On Gaseous Self-Diffusion in Long Capillary Tubes*

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A calculation is made of the rate of diffusion of "tagged" molecules in a pure gas at uniform pressure in a long capillary tube of half-length L and radius a. At pressures for which the mean free path $\lambda \gg a$, the result in the limit $L \to \infty$ reduces to that already obtained by M. Knudsen, the diffusion coefficient D being given by $2a\bar{v}/3$, where $\bar{v}$ is the mean molecular speed. For a capillary of finite length the diffusion coefficient is, to first order in a/L, smaller than this by a factor $1 - 3a/4L$. In the opposite limit of high pressures, for which $\lambda \ll a$, the result reduces to the elementary kinetic theory expression for the self diffusion coefficient, $D = \lambda\bar{v}/3$. One of the most significant features of the result is that in a long tube the diffusion coefficient drops very rapidly with increasing pressure from its initial value for $\lambda \gg L$. Thus the initial slope of D as a function of pressure is given by $dD/d(a/\lambda) \cong -\tfrac{1}{4}\bar{v}a \ln L/a$. It is shown that these results account for the anomalous low pressure minima observed by several investigators who have measured the specific flow $G/\Delta p$ through long capillary tubes as a function of mean pressure $\bar{p}$. The failure to observe such minima with porous media, for which effectively $L \approx a$ in each pore, is also explained by these results. The formulae obtained here represent a rigorous solution to the long capillary diffusion problem, valid at all pressures and subject only to the limitations of the mean free path type of treatment.

T HE flow of a gas through a long tube at pressures for which the mean free path is much greater than the tube radius has been investigated experimentally by Knudsen,[1] Gaede,[2] and Adzumi.[3] Knudsen showed by an elementary argument that a diffusive transport proportional to the pressure gradient but independent of the density of the gas was to be expected in this limit. In this derivation it is assumed that all momentum transfers take place at the tube walls and none in the gas. In a circular capillary of radius a, a section of the wall of length dx is subject to gas molecule collisions at a frequency $(1/4)n\bar{v} \cdot 2\pi a dx$, where n is the numerical density and $\bar{v}$ the mean molecular speed. If the average flow velocity of these molecules along the tube is u, and if u is assumed not to vary with distance from the axis, the rate at which they transfer

momentum to the tube wall is $(1/2)\pi a n\bar{v}mudx$, where m is the molecular mass (cf., Appendix I). It is assumed that there is no preferential direction of reflection. Balancing this rate of momentum transfer by the force $-\pi a^2 dp$, due to the pressure difference between the faces of the segment, and neglecting the inertia force, which is negligible in the case of a long tube, the gas transport G in molecules per second is found to be[4]

$$G = \pi a^2 nu = -\frac{2\pi a^3}{m\bar{v}}\frac{dp}{dx}. \tag{1}$$

Knudsen also gives an alternative treatment of this problem[5] using a more reliable method, an extension of which is employed in the present investigation. In this treatment an expression is found for the number of molecules crossing a given section of the tube in unit time due to reflection from an arbitrary element of surface on the tube wall. Integration of this expression

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[1] M. Knudsen, Ann. d. Physik 28, 75 (1909).
[2] W. Gaede, Ann. d. Physik 41, 289 (1913).
[3] H. Adzumi, Bull. Chem. Soc. Japan 12, 285 (1937).

[4] This result differs by a factor $8/3\pi$ from that obtained by Knudsen using this method. The discrepancy is due to an incorrect expression which he used for the momentum transferred to the wall. The problem of the rate of momentum transfer to the tube wall in a diffusing gas is considered in Appendix I.

[5] See also von Smoluchowski, Ann. d. Physik 33, 1559 (1910).

over the entire surface of the tube leads to the desired expression for the net transport. The result, which has the same form as the "momentum transfer" expression (1), except for the numerical factor, is

$$G = -\frac{16a^3}{3m\bar{v}}\frac{dp}{dx}.$$ (2)

The experimental investigations referred to above all show that the observed flow approaches a limiting value at zero pressure which is in good agreement with that given by relation (2). A comparison of these two treatments of free molecule flow is given in Appendix II.

These kinetic theory calculations of free molecule flow in a capillary tube are applicable only for values of the mean free path, λ, much greater than the tube radius, a. In the opposite limit of high pressure where $\lambda \ll a$ it is necessary to differentiate two distinct limiting forms for G: hydrodynamic viscous flow and gaseous self-diffusion. The first form occurs where a gradient of the total pressure exists and is given by the usual hydrodynamic treatment of the flow of a viscous fluid in a long circular tube as[6]

$$G = n\pi a^2\left[-\frac{a^2}{8\eta}\frac{dp}{dx}+u_0\right],$$ (3)

where η is the viscosity, n the molecular density, and u_0 the "slip" velocity at the tube wall. The gas molecules in this case possess an average drift velocity characteristic of the point in the tube at which they made their last collision.

The kinetic theory treatment of hydrodynamic flow is limited to an evaluation of the viscosity η and the slip velocity u_0 in terms of the mean free path λ and mean molecular speed $\bar{v}$. No kinetic theory derivation of the production of a molecular drift velocity from a pressure gradient has yet been developed to the authors' knowledge. It is therefore not yet possible to give a theoretical discussion of the transition from the limit represented by Eq. (2) to that represented by Eq. (3), although this transition is actually the one investigated experimentally by Knudsen, Gaede, and

Adzumi. Using the kinetic theory values[7] of η, p, and u_0, Eq. (3) may be written in the form

$$G = -\left[\frac{\pi a^3}{m\bar{v}}+\frac{3\pi a^3}{8m\bar{v}}\frac{a}{\lambda}\right]\frac{dp}{dx}.$$ (4)

The experiments of course verified the Poiseuille term. In the low pressure limit Eq. (4) reduces to the slip term which has the same form as the free molecule flow but is smaller by a factor of $3\pi/16$. This factor is independent of the relation between η and λ. If Eq. (4) is integrated and the specific flow $G/\Delta p$ is plotted against the mean pressure, a straight line is obtained and the ordinate intercept measures the slip term according to (4). Since the intercept lies below the free molecule flow, the specific flow curve should have a minimum at low pressures. The experiments demonstrated the existence of a minimum in the neighborhood of $a/\lambda = 0.2$. However, the minimum was less pronounced and the intercept of the straight-line portion higher than one would have expected from Eq. (4). Approximations such as those made in the classical treatment of slip lead to appreciable uncertainties in numerical factors, so that not only may the factor $3\pi/16$ be incorrect but the prediction of a minimum on the basis of Eqs. (3) and (4) may be essentially fortuitous. The experimental curves when extrapolated to zero pressure agreed within one or two percent with the Knudsen formula (2). The experiments of Gaede showed that the drop below (2) set in at very low pressures corresponding to $\lambda/a \approx 100$. No satisfactory explanation of this behavior has as yet been given and we shall return to this point later.

The other high pressure limiting form is obtained at uniform total pressure and represents a transport due to random motion without drift. If a certain fraction of all the molecules is "tagged" by some means without the molecules losing their identity in other respects with the untagged molecules, a transport due to inter-diffusion is associated with a partial pressure

[6] E. H. Kennard, *Kinetic Theory of Gases* (McGraw-Hill Book Company, Inc., New York 1938), p. 293.

[7] The Maxwell expression for the slip velocity u_0 is $-(2\eta/nm\bar{v})(du/dr)_{r=a}$. We take $\eta=(1/3)nm\bar{v}\lambda$ and $p=(\pi/8)nm\bar{v}^2$ in the following. Some results clearly depend on the form chosen for the relation between η and λ. The factor $1/3$ is used here rather than the Chapman-Enskog value $1/2$ in order to have the result correspond with the simple kinetic theory treatment employed in this paper.

gradient of the tagged molecules by the relation

$$G_1 = -\frac{\pi a^2 D_{11}}{kT}\frac{dp_1}{dx},\qquad (5)$$

where p_1 is the partial pressure of the tagged molecules and D_{11} is the self-diffusion coefficient of the gas. In the absence of a total pressure gradient and the associated molecular drift velocity, the diffusive transports which may occur are amenable to kinetic theory treatment so that it should be possible to discuss theoretically the transition in a capillary tube from the tagged molecule transport given by (2), i.e., $G_1 = -(16a^3/3m\bar{v})dp_1/dx$, to that given by (5) as the gas density in the tube is increased from zero to very large values. This is the problem which we undertake to treat here. Unfortunately, no experimental investigations of this type of transition are available, but the results of this study indicate that such experiments should be of considerable interest.

Before proceeding with the formulation of this problem, it will be convenient to express the two limiting forms in terms of appropriate diffusion coefficients. For this purpose we denote by $\bar{\Gamma}$ the average transport per unit cross-sectional area of the capillary so that $\bar{\Gamma} = G/\pi a^2$, and we define a generalized diffusion coefficient D by means of the usual relation

$$\bar{\Gamma} = -D(dn/dx),\qquad (6)$$

where n is the molecular density. Putting $p = nkT = \pi n m \bar{v}^2/8$ in Eq. (2), the zero pressure or Knudsen limit of D is found to be

$$D = (2/3)\bar{v}a,\qquad (a/\lambda\to 0),\qquad (7)$$

whereas from (5) the high pressure or gas diffusion limit is D_{11}. The elementary kinetic theory expression for the self-diffusion coefficient, which is appropriate to the treatment employed here,

then gives as the high pressure limit of D,

$$D = (1/3)\bar{v}\lambda,\qquad (a/\lambda\to\infty).\qquad (8)$$

We undertake now to determine the form of the diffusion coefficient D for intermediate values of a/λ.

THE GAS DIFFUSION COEFFICIENT FOR A CAPILLARY TUBE OF INFINITE LENGTH

Consider the flow of molecules across an element of area dS in a cross section of the capillary, as shown in Fig. 1. These molecules will either arrive at dS directly from some point on the tube wall or they will have been deflected through dS from an encounter with another molecule in the gas. Thus we consider two groups of molecules passing through this element. Of the first group, we denote by $-dN_w$ the number of molecules passing through dS in unit time which come without collision from an element dS' of the tube wall located at a distance x from the section in which dS lies and at an angle θ from a fixed diameter of the tube. (The flow is taken positive in the direction of increasing x.) Of the second group, we denote by $-dN_g$ the number of molecules passing through dS in unit time which come from an element of volume $d\tau$ in which they made their last encounter with a gas molecule. The spherical coordinates of $d\tau$ are ρ, ψ, φ, and those of dS' are r', ψ, φ, in a coordinate system centered at dS.

To evaluate dN_w we note that when the surface element dS' is in equilibrium with the gas, of density $n(x)$, in its immediate vicinity, the number of molecules which start from dS' in unit time in such a direction as to pass through dS is given by

$$(d\omega/4\pi)\cdot n\bar{v}dS'\cos\alpha,$$

where $d\omega$ is the solid angle subtended by dS at dS', $\bar{v}$ is the mean molecular velocity, and α is
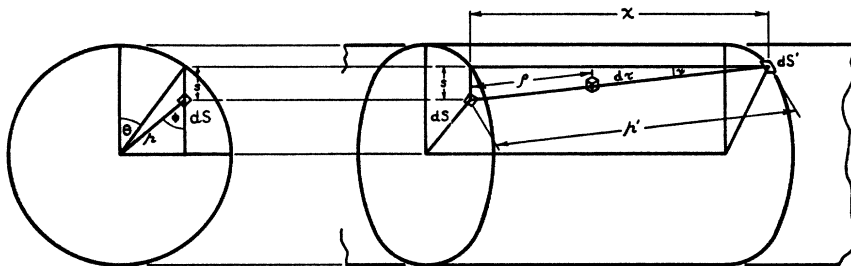

Fig. 1. Coordinate system and notation.

the angle between r' and the normal to dS'. Of these a fraction $e^{-r'/\lambda}$ will arrive at dS without collision. Thus,

$$-dN_w = \frac{n\bar{v}}{4\pi r'^2} dSdS' \cos\psi \cos\alpha \cdot e^{-r'/\lambda},$$

where we have put $d\omega = dS \cos\psi/r'^2$. We now put $d\omega' = dS' \cos\alpha/r'^2 = \sin\psi d\psi d\varphi$ and $s = r' \sin\psi$ with the result

$$-dN_w = (n\bar{v}dS/4\pi) \cos\psi \sin\psi e^{-s \csc\psi/\lambda} d\psi d\varphi.$$

The net number passing from left to right through the tube cross section at this point in unit time which come directly from the tube wall is thus

$$N_w = \int dN_w = -\frac{\bar{v}}{4\pi} \int \int dS \int_0^{2\pi} d\varphi \int_0^\pi n(x)$$

$$\times \cos\psi \sin\psi e^{-s \csc\psi/\lambda} d\psi,$$

where the integration extends over all values of ψ for a tube of infinite length. Since the integral does not depend on φ, this result simplifies to

$$N_w = -(1/2)\bar{v} \int \int dS \int_0^\pi n(x)$$

$$\times \cos\psi \sin\psi e^{-s \csc\psi/\lambda} d\psi. \quad (9)$$

In order to get the number dN_g which comes from gas collisions, we note that the collision frequency in the volume element $d\tau$ is $n\bar{v}d\tau/\lambda$, so that

$$-dN_g = \frac{n\bar{v}d\tau}{\lambda} \frac{d\omega}{4\pi} e^{-\rho/\lambda}.$$

Putting $d\omega = dS \cos\psi/\rho^2$ and $d\tau = \rho^2 \sin\psi d\rho d\psi d\varphi$, we obtain

$$-dN_g = \frac{n\bar{v}dS}{4\pi\lambda} \cos\psi \sin\psi e^{-\rho/\lambda} d\rho d\psi d\varphi.$$

The integration over ρ is terminated by the tube wall at $\rho = s \csc\psi$. Thus the net transport across the section in question due to diffusion from the gas is given by

$$N_g = -\frac{\bar{v}}{2\lambda} \int \int dS \int_0^\pi \cos\psi \sin\psi d\psi$$

$$\times \int_0^{s \csc\psi} n(x)e^{-\rho/\lambda} d\rho. \quad (10)$$

In order to proceed further it is necessary to make a specific assumption with respect to the molecular density n as a function of position x in the tube. We shall show later when we treat a tube of finite length that this function for an infinite tube is given by

$$n(x) = n_0 + x(dn/dx), \quad (11)$$

where dn/dx is constant. This variation of n implies a corresponding variation of λ and invalidates the use of the factor $e^{-\rho/\lambda}$ as a measure of the probability of a free path of length ρ. We show in Appendix III, however, that the proper inclusion in these expressions of the variation of λ with position in the tube leads to the same final expression as that obtained in Eq. (15) for a fixed value of λ appropriate to the gas density at the point where the flow is measured. It is therefore sufficient to use the value of λ corresponding to the value of n_0 above and to include only the variation of n.

The foregoing considerations apply directly to the case of a pure gas diffusing under a pressure gradient. If there is no pressure gradient, the same expressions apply to the self-diffusion if N_w, N_g, and $n(x)$ in Eqs. (9), (10), and (11) are interpreted as the number and density of the tagged molecules. Furthermore, in the case of the self-diffusion, the mean free path λ is interpreted as $(n_1\sigma_{11} + n_2\sigma_{12})^{-1}$, where n_1 and n_2 are the densities of tagged and untagged molecules and σ_{11} and σ_{12} are the collision cross sections for like and unlike encounters. Thus, λ is inversely proportional to the total pressure and is constant along the entire length of the tube.

In the integral for N_w, Eq. (9), we put

$$n = n_0 + s \cot\psi(dn/dx).$$

The integral over the term in n_0 then vanishes by symmetry and the term in dn/dx gives

$$N_w = -\bar{v}\frac{dn}{dx} \int \int dS \int_0^{\pi/2} s \cos^2\psi e^{-s \csc\psi/\lambda} d\psi. \quad (12)$$

This expression was first obtained by Knudsen and he evaluated it in the special case of $\lambda = \infty$, where the exponential term can be set equal to unity, with the result already given in Eqs. (2) or (7).

In the integral for N_g we put

$$n = n_0 + \rho \cos\psi (dn/dx),\qquad (13)$$

so that Eq. (10) reduces to

$$N_g = -\bar{v}\lambda\frac{dn}{dx}\int\int dS\int_0^{\pi/2}\cos^2\psi\,\sin\psi$$

$$\times\left[1-\left(1+\frac{s\,\csc\psi}{\lambda}\right)e^{-s\,\csc\psi/\lambda}\right]d\psi.\quad (14)$$

The total flow of both groups of molecules through the section is given by the sum of the two flows N_w and N_g in Eqs. (12) and (13). It has the value

$$N = N_w + N_g = -\bar{v}\lambda\frac{dn}{dx}\int\int dS\int_0^{\pi/2}$$

$$\times(1-e^{-s\,\csc\psi/\lambda})\cos^2\psi\,\sin\psi d\psi.\quad (15)$$

It is readily verified from Fig. 1 that

$$\int\int dS = a\int_{-\pi/2}^{\pi/2}\cos\theta d\theta\int_0^{2a\cos\theta}ds.\quad (16)$$

Applying this to Eq. (15) and interchanging the order of integration over ψ and s, we obtain

$$N = -\frac{\pi a^2\bar{v}\lambda}{3}\left[1-\frac{3\lambda}{8a}+\frac{6\lambda}{\pi a}Q(a/\lambda)\right]\frac{dn}{dx}$$

where

$$Q(a/\lambda) = \int_0^{\pi/2}\cos\theta d\theta\int_0^{\pi/2}e^{-2a\cos\theta\,\csc\psi/\lambda}$$

$$\times\cos^2\psi\,\sin^2\psi d\psi.\quad (17)$$

It has not been possible to evaluate the integral for Q explicitly for all values of a/λ, but it has been evaluated numerically for a few values and an expression which can be used for small values of a/λ has been obtained and is discussed in Appendix IV. It is shown there that

$$Q(a/\lambda) = \frac{\pi}{16}-\frac{\pi a}{6\lambda}+\frac{\pi a^2}{3\lambda^2}$$

$$-\frac{\pi}{3}(1.2264-\tfrac{3}{4}\ln 2\gamma a/\lambda)\frac{a^3}{\lambda^3}+\cdots,\quad (18)$$

where γ is Euler's constant. For large values of

a/λ it is clear that Q must vanish somewhat as $e^{-a/\lambda}$.

Using this result it is possible to obtain expressions for the diffusion coefficient in the capillary which are valid for small and for large values of a/λ. The diffusion coefficient is given by Eq. (6) as

$$D = -\bar{\Gamma}\Big/\frac{dn}{dx} = -N\Big/\left(\pi a^2\frac{dn}{dx}\right)$$

$$=\frac{1}{3}\bar{v}\lambda\left[1-\frac{3\lambda}{8a}+\frac{6\lambda}{\pi a}Q(a/\lambda)\right].\quad (19)$$

Thus using (18) we find in the two limiting cases

$$D=\frac{2}{3}\bar{v}a\left[1-(1.2264+\tfrac{3}{4}\ln(\lambda/2\gamma a))\frac{a}{\lambda}+\cdots\right],$$
$$\lambda\gg a,\quad (20)$$

and

$$D=\frac{1}{3}\bar{v}\lambda\left[1-\frac{3\lambda}{8a}\right],\quad \lambda\ll a.\quad (21)$$

These results show that in the two extreme limits $\lambda/a\to\infty$ and $\lambda/a\to 0$, the present calculation gives limiting forms of the diffusion coefficient in agreement with those given by Eqs. (7) and (8).

A perhaps surprising feature of this result is the appearance of the logarithm term in the coefficient of a/λ, Eq. (20). The effect of this term is to make the slope of the curve for the diffusion coefficient as a function of pressure negatively infinite at zero pressure. Thus we have from (20)

$$\frac{dD}{d(a/\lambda)} = -\tfrac{1}{2}\bar{v}a[0.6352+\ln(\lambda/2\gamma a)]\quad (22)$$

and this approaches $-\infty$ as p (or $1/\lambda$) approaches zero.

It should be noted that although the diffusion coefficient has an apparently infinite slope, the diffusive flow has a finite slope as p approaches zero. It is, of course, impossible for a measurable physical quantity such as the diffusion coefficient to vary with pressure in such a way that at zero pressure the graph has a vertical tangent. This behavior would imply that an infinitesimal amount of gas could produce a finite drop in the diffusion coefficient. One must recall, however, that in the derivation of Eqs. (20) and (22) the

capillary was assumed to be infinite in length. For a tube of length $2L$, these equations are therefore valid only for mean free paths in the range $a \ll \lambda \ll L$ and cannot be applied at pressures so low that $\lambda \gtrsim L$. Consequently, there is no vertical tangent at zero pressure and the shape of the curve when $\lambda \gtrsim L$ must be determined from a separate calculation for a finite tube.

THE DIFFUSION COEFFICIENT FOR A CAPILLARY OF FINITE LENGTH

The diffusive transport in a tube of finite length will differ from that obtained in Eq. (15) for an infinite tube in two respects. First, in the various integrals for N_w and N_g, the lower limit on ψ is no longer 0 but the value appropriate to the end of the tube. The other effect arises from the fact that the molecular density $n(x)$ can no longer be represented by the simple linear function (11) because the density must become constant beyond the tube ends and equal to the values appropriate to each of the connecting chambers. The manner in which the transition occurs from these constant values to the approximately linear variation at the center of the tube depends on the ratio of its diameter to its length.

We consider first the effect on the molecular density. Let n_0 be the density and dn/dx the density gradient at the center of the tube, $x = 0$. Let L be the half-length of the tube and n_1 and n_2 the densities in the connecting chambers at $x = -L$ and $x = +L$, respectively. We may expand the density $n(x)$ in a Taylor series

$$n = n_0 + x\frac{dn}{dx} + x^2 A + x^3 B + \cdots. \qquad (23)$$

Adjusting this to n_1 at $-L$ and to n_2 at $+L$, we find

$$A = (1/L^2)(\tfrac{1}{2}(n_1 + n_2) - n_0) = (1/L^2)(\bar{n} - n_0),$$

$$B = \frac{1}{L^2}\left(\frac{n_2 - n_1}{2L} - \frac{dn}{dx}\right) = \frac{1}{L^2}\left(\frac{\Delta n}{\Delta x} - \frac{dn}{dx}\right).$$

Thus the coefficient A measures the difference between the average of the densities in the connecting chambers and that at the center of the tube while B measures the corresponding dif-

ference for the density gradient. Both are proportional to $1/L^2$.

An appropriate way, in principle, to determine the values of A and B would be to set up the equivalent of Eqs. (9) and (10) for a tube of finite length using (23) for n. Expressions could be found for the total transport $N = N_w + N_g$ at either end of the tube and at its center. Values could then be chosen for A and B which would make all three transports the same. In like manner, higher order coefficients in the Taylor expansion of n could be determined by equating the transports at other sections. Such a procedure is very involved in practice and will not be attempted here. It can, however, be easily shown that the integrals arising from terms in x^{2n} and x^{2n+1} are of order a^2 times those arising from terms in x^{2n-2} and x^{2n-1}, respectively. It follows that inclusion of terms in x^2 and x^3 in (23) results in additional contributions to the transport proportional to $a^2 A$ and $a^2 B$ and thus in terms of order a^2/L^2. In this treatment we restrict ourselves to long tubes and a determination of the end effects only to order a/L. Thus in this approximation we can continue to use Eq. (11) to represent the density $n(x)$.

The first effect referred to above results in terms of order a/L and we proceed to take account of it in Eqs. (9) and (10). Referring to Fig. 1, we let ψ_0 be the value of ψ for a point on the tube rim so that $\tan\psi_0 = s/L$. Using (11) for n this replaces Eq. (9) by

$$N_w = -\frac{1}{2}\bar{v}\frac{dn}{dx} \int\int dS \int_{\psi_0}^{\pi-\psi_0} s$$

$$\times \cos^2\psi\, e^{-s\, \csc\psi/\lambda} d\psi. \qquad (24)$$

The modification in the integral for N_g is more pronounced. For values of ψ lying between ψ_0 and $\pi - \psi_0$ the integration over ρ is ended by the tube wall at $\rho = s \csc\psi$, but for values smaller than ψ_0 or greater than $\pi - \psi_0$, this integration must be extended beyond the tube ends into the gas in the connecting chambers. In this latter case, we must use (13) for n for $0 \leqslant \rho \leqslant |L \sec\psi|$ while for $\rho > |L \sec\psi|$ we must use $n = n_2$ when $0 \leqslant \psi \leqslant \psi_0$ and $n = n_1$ for $\pi - \psi_0 \leqslant \psi \leqslant \pi$. Thus, the net transport across the central section due to

diffusion from the gas is

$$N_g = -\frac{\bar{v}}{2\lambda}\frac{dn}{dx}\int\int dS\int_{\psi_0}^{\pi-\psi_0}\cos^2\psi$$

$$\times\sin\psi d\psi\int_0^{s\,\csc\psi}\rho e^{-\rho/\lambda}d\rho$$

$$-\frac{\bar{v}}{2\lambda}\frac{dn}{dx}\int\int dS\left[\int_0^{\psi_0}+\int_{\pi-\psi_0}^{\pi}\right]\cos^2\psi$$

$$\times\sin\psi d\psi\int_0^{|L\,\sec\psi|}\rho e^{-\rho/\lambda}d\rho$$

$$-\frac{\bar{v}}{2\lambda}\int\int dS\left[n_2\int_0^{\psi_0}+n_1\int_{\pi-\psi_0}^{\pi}\right]\cos\psi$$

$$\times\sin\psi d\psi\int_{|L\,\sec\psi|}^{\infty}e^{-\rho/\lambda}d\rho. \quad (25)$$

The neglect of terms of order a^2/L^2 leads to the neglect of the x^3 term in (23) whose coefficient B is proportional to $\Delta n/\Delta x - dn/dx$. Thus, in this approximation we may put $(n_2-n_1)/2L = dn/dx$. On performing the integrations over ρ, Eq. (25) with this approximation simplifies to

$$N_g = -\bar{v}\lambda\frac{dn}{dx}\int\int dS\Bigg\{\int_{\psi_0}^{\pi/2}(1-e^{-s\,\csc\psi/\lambda})$$

$$\times\cos^2\psi\,\sin\psi d\psi$$

$$+\int_0^{\psi_0}(1-e^{-L\,\sec\psi/\lambda})\cos^2\psi\,\sin\psi d\psi$$

$$-\frac{1}{\lambda}\int_{\psi_0}^{\pi/2}s\,\cos^2\psi e^{-s\,\csc\psi/\lambda}d\psi\Bigg\}.$$

On combining this with Eq. (24) for N_w we obtain finally

$$N = N_w + N_g = -\bar{v}\lambda\frac{dn}{dx}\int\int dS\int_0^{\pi/2}$$

$$\times(1-e^{-s\,\csc\psi/\lambda})\cos^2\psi\,\sin\psi d\psi$$

$$+\bar{v}\lambda\frac{dn}{dx}\int\int dS\int_0^{\psi_0}(e^{-L\,\sec\psi/\lambda}$$

$$-e^{-s\,\csc\psi/\lambda})\cos^2\psi\,\sin\psi d\psi, \quad (26)$$

where we have substituted

$$\int_0^{\pi/2}-\int_0^{\psi_0}\quad\text{for}\quad\int_{\psi_0}^{\pi/2}.$$

The first term is identical with Eq. (15) which was derived for a tube of infinite length so that the second term clearly represents the correction to N due to the finite length of the tube.

We now obtain the diffusion coefficient D corresponding to this expression for N, and denote by D_∞ the value given by (19) for an infinite tube and by ΔD_L the correction to this value arising from the finite length of the tube. Thus

$$D = D_\infty - \Delta D_L \quad (27)$$

with

$$\Delta D_L = \bar{v}\lambda\int\int\frac{dS}{\pi a^2}\int_0^{\psi_0}(e^{-L\,\sec\psi/\lambda}$$

$$-e^{-s\,\csc\psi/\lambda})\cos^2\psi\,\sin\psi d\psi.$$

On expanding the trigonometric functions in powers of ψ and representing ΔD_L in units of $\bar{v}a$, it is found that the leading term is of order a/L with the next term of order $(a/L)^3$.

Thus, to the required order in a/L we may put $\tan\psi_0 = \psi_0 = s/L$, $\sin\psi = \tan\psi = \psi$, and $\cos\psi = \sec\psi = 1$. This gives

$$\Delta D_L = \bar{v}\lambda\int\int\frac{dS}{\pi a^2}\int_0^{\psi_0}(e^{-L/\lambda}-e^{-L\psi_0/\lambda\psi})\psi d\psi.$$

Using $\psi_0 = s/L$ together with (16), we obtain finally

$$\Delta D_L = \frac{1}{2}\bar{v}a\left[e^{-L/\lambda}+\frac{L}{\lambda}Ei\left(-\frac{L}{\lambda}\right)\right]\frac{a}{L}. \quad (28)$$

If we now combine this result with Eq. (19) for D_∞ according to (27), the diffusion coefficient for a finite tube, good to order a/L, is found to be given by

$$D = \frac{1}{3}\bar{v}\lambda\Bigg\{1-\frac{3}{8}\frac{\lambda}{a}+\frac{6}{\pi}\frac{\lambda}{a}Q(a/\lambda)$$

$$-\frac{3}{2}\frac{a^2}{L^2}\frac{L}{\lambda}\left[e^{-L/\lambda}+\frac{L}{\lambda}Ei\left(-\frac{L}{\lambda}\right)\right]\Bigg\}. \quad (29)$$

The behavior of the correction term ΔD_L at very low pressures for which $\lambda \gg L$ is found from an expansion of (28) to be

$$\Delta D_L = \frac{1}{2}\bar{v}a\left[\frac{a}{L}-(1-\ln\gamma L/\lambda)\frac{a}{\lambda}\right], \quad \lambda \gg L. \quad (30)$$

For larger values of L/λ this term decreases very rapidly, becoming asymptotic to

$$\Delta D_L \simeq \tfrac{1}{2}\bar{v}\lambda(a/L)^2 e^{-L/\lambda}, \quad \lambda \ll L. \tag{31}$$

Thus the correction term is negligible for mean free paths a few times shorter than the half-length of the tube.

Equation (30) is of primary interest at pressures lower than that for which $\lambda \sim L$. In this range we may combine Eqs. (20) and (30) to obtain

$$D = \frac{2}{3}\bar{v}a\left[1 - \frac{3}{4}\frac{a}{L} - \left(0.4764 + \frac{3}{4}\ln\frac{L}{2a}\right)\frac{a}{\lambda}\right],$$
$$\lambda \gg L \gg a. \tag{32}$$

This result shows (a) that the Knudsen diffusion coefficient in a tube of finite length is less than that, Eq. (7), for an infinite tube by the factor

$$\operatorname*{Lim}_{\lambda\to\infty} \frac{D}{D_\infty} = 1 - \frac{3}{4}\frac{a}{L}, \tag{33}$$

and (b) that the slope in the limit $\lambda \to \infty$ is no longer infinite as in (22) but has the finite value

$$\frac{dD}{d(a/\lambda)} = -\tfrac{1}{2}\bar{v}a[0.6352 + \ln L/2a] \quad (\lambda \gg L)$$
$$\simeq -\tfrac{1}{2}\bar{v}a\ln L/a. \tag{34}$$

DISCUSSION OF RESULTS

We wish first to comment on the behavior noted in (a) above and in Eq. (33) which shows that among several tubes of the same radii but different lengths the Knudsen flows maintained in each by the same pressure gradient approach different limits at zero pressure, the values being smaller the shorter the tube. If we compare the diffusion process under a given density gradient dn/dx in the limit $\lambda \to \infty$ for an infinite tube with that for a tube of the same radius but finite length, it is seen that the chief difference arises from the fact that the density $n(x)$ increases without limit in the former, but assumes constant values in the connecting chambers where $x < -L$ and $x > L$ in the latter. A comparison of Eqs. (24) and (25) for N_w and N_g in a finite tube with the corresponding Eqs. (12) and (14) for an infinite tube shows that this difference is indeed responsible for the dependence of diffusion coefficient on tube length.

The effect of cutting off the tube at $x = \pm L$ appears in Eqs. (24) and (25) in two ways. The first is through the substitution of limits ψ_0 and $\pi - \psi_0$ in place of 0 and π for the integration over ψ. The other is through the second term in Eq. (25), which merely includes a portion of N_g for the region $-L \leqslant x \leqslant L$ which was left out of the first term in this equation by setting these limits on ψ. In the limit $\lambda \gg L$ these modifications are found to subtract an amount $\bar{v}a^2/L$ from the corresponding limiting value $2\bar{v}a/3$ for the diffusion coefficient of an infinite tube. On the other hand, the contribution from the regions $x < -L$ and $x > L$ in the connecting chambers, where the density is now constant, is represented by the last term in Eq. (25). In the limit $\lambda \gg L$ it is found that this term adds only $\tfrac{1}{2}\bar{v}a^2/L$ to the diffusion coefficient. Thus, the substitution of constant density chambers for additional capillary maintaining the gradient dn/dx beyond $x = \pm L$ results in a net loss of $\tfrac{1}{2}\bar{v}a^2/L$ in the zero-pressure limit for the diffusion coefficient. This accounts for the dependence of this limit on tube length expressed in Eq. (33).

The Knudsen diffusion coefficient in a tube of finite length in the limit $\lambda \to \infty$ has been determined for all values of a/L by Clausing.[8] He employs a method in which all terms in the Taylor expansion for $n(x)$, Eq. (23), are included by setting up an integral equation involving $n(x)$, which insures that the total transport across all sections of the tube is the same. The result obtained here in Eq. (33) agrees with his within the limits set by the neglect of terms in a^2/L^2.

We turn next to a consideration of the behavior noted in (b) at the end of the preceding section together with the asymptotic behavior of the correction term ΔD_L given in Eq. (31). The latter causes the diffusion coefficient to merge with that for an infinite tube of the same radius when $\lambda \lesssim L$.

We have seen that among several tubes of different lengths the Knudsen flows maintained in each by the same pressure gradient approach limits at zero pressure which are smaller the shorter the tube. Equation (34) shows, on the other hand, that as the pressure is increased, these flows are decreased at a rate which is

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[8] P. Clausing, Physica 9, 65 (1929).

smaller the shorter the tube. Thus the smaller the initial value of the flow, the less rapid is its decline with increasing pressure. In terms of these two effects the asymptotic behavior of ΔD_L means that the dependence of the initial slope on tube length is so related to that of the intercept that, in a tube of given L, the flow is brought into coincidence with that in all longer tubes of the same radius when the pressure in all of them has been increased to values for which $\lambda < L$.

Physically this behavior has a simple interpretation. The transport across any given section of the tube will be determined largely by molecules starting free paths within a distance $|x| \sim \lambda$ on either side of the section. If $\lambda \gg L$, all portions of the tube are effective in determining the transport, and the Knudsen diffusion coefficient characteristic of the tube length L, as given in (33), is realized. When, however, $\lambda < L$, only the portions of the tube within a distance λ from the central section are effective in determining the transport across it. Thus, if additional lengths of the same tubing were added at the ends without changing the density gradient in the central portion, the transport there would not be appreciably altered. It follows that the diffusion coefficient in all tubes longer than a given value L should be the same at pressures for which $\lambda < L$.

The evaluation of the function $Q(a/\lambda)$ defined in Eq. (17) is described in Appendix IV. Using this evaluation, the diffusion coefficient D has been determined as a function of a/λ for an infinite tube by means of Eq. (19). The result is shown in Fig. 2 where $D/a\bar{v}$ is plotted as a function of a/λ in the lower full curve. The broken curve above it represents the gas diffusion coefficient $D_{11} = \bar{v}\lambda/3 = \bar{v}a/3(a/\lambda)$. It is seen that the coefficient of diffusion in a capillary tube falls below that for self-diffusion in the gas at pressures for which the tube radius is equal to a small number of mean free paths and that at pressures for which λ is of order a, the diffusion is primarily limited by wall collisions. In the more elaborate Chapman-Enskog theory of diffusion, the factor $\frac{1}{3}$ would not of course be obtained for the high pressure limiting form of the self-diffusion coefficient. The value at zero pressure would, however, still be $2\bar{v}a/3$, and the curve for D as a function of a/λ would still be asymptotic at high pressure to that for D_{11} in

much the same way as we have found here. It is clear that the value of λ can be adjusted to give D_{11} correctly for any particular gas.

It is of interest to compare these results with an interpolation formula developed by Bosanquet[9] for the diffusion coefficient as a function of pressure in a capillary tube. Bosanquet considers the diffusion process in the tube as a random walk in which the successive steps of individual molecules are terminated either by collisions with other molecules or with the tube wall. In this process the frequencies of the two types of collisions are additive. The mean step size l for this random walk can then be related to the mean free paths l_w for wall collisions and l_g for gas collisions by taking the total collision frequency to be $\bar{v}/l$, so that

$$(\bar{v}/l) = (\bar{v}/l_w) + (\bar{v}/l_g).$$

On the other hand, the diffusion coefficients associated with each of these mean steps may be taken to be proportional to $\bar{v}$ times the mean step size, so that we have

$$(1/D) = (1/D_w) + (1/D_g).$$

Putting $D_w = 2\bar{v}a/3$ and $D_g = \bar{v}\lambda/3$, we obtain

$$D = \frac{2}{3} \frac{\bar{v}a}{1 + (2a/\lambda)}. \tag{34}$$

The broken curve superimposed on the full one in Fig. 2 is plotted from this relation. The agreement between the two curves is quite good and may be taken as a justification for the applicability of the elementary considerations leading to Eq. (34).

Unfortunately, no experimental data on the variation of D with pressure are available for comparison with these results. In making such a comparison the mean free path at unit pressure $\lambda_1 = p\lambda$ is to be regarded as a parameter and adjusted to make $\bar{v}\lambda_1/3p$ agree with the measurements of D_{11} at high pressures.

ORIGIN OF THE MINIMUM IN THE SPECIFIC FLOW *VERSUS* PRESSURE CURVES

In the previous section, at high pressures, the pressure and density gradients referred to were

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[9] C. H. Bosanquet, British TA Report BR-507, September 27, 1944.

always partial gradients for the tagged molecules, the total pressure being uniform. We have already noted in the introduction that the theory developed here is not applicable to flows maintained in the capillary by finite total pressure gradients because of the production of molecular drift velocities under such conditions. The theory can, however, be used to obtain a qualitative insight into the mechanism of the flow behavior observed by Knudsen, Gaede, and Adzumi. This is possible because the flow at pressures for which $\lambda \gg a$ has a negligible contribution from drift and so can be described by the relations derived here.

When the coefficient of specular reflection is zero, the molecules are reflected or evaporated from the tube wall in a completely random manner at all pressures, so that each molecule

starts a free path from the wall with no drift velocity component. In order to acquire a drift it is necessary for such a molecule to collide with another, and thus we may get some measure of the amount of drift developed at low pressures by considering the average number of gas collisions made by a molecule between successive wall collisions. This number is equal to the gas collision frequency divided by the wall collision frequency. For a unit length of the tube, this ratio is

$$\frac{\pi a^2 n \bar{v}/\lambda}{2\pi a \cdot \frac{1}{4} n \bar{v}} = \frac{2a}{\lambda}. \tag{35}$$

Thus each molecule makes on the average $2a/\lambda$ gas collisions between successive wall collisions. At low pressures for which $L > \lambda \gg a$, the average molecule only occasionally collides with another before completing a path across the tube. The
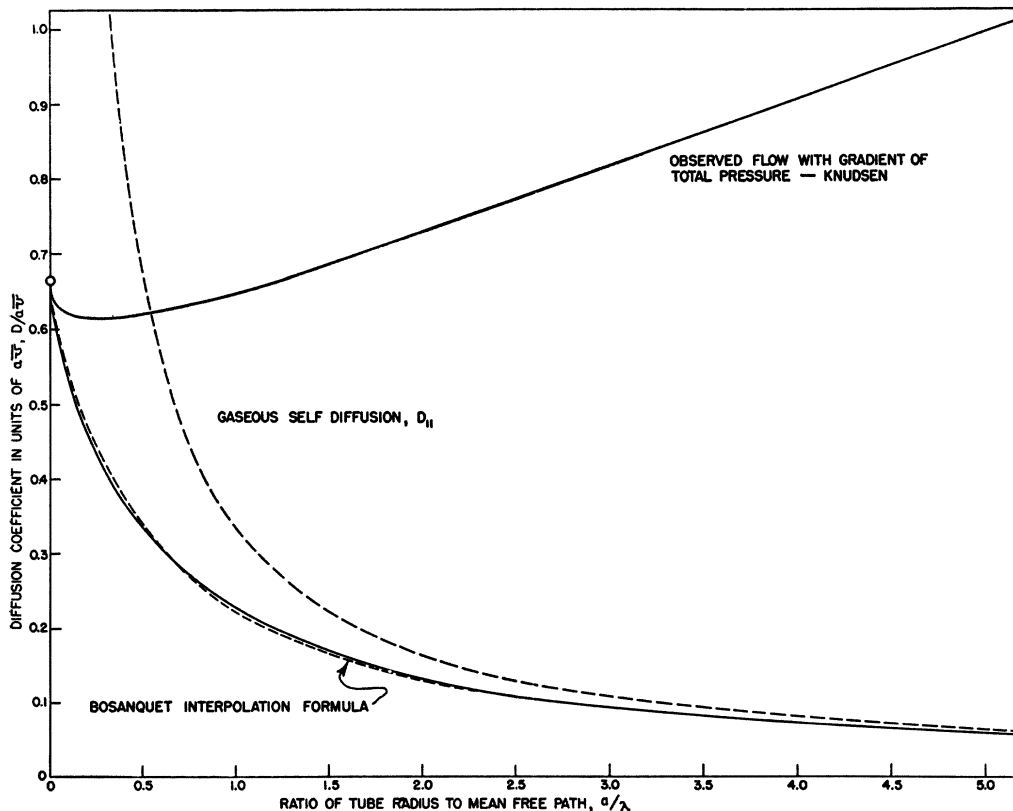

Fig. 2. Transport in molecules per unit time per unit area per unit pressure gradient as a function of the ratio of tube radius to mean free path for various cases of gas flow and diffusion in long capillary tubes. Upper full curve drawn from a composite of a large number of observations of M. Knudsen on the flow of several different gases through various capillary tubes. Lower full curve: Self-diffusion coefficient at constant total pressure according to Eq. (19) with the corresponding curve (— — —) from the Bosanquet interpolation formula, Eq. (34), superimposed on it. Broken curve: Self-diffusion coefficient D_{11} of the gas.

small drift component which can be developed under these circumstances is, to first order in a/λ, proportional to the chance of an intermolecular collision and thus to a/λ itself.

At zero pressure ($\lambda \gg L$) the entire transport comes from the Knudsen or wall diffusion. As the pressure is increased to small values such that $L > \lambda > a$, this flow is on the one hand decreased because of the obstruction of the long diffusion paths by the added molecules and, on the other hand, it is increased through the development of a drift transport. Now it is clear from the foregoing discussion of both tendencies that the former, because of the near infinite initial slope of the diffusion coefficient, must always outweigh the latter so that the total flow must initially decrease with pressure. Another way of putting this is that the obstruction of the long diffusion paths (depending on the ratio of mean free path λ to tube length L) sets in earlier than the drift which depends on the ratio a/λ. In a tube of given radius, the first effect can always be made to counteract the second simply by making the tube long enough.

These considerations give rise to the expectation that, starting with the Knudsen value at $p=0$, the specific flow in a long tube must initially decrease with pressure, pass through a minimum value, and at higher pressures increase toward the Poiseuille form. This is, of course, the behavior observed experimentally as shown by the upper solid curve of Fig. 2 which represents Knudsen's experimental data. This curve was contributed by Melkonian[10] and was prepared by plotting Knudsen's specific flow data for a number of different gases and capillaries, using the quantity $kTGl/\pi \bar{v} a^3 \Delta p$ as ordinate and $a/\bar{\lambda}$ as abscissa. Here l is the length of the capillary, Δp the pressure drop across it, G the flow in molecules per sec., and $\bar{\lambda}$ the mean free path computed from the average pressure in the tube. Plotted in this way all of the data defined a fairly unique curve with very little scatter and this is the one shown in Fig. 2. Gaede gives no data suitable for inclusion in this plot, but in this connection his observation that the drop below the limiting value of $\frac{2}{3}$ sets in at very low pressures corresponding to $\lambda \approx 100a$ is significant.

[10] E. Melkonian, Manhattan Project Report M-1485, January 11, 1945.

This behavior is in accord with the logarithmic term of Eq. (20).

An important consequence of this explanation of the Knudsen minimum is that it should not be observed in an irregular capillary or in a porous medium. In these cases free paths much longer than the mean radius cannot occur. The possibility that the observed minima were associated with the long free paths in a straight capillary or between parallel plates (cf., Gaede, reference 2) was first suggested by R. M. Badger and is, of course, confirmed by the present investigation. Experimental confirmation of this explanation is provided by the failure to observe any evidence of such minima with porous media.[11] These observations have shown the relation between specific flow and average pressure to be accurately linear down to pressures for which the mean free path is of the order of several hundred times the mean pore radius.

APPENDIX I

Momentum Transferred to Wall

Knudsen believed that the reason for the small numerical discrepancy between the results given by the momentum transfer and the diffusion treatments of free molecule flow (Eqs. (1) and (2), respectively) was to be found in the inapplicability of the usual relation $\frac{1}{4}n\bar{v}$ for the molecular flux when the gas is in motion. It is desirable therefore to consider the flux of momentum in a moving gas.

The Maxwell distribution function for a gas drifting in the x direction with velocity u is

$$f(\mathbf{v})d\mathbf{v} = A e^{-\beta^2(v_x-u)^2}dv_x e^{-\beta^2 v_y^2}dv_y e^{-\beta^2 v_z^2}dv_z,$$

where $\beta = 2/\bar{v}(\pi)^{\frac{1}{2}}$ and $\bar{v}$ is the average molecular speed. Since $u \ll v_x$, we can drop terms in u^2 and expand. We then have to first order in u/v_x

$$f(\mathbf{v})d\mathbf{v} = A e^{-\beta^2 v^2}(1+2\beta^2 u v_x)dv_x dv_y dv_z.$$

The normalization constant A can in first order be replaced by its value for a stationary gas: $(\beta/(\pi)^{\frac{1}{2}})^3$.

We transform to spherical polar coordinates with the polar (z) axis taken perpendicular to the wall. Then

$$f(\mathbf{v})d\mathbf{v} = A e^{-\beta^2 v^2}(1+2\beta^2 u v \sin\theta \cos\phi)v^2 dv \sin\theta d\theta d\phi.$$

The number of molecules with velocities between $\mathbf{v}$ and $\mathbf{v}+d\mathbf{v}$ striking unit area of the wall per unit time is $nv \cos\theta f(\mathbf{v})d\mathbf{v}$, where n is the molecular density. If each molecule is absorbed by the wall it transfers momentum mv_x in the x direction, and the total x momentum trans-

[11] H. Kuhn, letter from N. Kurti to F. G. Slack, Manhattan Project, March 8, 1944; A. D. Callihan, Manhattan Project Report M-1157, September 4, 1944; K. Schleicher, Manhattan Project Report M-1472, January 5, 1945.

ferred to unit area per second is

$$M = mnA \int_0^\infty \int_0^{\pi/2} \int_0^{2\pi} v^4 e^{-\beta^2 v^2}(1+2\beta^2 uv \sin\theta \cos\phi)$$
$$\times \sin^2\theta \cos\theta \cos\phi\, dv\, d\theta\, d\phi.$$

The first term of the parenthesis vanishes on integrating over ϕ. This corresponds to the fact that a stationary gas communicates no x momentum to the wall. On carrying out the integrations, one finds

$$M = \frac{nmu}{2\beta(\pi)^{\frac{1}{2}}} = \frac{n\bar{v}}{4} \cdot mu,$$

which agrees with the elementary result.

It is assumed in this treatment (1) that the drift velocity is the same at all points of the gas (cf., Appendix II), and (2) that the molecules, after being adsorbed on the wall, are re-emitted in random directions.

APPENDIX II

Comparison of Diffusion and Momentum Transfer Treatments of Knudsen Flow

It was noted in the introduction that the expression for the Knudsen flow which is given by the method employed here differs by a factor $8/3\pi$ from that given by the momentum transfer treatment. Although a comparison of these two treatments is secondary to the primary problem under consideration, it is nevertheless of some interest and we include a discussion of it here.

In order to make such a comparison we first determine the flow per unit area $\Gamma = dN/dS$ in the limit of zero pressure from Eq. (15). Since this eliminates the integration over dS, it is necessary to reintroduce the integration over ϕ which was performed in Eq. (9). Taking the limit as $\lambda \to \infty$, we find then from (15) that the flow dN through the element dS is

$$dN = -\frac{\bar{v}}{2\pi}\frac{dn}{dx}dS\int_0^{2\pi} d\phi \int_0^{\pi/2} s \cos^2\psi d\psi.$$

Thus

$$\Gamma = \frac{dN}{dS} = -\frac{\bar{v}}{8}\frac{dn}{dx}\int_0^{2\pi} s d\phi.$$

From Fig. 1 we note that the polar coordinates of dS in the plane of the cross section are r, ϕ, and that

$$s = (a^2 - r^2 \sin^2\phi)^{\frac{1}{2}} - r \cos\phi.$$

Hence

$$\Gamma = \frac{dN}{dS} = -\frac{1}{2}\bar{v}\frac{dn}{dx}\int_0^{\pi/2} (a^2 - r^2 \sin^2\phi)^{\frac{1}{2}} d\phi$$
$$= -\frac{1}{2}\bar{v}aE(r/a)\frac{dn}{dx},$$

where E denotes the complete elliptic integral of the second kind. Thus on the tube axis we have

$$\Gamma_{r=0} = -\frac{\pi}{4}\bar{v}a\frac{dn}{dx},$$

and at the tube wall

$$\Gamma_{r=a} = -\frac{1}{2}\bar{v}a\frac{dn}{dx}.$$

In the case of the momentum transfer treatment it is necessary to assume that all molecules have the same

average transport velocity u and thus that Γ is independent of r. This constant value of Γ is, from Eq. (1),

$$\Gamma = \frac{G}{\pi a^2} = -\frac{2akT}{m\bar{v}}\frac{dn}{dx} = -\frac{\pi}{4}\bar{v}a\frac{dn}{dx},$$

and is therefore equal to the correct value on the tube axis.

APPENDIX III

Effect of Change of Mean Free Path with Pressure

We consider here the effect of variations in the mean free path λ due to a pressure gradient on our final result, Eq. (15), for the total flow through a section of the infinite tube. For this purpose it is necessary to modify the expression for the probability that a molecule will traverse a distance ρ without collision. When the density is fixed at a value n_0, this probability is given by $P(\rho) = e^{-\rho/\lambda_0}$. When, however, the density varies along the tube in the manner given by Eq. (11), this probability is given by

$$\exp\left[-\frac{\rho}{\lambda_0}\left(1+\frac{x}{2n_0}\frac{dn}{dx}\right)\right].$$

Expanding the exponential of the small term proportional to dn/dx, this takes the form

$$P(\rho) = [1 - (\rho x/2n_0\lambda_0)(dn/dx)]e^{-\rho/\lambda_0}.$$

In determining the transport N_w from wall collisions, it is necessary to use the expression

$$\left(1 - \frac{s^2 \cot\psi \csc\psi}{2n_0\lambda_0}\frac{dn}{dx}\right)e^{-s \csc\psi/\lambda_0}$$

in Eq. (9) in place of the term $e^{-s \csc\psi/\lambda}$. This gives

$$N_w = -\bar{v}\frac{dn}{dx}\int\int dS\int_0^{\pi/2} s \cos^2\psi[1-(s \csc\psi)/2\lambda_0]$$
$$\times e^{-s \csc\psi/\lambda_0}d\psi.$$

For the transport N_g it is necessary to make two changes. Not only must the expression for $P(\rho)$ above be used in place of $e^{-\rho/\lambda}$ in Eq. (10), but the collision frequency $\bar{v}d\tau/\lambda$ in the volume element $d\tau$ must include the effect of the variation in λ along the tube. Since $1/\lambda$ is proportional to n, we may use for this collision frequency the expression

$$\frac{\bar{v}}{\lambda_0}\left(1+\frac{x}{n_0}\frac{dn}{dx}\right)d\tau.$$

The integral over ρ in Eq. (10) is then replaced by

$$\int_0^{s \csc\psi}\left(n_0+\rho \cos\psi\frac{dn}{dx}\right)\left(1+\frac{\rho \cos\psi}{n_0}\frac{dn}{dx}\right)$$
$$\times\left(1-\frac{\rho^2 \cos\psi}{2n_0\lambda_0}\frac{dn}{dx}\right)e^{-\rho/\lambda_0}d\rho.$$

This gives for N_g in place of Eq. (14)

$$N_g = -\bar{v}\lambda_0\frac{dn}{dx}\int\int dS\int_0^{\pi/2}\cos^2\psi \sin\psi$$
$$\times\left[1-\left(1+\frac{s \csc\psi}{\lambda_0}-\frac{1}{2}\frac{s^2 \csc^2\psi}{\lambda_0^2}\right)e^{-s \csc\psi/\lambda_0}\right]d\psi.$$

If we now add these expressions for N_w and N_g, the total

transport is found to reduce to

$$N = N_w + N_v = -v\lambda_0 \frac{dn}{dx} \int \int dS \int_0^{\pi/2} (1 - e^{-s \csc\psi/\lambda_0})$$
$$\times \cos^2\psi \sin\psi d\psi.$$

Since this is the same as Eq. (15) with λ_0 in place of λ, the statement made in the body of the text is established.

APPENDIX IV

The Evaluation of the Integral Q

The integral is defined by

$$Q = \frac{1}{2} \int_0^{\pi/2} d\psi \cos^2\psi \sin^2\psi \int_{-\pi/2}^{\pi/2} d\theta \cos\theta e^{-2a \csc\psi \cos\theta/\lambda}.$$

We consider first the problem of expanding Q in a power series in a/λ. Reversing the order of integration and substituting $x = \csc\psi$, we obtain

$$Q = \int_0^{\pi/2} d\theta \cos\theta \int_1^{\infty} dx \frac{e^{-qx}}{x^4} \left(1 - \frac{1}{x^2}\right)^{\frac{1}{2}}$$
$$= \int_0^{\pi/2} d\theta \cos\theta \int_1^{\infty} dx \frac{e^{-qx}}{x^4} \left\{1 - \frac{1}{2x^2} - \frac{1}{8x^4} \cdots\right\},$$

where $q = 2a \cos\theta/\lambda$. We define

$$L_n = \int_1^{\infty} dx \frac{e^{-qx}}{x^n} = \frac{1}{n-1}\{e^{-q} - qL_{n-1}\}$$

$$L_1 = -Ei(-q) = -\log\gamma q + q - \frac{q^2}{2!2} + \frac{q^3}{3!3} \cdots,$$

where γ is Euler's constant ($\log\gamma = 0.5772\cdots$).

$$\therefore \quad Q = \int_0^{\pi/2} d\theta \cos\theta \{L_4 - \frac{1}{2}L_6 - \frac{1}{8}L_8 \cdots\}.$$

Retaining terms through $(a/\lambda)^3$ we have to the desired order of approximation

$$L_4 = \frac{1}{3} - \frac{q}{2} + \frac{q^2}{2} - \frac{11}{36}q^3 + \frac{q^3}{6}\log\gamma q$$

$$L_n = \frac{1}{n-1} - \frac{q}{n-2} + \frac{q^2}{2(n-3)} - \frac{q^3}{6(n-4)}, \quad n > 4,$$

from which we find that

$$Q = \int_0^{\pi/2} d\theta \cos\theta \left\{C_1 - C_2 q + \frac{C_3}{2}q^2 - \frac{C_4}{6}q^3 + \frac{q^3}{6}\log\gamma q\right\},$$

where

$$C_1 = \frac{1}{3} - \sum_1^{\infty} \frac{(2k-2)!}{k!(k-1)!2^{2k-1}(2k+3)} = \frac{\pi}{16},$$

$$C_2 = \frac{1}{2} - \sum_1^{\infty} \frac{(2k-2)!}{k!(k-1)!2^{2k-1}(2k+2)} = \frac{1}{3},$$

$$C_3 = 1 - \sum_1^{\infty} \frac{(2k-2)!}{k!(k-1)!2^{2k-1}(2k+1)} = \frac{\pi}{4},$$

$$C_4 = \frac{11}{6} - \sum_1^{\infty} \frac{(2k-2)!}{k!(k-1)!2^{2k-1}2k} = 1.5265.$$

On carrying out the integration over θ we obtain

$$Q = \frac{\pi}{16} - \frac{\pi}{6} \cdot \frac{a}{\lambda} + \frac{\pi}{3} \cdot \left(\frac{a}{\lambda}\right)^2$$
$$- \left(\frac{\pi C_4}{4} - \frac{4C_5}{3}\right) \cdot \left(\frac{a}{\lambda}\right)^3 + \frac{\pi}{4}\left(\frac{a}{\lambda}\right)^3 \log\left(\frac{2\gamma a}{\lambda}\right),$$

where

$$C_5 = \int_0^{\pi/2} \cos^4\theta \log\cos\theta d\theta = -0.06405.$$

This is the desired expansion for small a/λ. In order to evaluate Q at larger values of a/λ we make use of the relation

$$\int_{-\pi/2}^{\pi/2} e^{-y\cos\theta} \cos\theta d\theta = 2 - \pi\{\mathbf{H}_1(iy) - iJ_1(iy)\}$$

in which $J_1(iy)$ and $\mathbf{H}_1(iy)$ are, respectively, the Bessel and Struve functions of first-order and imaginary argument. Then $Q = \pi/16 - (\pi/2)K$ where

$$K = \int_0^{\pi/2} d\psi \cos^2\psi \sin^2\psi \{\mathbf{H}_1(2ai/\lambda \sin\psi) - iJ_1(2ai/\lambda \sin\psi)\}$$

and K has been evaluated numerically with the following results:

$a/\lambda =$	0.25	0.5	1	2	∞ ;
$K =$	0.0560	0.0834	0.1066	0.1186	0.1250.