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EFFECT OF PRESSURE ON THE THERMAL CONDUCTIVITY OF A GAS

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ABSTRACT

The thermal conductivity of a pure gas or a mixture of gases has been studied with a new experimental technique which consists of measuring the increase in pressure produced when a temperature gradient is set up in a gas at constant volume during a steady-state flow of heat from a hot wire along the axis of a tube. The observed increase in pressure is used to calculate the true mean temperature of the gas as it conducts heat. It has been observed that the mean temperature increases as the pressure of the gas is decreased, thereby showing that at a given temperature the thermal conductivity of the gas must decrease as the pressure is reduced. Some of the interesting conclusions to be drawn from these experiments are: (a) the mean temperature is never $(T_{hot} + T_{cold})/2$; (b) the temperature-distribution curves are rectangular hyperbolas with their asymptotes as coordinate axes; (c) most of the drop in temperature between the hot wire and the cold tube is across a thin layer of gas a few tenths of a millimeter thick surrounding the hot wire.

PROBLEM STATUS

This is an interim report; work on this problem is continuing.

AUTHORIZATION

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EFFECT OF PRESSURE ON THE THERMAL CONDUCTIVITY OF A GAS

INTRODUCTION

When a conventional thermal conductivity bridge is to be used for determining the composition of a binary mixture of gases, it is always necessary to calibrate the apparatus with mixtures of known composition. Even though the thermal conductivities of the pure component gases are accurately known, it is found that the simple rule of mixtures cannot be employed to calculate thermal conductivities of such binary mixtures. The rule of mixtures states that K_m, the thermal conductivity of the mixture at a pressure of one atmosphere and a given temperature, is

$$ {}_1K_m = {}_1K_1\, p + {}_1K_2(1-p) \tag{1}$$

in which ${}_1K_1$ and ${}_1K_2$ are the thermal conductivities of the pure components at one atmosphere, and the given temperature, while p is the partial pressure expressed in atmospheres.

The simple rule of mixtures fails because the thermal conductivities of components are not constant but apparently vary with the composition of the mixture. A general expression for the thermal conductivity of binary mixtures of nonassociated gases could be written as

$$ {}_1K_m = ({}_pK_1)p + \left({}_{(1-p)}K_2\right)(1-p) \tag{2}$$

in which ${}_pK_1$ and ${}_{(1-p)}K_2$ are the thermal conductivities of the components at their concentration in the mixture. Now Eq. (2) implies that the thermal conductivity of a gas must vary with pressure, which conclusion is in conflict with the experimentally confirmed prediction of kinetic theory that the thermal conductivity of a pure gas is independent of pressure. Since the thermal conductivity of a pure gas seems to be almost independent of pressure, it does not appear reasonable to assume that the thermal conductivity of a gas varies with its partial pressure in a binary mixture with another gas as expressed in Eq. (2). However, this assumption was made by Minter and Schuldiner (1) to derive an equation for the thermal conductivity of hydrogen-deuterium mixtures which yields results in excellent agreement with experimental measurements.

DERIVATION OF EQUATION FOR BINARY MIXTURES

Although experiment shows that the thermal conductivity of a pure gas does not vary appreciably as the pressure is decreased below atmospheric until rather low pressures are reached, it is here assumed that when two gases at atmospheric pressure are mixed, their thermal conductivities in the mixture are lower than for the pure state because the gases dilute each other to an extent depending on their relative concentrations in the mixture.

Let ${}_1K_1$ be the thermal conductivity of gas 1 at 1 atm and a given temperature. Let ${}_pK_1$ be the thermal conductivity of gas 1 at partial pressure p and the same temperature. It is now assumed that when gas 1 is mixed with gas 2, its thermal conductivity is reduced and that the percent change in thermal conductivity is directly proportional to the percent change in partial pressure, which in the limit becomes

$$\frac{d\,({}_pK_1)}{{}_pK_1} = N_1 \frac{d\,p}{p} \tag{3}$$

in which N_1 is a constant of proportionality. The solution of Eq. (3) is

$$\ln\,({}_pK_1) = N_1 \ln p + C \tag{4}$$

When $p = 1$, ${}_pK_1 = {}_1K_1$ and $C = \ln {}_1K_1$. Substituting in Eq. (4) and reducing we find

$$ {}_pK_1 = {}_1K_1 p^{N_1} \tag{5}$$

An expression similar to Eq. (5) can be obtained for gas 2, and for the two gases we have

$$\left.\begin{aligned} {}_pK_1 &= {}_1K_1 p^{N_1} \\ {}_{(1-p)}K_2 &= {}_1K_2\,(1-p)^{N_2} \end{aligned}\right\} \tag{6}$$

Substituting Eq. (6) in Eq. (2) we have for the thermal conductivity of binary mixtures

$$ {}_1K_m = {}_1K_1 p^{(1+N_1)} + {}_1K_2\,(1-p)^{(1+N_2)} \tag{7}$$

An alternate form of Eq. (7) can be obtained by expanding $p^{(1+N_1)}$ and $(1-p)^{(1+N_2)}$ into a logarithmic series and neglecting terms higher than the first power. These expansions yield the equation

$$ {}_1K_m = {}_1K_1\,(1 + N_1 \ln p)\,p + {}_1K_2[1 + N_2 \ln\,(1-p)]\,(1-p) \tag{8}$$

Calculations show that there is a negligible difference between the results obtained with Eqs. (7) and (8), so that either can be used for binary mixtures.

APPLICATION OF THE NEW EQUATION TO SOME BINARY MIXTURES

As already stated, Eq. (7) was derived by Minter and Schuldiner in order to check the experimentally observed thermal conductivities of hydrogen-deuterium mixtures. Agreement between observed and calculated values is quite good, as can be seen from Fig. 1, and it is thought that the deviation of about 1% on the lower end of the curve is due to an error in the composition of the mixtures containing a low percentage of hydrogen. The same equation was applied with good results by Minter and Schuldiner to the equilibrated mixture of H_2, HD, and D_2, consisting of the three binary mixtures H_2-D_2, H_2-HD, and HD-D_2, as can be seen by referring to Ref. 1.

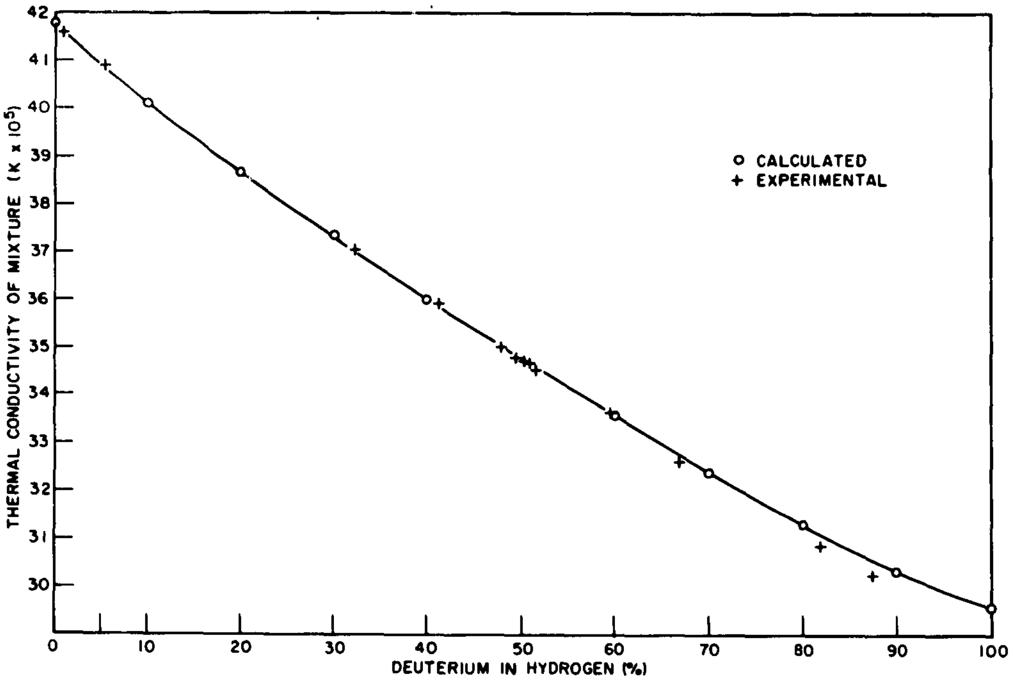

Fig. 1 - The thermal conductivity of hydrogen-deuterium mixtures at 1 atmosphere

Equation (7) has also been applied to some experimental data published by Ibbs and Hirst (2). Values of the constants N_1 and N_2 for a given pair of gases were calculated by taking observed conductivity values for two different concentrations. The empirically derived values of N_1 and N_2 are then put in Eqs. (7) or (8) and the conductivities of the other mixtures calculated. When the values so calculated are compared with the experimental values of Ibbs and Hirst it can be seen from Table 1 that the agreement is excellent.

It must be emphasized that Eqs. (7) and (8) are to be used for binary mixtures of nonassociated gases. The behavior of binary mixtures containing an associated gas such as water vapor, ammonia, or a hydrocarbon cannot be predicted by the simple formulas given above.

DISCUSSION

While it is obvious that Eq. (7) for binary mixtures yields calculated values that agree well with experimental results, there appears to be no theoretical basis for the assumption made in its derivation. The statement made in the introduction is not (A) that the decrease in thermal conductivity of a component in the mixture is proportional to the decrease in its partial pressure, but (B) that the percent decrease in thermal conductivity is proportional to the percent decrease in partial pressure – or proportional

Table 1
Comparison of Observed and Calculated Thermal Conductivities of Some Binary Mixtures

Mixture	Percent of First Gas	Thermal Conductivity of Mixture ($K \times 10^5$ cal $cm^{-1}sec^{-1}$ $°C^{-1}$)	
		Calculated*	Observed†
H_2-CO_2	35.5	9.88	10.00
	50.0	13.22	13.50
H_2-A	40.00	12.56	12.60
	80.20	26.16	27.00
H_2-N_2	65.2	19.51	19.40
	80.3	25.60	25.70
He-A	45.37	10.74	10.77
	94.61	29.21	29.29
H_2-N_2O	20.90	7.33	7.10
	38.60	10.60	10.70
	59.90	16.61	17.00
	81.20	27.10	27.20

*From Eq. (7).
†T. L. Ibbs, and A. A. Hirst, Proc. Roy. Soc. A123:134 (1929).

to the percent decrease in density or concentration in the mixture. This distinction should be emphasized. To express statement (A) we should have to write

$$(dK)/(dp) = \text{constant} \tag{9}$$

which would mean that the thermal conductivity of a gas in a mixture is directly proportional to its partial pressure, which is obviously untrue. For statement (B) on the other hand we can write

$$(dK)/(dp) = N(K/p) \tag{10}$$

where N is a constant of proportionality.

Equation (10) states that the rate at which the thermal conductivity of a gas in a mixture changes with its partial pressure is directly proportional to the thermal conductivity of the gas at that pressure and inversely proportional to the pressure. Or, expressed another way, the rate of change of thermal conductivity with pressure is proportional to the ratio of thermal conductivity to pressure.

Up to this point the principal object of this analysis has been to ascertain whether or not the thermal conductivity of a gas in a binary mixture changes as the partial pressure in the mixture is changed. The result of this analysis shows that by making the assumption that thermal conductivity does vary with partial pressure in the mixture it is possible to calculate values for the thermal conductivities of mixtures that agree well with experimental observation. On account of this agreement between calculated and observed values for mixtures it seems reasonable to conclude that the rate at which the thermal conductivity of a gas in a binary mixture changes with its partial pressure is correctly expressed by Eq. (10). It is therefore only natural to expect that Eq. (10) might also express the variation of thermal conductivity of a pure gas with pressure. However Eq. (10) has never been employed for a pure gas for the following two reasons: (a) the kinetic theory of gases predicts that thermal conductivity should be independent of pressure, and (b) this prediction has been confirmed experimentally.

Clerk Maxwell predicted on purely theoretical grounds, about a hundred years ago, that viscosity and thermal conductivity should be independent of density. When this prediction was confirmed experimentally by numerous investigators, the kinetic theory was accepted by most scientists as having much validity. In the original kinetic theory as derived by Maxwell the thermal conductivity K at a given temperature was expressed as

$$K = (1/3)C_v \rho L\bar{c} \tag{11}$$

in which C_v is the specific heat at constant volume, ρ is the density, L is the mean free path of the molecules, and $\bar{c}$ is their mean velocity of translation. Maxwell pointed out that since ρ and L are respectively directly and inversely proportional to pressure, the product ρL should be independent of pressure, thereby giving a constant thermal conductivity as the pressure is varied.

This theoretical prediction is not completely confirmed experimentally as can be seen in Fig. 2 which shows the observed heat loss from a hot wire along the axis of a tube containing air as obtained by Gregory and Archer (3). These investigators assumed that the heat loss from a current-heated filament can be equated to the thermal conductivity of the gas in the tube, and it is seen in Fig. 2 that the thermal conductivity remains practically constant as the pressure is reduced below atmospheric until about 75 mm Hg is reached, below which there is a rapidly decreasing conductivity as the pressure is still further lowered. Kinetic theory does not predict at what pressure the product ρL in Eq. (11) ceases to be constant. However it is to be expected that when the pressure is zero the thermal conductivity will have to be zero.

It can be observed experimentally that the greatest rate of increase of thermal conductivity occurs when the pressure is increased slightly above zero. It can also be observed that the rate of increase of thermal conductivity diminishes as the pressure is still further increased until the rate of change finally becomes zero or negligible above a certain pressure. If Eq. (10) is considered in the light of the experimental curve in Fig. 2, it can be seen that for pressures where the kinetic theory prediction fails, the experimental curve has those characteristics which can be predicted by Eq. (10) – that is, the rate of increase is directly proportional to conductivity, but inversely proportional to pressure. Now it is well known that when the reciprocal of a number is greater, the number is smaller, and consequently it is to be expected that, if the rate of change of thermal conductivity is inversely proportional to pressure, the effect of reducing the pressure will increase as the pressure is lowered, and will be greatest at the lowest pressures. Although Eq. (10) states that the rate of change of conductivity is proportional to the product of a number (K) and the reciprocal of another number (p), it is obvious that when K and p are both small the change in $(1/p)$ has a greater influence on the change in (dk/dp) than does the change in (K).

The experimental curve showing the effect of pressure on thermal conductivity can be divided into two parts, namely the low pressure region where the thermal conductivity varies with pressure and the higher pressures where the thermal conductivity appears to be independent of pressure. It can be seen in Fig. 2 that the kinetic theory prediction is confirmed for the higher pressures but fails at the lower pressures. On the other hand,

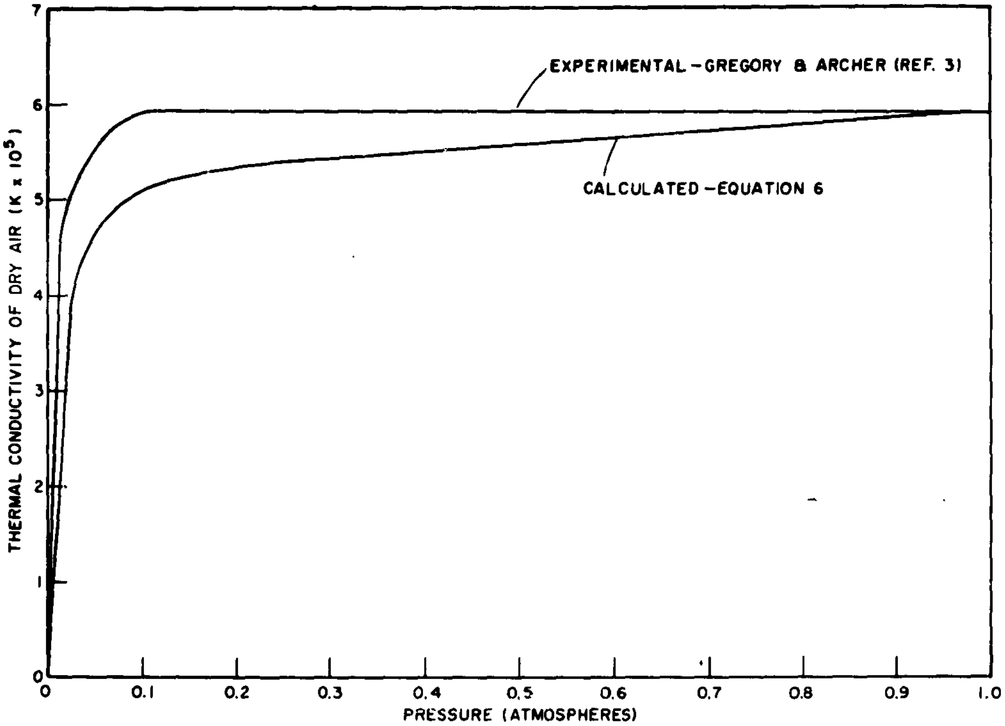

Fig. 2 - The difference between experimental and calculated thermal conductivities of air at several pressures

Eq. (6) derived for a pure gas appears to agree with experiment for the low pressure region but fails at the higher pressures. However it has been concluded that Eq. (6) has been confirmed experimentally over the whole range of pressures when used to calculate the effect of partial pressure on the thermal conductivities of the components in a binary mixture. The fact that when used for a pure gas it does not agree with experiment over the whole range of pressures has posed a question to which the author has been seeking a satisfactory answer for many years.

ANALYSIS OF THE EXPERIMENTAL METHOD

In a final effort to resolve this dilemma, a critical analysis of the experimental method used to test the effect of pressure on thermal conductivity was undertaken, and it has been found that in the experimental method employed there is a "hidden parameter" which obscures the effect of pressure on thermal conductivity. This hidden parameter is the mean temperature of the gas in the tube when the wall temperature is T_w, with a hot wire along the axis at a temperature T_f. As the pressure is reduced below atmospheric, it is assumed here that the mean temperature increases, causing the thermal conductivity to increase, thereby obscuring the reduction in conductivity caused by lowering the pressure. Variation of the mean temperature of the gas with pressure can be easily observed by means of a simple experimental setup. However, before taking up the experimental part of this investigation it is felt that a resume of the apparatus and method used in previous experiments would make it clear why earlier investigators reached the erroneous conclusion that thermal conductivity is independent of pressure.

EVALUATION OF EARLIER WORK

In Fig. 3 a wire of radius x_f is mounted along the axis of a cylindrical tube having an inside radius x_w. The tube is placed in a thermostat maintained at a constant temperature ($T_w - \Delta T_w$) and filled with a gas at a pressure of 1 atmosphere. An electrical current is now passed through the wire which can be maintained at a constant temperature $T_f (T_f > T_w)$ while heat flows from the wire to the tube at a steady rate.

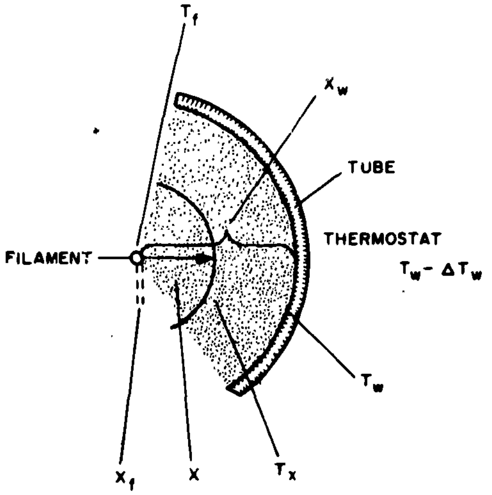

Fig. 3 - Schematic diagram of conventional thermal conductivity tube

T_f - TEMPERATURE OF FILAMENT
T_x - TEMPERATURE OF ISOTHERMAL LAYER OF GAS X DISTANCE FROM WALL OF TUBE
T_w - TEMPERATURE OF TUBE WALL
X_f - RADIUS OF FILAMENT
X_w - INSIDE RADIUS OF TUBE
X - ANY POINT BETWEEN TUBE WALL AND FILAMENT

When a steady-state condition prevails in the tube and no convection occurs it has been assumed by previous investigators such as Gregory and Archer (3) that the temperature gradient in the tube is constant, calling for a linear temperature-distribution curve. These investigators would then take the mean temperature to be $(T_f + T_w)/2$ and the power loss I^2R from the wire would then be taken as a measure of the thermal conductivity of the gas at the temperature $(T_f + T_w)/2$. Now when the pressure was reduced below atmospheric and it was observed that the I^2R loss did not change appreciably the mean temperature of the gas was again assumed to be $(T_f + T_w)/2$ and the conclusion was reached that the change in pressure had not affected the thermal conductivity of the gas. Even though experimental conditions were very carefully controlled and the measurements of pressure and power loss accurately made, these investigators reached the erroneous conclusion that they had experimentally confirmed the kinetic theory prediction that the thermal conductivity of a gas is independent of pressure. This conclusion is the result of two erroneous assumptions; (a) that the temperature-distribution curve is linear and (b) that the mean temperature of the gas is the same at all pressures. It is true that the experimental results appeared to confirm the kinetic theory prediction, but because of the erroneous assumptions the correct conclusion regarding the effect of pressure on thermal conductivity was not reached.

ANALYSIS OF THE CLASSICAL EQUATION

Regarding the assumption that under all conditions of pressure the temperature-distribution curve is linear and the mean temperature $(T_f + T_w)/2$, it should be pointed out that from elementary physical considerations alone a linear temperature-distribution curve is not expected under any conditions. We can write for the quantity of heat Q flowing in unit time through unit length of an annular layer of gas having a thickness dx

$$Q = AK(dT/dx) \tag{12}$$

in which A is the area of the layer, K is the thermal conductivity of the gas in the layer, and dT/dx is the gradient across the layer. Since $A = 2\pi x$ we can write for the heat flux density

$$\Phi = Q/2\pi x = K(dT/dx) \tag{13}$$

Since $Q/2\pi x$ decreases as x increases it follows that if thermal conductivity K is assumed constant, as in the classical theory of conductivity, then the temperature gradient dT/dx must decrease as x increases. This consideration alone leads to the necessary conclusion that the temperature-distribution curve cannot be linear. Therefore a hyperbolic curve is assumed to be the form of the temperature-distribution curve to be expected under the conditions of the experiment.

Although Eq. (13) was originally intended to apply to the flow of heat through a cylindrical solid conductor electrically heated by a wire stretched along its axis, it has been assumed in the past that it could be applied to conduction through a gas if there is no transfer of mass, as in convection. The temperature distribution curve for conduction through a solid can be obtained by assuming K is constant in Eq. (13), which can be integrated after separating the variables. Thus

$$\int_{T}^{T_f} dT = \frac{Q}{2\pi K}\int_{x_f}^{x} \frac{dx}{x} \tag{14}$$

yields

$$T_x = T_f - \frac{Q}{2\pi K} \ln \frac{x}{x_f} \tag{15}$$

in which T_x in the temperature of an isothermal layer in the gas a distance x from the axis of the tube, T_f is the temperature of the hot wire, and x_f is its radius. Equation (15) cannot properly be applied to conduction in gases for two reasons; (a) the thermal conductivity of a gas increases as the temperature increases and (b) there is necessarily a density gradient in the gas because of the temperature gradient. However, if K is assumed uniform all through the body of gas in order to integrate Eq. (13), it will mean that the increase in thermal conductivity caused by increasing the temperature in any concentric, isothermal layer in the gas is exactly balanced by the decrease in thermal conductivity in that layer caused by the reduction in density accompanying the increase in temperature. Since ${}_p\rho_T = {}_p\rho_0 \frac{273}{T}$ at a given pressure, it follows that ${}_pK_T = {}_pK_0 \frac{T}{273}$, or $({}_pK_0)({}_p\rho_0) = ({}_pK_T)({}_p\rho_T)$ which leads finally to

$${}_pK_0 = {}_pK_{T_m} \frac{273}{273 + {}_pT_m} \tag{15a}$$

giving the thermal conductivity at 0°C, the pressure p as a function of the thermal conductivity at the mean temperature T_m observed at that pressure.

In regard to the erroneous assumption that the mean temperature of the gas in the tube is the same at all pressures, it can also be shown from elementary physical considerations that a constant mean temperature for all pressures is not to be expected. Having shown that a hyperbolic temperature-distribution curve is to be expected instead of the linear distribution curve, it follows that, if the shape of the temperature-distribution curve changes as the pressure is varied, then the mean temperature of the gas in the tube will have to vary with pressure.

DERIVATION OF THE NEW TEMPERATURE-DISTRIBUTION EQUATION

The new temperature-distribution equation is derived solely from elementary physical considerations in combination with the perfect gas laws. The system to which these considerations are applied consists of a gas sealed in a cylindrical tube having a filament wire stretched along its axis. The operations performed on this simple system consist solely in (a) maintaining the tube at a constant temperature T_w, (b) maintaining the filament at a constant temperature T_f $(T_f > T_w)$, (c) measuring the power required to maintain a steady flow of heat from the wire through the gas to the wall of the tube, and (d) measuring the increase in pressure of the gas in the sealed tube caused by the temperature gradient.

Let the gas be originally at the uniform temperature of the bath 0°C and at a pressure P. When the wire is heated to a temperature T_f, a sort of "structure" is formed in which gradients of temperature and density are set up in the gas and the pressure increases to $P_h = P + \Delta P$.

The significance of the measurement of the pressure increase ΔP, when the gas in the sealed tube is conducting heat, is that now for the first time it is possible to obtain an indication of the true mean temperature of a gas conducting heat under steady-state conditions. If the filament temperature is T_f and the bath temperature is T_o, the assumed mean temperature according to classical theory is $(T_f + T_o)/2$. In the new method however no assumption is made about the mean temperature – it is measured very simply by means of the simple gas laws. For if P_h is the pressure in the sealed tube when the filament is hot and P is the pressure when it is cold and we know that T_o is the cold temperature of the gas and T_m is the mean temperature, then

$$T_m/T_o = P_h/P, \text{ or } T_m = 273\,(P_h/P)$$

when $T_o = 273$. We can also write

$$T_m = 273\left(1 + \frac{\Delta P}{P}\right)$$

which gives the mean temperature in degrees Kelvin. Since $T_m - 273 = 273\,\frac{\Delta P}{P}$ we have finally $\Delta T_m = 273\,\Delta P/P = T_m\,°C$. The expression for ΔP can be derived from the gas laws in another manner.

Since $P = P_o\,(1 + \alpha T_m\,°C)$ for heating at constant volume

$$\frac{P - P_o}{P_o} = \alpha T_m$$

or

$$T_m = \frac{\Delta P}{\alpha P} \qquad (16)$$

where α is the temperature coefficient of pressure increase at constant volume.

After obtaining the mean temperature the next step in the derivation of the temperature-distribution equation is to find out how far the mean temperature layer is from the axis of the tube. That is, if the point (T_m, x_m) is on the curve $T = T(x)$, what is the value of x_m when T_m is known? Now the area between the curve and the x axis from the ordinate x_f to the ordinate x_w is

$$A = \int_{x_f}^{x_w} T(x)dx = T_m(x_w - x_f)$$

and is obtained by taking the product of the observed mean temperature T_m and the known dimensions $(x_w - x_f)$. In a similar manner the same area can be expressed as

$$A = (x_m - x_f)\, T_f = \int_{T_w}^{T_f} x(T)dT$$

Therefore:

$$(x_m - x_f)(T_f - T_w) = T_m\,(x_w - x_f)$$

or neglecting T_w

$$x_m = \frac{T_m(x_w - x_f) + x_f T_f}{T_f} \tag{17}$$

gives the distance of the mean temperature layer from the axis of the tube.

It has been shown above that by means of the simple expedient of measuring the increase in pressure which occurs when a temperature gradient is set up in a gas at constant volume, it is possible to determine not only the mean temperature T_m of the gas but also the distance x_m of the mean temperature layer from the axis. Obviously the point (T_m, x_m) lies on a $(T \text{ vs } x)$ graph, and it will now be shown how the equation of such a graph can be derived. To derive such a temperature-distribution equation when the gas is conducting heat, it is necessary to make the following assumptions:

1. The pressure is the same at all points in the gas and follows the simple gas law ρT = constant, where ρ is density and T is absolute temperature,

2. The increase in pressure ΔP in each isothermal layer of gas when heat is flowing is the same as would be obtained by increasing the temperature of the entire body of gas at constant volume by T_m°C,

3. The temperature-distribution equation $T = T(x)$ is a continuous, monotonic function of x, and so is its first derivative $dT/dx = T'(x)$.

When the temperature of a gas is increased at constant volume from 0°C to T°C, it is known by the simple gas law that the increase in pressure ΔP is proportional to the increase in temperature, or $\Delta P \propto NT$ where N is the number of moles in the given volume. Since N = (mass/mol wt), we have

$$\Delta P = \frac{(\text{mass})}{M}\, T = \frac{(\text{volume})\ x(\text{density})}{M}\, T \tag{18}$$

When the above equation is applied to an elementary isothermal layer in a gas conducting heat we can write

$$MB\Delta P = 2\pi x \left(\frac{273}{273 + T}\right)\left(1 + \frac{\Delta P}{P}\right)T \tag{19}$$

in which x is the distance of the layer from the axis of the tube, T is increase in temperature of the layer in degrees C, and B is a constant of proportionality. In this equation $2\pi x$ is the "relative" volume and $\left(\frac{273}{273 + T}\right)\left(1 + \frac{\Delta P}{P}\right)$ is the "relative" density. If Eq. (19) is solved for T, we have

$$T = \frac{273\, B\Delta P}{273\left(1 + \frac{\Delta P}{P}\right)x - B\Delta P} \tag{20}$$

which is the relative temperature increase of a layer at x as required by the simple gas law, which takes into account the effect of density on temperature distribution. The correction in the denominator $B\Delta P$ is small but it has a large effect on temperature distribution when x is small, which is to be expected.

In order for the relative temperatures at two different values of x to fall on the same temperature-distribution curve, we can express the difference between the temperature T at x and the mean temperature T_m at x_m as

$$(T - T_m) = C\left[\frac{273\, B\Delta P}{273\left(1+\frac{\Delta P}{P}\right)x - B\Delta P} - \frac{273\, B\Delta P}{273\left(1+\frac{\Delta P}{P}\right)x_m - B\Delta P}\right] \tag{21}$$

in which C is a constant.

Equation (21) can be reduced and solved for T, which is found to be

$$T = T_m - \frac{\overline{BC}\,\Delta P}{\left(1 + \frac{\Delta P}{P}\right)}\left(\frac{1}{x_m - a} - \frac{1}{x - a}\right) \tag{22}$$

in which

$$a = \frac{B\Delta P}{273\left(1 + \frac{\Delta P}{P}\right)}$$

Since the location of the point (T_m, x_m) on the temperature-distribution curve is obtained from experimental observations, and the point (T_f, x_f) is known, it is necessary to know the temperature at the wall so that a third point on the curve (T_w, x_w) can be located. To obtain a value for the temperature T_w at the wall of the tube, it is necessary to use the classical integrated equation which has always been used to calculate temperature differences across an annular space where the thermal conductivity is known. Thus, we can rewrite Eq. (15) as

$$T_w - T_o = \frac{W \ln (OD/ID)}{2\pi JLK}$$

in which OD and ID are outside and inside diameters of the glass tube. For a tube of given dimensions and a known thermal conductivity we can write, since

$T_o = 0$; T_w = constant $\times W$, where W is the observed heat loss in watts. The Pyrex tubes used had a thermal conductivity given in the literature to be 0.0027, which value is incorporated in the constant.

To obtain the values of the constants BC and a in Eq. (22), it is necessary to solve two expressions of Eq. (22) simultaneously – one containing the points (T_m, x_m) and (T_f, x_f), and the other containing points (T_m, x_m) and (T_w, x_w). For a given bath temperature the values assumed by BC and a will vary with filament temperature and the radius of the tube x_w, and these constants must be known if the entire temperature-distribution curve is to be calculated, or if the value of the temperature gradient dT/dx across any layer is needed.

EXPERIMENTAL PART

The apparatus used for measuring the thermal conductivity of air by both methods is shown schematically in Fig. 4. By means of a helical spring, a 0.0038-cm-diameter nickel filament L cm long is stretched along the axis of a cylindrical glass tube. The filament is welded to leads sealed into the ends of the tube so that it can be connected into a Wheatstone bridge circuit whereby it is heated electrically and its temperature determined by measuring its electrical resistance. A capillary tube of 1-mm bore sealed to the bulb is used for evacuating and filling the system with gas at a known pressure. The system is shown connected to a 1-mm-bore U-tube containing a light manometric liquid which is a vacuum pump fluid known as Octoil-S having a specific gravity of 0.9103. By means of stopcock A, the bulb can be sealed off from the rest of the system so that the increase in pressure, which occurs when the filament is heated electrically, can be observed by reading the manometer. The bulb is mounted in a large Dewar flask (not shown) containing a mixture of crushed ice and water, which can be vigorously stirred to maintain a constant temperature at 0°C. The only difference between the conventional experimental apparatus and the author's apparatus is that in the earlier method no attempt is made to measure the increase in pressure which occurs when heat is flowing through the gas in a sealed bulb.

The electrical circuit is also shown in Fig. 4. By means of parallel sets of decade resistances it was possible to measure the filament resistance to the second decimal so that its average temperature could be accurately determined. An adjustable power supply provides a constant dc voltage for the bridge current, which was measured by a Weston Model 622 milliammeter. Different wire temperatures could be obtained by setting the decade resistances to obtain the desired filament resistance and then adjusting the current through the bridge until the sensitive null indicator showed that the bridge was in balance.

Measurement of power dissipated by the filament is the same in both the old and the new methods and it is obvious that a single set of I^2R measurements at different filament temperatures can be used to calculate K_o according to the two methods. To calculate K_o by the classical method, it is necessary to know the filament temperature, the tube temperature, and the I^2R loss, as well as the diameters of the wire and the tube. In calculating K_o by the new method the same data must be known, and in addition the mean temperature ΔT_m as determined from the observed increase in pressure ΔP which occurs when heat flows through the gas at constant volume must also be known.

One of the preliminary experimental steps consisted in determining the resistance of the 12.7-cm-long filament of 0.0038 nickel wire between 0° and 100°C. The bulb containing the filament was placed in the water bath, which could be thermostatted at any desired temperature up to 95°C. With a low current of only 200 μa through the bridge to insure no self-heating of the filament, the parallel sets of decade resistances shown in Fig. 4 were adjusted until the sensitive null indicator showed the bridge was in

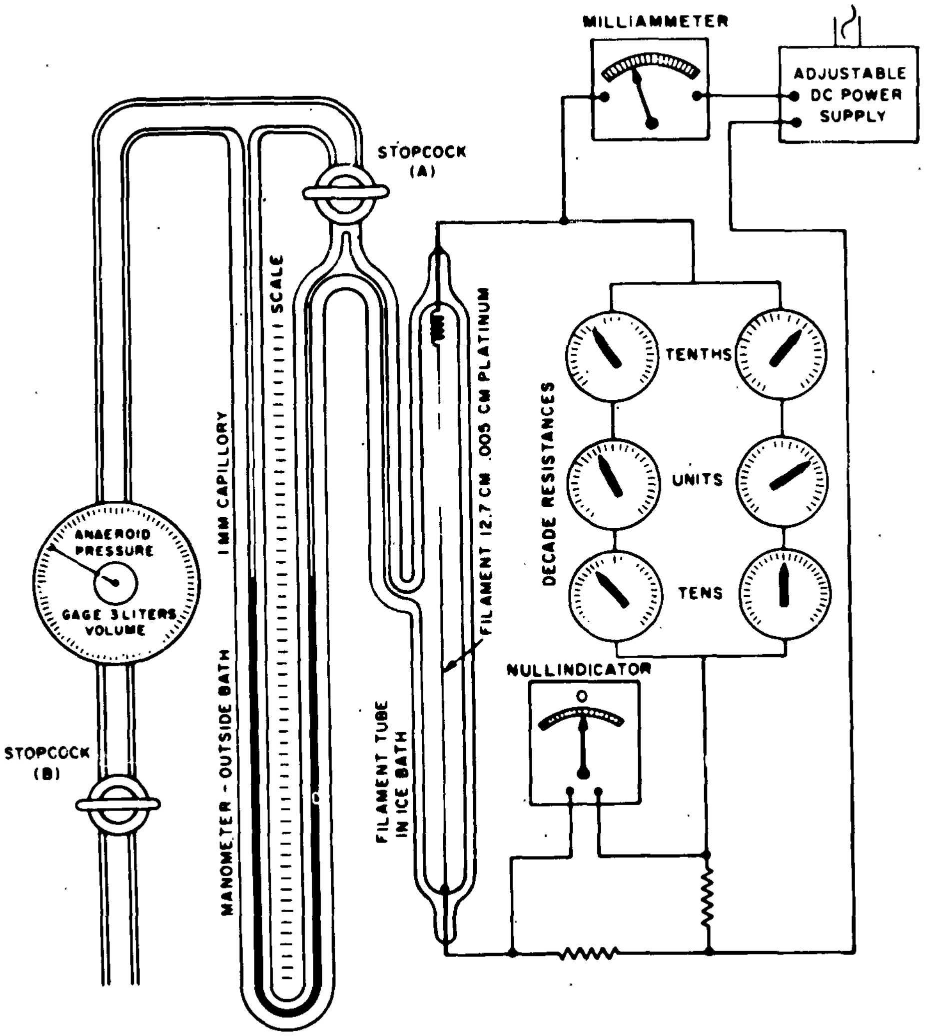

Fig. 4 - Schematic of experimental apparatus used in this investigation

balance. Since tubes of three different diameters were used in the measurements, it was necessary to use three different wires and every care was taken to insure that the three wires were as nearly alike as possible.

Before making measurements of heat loss through the gas it was also necessary to measure the power loss from the hot wire due to radiation and end-loss when the pressure is very low. The measurements are plotted in Fig. 5 for several filament temperatures. When the graphs so obtained are extrapolated to zero pressure, the power dissipated at zero pressure is a correction factor which must be subtracted from the measured I^2R to obtain the power actually dissipated through the gas.

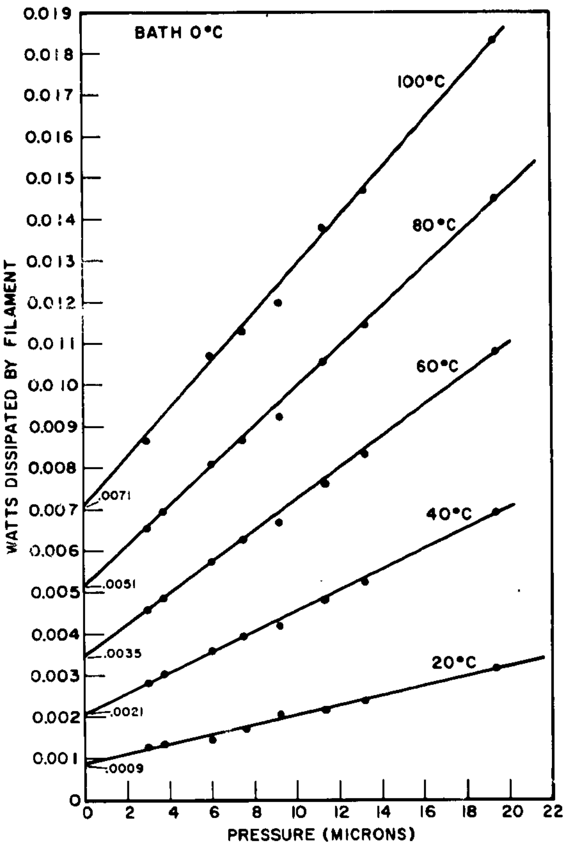

Fig. 5 - Effect of filament temperature and pressure on heat loss from filament wire

EXPERIMENTAL RESULTS

The experimental procedure (Fig. 4) consists in (a) bringing the bulb to the temperature in the ice-water bath, (b) with stopcocks A and B open, evacuating and filling the bulb at a known pressure with the gas to be tested, after which the stopcocks are closed, (c) setting on the parallel sets of decade resistances the resistance of the filament at the desired temperature of operation, (d) adjusting the power supply to vary the current through the bridge until the null indicator shows the bridge is balanced, and (e) measuring the increase in pressure in the bulb by reading the manometer.

Corrections must be applied to the two experimental observations made in this investigation. The resistance used in calculating the I^2R loss through the gas must contain only the resistance of the filament. While resistance of the heavy flexible copper leads used to connect the filament into the bridge circuit was negligible, the resistance of the 0.003-inch tungsten spring at 0°C amounted to 0.30 ohm and has to be subtracted from the total resistance in order to get the true resistance of the filament. The power loss from the filament is therefore calculated according to the relation $W = (I/2)^2 (R - 0.30)$. The measured I^2R must be reduced by an amount depending on the filament temperature, the correction being taken from Fig. 5.

There are two corrections to be applied to the manometric difference H. In the first place heat does not flow through all the gas in the closed system. There is approximately 50 cm of 1-mm-bore capillary tubing in the closed system which will add about 0.5 ml of "dead space" thereby causing the observed increase in pressure $\Delta P'$ to be too low. The true value of ΔP can be obtained by multiplying $\Delta P'$ by $(1 + 0.4/V)$ where V is the volume of "hot" gas in the tube. Another small correction to the observed $\Delta P'$ is necessary because of the increase in volume which occurs when the filament is hot. The ΔV in this case is $(\pi/4) r^2 (H'/2)$, which for a capillary of 1-mm bore is equal to $0.0003927\ H'$. If H' is expressed in millimeters, ΔV will be given in milliliters. Combining the two corrections we have finally for the true pressure increase

$$1 + \left[\frac{0.5 + 0.0003927H'}{V}\right] H' = H \tag{23}$$

It can be seen from Eq. (23) that when the volume V is small, the correction can be appreciable. Since the volume of the system on the other side of the U-tube is about three liters, the change in external pressure due to the movement of the manometric fluid is negligible.

RESULTS AT ATMOSPHERIC PRESSURE

Before taking up the effect of pressure on mean temperature, measurements were made on dry air at atmospheric pressure for several filament temperatures and three tube sizes (Table 2). As would be expected, the mean temperature T_m increased as the filament temperature increased, the bath remaining constant at 0°C. At a given filament temperature the mean temperature increased as the radius of the tube was increased even though the quantity of heat flowing through the gas was diminished. Table 3 shows that T_m varied little with the nature of the gas, appearing to be inversely proportional to α, the temperature coefficient of pressure increase.

It can be seen in Tables 2 and 3 that the observed mean temperature is quite different from the mean temperature $(T_f + T_w)/2$ assumed in the classical treatment of thermal conductivity. When the classical temperature-distribution curve is compared in the same graph with the new temperature-distribution curve, the difference in the characteristics of the two is striking. Figure 6 shows the two curves when the filament temperature is 60°C in a tube of 0.50 cm radius. The classical temperature-distribution curve was calculated according to Eq. (15) assuming a value for the mean thermal conductivity K_m at the assumed mean temperature $(T_f + T_w)/2$. The new temperature-distribution curve was calculated by means of Eq. (22). The two graphs are entirely dissimilar for the simple reason that Eqs. (15) and (22) represent two entirely different functions. In Eq. (15) an assumed value of the thermal conductivity has to be employed in order to calculate the graph, while in Eq. (22) the thermal conductivity K_m does not enter in any manner. The "relative" temperature distribution as expressed in Eq. (20) is solely a function of the simple gas laws, and for that reason it is expected that the temperature-distribution curves would be practically the same for all gases regardless of the nature of the gas. In fact the results in Table 3 show that the mean temperature for a given filament temperature is practically the same for carbon dioxide as for

Table 2
Effect of Filament Temperature T_f and Tube Radius x_w on Mean Temperature T_m*

Filament Temp. (°C)	Radius of Tube x_w (cm)								
	0,25			0.50			1.27		
	T_m† (°C)	x_m‡ (cm)	Total Power (watts)	T_m† (°C)	x_m† (cm)	Total Power (watts)	T_m† (°C)	x_m‡ (cm)	Total Power (watts)
20	0.420	0.007	0.0942	0.800	0.0219	0,0744	1.119	0.0729	0.0718
40	0.756	0.0066	0.1709	1.470	0.0203	0.1445	1.917	0.0629	0.1388
60	1.121	0.0066	0.2567	2.250	0.0206	0.2207	2.660	0.0584	0.2118
80	1.517	0.0066	0.3508	3.015	0.0207	0.3043	3.405	0.0582	0.2956
100	1.912	0.0067	0.4606	3.920	0.0215	0.4021	4.252	0.0559	0.4002

*Filament radius = 0.0019 cm; filament length = 12.7 cm ± 5%; bath temperature = 0°C; pressure = 1.00 atm.

†From Eq. (16).

‡From Eq. (17).

Table 3
Effect of the Nature of the Gas on Mean Temperature T_m at Three Filament Temperatures*

Filament Temp. (°C)	Dry Air			Carbon Dioxide			Helium		
	T_m† (°C)	x_m‡ (cm)	Total Power (watts)	T_m† (°C)	x_m‡ (cm)	Total Power (watts)	T_m† (°C)	x_m‡ (cm)	Total Power (watts)
20	0.932	0.0251	0.0857	0.896	0.0242	0.0535	0.930	0.0250	0.4985
30	1.265	0.0229	0.1177	1.222	0.0221	0.0731	1.279	0.0231	0.6825
40	1.623	0.0221	0.1524	1.572	0.0215	0.0959	1.597	0.0218	0.8787

*Pressure = 1.00 atm; bath temperature = 0°C; tube radius = 0.50 cm.

†From Eq. (16).

‡From Eq. (17).

helium, which has about 10 times the thermal conductivity of carbon dioxide. From these results it can be concluded that for radial flow of heat in a gas, the characteristics of the temperature-distribution curve are essentially independent of the nature of the gas.

Another interesting conclusion which emerges from Eq. (22) and the new temperature-distribution curve in Fig. 6 is that the graph appears to be a rectangular hyperbola with its asymptotes as coordinate axes. It can be seen that the curve "corners" at the mean temperature point (T_m, x_m) which is calculated by means of Eqs. (16) and (17). It would seem therefore that the gas between the filament and the wall of the tube is really divided into two distinct parts: (a) that between (T_f, x_f) and (T_m, x_m) and (b) that between (T_m, x_m) and (T_w, x_w). It can be calculated that the ratio x_w/x_m is practically constant regardless of the radius of the tube, having an approximate value of 24. This means that more than 99.80% of the gas in a tube of any radius is contained between points (T_m, x_m)

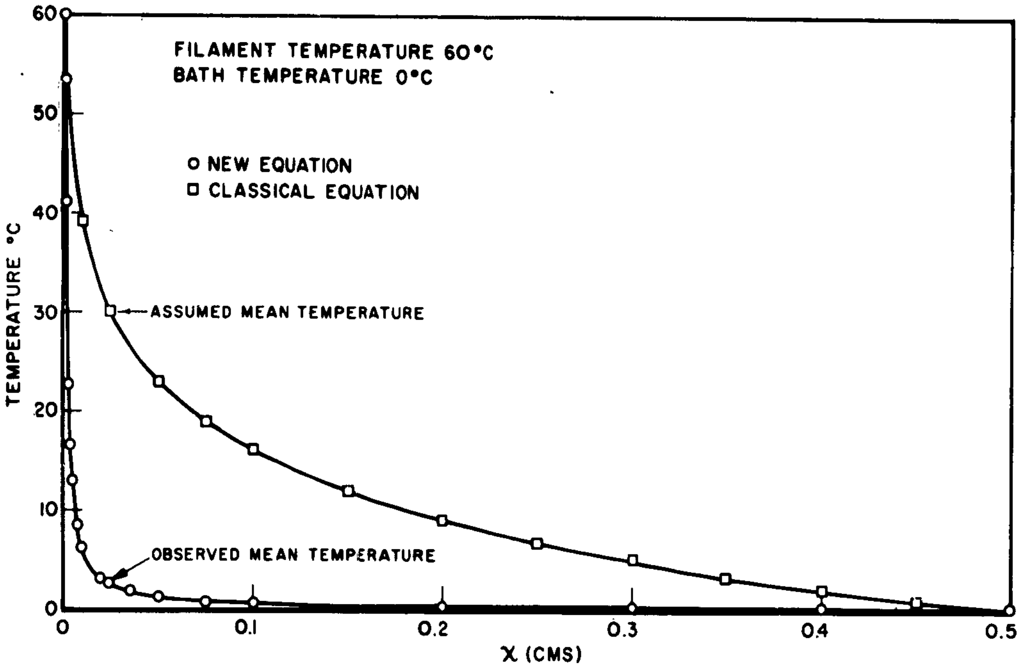

Fig. 6 - Classical temperature-distribution curve compared with new hyperbolic temperature-distribution curve

and (T_w, x_w) and its temperature is below the mean temperature T_m. It is obvious that most of the drop in temperature between the filament and the wall of the tube occurs in a thin film, $(x_m - x_f)$ cms thick, surrounding the filament.

In 1912 Langmuir (4) stated "the viscosity of the gas causes the heat to flow from a hot wire as though there were around the wire a stationary cylindrical film of gas (of diameter b) through which heat is carried only by conduction." The experimental evidence given in this report certainly supports the assumption that such a film surrounds a hot wire, but the data show that the actual thickness of the film, $(x_m - x_f)$ cm, is only a small fraction of the thickness of the Langmuir film.

EFFECT OF PRESSURE ON MEAN TEMPERATURE

Pressures below atmospheric can be maintained in the system shown in Fig. 4. With stopcocks A and B open the system is pumped down to the desired pressure indicated on the aneroid pressure gage, and stopcock B is then closed. With no current flowing through the filament, stopcock A is closed, and the filament is brought to the desired operating temperature whereby an increase in pressure in the tube is shown on the manometer. Following the above procedure it was apparent that as the pressure P was reduced, ΔP did not decrease as fast as P; consequently the ratio $\Delta P/P$ increased as P was diminished.

Some of the experimental observations with dry air in the tube are given in Tables 4 and 5, and in Fig. 7. An idea of the magnitude of the change involved is shown in Fig. 7 in which the point (T_m, x_m), calculated by means of Eqs. (16) and (17), is plotted for three pressures when the filament temperature T_f is 40°C in a tube of 0.50 cm radius. The graphs show that as the pressure is reduced the temperature increases in every concentric layer of the gas, and it is this increase in temperature which tends to counteract the small decrease in thermal conductivity caused by lowering the pressure. The fact that the temperature of all parts of the gas increases as the pressure is reduced requires that, if

Table 4
The Effect of Pressure on the Thermal Conductivity of Dry Air at 0°C Bath Temperature and 40°C Filament Temperature *

Pressure (mm Hg)	T_m † (°C)	x_m ‡ (cm)	Total Power (watts)	Calculated Thermal Conductivity (cal sec^{-1} cm^{-1}°C^{-1} × 10^5)		
				$K_{20°} = \frac{W \ln \frac{x_w}{x_f}}{2\pi JL(T_f - T_w)}$ §	Classical Method $K_o = \frac{K_{20}}{1.05}$	$K_o = K_{20} \frac{273}{273 + T_m}$ ¶
763.0	1.619	0.0221	0.1524	6.364	6.060	6.326
635.0	1.808	0.0244	0.1523	6.360	6.057	6.318
508.0	1.975	0.0265	0.1522	6.355	6.052	6.309
381.0	2.227	0.0296	0.1520	6.347	6.044	6.295
254.0	2.505	0.0331	0.1516	6.330	6.028	6.272
127.0	2.806	0.0368	0.1512	6.314	6.013	6.249
102.0	2.937	0.0385	0.1504	6.280	5.980	6.212
76.3	3.033	0.0397	0.1496	6.247	5.950	6.178

*Tube radius = 0.50 cm; filament radius = 0.0019 cm; filament temperature = 40 °C; bath temperature = 0°C; filament length 12.7 cm; J = 4.185.

†From Eq. (16).

‡From Eq. (17).

§From Eq. (24).

¶From Eq. (15a).

Table 5
The Effect of Pressure on the Thermal Conductivity of Dry Air at 0°C Bath Temperature and 100°C Filament Temperature *

Pressure (mm Hg)	T_m † (°C)	x_m ‡ (cm)	Total Power (watts)	Calculated Thermal Conductivity (cal sec^{-1} cm^{-1}°C^{-1} × 10^5)		
				$K_{50} = \frac{W \ln \frac{x_w}{x_b}}{2\pi JL(T_f - T_w)}$ §	Classical Method $K_o = \frac{K_{50}}{1.125}$	$K_o = K_{50} \frac{273}{273 + T_m}$ ¶
763.0	3.824	.0210	.4029	6.730	5.982	6.637
635.0	4.302	.0233	.4024	6.721	5.974	6.616
508.0	4.731	.0255	.4019	6.713	5.967	6.599
381.0	5.361	.0286	.4009	6.696	5.952	6.567
308.0	5.746	.0305	.3998	6.678	5.936	6.540
254.0	6.270	.0331	.3990	6.665	5.924	6.515
190.0	6.720	.0355	.3977	6.643	5.904	6.483
127.0	7.290	.0382	.3967	6.626	5.889	6.453
102.0	7.619	.0399	.3952	6.601	5.867	6.421
76.3	7.900	.0413	.3926	6.558	5.829	6.373
50.8	8.274	.0431	.3888	6.494	5.772	6.303
38.0	8.550	.0445	.3836	6.467	5.695	6.212
25.4	9.025	.0469	.3749	6.262	5.566	6.062
19.0	9.620	.0499	.3675	6.138	5.456	5.930
12.74	10.109	.0524	.3552	5.933	5.273	5.721

*Tube radius = 0.50 cm; filament radius 0.0019 cm; filament temperature = 100°C; bath temperature = 0°C; filament length = 12.7 cm; J = 4.185.

†From Eq. (16).

‡From Eq. (17).

§From Eq. (24).

¶From Eq. (15a).

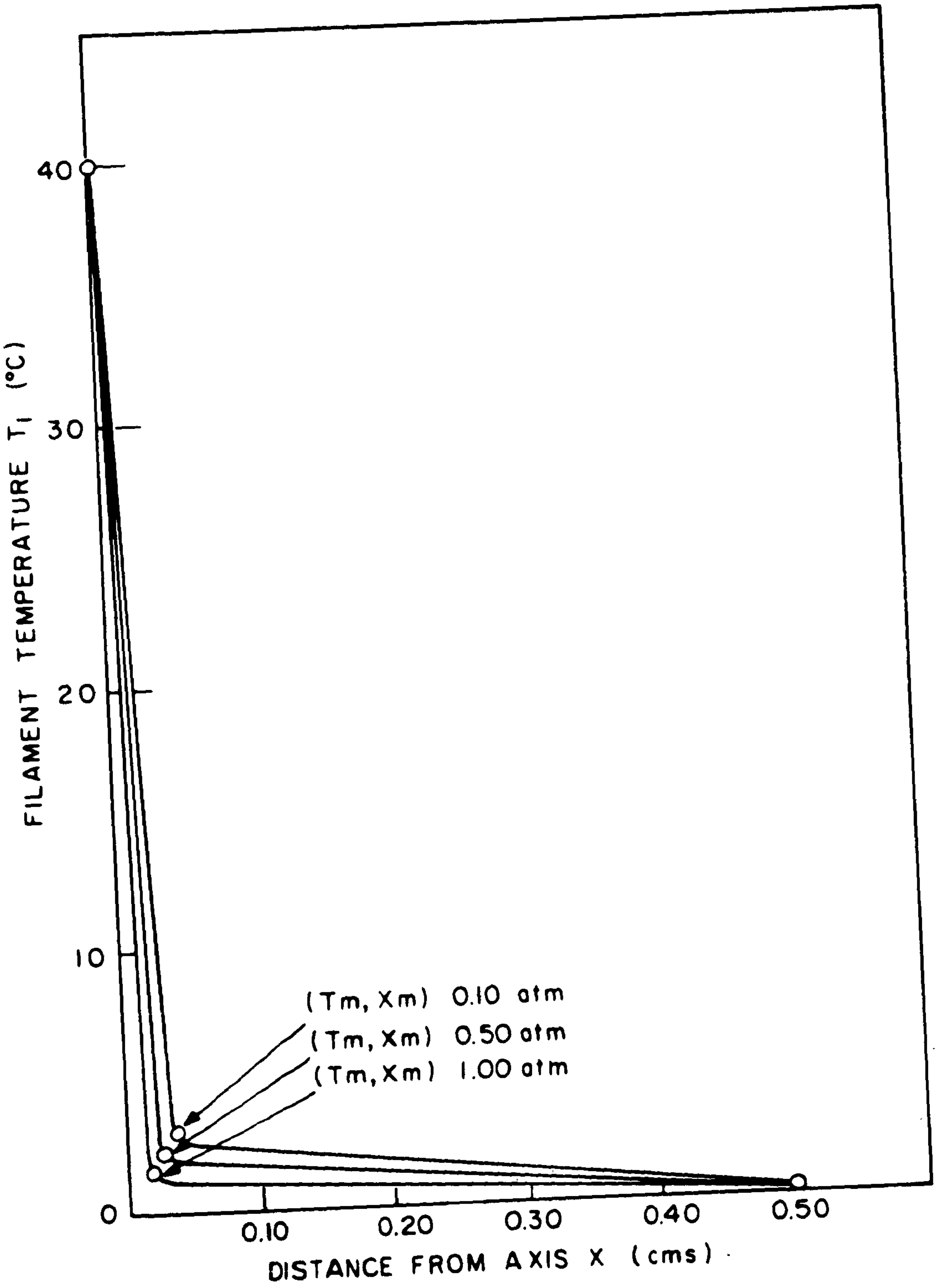

Fig. 7 - The effect of pressure on mean temperature in a gas

the temperature coefficient of thermal conductivity is independent of pressure, the thermal conductivity of air must diminish in a regular, though nonlinear, manner as its density is reduced, even though the heat lost by the hot wire remains nearly constant as the pressure is reduced from 1.0 atm to 0.10 atm.

Without the knowledge that the mean temperature in a gas conducting heat radially from a hot wire increases as the pressure is reduced, it would be natural to conclude that a constant power loss from such a wire would indicate that the thermal conductivity of the gas is independent of pressure, as predicted from kinetic theory by Maxwell.

DISCUSSION OF RESULTS

It can be seen in Tables 4 and 5 and in Fig. 7 that the mean temperature in a gas conducting heat increases as the pressure is reduced. Interpretation of this behavior in terms of the effect of pressure on the thermal conductivity of air will be undertaken according to two procedures: the classical approach and the new approach described in this report.

Taking up first the classical approach there is shown in column 5 of Tables 4 and 5 the values for the mean thermal conductivity K_m calculated for the classical mean temperature $(T_f + T_w)/2$ by means of the equation

$$K_m = \frac{W \ln(x_w/x_f)}{2\pi JL(T_f - T_w)} \tag{24}$$

Since we are interested in obtaining the thermal conductivity K_o at 0°C from the observation of K_m at $[(T_f + T_w)/2]$ °C, the figures in column 5 have to be inserted in the relation

$$K_o = \frac{K_m}{1 + 0.0025\,(T_f + T_w)/2}$$

in which 0.0025 is the accepted value for the temperature coefficient of thermal conductivity of air. The values of K_o so calculated are given in column 6 of Tables 4 and 5. It can be seen that the values for K_o when the filament temperature is 40°C are between 1% and 2% higher than when the filament temperature is 100°C. This agreement is satisfactory considering that different tubes were used for the two filament temperatures.

While the classical values of K_o calculated from observations at two filament temperatures are in good agreement with one another, the calculated values for 1 atm are about 5% to 6% higher than the accepted value for air, which is 5.66×10^{-5} cal $\sec^{-1}\mathrm{cm}^{-1}\,{}^\circ\mathrm{C}^{-1}$. These discrepancies indicate that "convection" effects were operating in the 0.50-cm-radius tube to increase the power dissipated by the hot wire, thereby causing the apparent thermal conductivity to be greater. Convection can be described as a steady-state mass movement caused by differences in the action of gravity on adjacent parts of a body of fluid in which temperature and density gradients exist. The effect of convection is to increase the value of W in Eq. (24), whereby the calculated value of K_m will be greater. It has been shown by several investigators such as Gregory and Archer (5) that in radial flow of heat from a hot wire in a tube the convection effect varies in the following manner: (a) for a given filament temperature, convection increases as the diameter of the tube increases, (b) for a given set of conditions, convection decreases as the specific gravity of the gas is reduced, and (c) for a given gas in a given tube, convection diminishes with pressure in a manner characteristic of the gas.

To determine the actual relation between pressure and the thermal conductivity of air, it will be necessary to carry out the investigation in such a manner that convection is entirely suppressed at atmospheric pressure. The figures for K_o at one atmosphere in Tables 4 and 5 show that some convection operated to increase the apparent thermal conductivity. The effect of convection would diminish as the pressure is reduced in such a tube and for this reason the value of K_m calculated according to Eq. (24) would also appear to diminish appreciably as the pressure is reduced. If there were no convection at one atmosphere, the power loss W would remain more nearly constant as the pressure is reduced.

The values of K_o in Tables 4 and 5 calculated according to the new Eq. (15a) also depend on the values of K_m calculated according to Eq. (24). The first difference between the classical K_o and the new K_o is that in calculating the former the mean temperature for K_m is taken as $(T_f + T_w)/2$, while in calculating the latter, K_m is taken at the observed mean temperature T_m. Another difference lies in the value taken for the temperature coefficient of thermal conductivity, which for the classical K_o is 0.0025, while 0.0036 is taken as the coefficient in calculating the new K_o.

It is principally the difference in the mean temperature used in calculating K_o according to the two procedures that causes K_o at one atmosphere to be higher when calculated according to the new method. This means, therefore, that if we are to accept the experimental mean temperature described in this report as the true mean temperature in a gas conducting heat, then all calculated values for K_o will be greater than the currently accepted values because the observed mean temperatures are lower than the assumed mean temperature $(T_f + T_w)/2$ of classical theory.

Regarding the effect of pressure on thermal conductivity, the only definite conclusion which can be drawn from the experimental results given in this report is that the thermal conductivity of air diminishes in a regular manner as the pressure is lowered. Although the values of K_o in column 6 (Tables 4 and 5) also diminish as the pressure is reduced, it has been pointed out above that this effect is obviously caused by the increase in the value of W at the higher pressures. In any case the rate at which K_o in column 6 decreases with pressure is lower than the rate of decrease of K_o in column 7. In addition it is thought that if the effect of pressure is investigated in a tube in which convection is absent at all pressures the rate of decrease of K_o as the pressure is reduced will be greater than that shown in column 7.

The results obtained with the 0.50-cm tube indicate that although the thermal conductivity diminishes regularly as the pressure is reduced, the experimental pressure-conductivity relation does not follow that predicted by Eq. (6) and shown in Fig. 2. However, a final conclusion concerning the validity of Eq. (6) for a pure gas will not be possible until the tube is reduced in diameter so that no convection can occur at atmospheric pressure, and steps are taken to align the hot wire exactly on the axis of the tube.

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Naval Research Laboratory. Report 5907. EFFECT OF PRESSURE ON THE THERMAL CONDUCTIVITY OF A GAS, by C.C. Minter. 21 pp. and figs., February 20, 1963.

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