion-tube technique for higher temperatures is the need for some kind of a moving partition between the two sections of the tube.

For absolute determinations, all three transport-property techniques require that the dimensions of the various cells be known at all the temperatures used. Because of this and the other problems involved, many investigators have been satisfied with relative measurements.

Since high temperatures magnify these problems, it is not surprising that the number and accuracy of the available measurements decrease with increasing temperature. We know of only one report of diffusion-coefficient measurements above 500°K by a variation of the classical method, and the data scattered by as much as ± 10%; this was for the gas pairs CO_2–air and H_2O–air. The number of conventional thermal-conductivity measurements for most gases is small, and the disagreement among the various investigators is often pronounced. For example, for nitrogen and carbon dioxide there is a scatter of about 6% in the results within the 500-to-1000°K interval, with no clear grouping. There is only one known measurement on oxygen above 800°K, while the two known independent measurements for water at 800°K differ by about 20%. There are many data on viscosity at high temperatures, and measurements for a large number of gases have been made up to as high as 1800°K. Further, the accuracy claimed is of the order of 1% at elevated temperatures for a number of investigations. This is because viscosity measurements at high temperatures are simpler than for the other coefficients.

The New Source-in-Flow Method

The new approach to measuring the major transport properties over a fairly wide temperature range uses a laminar flow system containing a continuous source, or sink, of the particular quantity of interest, i.e., mass, heat, or momentum. In the case of mass diffusion, referring to Fig. 1, consider a point source of one gas (the trace) injected at a steady rate Q (in cm^3/sec) into a uniform laminar stream of a second gas (the carrier) flowing at constant velocity U (in cm/sec). With constant temperature and pressure, no chemical reaction, and such small source rate that the density may be called constant, distribution of the trace-gas concentration in mole fraction is given by:

$$C = \frac{Q}{4\pi Dr} \exp \left[(x-r) \, U/2D \right]; \qquad (1)$$

D (in cm^2/sec) is the binary diffusion coefficient for the trace carrier pair, and r (in cm) is the distance coordinate given by $r^2 = x^2 + y^2 + z^2$, where x is the axial distance (in cm) from the source. We can then determine D by measuring the concentration C_m at a known distance x on the flow axis just downstream of the source $(x = r)$, if Q is also known; thus, from Eq. (1),
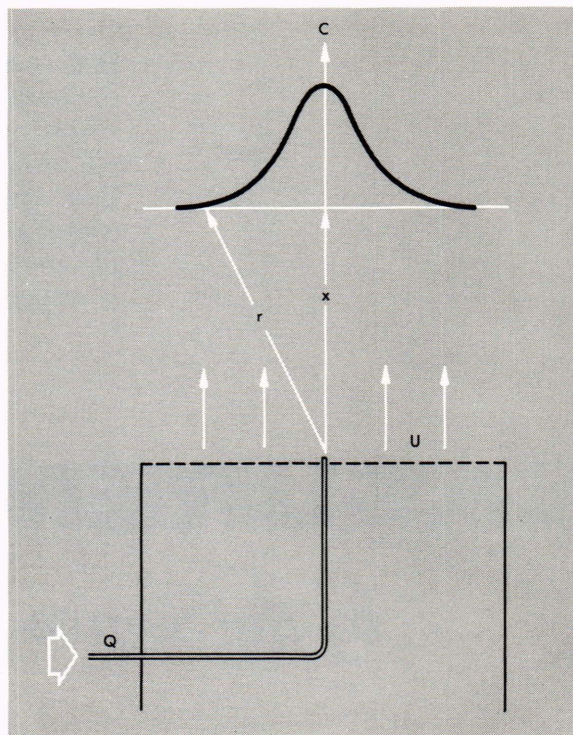

Fig. 1—The source-in-flow method of measuring mass diffusion coefficient.

$$D = \frac{Q}{4\pi x C_m} \, . \qquad (2)$$

In principle, of course, D could also be found by using the exponential part of Eq. (1) if U is known.

We can treat the case of heat diffusion for thermal conductivity in much the same way. If the point source of mass is replaced by one of heat H, then the distribution of temperature rise $\triangle T$ above that of the free stream is given by

$$\triangle T = \frac{H}{4\pi\lambda r} \exp \left[(x-r) \, UC\rho/2\lambda \right]; \qquad (3)$$

λ is thermal conductivity of the gas, C is specific heat at constant pressure, and ρ is density. Presumably, the $\triangle T$ values are so small that all the gas properties are essentially constant. We may then find λ in the way described for mass diffusion. One can readily see that an experimental approximation to a point source of mass is easier to attain than one of heat; for a line source the reverse is true. For an infinite line source of heat in the z-direction, the governing relation is

$$\triangle T = \frac{h}{(4\pi UC\rho\lambda r)^{1/2}} \exp \left[(x-r) \, UC\rho/2\lambda \right], \qquad (4)$$

where h is the heat transferred to the gas per unit length of source, and $r^2 = x^2 + y^2$.

Finally, if we consider a line sink for momentum in the laminar flow, there will be a velocity deficit $\triangle U$ in the wake of the sink; its distribution may be shown to be

$$\triangle U = \frac{-d}{(4\pi U \rho \mu r)^{1/2}} \exp \left[(x-r)\rho \ U/2\lambda \right], \quad (5)$$

where μ is the gas viscosity and d is the momentum sink strength or drag per unit length of the sink.

Apparatus

The one basic requirement common to all three transport-property equations is a steady, uniform, laminar gas flow that can be heated. The laboratory apparatus to deliver this flow is described as follows: A constant flow of the desired carrier gas is metered at an appropriate rate into a 1.5-in.-diameter pipe housed in a wire-wound furnace; the pipe exit is fitted with a series of 100-mesh precision screens to smooth out the flow. We thus have a laminar free jet that is uniform in velocity and temperature to about 1% in a central core region where the measurements are made. The jet temperature is then determined with a fine Pt, Pt-10% Rh thermocouple.

For diffusion experiments we must furnish a "point" source of a tracer gas. This is done by metering it into a 10-mil stainless steel hypodermic tube threaded through the screens from below and projecting slightly beyond the final screen into the jet. At the distances used, this tube is a close enough approximation to a point source for the theory to apply. The gas mixture in the diffusion region downstream of the source is sampled continuously with a quartz microprobe and analyzed in a precision, thermal-conductivity, gas-analysis cell. The probe is mounted on a three-dimensional micrometer for positioning. We can then measure the required quantities in Eq. (2), i.e., trace flow rate Q, distance x, and trace concentration C_m.

For thermal conductivity, the point source of matter must be replaced by a line source of heat. This is easily obtained by using a fine resistance wire (0.5-mil Pt or Rh) stretched across the jet a few millimeters above the final screen. The wire can be heated electrically to give a good approximation to a steady line source of heat. To avoid having to measure absolute values of the heat transfer rate h of Eq. (4), which would not be simply the electrical

power input if the wire lost some heat by radiation, we should use only the exponential part of Eq. (4) in determining λ. In other words, we measure the width of the transverse $\triangle T$ profile at some convenient fraction of the maximum $\triangle T$ (for $x = r$), say at half-maximum, for a series of distances x downstream of the source. In this way, only relative $\triangle T$ measurements are needed, an advantage at high temperatures where the thermoelectric power of the thermocouple may be uncertain. The quantity $\triangle T$ is measured by a differential thermocouple arrangement; one junction is held stationary somewhere in the free stream while the other, mounted on the three-dimensional movement, senses the temperature rise above the free stream in the thermal wake of the source.

Note that the exponential term in Eq. (4) contains the gas velocity U, which must, therefore, be measured; we assume that ρ and C can be obtained from standard sources. Measuring low velocities (about 100 cm/sec) has been considered such a very difficult task that the method in these experiments deserves special comment. The anemometer developed for this purpose uses two hot wires of the Wollaston type. One is fixed in position and is pulsed at a low audio frequency, typically 100 cps (Fig. 2). The other is movable and acts as a sensitive resistance thermometer to detect the fluctuating temperature in the wake of the first wire. The idea is to measure the phase difference between the detector signal at two positions a known distance apart and downstream (this phase difference is inversely proportional to the flow velocity). The phase comparison is made by applying a multiple of the original source frequency (which
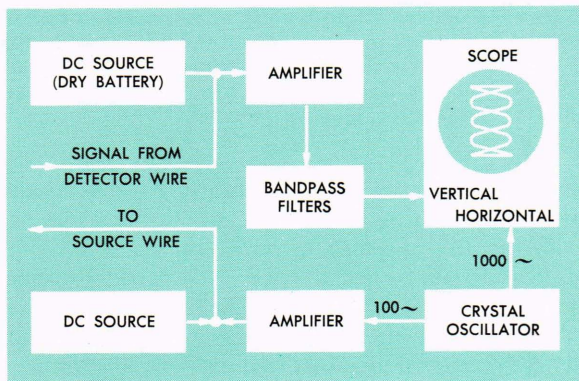
Fig. 2—Two-wire low-speed anemometer. Velocity of the flow is given by $U = 2000 \triangle x/N$, where $\triangle x$ is movement of the detector wire causing a phase change corresponding to N pattern repetitions of the 10:1 Lissajous figure.

is therefore locked in phase to the source) to the horizontal oscilloscope input, while the detector signal is applied to the vertical. The resulting Lissajous figure (Fig. 2) is then used to measure the phase change as the detector wire is moved downstream, since the figure repeats itself at certain known phase intervals. With this anemometer, velocity measurements to an accuracy of about 2% may be made in the range 40 to 300 cm/sec.
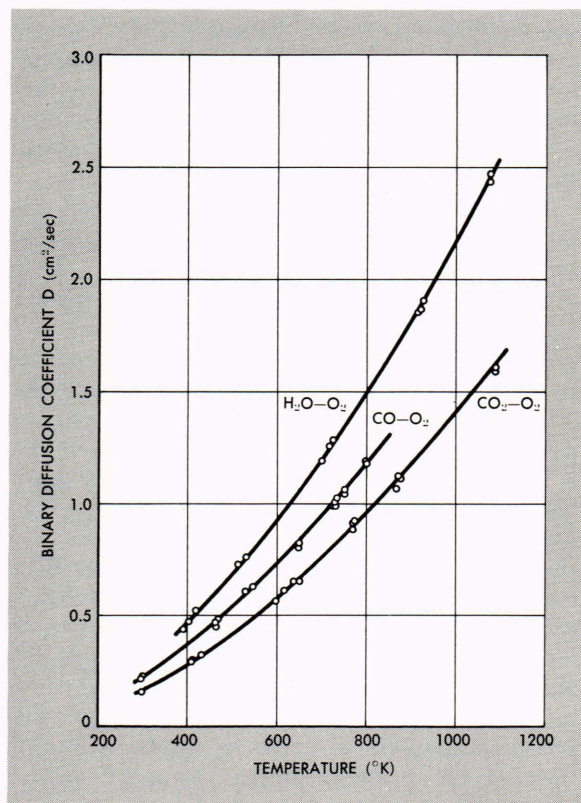
Fig. 3—Diffusion coefficient D as a function of temperature for gas pairs $H_2O - O_2$, $CO - O_2$ and $CO_2 - O_2$, obtained by the source-in-flow method. The $CO - O_2$ data could not be extended above 800°K because of ignition of the CO tracer.

The third property, viscosity, has not been actually measured experimentally by this method. In principle, we could use Eq. (5) by exploiting the exponential term in the same way as for thermal conductivity. We could provide the line sink for momentum by a taut wire (unheated in this case) across the jet, and we would have to measure relative values of the velocity decrement $\triangle U$ in the wake. A suitable method for precisely measuring $\triangle U$ would probably be the chief difficulty. The regular two-wire anemometer just described could not be used because its spatial resolution would not

suffice. A carefully calibrated single hot wire suggests itself at once, but such calibration is far from simple. Therefore, use of this method in viscosity measurement has not been carried out; nor is it likely to be since conventional methods are more suitable for high-temperature viscosity work than for the other transport properties.

Results

These new techniques have been extensively studied and checked for both diffusion and thermal conductivity in order to prove that the basic model was followed experimentally. This indeed was the case. Results for common test gases were then compared with known, published values obtained by the conventional means. Because agreement was excellent, the source-in-flow methods were shown to be reliable.

For binary diffusion, the following gas pairs have thus far been studied over the approximate temperature range of 300 to 1100°K: He − N_2, He − Ar, $CO_2 − N_2$, $CO_2 − O_2$, $CO − O_2$, $H_2 − O_2$, $H_2 − Ar$, $CH_4 − O_2$, and $H_2O − O_2$. Figure 3 shows some examples of these results. The data obtained cover a wide enough range of temperatures to make possible an interpretation in terms of the Chapman-Enskog[2] kinetic theory of dilute gases. We did this by finding constants for various intermolecular potential energy functions that best fit the data. This threw some light on the binary collision processes characterized by these potential functions. One set of significant data involved the He−Ar system. The potential function for this pair of gases had been determined as a simple inverse power of the molecular separation distance in an entirely different experiment carried out elsewhere. This was a molecular beam-scattering experiment, and as such was a more direct measure of the He−Ar interaction. We could then use this scattering potential to predict the He−Ar diffusion coefficient as a function of temperature by means of kinetic theory (i.e., the reverse of deriving the potential from diffusion data). Also, the scattering predictions had an expected range of validity that overlapped the upper end of the experimental temperature range covered in the direct APL diffusion measurements. Thus, an interesting cross check on both experiments and theory was possible. The results of this procedure, where

[2] S. Chapman and T. G. Cowling, "Mathematical Theory of Non-Uniform Gases," Cambridge University Press, London, 1939.

the direct data and the scattering prediction fit together with gratifying smoothness, are shown in Fig. 4.

The diffusion data obtained by the new method have also been put to good use in the quantitative analysis of laminar flame structure since the pairs $CH_4 - O_2$, $H_2 - O_2$, $CO - O_2$, $CO_2 - O_2$, and $H_2O - O_2$ account for all the stable species found in lean methane-oxygen flames. The high-temperature diffusion data have permitted a much more reliable extrapolation to flame temperatures, where diffusion of all species strongly affects interpretation of the flame structure data.[1]

To summarize, there are two advantages of the point source diffusion technique: (a) it permits reliable data ($\pm 2\%$) to be obtained up to quite high temperature, the upper limits being set by materials problems; and (b) since it is a trace technique, ambiguities due to the concentration dependence of the diffusion coefficient are avoided in cases where they are significant. The main disadvantage of the technique is the need for large gas flows.

We have now obtained thermal conductivity data for O_2, N_2, CO_2, and $N_2 - CO_2$ mixtures over the entire composition range. To some extent, these were regarded as test cases since data have been reported previously for these gases. Figure 5 shows the new data for
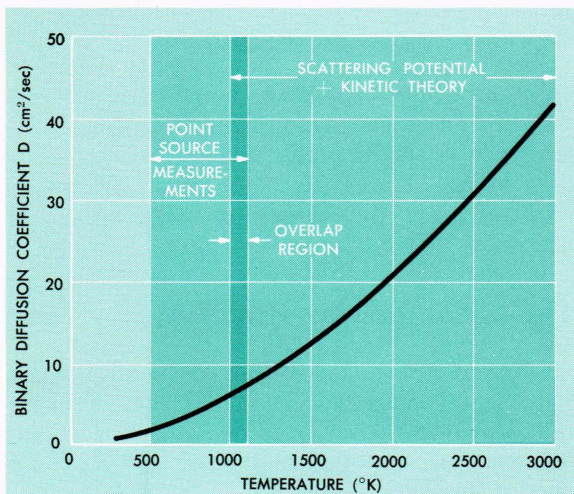
Fig. 4—Diffusion coefficients for the helium (trace)-argon system. Values up to about 1200°K were obtained by source-in-flow measurements. The high-temperature portion of the curve was calculated by applying kinetic theory to the helium-argon potential function obtained from molecular beam-scattering experiments. A cross-check on both experiments and theory was provided in the overlap region.
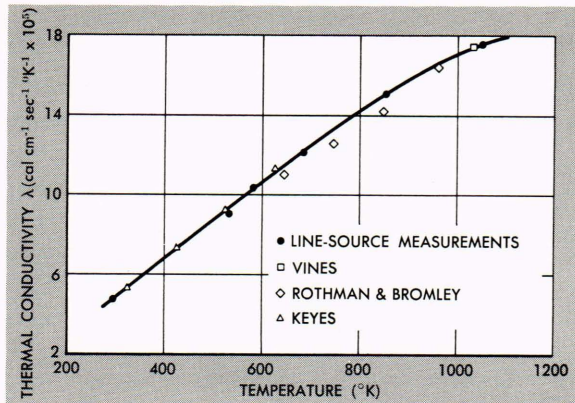
Fig. 5—Comparison of the thermal conductivity λ of the gas mixture 50-50 mole percent $CO_2 - N_2$ as measured by the source-in-flow method and by classical methods.

a 50-50 mole percent mixture of N_2 and CO_2 and older results [3] obtained conventionally. Agreement is generally very good. One reason for studying this mixture was our expectation that the data could provide a good case for checking the predictions of kinetic theory. A fairly rigorous theoretical calculation of the thermal conductivity of a binary mixture of non-polar gases can be made. However, data on the thermal conductivity and viscosity of the pure components must be available, plus the binary diffusion coefficient of the pair. Both the pure gas thermal conductivities and the binary diffusion coefficient were available from the APL experiments, while reliable viscosity data were available in the literature. Therefore, a direct application of the mixture theory was feasible for comparison with experiment over the whole temperature and composition range. Results showed general agreement at the lower temperatures but possibly some deviation at the highest, although the experimental scatter was enough to preclude a definitive conclusion.

Other thermal-conductivity measurements with the line-source technique are now in progress, particularly on mixtures with polar molecules for which the appropriate kinetic theory is only now being worked out. From a more immediately practical point of view, data on polar gases would also be of value in various rocket and ramjet heat transfer applications since they are now almost completely lacking.

[3] R. G. Vines, "Measurement of the Thermal Conductivities of Gases at High Temperatures," *J. Heat Transfer (Trans. Am. Soc. Mech. Engrs.)*, 82, 1960 48-52; A. J. Rothman and L. A. Bromley, "High Temperature Thermal Conductivity of Gases," *Ind. and Engr. Chem.*, 47, 1955, 899-906; and F. G. Keyes, "Additional Measurements of Heat Conductivity of Nitrogen, Carbon Dioxide, and Mixtures," *Trans. Am. Soc. Mech. Engrs.*, 74, 1952, 1303-1306.