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THE STATUS OF TRANSPORT PROPERTIES OF AIR

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V. E. Schrock

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NOMENCLATURE

c_v	Constant-volume specific heat
c_p	Constant-pressure specific heat
D	Diameter
f	Property group $c_v \eta/k$
g_c	Gravitational constant
h	Boltzmann constant
k	Thermal conductivity
\dot{m}	Mass flow rate
M	Molecular weight
p	Pressure
Pr	Prandtl number
\vec{r}	Distance from center of mass
T	Temperature
V	Volume
x	Distance along tube
γ	c_p/c_v
ϵ	Energy parameter
η	Viscosity
ρ	Density
ϕ	Force potential for molecular encounters
Ω	Transport integral defined in Eq. (4)

THE STATUS OF TRANSPORT PROPERTIES OF AIR

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September 25, 1962

I. INTRODUCTION

As materials technology permits higher temperature operation of propulsion equipment, accuracy of performance predictions becomes lower due to uncertainty in the physical properties of materials. Of particular concern in jet-propulsion devices are of course the properties of gases. Thermodynamic functions, are known to a comparatively high degree of accuracy. Transport properties, viscosity, thermal conductivity, and the mass diffusion coefficients, are difficult to measure with a high degree of accuracy and therefore are not as well known, particularly at high temperature. Viscosity, thermal conductivity, and Prandtl number are of primary importance in high-temperature heat transfer to gases. The purpose of this report is to explore the status of experimental data for air and to review the measurement problem and techniques and the predictions available from the general transport theory of Boltzmann. Because the constant-pressure specific heat is known to a high degree of accuracy, the Prandtl number $c_p \eta / k$ is customarily calculated from it and the best available viscosity and thermal conductivity. For this reason emphasis is given here to viscosity and thermal conductivity.

II. THEORETICAL PREDICTION OF THERMAL CONDUCTIVITY
AND VISCOSITY

Maxwell and Boltzmann established the general transport equation for the kinetic theory of gases. This theory is described in great detail by Chapman and Cowling¹ and Hirschfelder et al.² Chapman and Enskog independently obtained solutions for the transport properties. These solutions

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are rigorous for dilute monatomic gases, but are approximate to some degree for the more complex polyatomic molecules. The process of momentum exchange, characterized by viscosity, is predicted with negligible error at ordinary temperature for the polyatomic gas because internal modes of motion play a relatively unimportant role in momentum consideration. In the case of thermal conductivity (energy transport) the internal motions are very important and the theory must be corrected to yield suitable results even at moderate temperatures. The correction factor was first derived by Eucken³ by consideration of transfer of energy between translational and internal (rotation and vibration) modes.

As the temperature increases, all transport properties, particularly the thermal conductivity, become less certain theoretically. This is apparently due to lack of understanding of the fundamental force potential for molecular encounters. Since this potential is not directly measurable, it is commonly inferred from transport properties and this interest, among others, has helped to stimulate interest in accurate direct measurements of transport properties. Several models have been proposed for the force potential, e. g. , Lennard-Jones, Sutherland, Buckingham, etc. , but so far none has proven entirely satisfactory nor is there general agreement as to which potential is most nearly correct.

From the Chapman-Enskog solution the relation between viscosity and thermal conductivity is, to the first approximation:

$$k = f c_v \eta \quad (1)$$

where k is the thermal conductivity, c_v is the constant-volume specific heat, η is the viscosity, and the factor $f = 5/2$ for spherically symmetric non-rotating molecules. For higher approximations f approaches 2.522. For rotating molecules (considering internal modes only) $f = 1$, so the actual value is between 1 and 2.522.

It might be worthwhile to note that the factor f is related to Prandtl number, i. e. ,

$$\text{Pr} = \gamma / f \quad (2)$$

where $\gamma = c_p / c_v$, the specific heat ratio.

The Eucken correction for polyatomic molecules is based on the additive values of f for internal motion and f for translation with their contributions determined by γ so that

$$k = (1/4)(9\gamma - 5)c_v\eta \quad (3)$$

for polyatomic molecules. Chapman and Cowling question the separability of the translational and internal contributions. In essence, thermal conductivity is more complicated due to the sensitive dependence of transition probabilities for the transfer of energy between various degrees of freedom of the molecule and the effect this has upon energy exchange between molecules experiencing inelastic collisions. The Eucken correction is an approximation which assumes rapid transfer such that the energy distribution among molecular states is essentially the equilibrium distribution corresponding to the local temperature.

Bromley³⁷ extended the Eucken correction by considering more detail of the internal energy modes. Internal rotation was considered separately from overall rotation and vibration. Electronic transitions were also included. The resulting equation for the factor $f = k/c_v\eta$ in the pressure-independent range (low pressure) includes temperature dependence.

In the kinetic theory (dilute gas) prediction of the transport coefficients the integral transport equations based on the conservation principles are solved by expanding scalar functions in Sonine polynomials which depend upon a double integral*

$$\Omega^{\ell, s} = \frac{2\pi kT}{\mu_{ij}} \int_0^\infty \int_0^\infty e^{-\gamma_{ij}^2} \gamma_{ij}^{2s+3} (1 - \cos^\ell \chi) b db d\gamma_{ij} \quad (4)$$

This is written for a collision between molecules of types i and j ; μ_{ij} is the reduced mass of the colliding pair, γ_{ij} is the reduced initial relative speed of the colliding molecules, χ is the angle of deflection in the center-of-mass system, and b is the impact parameter (distance between molecules at the projected closest point of approach). Parameters are tabulated in Hirschfelder, et al.

*For details see Hirschfelder, et al. Ref. 2.

The theory predicts the transport properties in terms of $\Omega^{(\ell, s)}$ and properties of the potential functions which are of the general form:

$$\phi(\vec{r}) = \epsilon f\left(\frac{\vec{r}}{\sigma}\right) \quad (5)$$

in which ϵ is the energy constant and σ is the molecular diameter. Thus, for coefficient of shear viscosity of a pure gas

$$[\eta]_k = [\eta]_1 f_\eta(k) \quad (6)$$

where $[\eta]_1$, is the first order approximation,

$$[\eta]_1 \times 10^7 = 266.93 \frac{\sqrt{M/T}}{\sigma^2 \Omega^{(2,2)} T^*} \quad (\text{poise}) \quad (7)$$

where

M is molecular weight

T is temp., °K

$T^* = kT/\epsilon$

σ = collision diameter, Å

* on $\Omega^{(2,2)}$ refers to normalization to the hard sphere value of $\Omega^{(2,2)}$.

The correction $f_\eta(k)$ is a slowly varying function of T^* and is given in Chapter 8 of Hirschfelder. In the case of binary gases (air approximately) this result is complicated by collisions between unlike species and may be treated by methods described by Hirschfelder.

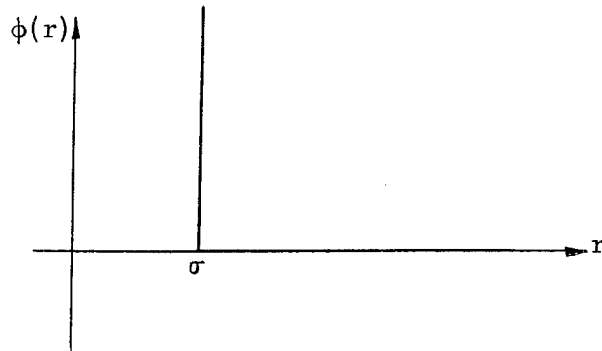
Thermal conductivity is given by

$$[k]_k = f_k(k) [k]_1 \quad \text{with}$$

$$[k]_1 \times 10^7 = 1989.1 \frac{\sqrt{T/M}}{\sigma^2 \Omega^{(2,2)} T^*} \quad (\text{cal/cm sec}) \quad (8)$$

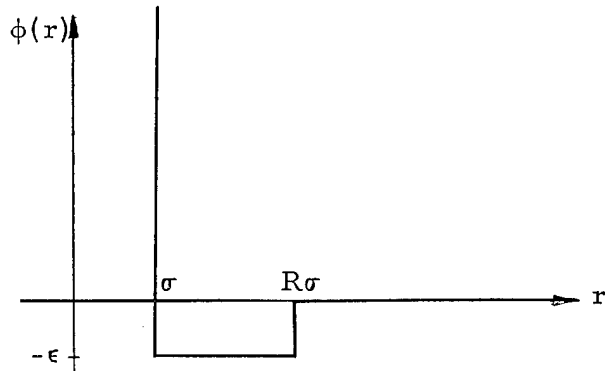
where $f_k(k)$ differs from $f_\eta(k)$ as explained above and approximately by the Eucken correction. For the binary mixture (multicomponent mixture in general) the expression is again more complex because of collisions of various types which are possible.

A. Rigid Sphere



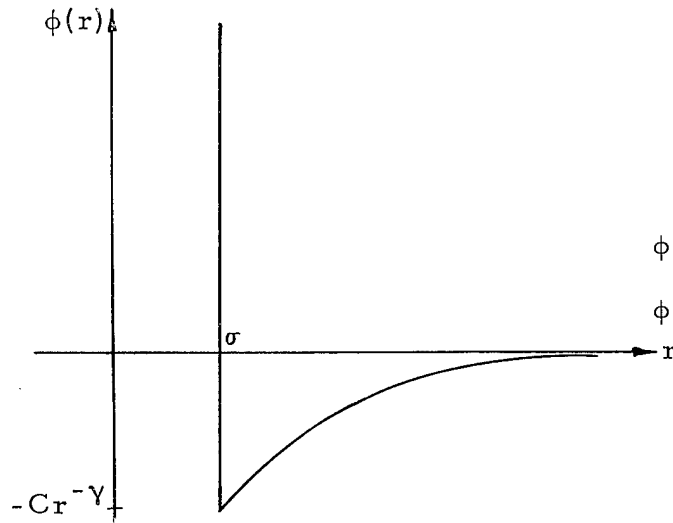
$$\begin{aligned} \phi(r) &= \infty, \quad r < \sigma \\ \phi(r) &= 0, \quad r > \sigma \end{aligned} \quad (9)$$

B. Square Well

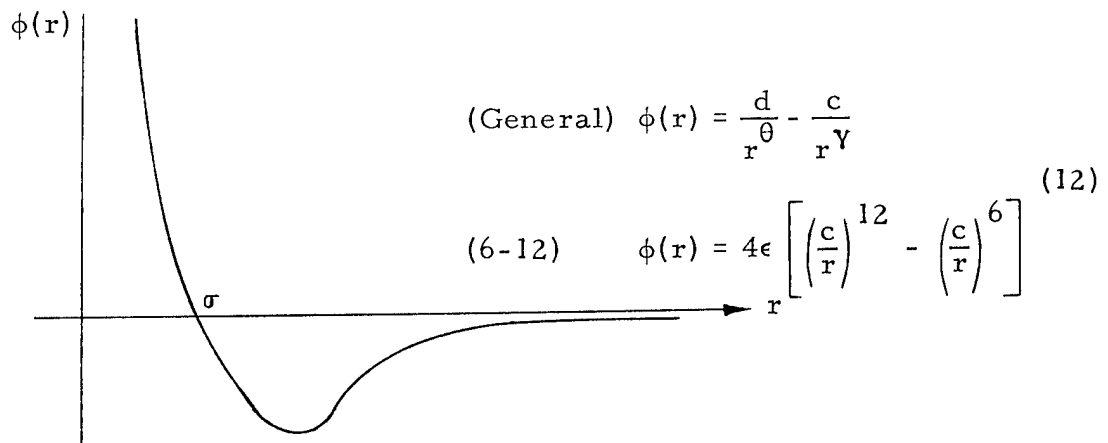
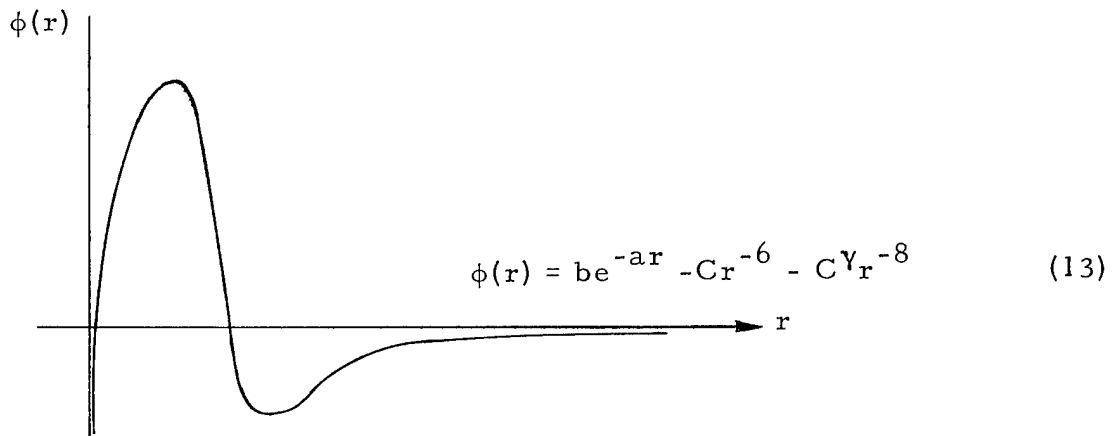


$$\begin{aligned} \phi(r) &= \infty, \quad r < \sigma \\ \phi(r) &= -\epsilon, \quad \sigma < r < R\sigma \\ \phi(r) &= 0, \quad r > R\sigma \end{aligned} \quad (10)$$

C. Sutherland



$$\begin{aligned} \phi(r) &= \infty, \quad r < \sigma \\ \phi(r) &= -Cr^{-\gamma}, \quad r > \sigma \end{aligned} \quad (11)$$

D. Lennard-JonesE. BuckinghamF. Modified Buckingham

$$\phi(r) = \frac{\epsilon}{1 - 6/a} \left\{ \frac{6}{a} \exp \left[a \left(1 - \frac{r}{r_m} \right) - \left(\frac{r_m}{r} \right)^6 \right] \right\}, \quad r \geq r_{\max} \quad (14)$$

$$\phi(r) = \infty, \quad r \leq r_{\max}$$

where r_m is the value for the energy minimum

a is the steepness of the exponential functions (13.5)

r_{\max} is the value for $\max \phi(r)$

ϵ is the depth of the potential well.

In each case there are involved molecular parameters (ϵ and σ) which are characteristic of the specie and which must be deduced from empirical values of one of the macroscopic properties (e. g. , viscosity). In a

sense, then, the theory does not provide predictions, but interpolation and extrapolation or interrelation of various properties. Hirschfelder, et al., (Chapter 8 and Appendix) give extensive values of the force constants. These are most frequently determined from measured viscosity. In addition, comparisons are given between calculated and measured viscosity in the high-temperature range for some pure gas. It appears that, for example, force constants can be chosen for the Lennard-Jones (6 - 12) potential which result in agreement within 1% between the predicted and measured viscosity of nitrogen (at 1 atm) in the temperature range 100 to 1100°K. All of the potential forms are capable of accurate predictions (or fitting of the data) in the low-temperature range 100 to 400°K.

The theory of the dilute gas has also been extended to the dense gas case and predictions of the effect of pressure upon the viscosity and thermal conductivity can be made with reasonable accuracy. In general the transport properties depend much more strongly upon temperature than pressure.

III. EXPERIMENTAL METHODS

A. Viscosity

Measurements of transport properties are usually based on the solution of a basic general equation for such a simple geometry and boundary conditions that an exact solution exists. The system must be chosen to give close approach to the ideal conditions and the solution must relate the property to be measured only to quantities which may be directly measured with suitable accuracy. Thus, to measure viscosity, solutions of the Navier-Stokes equations are employed; while for thermal conductivity, solutions of the Fourier equation are used. One-dimensional (or very simple two-dimensional) geometries are almost invariably selected for accurate measurements.

Viscosity is usually measured by techniques which may be classified as one of the following:

1. Capillary tubes
2. Rotating cylinder
3. Rotating disk
4. Falling sphere
5. Orifice flow
6. Flow in porous media.

Capillary Tubes

The principle of the capillary tube measurement rests on the Hagen-Poiseuille solution of the Navier-Stokes equations applied to flow in a circular pipe. This solution predicts

$$\eta = \frac{\pi g_c \rho D^4}{32 \dot{m}} \left(- \frac{dp}{dx} \right), \quad (15)$$

The measurements to be made are of ρ , D , \dot{m} and $(-dp/dx)$. Since D appears to the fourth power it must be measured with great precision. Accuracy between 1/4 and 1/2% appears feasible when such an experiment is done with great care and the best instrumentation. Some experimenters have coiled the capillary so that greater length could be used conveniently. In precision work this should be avoided because of the obvious departure from the conditions of Hagen-Poiseuille flow. It is desirable to make the tube long enough so as to produce a pressure gradient large enough to measure accurately, but not so long that the density of the gas changes appreciably.

The capillary method is suitable for use with both gases and liquids and may be used at high temperatures and pressure. In any case, the pressure taps must be free from burrs and the entrance and exit regions avoided to ensure adherence to the Hagen-Poiseuille flow condition.

Rotating Cylinder or Disk

Solutions are available for these geometries which are essentially exact. They are omitted here for brevity. In each case it is necessary to measure torque, rotational speed, dimensions of the apparatus, and the state of the fluid. Edge effects present problems as does concentricity of the parts. However, this technique has been used very successfully in producing precision data at ambient pressure and temperature. For high-pressure work it is difficult to handle a precision, rotating device. At high temperatures it may also be difficult to maintain the necessary dimensional control.

Falling Sphere, Orifice, Porous Media

These techniques are not based upon exact solutions of the N-S equations and consequently are to be regarded as secondary or comparison

methods. It is necessary to calibrate the device with a fluid of known viscosity. The falling sphere and orifice techniques are used with incompressible fluids, while the porous media may be used for gases.

B. Thermal Conductivity

Thermal conductivity meters or cells are designed around simple, one-dimensional geometries (slabs, cylinders, or spheres) for which the solution to the Fourier conduction equation in the steady state or transient case is well known. In any case the measurements to be made include heat flow, temperatures, and the dimensions of the cell, together with the state of the fluid. A chief difficulty in all cases is the conflicting requirement of using substantial temperature differences to get suitable accuracy and of using small enough differences to avoid thermal convection (mass motion superimposed on molecular motion).

In the case of gases, the measurements are particularly difficult because the low thermal conductivity and the resulting small heat flux, which demands greater accuracy in the correction for end or edge losses. In the high-temperature range, there is the added difficulty of thermal radiation becoming a significant part of the heat exchange between the confining surfaces. All cell designs attempt to make the best compromise of these factors for the specific fluid and conditions of interest.

Hot-wire cells consist of a fine wire mounted axially in a hollow cylinder. The wire serves both as a heater and a resistance thermometer. This simple device was modified by Eucken³ to automatically compensate for end losses. The chief difficulties lie in the concentricity and extreme dimensional accuracy required if the cell is to be used for absolute measurements. These requirements are not so severe when the apparatus is to be used to measure relative values. Measurement of the temperature of the outer surface is also difficult. The hot wire has, however, been one of the most successful techniques for use with gases.

Concentric cylinders have also been employed. Kannuliik and Martin⁴ used a thick wire in a hot-wire apparatus to reduce the uncertainty in wire mean diameter and to reduce the variation of heat flux at the wire surface. Glassman and Bonilla,⁵ Keyes and Sandill,⁶ and Vines⁷ have recently used the concentric cylinder in the high-temperature region. Glassman and

Bonilla employed a quartz outer cylinder to avoid radiation effects. Levinson⁸ designed a concentric cylinder device to operate at 3000°F, however it was never built.

Parallel plates have also been used extensively for gases. With horizontal orientation of the plates and downward heating, static stability of the gas is maintained with large temperature differences. However, guard heaters are necessary to control edge losses.

Concentric spheres are ideally suited to measurement of conductivity of liquids and were used for many early measurements on gases. The chief virtue of this configuration is the minimization of heat leakage which takes place only through spacers, thermocouple, and heater leads. For liquids the spacers may be made of material having comparable conductivities, but for gases the spacers are bound to carry a significant portion of the heat input. The other disadvantage is the difficulty and high cost of fabricating precision spheres of suitable size.

Secondary or indirect methods have also been proposed, e. g. , Eckert and Irvine,⁹ proposed measuring Prandtl number and then calculating thermal conductivity from known viscosity and density data, the latter two properties being better known and measured with less difficulty. They proposed measuring recovery factors for laminar boundary layer flow over a flat plate. Pohlhausen obtained the solution to this problem for the constant fluid properties case and Buseman showed that the recovery factor was just $Pr^{1/2}$. This solution of course contains the boundary layer assumptions, but this is not serious to the accuracy desired in the measured Pr . Eckert and Irvine employed a probe in a converging nozzle to measure the Prandtl number of air. High accuracy (1/2%) is claimed in calculated thermal conductivity based on these Prandtl number data.

IV. EXPERIMENTAL RESULTS

A. Viscosity

The Table of Gas Properties¹⁰ compiled by the National Bureau of Standards gives averaged 1-atm viscosity data for air based on references 11 through 21. The constants in a Sutherland-type equation

$$\eta \times 10^7 = \frac{AT^{3/2}}{T + B} \quad (\text{poise}) \quad (16)$$

based on these data were found to be $A = 145.8$ and $B = 110.4$. The tabulated data are in the form η/η_0 with $\eta_0 = 1716 \times 10^{-7}$ poise and are calculated from Eq. (16). These values are compared graphically with the data cited above and are shown to agree within 1/2% with all the data of Vasilesco¹¹ in the temperature range $100 < T^\circ\text{K} < 1900$. The other observer's data agree within 2-1/2% as a whole (below 800°K). No data are given for elevated pressure.

The NBS tabulation was based on all the available data known to the authors and presumably reflects some judgment in weighting the data. The absolute accuracy of course cannot be determined. It is strange, however, that the data of Bearden²² were omitted from this tabulation. Bearden measured the viscosity of air in order to improve the evaluation of the fundamental electronic charge by the Millikan oil-drop and x-ray methods. He claimed accuracy in viscosity of 3 parts in 10^5 , which is of an entirely different order from the data in the NBS compilation. Bearden's work was done at standard conditions minimizing experimental problems, but the meticulous care in the experiment is impressive none-the-less. One would certainly wonder at the omission by NBS of such excellent work. The data compare as follows:

$$\begin{array}{ll} \text{@ } 293^\circ\text{K} \text{ Bearden } \eta = (1812.26 \pm 0.06) \times 10^{-7} \text{ poise} \\ \text{NBS } \eta = 1819.20 \times 10^{-7} \text{ poise.} \end{array}$$

The two differ by 0.39%. In view of the quality of Bearden's work it would seem appropriate to force Eq. (16) to pass through his data. Comparison with Vasilesco's data, which are the most extensive, would not be seriously degraded.

Absolute accuracy is very difficult to assess, but it would appear that the viscosity of air at 1 atmosphere and 20°C is known to within a small fraction of 1%, and that at elevated temperature (to 1900°K) it is known to within about 1/2%. One point that must be stressed is that moisture content and other variations in the composition of "air" may have considerable effect upon the viscosity.

The effect of pressure upon viscosity has been measured by Kestin and Wong²³ and Kestin and Persen²⁴ using an oscillating disk viscosimeter. The apparatus was calibrated against the nitrogen data of Michels and Gibson²⁵ who used a Rankine capillary apparatus. The former measured viscosity to

80 atm, while the latter went to 1000 atm, but both sets of data were for moderate temperatures. It appears that the only means presently available for getting viscosity at both elevated pressure and temperature is by calculation using methods described in Chapter 9 of Hirschfelder et al. and the method of corresponding states, which has some basis in experiment from the data of Uhlir²⁶ for carbon dioxide over a wide range of pressure and temperature. There is good agreement between the pressure effect calculations and data of Michels and Gibson for nitrogen and Warburg and Babo²⁷ for carbon dioxide. The effect of pressure on viscosity of air is roughly an increase of 10% per 100-atm increase in pressure at 25°C, according to the data of Kestin, et al. Values calculated by Granet and Kass³⁵ based on the law of corresponding states predicts a somewhat stronger dependence on pressure as shown in Table I. Biles and Putnam³⁶ give high data for air at 75°F and 517°F for pressures to 850 psi. These data were obtained in a porous medium.

B. Thermal Conductivity

NBS 564 tabulates values of thermal conductivity of air at 1 atmosphere from the Sutherland type equation.

$$k = \frac{a\sqrt{T}}{1 + \frac{b \times 10^{-4}(C/T)}{T}} \quad (\text{cal/sec cm}) \quad (17)$$

with

$$a = 0.6325 \times 10^{-5}$$

$$b = 245.4$$

$$c = 12.$$

Equation (17) is based on the weighted average of the data of references 28 through 33. Comparison with the computed values from Eq. (17) shows the data to scatter in the range of +7.6% to -4%. The authors feel the absolute accuracy is within 5%. Eckert and Irvine⁹ claim their results based on Prandtl number measurement have an absolute accuracy of 1/2%. This is probably optimistic since the viscosity data used in the calculations are uncertain to that degree.

The best available data appear to be those of Stops³⁴ who made measurements in a quartz-platinum hot-wire cell to 1000°C. He found that his

data followed a Sutherland form up to 600°C, but could not fit any viscosity-temperature relation above that level.

The effect of pressure on thermal conductivity of gases has been measured by Lenoir,³⁸ Frank,³⁹ and Kannuluik and Donald.⁴⁰ Comings and Nathan⁴¹ have developed a generalized correlation based on the law of corresponding states and substantiated by the data of Lenoir. Granet and Kass³⁵ developed graphs of thermal conductivity (and viscosity) for dry air based on the low-pressure data of NBS 564 and the correlations of Gamson⁴² and Uyhara and Watson.⁴³ The calculated pressure effect is illustrated in Table I.

Table I. Effect of pressure on thermal conductivity and viscosity of dry air (from Granet and Kass, Ref. 35).

Temp (°F)	% increase for 2000 psi above ambient	
	k	η
100	26.0	26.6
500	8.1	4.5
1000	4.6	2.0
1500	4.4	2.5

The knowledge of thermal conductivity of air is considerably poorer than for viscosity. Here again the region of greatest uncertainty is for combined high pressure and high temperature. For gas mixtures, such as air, there has been some speculation that mass diffusion due to a temperature gradient may have some effect on measurements of thermal conductivity. Such an effect would be very important in heat transfer to gases with very large temperature differences.

A more extensive list of references for work on both thermal conductivity and viscosity is given by Touloukian⁴⁴ in the Retrieval Guide. These two sets of references are included here for convenience as a supplementary bibliography.

V. CONCLUSION

There is considerable need for new experimental and theoretical work in the area of high pressure and temperature transport properties. The need

is greatest for thermal conductivity, although viscosity data at simultaneously high temperature and pressure are almost totally lacking. New techniques are needed for the measurement of thermal conductivity at high temperature which are not seriously hampered by thermal radiation acting in parallel. In this regard the experiments of Eckert and Irvine are very promising. All new high-precision experiments should be done with air of accurately determined composition. There is also need of a recognized, standard composition of air for this purpose.

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