LA-2316
PHYSICS AND MATHEMATICS
(TID-4500, 14th edition)

LOS ALAMOS SCIENTIFIC LABORATORY
OF THE UNIVERSITY OF CALIFORNIA LOS ALAMOS NEW MEXICO

REPORT WRITTEN: April 1959

REPORT DISTRIBUTED: September 16, 1959

THERMAL CONDUCTIVITY OF HELIUM AND HYDROGEN
AT HIGH TEMPERATURES

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Contract W-7405-ENG. 36 with the U. S. Atomic Energy Commission

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ABSTRACT

A steady-state hot wire method for measuring the thermal conductivity of light gases in the temperature range 1200 to 2100°K is described. In contrast to other methods, free convection currents and large temperature gradients occur; convection effects are shown to be negligible, and an experimental procedure for eliminating the large gradient effects is described. The thermal conductivity of helium is found to follow the equation $\lambda \times 10^6 = 991 + 0.678(T - 1200)$ cal/sec cm deg over the temperature range covered. That for hydrogen is $\lambda \times 10^6 = 1434 + 1.257(T - 1200)$ cal/sec cm deg.

ACKNOWLEDGMENT

We wish to thank Eugene S. Robinson for bringing this problem to our attention. We are certainly indebted to B. B. McInteer for pointing out that laminar convective flow disturbs the temperature distribution only at the ends of the apparatus. We are grateful to Don L. Bunker for instruction in programming convection calculations for the IBM 704 Data Processing Machine.

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INTRODUCTION

The thermal conductivities at high temperatures of light gases, such as hydrogen and helium, have recently become of interest to this Laboratory. We embarked on a program to study methods by which reasonably accurate measurements of thermal conductivities from 1200 to 2000°K could be made, and to measure this quantity for helium and hydrogen in particular.

Many steady-state methods have been devised for thermal conductivity measurements of substances from 20 to 700°K.¹ The usual method is to contain the material under study to a volume of such geometry that a theoretical treatment of the data is readily made. A small temperature gradient (1 to 10 deg/cm) is applied across the gas, and the thermal conductivity is calculated from the power conducted against the gradient. A small temperature gradient is desirable for several reasons: (1) Only the ambient temperature thermal conductivity need be considered. (2) Convection current effects become negligible. (3) A gas may be treated as a continuum since the temperature change along a mean free path is small. (4) Radiation effects can be treated analytically.

Upon extending these techniques to high temperatures, one finds that the radiated power approaches the conducted power in magnitude. The bath temperature fluctuation, as compared to the applied temperature difference, causes serious difficulty for steady-state conditions. The deterioration of thermal and electrical insulation also becomes serious at high temperatures.

Many of these difficulties could be removed by using a dynamical rather than a steady-state system; for example, either a delta or a step function of heat could be applied to a wire in a gas, and the resultant temperature change detected as a function of time by a sensing element located a given distance from the heat source. With a dynamical system the following advantages would be obtained: Radiation effects are separated in time from conduction effects. The problem of convection is reduced. Temperature fluctuation effects are eliminated if the length of time required to make a measurement is short compared to the fluctuation time. On the other hand, the dynamical system requires more sophisticated calculations and temperature measurement schemes to attain the accuracy possible with steady-state systems.

The thermal conductivity of gases with molecular weights greater than that of neon is small, so that the radiated power loss becomes greater than the conducted power; for these gases a dynamical method would seem to be required.

The scheme we finally chose for use with helium and hydrogen was

a steady-state method in which large temperature gradients (of the order of 10^4 deg/cm) were applied, and free convection currents allowed. Specifically, the apparatus consisted of a vertical, water-cooled glass tube with a coaxial tungsten wire. The wire was heated electrically to the temperature at which the thermal conductivity of the gas was desired.

Under certain conditions, the gas in the tube will be in laminar, free-convection flow^{2,3} along the axis of the tube. This type of flow may be treated mathematically (see Appendix) to determine the flow velocity profile. Assuming conditions for laminar flow to hold, the heat flow equation becomes

$$\frac{\lambda}{r} \frac{\partial}{\partial r} r \frac{\partial T}{\partial r} + \lambda \frac{\partial^2 T}{\partial z^2} = c \rho v \frac{\partial T}{\partial z}$$

where the z axis is along the vertical axis of the tube, thermal conductivity is denoted by λ , r is the radius, T is the temperature, c is the specific heat, ρ is the density of the gas, and v is the flow velocity. The first term is seen to be the ordinary heat flow equation through an isotropic substance. The term on the right hand side of the equation arises because a small volume of gas may gain heat as it moves in the convective flow cycle. If the apparatus is sufficiently long so that in some region $\partial T / \partial z$ is much smaller than $\partial T / \partial r$, then both the convective heat loss and the heat conducted axially will be negligible compared to the transverse heat flux.

At the same time, it is obvious that the axial gradient can be small only if the heat source does not have an axial gradient in temperature. If the temperature distribution of the source (the tungsten wire) remains uniform in this region, with or without gas, then the transverse conducted power can be determined; it is the difference between the ohmic losses with the wire in gas and in vacuum.

The apparatus was made long enough so that the wire was uniform in temperature over most of its length. A crude model of the temperature distribution would then suffice to calculate the power losses in the uniform region.

Also worth mentioning is the fact that the radiation correction is smaller for our large gradient apparatus than for the small gradient system by a factor of 2 to 3. With a concentric cylinder system of inner radius a at temperature T_a and outer radius b at T_b , the ratio of radiated to conducted power is

$$\text{small gradient} \quad \frac{4a\epsilon\sigma T_a^3 \ln b/a}{\lambda}$$

$$\text{large gradient} \quad \frac{a\epsilon\sigma T_a^3 \ln b/a}{\bar{\lambda}}$$

where ϵ is the emissivity of the wire and σ is the Stefan-Boltzmann constant. The average thermal conductivity $\bar{\lambda}$ may be one-half to three-fourths of λ at T_a .

The virtue of our method lies chiefly in the fact that no

special materials are required for insulation and that maintaining the wall and wire temperatures constant is relatively easy.

Derivation of the basic equation used with the apparatus is straightforward. The defining equation for the thermal conductivity of a substance is

$$W = -\lambda \nabla T$$

W is the power conducted across a unit area of gas. For cylindrical geometry with only radial flow, integration gives for the conducted power per unit length of the wire

$$\frac{2\pi j}{\ln b/a} \int_{T_b}^{T_a} \lambda dT \quad (1)$$

where the wire of radius a is maintained at temperature T_a , and the cylinder of radius b at T_b . The term j is a conversion factor 4.184, since the power is expressed in watts, and λ in cal/sec cm deg.

The thermal conductivity at the wire temperature is given by

$$\lambda_{T_a} = \frac{\ln b/a}{2\pi j} \frac{dW}{dT_a} \quad (2)$$

APPARATUS

Glass Column

We made use of a thermal diffusion column, modifying it slightly for pumping accommodations and a gas inlet system. The column had an inside diameter of about 1.22 in. and was 20 ft long. A water jacket surrounded the column along its entire length.

Wire and Seals

The wire running along the axis was clean, bright tungsten, 0.015 in. diameter. It was held at each end by a $3/8$ in. diameter brass rod, with set screws at right angles to the axis for clamping the wire. Because of power limitations, only 8 ft of the column was used. The reduction in length was made by replacing the remaining 12 ft of wire with aluminum rod $5/16$ in. in diameter. Spiders were located along the rod for accurate centering. A glass-to-Kovar tube seal permitted entry of the power lead at the top. This was a $1/8$ in. diameter copper rod soldered inside the Kovar.

At the bottom, a smoothly ground steel rod $3/8$ in. in diameter was the power lead, and was part of a double-O-ring sliding vacuum seal. This allowed variation of the tension on the tungsten wire, and took up the thermal expansion. The region between the O-rings could be either evacuated or filled with gas.

Pumping System

At the bottom, a 3/4 in. diameter pumping tube led to an ion gauge, a liquid nitrogen cold trap, a 20 l/sec oil diffusion pump, and a fore-pump. The column could be pumped to a pressure of 0.02 μ Hg while the wire was maintained at 2000°K.

Gas System

The gas inlet system was simple. It consisted of a cylinder of hydrogen or helium gas, appropriate pressure-reducing valves, and a length of flexible vacuum tubing that ran to a stopcock at the center of the column. Facilities for pumping this system were provided from the main pumps. A Bourdon-type gauge, calibrated against a manometer, measured the pressure.

DC Power Supply

A 5 kw amplidyne generator was the power source for the wire. A fraction of the output voltage was fed into one input of a direct-coupled, push-pull power amplifier. The other input was a reference voltage. The output of the amplifier was the excitation current for the generator field windings. This negative feedback system gave about 0.1% regulation, and by varying the reference voltage, the generator voltage could be controlled from 0 to 250 volts. The alternating-current component was less than 1% of the direct current.

Temperature Measurements

A Leeds and Northrup portable pyrometer was used to measure the wire temperature midway along the wire length. A previous calibration of the pyrometer was made against two secondary standard lamps. The effective wavelength of this pyrometer may be taken as $0.653 \mu^4$.

Electrical Measurements

The potential across the tungsten wire was measured with a calibrated 1/4%, 0-150/300 volt dc meter. The current was determined by measuring the potential drop across a 0.01 ohm (0.04%, 100 amp capacity) series resistor with a Rubicon portable potentiometer.

Wire Length Measurements

Throughout the experiment, the length of the tungsten wire was measured. On installation the initial length was measured with a steel tape. Subsequent changes in length were measured with a cathetometer.

TECHNIQUE

Briefly, the operating technique for a typical gas run was as follows: The system was filled with gas to a pressure of about 61 cm Hg. From four to six temperature readings were taken at each power setting, and the current I, voltage E, and cathetometer reading recorded. The wire temperature was maintained approximately constant

by keeping the ratio E/I constant, and the pressure lowered slightly to another value and E , I , p , and cathetometer recorded. This was repeated for a total of 8 values of p ranging from 61 to 10 cm Hg. These readings constituted one temperature point. This procedure was repeated for six or seven temperatures in the range 1100 to 2100°K. Power measurements were taken at other temperatures, but at 61 cm Hg only.

At every temperature, an estimate was made of the length at each end of the wire which was at a lower temperature than the central section. This was strictly a "by eye" estimate but, as will be seen in the next section, was sufficiently accurate for the intended purpose.

The major difficulty encountered during a run was that of vibration of the wire. This seemed to come about because a combination of power fluctuation and sliding seal friction allowed the tension to decrease. Building vibrations would start the oscillation, which was very difficult to damp out. This was especially so in the case of a vacuum run.

TREATMENT OF DATA

Only 5%, at most, of the length of the tungsten wire was non-uniform in temperature. The wire temperature, as determined by the resistivity averaged over the wire length, and by resistivity

tables,⁵ agreed with the pyrometer temperature to within 15 to 20°K. Therefore, it was decided that a crude model would suffice to correct to the maximum resistance.

On the basis of the model in this sketch, the maximum resistance per unit length is given by

$$R_m = \frac{E/I - 0.0365}{l - 2z' \left[1 - \frac{T_m}{2.195(T_m - T_0)} \right]} \quad (3)$$

using the relation⁶

$$\frac{R}{R_0} = \left(\frac{T}{T_0} \right)^{1.195}$$

The number 0.0365 is the sum of series resistances in the line

leading from the voltmeter to the tungsten wire. The value of R_m is insensitive to T_o provided it remains much smaller than T_m . A value of 350°K was chosen. It is evident that our choice of distribution in the region of z' is immaterial. If we let the resistance be linear with z instead of T , for example, the number 2.195 changes to 2.

The value of z' used was taken from a plot of many of the "by eye" estimates mentioned earlier. Vacuum runs and gas runs were treated separately. See Fig. 1. The resulting length correction term was generally about 1% of the total length (approximately 240 cm).

The power loss per unit length where $T = T_m$ was then given by $I^2 R_m$. This method was preferred over the use of resistivity tables, either as a measure of T_m or of R_m , because any change in the cross sectional area due to stretching of the wire, or thermal expansion, was automatically included. Also, any deviations in resistivity from sample to sample of wire did not have to be included.

Four runs were made with the column evacuated. A plot of power as a function of temperature was drawn. This was called W_r , the radiated power; see Fig. 2. If the emissivity ϵ of the wire was given its proper T dependence,⁶ then the curve was found to fit very well an equation of the type

$$W_r = 2\pi a \epsilon \sigma (T^4 - T_o^4) \quad T_o = 286^\circ K$$

Fig. 1 Wire length in which temperature is nonuniform

Fig. 2 Radiated power and conducted power per unit length

That value of power obtained by subtracting $I^2 R_m$ with the wire in vacuum from that with the wire in gas we called the conducted power W_c .

$$W_c(T_a) = W_{gas}(T_a) - W_r(T_a)$$

For those temperatures at which the pressure had been varied, a plot of $1/W_c$ vs $1/p$ was made. Small deviations in temperature from one value of pressure to another were detected by comparing values of R_m . All temperatures were corrected to a common value using a plot of R_m vs T , and an approximate value of

$$\Delta W_c = \frac{2\pi j}{\ln b/a} \lambda \Delta T \quad (4)$$

Figures 3 and 4 are typical curves of $1/W_c$ vs $1/p$ for helium and hydrogen, respectively.

The straight line portion of the curve was then extrapolated to $1/p = 0$ and the value of power obtained called $W_\infty(T)$.

There were several reasons for the above procedure. First, there exists a critical pressure above which the flow of gases ceases to be laminar and becomes turbulent. Generally, a large increase in power results, and a break in our curves would be evidence of this. Second, when the wire temperature is near 2000°K, the mean free path in the gas immediately surrounding the wire might be sufficiently large that the temperature change in a mean free

Fig. 3 $1/W_c$ vs $1/p$ for helium at $T = 1676^\circ\text{K}$; slope = 0.46

Fig. 4 $1/W_c$ vs $1/p$ for hydrogen at $T = 1720^\circ\text{K}$; slope = 0.31

path length could be large. Third, there is evidence that, except under carefully controlled circumstances, the accommodation coefficient of hydrogen on tungsten could be small enough to be important even at atmospheric pressure.⁷ The latter two conditions are inter-related, and lead physically to a temperature discontinuity between the gas and the wire. We will now show that a plot of $1/W_c$ vs $1/p$ should be a straight line, and that an extrapolation of this line to $1/p = 0$ will intersect the axis at the reciprocal of the power expressed in Eq. (1).

The temperature "jump" can be expressed as⁸

$$T_a - T_K = -g \frac{dT}{dr} \quad (5)$$

where g is called the "temperature jump distance", and is of the order of a few mean free paths. T_a is the wire temperature, and T_K is the temperature obtained by extrapolating dT/dr to the wire from that region in the gas where we may treat the gas as a continuum.

If the ratio of g to L , the mean free path, is not large, then g is given by⁸

$$g = \frac{2 - \alpha}{\alpha} \frac{4c}{\gamma + 1} \frac{\lambda}{\eta c_V} L \quad (6)$$

where α is the accommodation coefficient, c is a constant, γ is the specific heat ratio, c_V is specific heat at constant volume, η is viscosity, and λ is thermal conductivity as before. Equation (6) can

more simply be stated as

$$g = mL \quad (7)$$

where m is a constant presumably independent of pressure. At any temperature, L varies as $1/p$. We may write

$$W_c = \frac{2\pi j}{\ln b/a} \int_{T_b}^{T_a - \Delta T} \lambda \, dT \quad W_\infty = \frac{2\pi j}{\ln b/a} \int_{T_b}^{T_a} \lambda \, dT \quad (8)$$

Taking $T_a - T_K = \Delta T$, we get

$$W_c = W_\infty + \frac{2\pi j}{\ln b/a} \lambda g \frac{dT}{dr} \quad (9)$$

Since, to a good approximation

$$-2\pi j a \lambda \frac{dT}{dr} = W_c \quad (10)$$

then

$$\frac{1}{W_c} = \frac{1}{W_\infty} + \frac{B}{p} \quad (11)$$

where B involves α , T , and the other gas constants in g . This is the equation of a straight line in $1/W_c$ and $1/p$, with the intercept given by $1/W_\infty$.

Under our experimental conditions, the ratio of g to L varied from 20 to 50. Because of the magnitude of this ratio, there could

be some doubt about applying the above theory to our cases. However, helium (Fig. 3 is typical) followed the theory very well over the entire temperature range covered. We feel that this bears out the necessity of following our procedure to eliminate the effects of the large temperature gradients.

Some difficulty was encountered in the case of hydrogen. At the lowest temperature points (1100 to 1300°K), curves similar to those for helium were obtained, but as the temperature was increased, departures from linearity were found (see Fig. 4). For pressures less than 30 cm Hg, the points could be connected by a straight line, but higher pressure points deviated sharply from this line. The magnitude of this deviation increased slowly with temperature, but no significant temperature-pressure relation at which deviation started was evident.

Even though the helium curves bear out the theory, it might be argued that because hydrogen is a diatomic gas, it should not behave so simply. Each of its modes of motion may have a different accommodation coefficient and mean free path. However, crude calculations show that our pressure region was always sufficiently high that curves of the type of Fig. 3 should be very closely straight lines, if one does include both rotation and translation. Any deviations should occur at low pressures, rather than at high pressures.

Another argument can involve the hypothesis that some impurity, either reacting with hydrogen or dissociating at high temperatures,

caused a change in the apparent thermal conductivity of hydrogen as a function of pressure. This does not seem reasonable, since the large thermal conductivity of hydrogen would require a larger amount of impurity to be present than we feel was possible. Also, such a reacting mixture would probably increase the apparent thermal conductivity rather than decrease it.

Our conclusion about hydrogen is that the apparent change in thermal conductivity with pressure is caused by a change in the accommodation coefficient. A small amount of impurity, or hydrogen reaction, can change the surface conditions on the wire drastically, although no mechanism has yet been found to account for the strong pressure dependence. Our extrapolation procedure implies that we are taking the accommodation coefficient to be constant where the points lie on the straight line, and that it decreases in the higher pressure region where the points lie above the line. Even if the accommodation coefficient does vary slightly with pressure in the region where we have drawn the straight line, no large error would result, and our final answer would not be greatly affected. We should emphasize that the slope of the straight lines for hydrogen and helium agree very well.

With W_c at 61 cm Hg, a plot of the quantity

$$\frac{W_{\infty} - W_c}{W_c} \tag{12}$$

vs temperature was made; interpolation gave W_{∞} for those temperatures at which only W_c was measured. Figure 5 is a typical curve of Eq. (12).

As mentioned earlier, the brightness temperature of the wire was measured with a pyrometer. For ease of conversion to true temperature, a plot of the true temperature, T , vs the apparent brightness of the wire, S , was made using the equation⁹

$$\frac{1}{T} - \frac{1}{S} = \frac{\lambda}{C_2} \ln \epsilon_{\lambda} \tau_{\lambda} C_1 \quad (13)$$

Here C_2 is Wien's constant, ϵ_{λ} is the spectral emissivity of tungsten at the effective wavelength of the pyrometer,¹⁰ τ_{λ} the transmission at the same wavelength of the water jacket and glass, and C_1 ($= 1.028$) corrects for the fact that we were observing a wire rather than a flat surface. The transmission τ ($= 0.844$) was found by observing a tungsten ribbon in an evacuated bulb both inside and outside the column at 9 different temperatures from 1100 to 1960°K.

As indicated earlier in Eq. (2), the thermal conductivity at any temperature is directly proportional to the derivative of the conducted power vs temperature curve. The derivatives were found by numerical differentiation based on Stirling's interpolation formula.¹¹ Five points, at 40° intervals, were used for each derivative. The points were read from the smoothed curve drawn through the observed power points for each run.

Fig. 5 Ratio $(W_\infty - W_c)/W_c$ vs temperature with W_c at 61 cm Hg

RESULTS AND DISCUSSION

Results

Figure 2 shows the curves obtained for power vs temperature by averaging over four runs for helium and six runs for hydrogen. The indicated errors are the standard deviation from the mean.

The thermal conductivity resulting from these runs is shown, as an average, in Fig. 6. Here again the indicated errors are standard deviations from the mean of the individual runs. The points are seen to lie almost on a straight line. A least squares fit of the individual runs results in the equation:

$$\begin{aligned} \text{for helium} \quad \lambda \times 10^6 &= 991 + 0.678(T - 1200) & \sigma &= 3.1 \times 10^{-5} \\ \text{for hydrogen} \quad \lambda \times 10^6 &= 1434 + 1.257(T - 1200) & \sigma &= 4.5 \times 10^{-5} \end{aligned} \quad (14)$$

For comparison in the case of hydrogen, we have included two additional curves. The curve labelled NBS was obtained by extrapolation from a formula in a National Bureau of Standards publication.¹² This formula is a semi-empirical fit of data for the thermal conductivity of hydrogen for temperatures ranging only up to 700°K. A previous publication¹³ gave quite similar results, although the form of the equation differed slightly from the one we used. The curve labelled THEORETICAL was calculated using a modified Buckingham (exp -6) potential for the viscosity of hydrogen,¹⁴ and an improved Eucken factor as outlined by Hirschfelder.¹⁵

Fig. 6 Thermal conductivity for hydrogen and helium vs temperature

The curve for helium has been extrapolated to room temperature because it agrees very well, perhaps fortuitously, with theoretical and experimental values at room temperature. A theoretical calculation¹⁴ (modified Buckingham potential) of the thermal conductivity in the temperature range of this experiment gives values which are too low, by about 7% at 1200° and 13.7% at 1830°K.

Errors

There were two principal sources of random error in this experiment. One was the measurement of T , and the other the procedure for finding W_{∞} .

A good color match between the rather small tungsten wire and the pyrometer filament was often difficult to obtain. This was a rather subjective phenomenon with the observer, and is difficult to express quantitatively. However, the agreement obtained between our curve of radiated power vs T , and the theoretical curve, leads us to believe that our measurements are probably correct to within 10°K.

Probably the larger of the sources of error was that involved in extrapolating W_c to infinite pressure to find W_{∞} (see Figs. 3 and 4), especially for hydrogen. Although our accuracy in measuring W_c was good -- indeed, except as noted below, rarely did a point deviate from the straight line by more than 1/2% -- it was often possible to draw two lines that fit the points fairly well, but differed at the

intercept by 1-1/2% to 2%. One could hope to reduce this by extending the data to higher pressures. However, in the case of hydrogen, this would not have been feasible because of the deviation from the straight line curve observed in Fig. 4.

Some of the more likely sources of systematic errors were considered in detail. Although great care went into the pyrometer calibration and factors determining calculation of wire temperature, there remains some uncertainty. The possible variation of the spectral emissivity of the wire from sample to sample, or of our samples from those recorded in literature tables, is difficult to judge. Actually, a difference of 6% in ϵ_λ is necessary to cause a 10°K change at 2000°K, so that we feel this source of error is not very important.

Other possible sources of systematic errors are (1) an off-axis wire; (2) a shift along the temperature axis of the radiated power curve relative to the total power curve; and (3) cooling water temperature variations. However, the magnitude of the errors appeared to be so small as to be insignificant compared to our statistical errors (σ of Eq. 14).

Both the helium and hydrogen curves of λ vs T can be connected nicely to the lower temperature data by smoothed curves that appear to be reasonable. However, if these curves are integrated as indicated by Eq. (1) from 280 to 1200°K, a discrepancy between the power calculated and that measured at 1200°K appears. For helium the

calculated value is about 3.7 watts/cm, 0.1 lower than the observed value. For hydrogen the calculated value is about 4.9 watts/cm, 0.2 above the observed value. This seems to be outside the permissible limits of error. Everything could be made to agree by shifting all the curves along the temperature axis. A shift of +15°K for helium and -20 to -30°K for hydrogen would be necessary. The result would be to change the thermal conductivity by about 0.7% for helium and 2% for hydrogen. As mentioned in the preceding section, such an error in temperature scale does not seem very likely, especially in the case of hydrogen. We could also force agreement by shifting our power curves along the power axis by the appropriate amount. Bearing in mind the accuracy of the current and voltage measurements, a power shift such as this is inexplicable; at any rate, the shift would leave λ unaltered.

In summary, the observed thermal conductivities for hydrogen and helium are given by Eq. (14). The random errors (σ of Eq. 14) amount to 3%, or less, of the thermal conductivity values. Such errors as pyrometer instability and uncertainty in extrapolation of conducted power to infinite pressure are included in this figure. We feel that any systematic errors which might be present could cause at most an additional uncertainty of 1%.

REFERENCES

- (1) H. S. Carslaw and J. C. Jaeger, "Conduction of Heat in Solids," Oxford University Press (1948), Sec. 15, p. 31.
- (2) L. Onsager and W. W. Watson, Phys. Rev. 56, 474 (1939).
- (3) R. Simon, Phys. Rev. 69, 596 (1946).
- (4) K. A. Walch and R. C. Stroud, "Manufacture of L. and N. Pyrometers," Leeds and Northrup Company, Philadelphia, Pa. (No date).
- (5) C. J. Smithells, "Tungsten," Chemical Publishing Co., Inc. (1953), Table XXVIII, pp. 178-180.
- (6) Ibid., p. 177.
- (7) K. B. Blodgett and I. Langmuir, Phys. Rev. 40, 78 (1932).
- (8) E. H. Kennard, "Kinetic Theory of Gases," McGraw-Hill Book Company, Inc., (1938), pp. 311-315.
- (9) W. R. Forsythe, "Measurement of Radiant Energy," McGraw-Hill Book Company, Inc. (1937), see Eq. 83 p. 366, and Eq. 85 p. 380.
- (10) "Handbook of Chemistry and Physics," 32nd Ed., Chemical Rubber Publishing Company, p. 2450 (1950).
- (11) J. B. Scarborough, "Numerical Mathematical Analysis," 3rd Ed., Johns Hopkins Press (1955), p. 70.
- (12) Joseph Hilsenrath, et al., "Tables of Thermal Properties of Gases," NBS Circular 564, U.S. Dept. of Commerce (1955).
- (13) H. W. Woolley, R. B. Scott, F. G. Brickwedde, "Thermal Properties of Hydrogen," NBS Research Paper 1932, 41 (1948).
- (14) E. A. Mason and W. E. Rice, J. Chem. Phys. 22, 522 (1954).
- (15) J. O. Hirschfelder, J. Chem. Phys. 26, 282 (1957).

APPENDIX

FREE CONVECTION OF HYDROGEN

It seemed advisable to determine the flow characteristics of the gas in our column. This was done for hydrogen gas only, assuming the column long enough that the characteristics were determined primarily by a region of zero axial temperature gradient. This involved solution of the equation

$$\nabla \eta \nabla \cdot \vec{v} = -(\rho - \bar{\rho} + \rho^*)\vec{g} \quad (\text{A-1})$$

where η is the viscosity, ρ the density, v the velocity of the gas, and g now stands for the acceleration of gravity. Also to be satisfied is the equation of continuity, $\nabla \cdot \rho \vec{v} = 0$. Letting the tube axis be the z direction, and assuming $\vec{v} = v_z \vec{k}$, the boundary conditions become $v = 0$ at $r = a, b$. The average density, $\bar{\rho}$, is defined as

$$\bar{\rho} = \frac{2}{b^2 - a^2} \int_a^b \rho r \, dr$$

It was necessary to introduce the quantity ρ^* as a small correction to $\bar{\rho}$, to make the net mass flow, $\int \rho v r \, dr$, of gas zero; i.e., ρ^* is introduced in lieu of accurate calculations at the column ends, which are too difficult to include analytically. ρ^* was typically of the order of one-tenth $\bar{\rho}$.

The first integration of Eq. (A-1) gives

$$v = g \int_a^r \frac{dr'}{\eta r'} \int_a^{r'} (\rho - \bar{\rho} + \rho^*) r dr + C \int_a^r \frac{dr}{\eta r} \quad (A-2)$$

where C is a constant determined by the condition $v = 0$, $r = b$. The problem was programmed for the IBM-704 machine, and run at various wire temperatures, pressures, wire radii, etc. The temperature distribution, neglecting "temperature jump" effects, in the gas depends on the thermal conductivity; this was assumed to vary linearly with temperature, from 0.00042 at 300° to 0.0024 at 2000°K. The temperature dependence of the viscosity was taken from the literature;¹² the density was not assumed to be constant, but was varied inversely with temperature.

Figure A-1 is a plot of T vs r for $T_a = 2000^\circ\text{K}$, while Fig. A-2 is a plot of the axial velocity vs r for several values of T_a . The heat carried by the flowing gas, in excess of the room temperature enthalpy, was found by numerical integration of the integral

$$\int_a^r \rho v r \left\{ \int_{288}^T c_p dT \right\} dr$$

At a wire temperature of 2000° the heat flowing upwards amounted to only 0.60 watt; the downward flow was 0.13 watt. These heat flows are negligible compared to the total power input to the apparatus of

Fig. A-1 Temperature of hydrogen gas in hot wire column

Fig. A-2 Speed profile for vertical flow of hydrogen gas; $p = 61$ cm Hg

about 4000 watts.

With the above results it is now possible to estimate the disturbed length in the gas at the ends of the column; that is, what is the distance along z in the gas in which $\partial T/\partial z$ is not negligibly small? The energy equation is written adequately as

$$-c_p \rho v \frac{\partial T}{\partial z} + \lambda \nabla^2 T = 0 \quad (A-3)$$

where, as before, v is the vertical convection speed, λ is thermal conductivity (assumed constant for simplicity), c_p is specific heat, and ρ is density.

It can be shown on the simple model depicted in Fig. A-2 that the first term can be neglected for hydrogen. It leads to a relaxation length of the order of

$$l_1 = \frac{b^2 \rho v c_p}{\lambda} \approx 0.1 \text{ cm} \quad (A-4)$$

On the other hand, the term $\lambda \nabla^2 T$ can be solved approximately at the ends of the tube, and leads to a relaxation length of

$$l_2 \approx b = 1.6 \text{ cm}$$

This indicates that $\partial T/\partial z$ becomes very small in a distance of 10 to 15 cm from either end. A column 30 cm long would have been sufficiently long to fulfill those requirements discussed in the introduction. However, more care would have been necessary in calculating R_m from the wire temperature distribution.