The Flow of Rarefied Gases

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It has been shown experimentally by Knudsen and others that gases flowing at decreasing total pressures through small capillaries pass from a region of Poiseuille flow to a so-called *slip* flow region which contains a flow minimum. Frequently the practice has been followed of approximating this behavior with a linear relationship which, although it gives a fairly good approximation to the actual curve, is incomplete in theory.

A new equation for the flow of gases in capillaries is presented, in which all flow constants can be calculated from the simple kinetic theory of gases. It is shown that this equation reproduces the experimental results of Knudsen and others over the entire range of laminar, slip, and Knudsen flow within the accuracy that might be expected from the simple kinetic model adopted.

Some discussion of the use of this equation in the design of vacuum piping and its applicability to flow through porous solids is also given.

The flow of gases under high vacuum, through fine capillaries, or through the small pores of a solid has been divided into three regimes, that of laminar or Poiseuille flow, the so-called *slip* flow region, and a region of molecular streaming or Knudsen flow. Physically these flow regimes are the result of the increasing frequency of molecular wall collisions relative to intermolecular collisions, as the ratio of the channel dimensions to the molecular mean free path decreases. That is when this ratio is large, Poiseuille flow is observed; when its value approaches unity, slip flow results, and for conditions such that the mean free path greatly exceeds the radius of the channel, Knudsen flow occurs. In the limiting case of Poiseuille flow the fluid can be treated as a continuum, and in the other extreme represented by Knudsen flow each molecule of the gas behaves independently of the others. Adequate formulas for both these regimes have been developed. In the slip region of flow however the rate of wall collisions is comparable with the rate of intermolecular collisions, and this situation presents somewhat more of a problem.

It has been the practice in the past to express flow rates in the slip region by a modification of the Poiseuille equation which contains a slip correction term. This correction factor is derived by assuming that the flow velocity at the wall is not zero and by making an estimate of the magnitude of the wall velocity from simple molecular momentum transfer theory for dilute gases.

Equations of this type are usually written in terms of a specific flow rate $G' = G/\Delta p$ for a given gas and capillary:

$$G' = A\bar{p} + B \qquad (1)$$

Present (*1*) gives a detailed derivation of such an expression.

The above equation is commonly applied to the flow of gases in capillaries and in porous solids. It implies that the specific flow rate should be linear with pressure, and it also might be expected that the quantity B would be identical with the expression for Knudsen flow as the pressure approached zero. However experiments of Knudsen (*2*) and others in circular capillaries have demonstrated the existence of a minimum in the specific flow rate-pressure curve and have shown that the value of the slip correction term obtained from the straight-line intercept of such a plot is considerably lower than the experimentally determined limiting flow or the minimum flow. Therefore the flow expression of the form of Equation (1) cannot be complete for the flow regimes described earlier. Knudsen proposed an empirical modification of Equation (1) of the form

$$G' = A\bar{p} + B\,\frac{1 + c_1\bar{p}}{1 + c_2\bar{p}} \qquad (2)$$

where all constants were determined from experimental results. A more theoretical expression which would qualitatively or quantitatively account for the observed experimental behavior in flow through circular capillaries does not appear to have been presented as yet. The problem has been discussed by Present (*1*).

Although tentative explanations of the occurrence of a flow minimum have been offered by Present and Pollard (*3*) and by Wicke and Vollmer (*4*), these do not give any indication as to the mathematical form for a more general expression, based on the physical picture they suggest, that would even qualitatively describe these experimental curves.

DERIVATION OF A MODIFIED FLOW EQUATION FOR CIRCULAR CAPILLARIES

It has been pointed out by several authors that the shortcomings of Equation (1) may be owing to the fact that the elementary mean free path theory used in the derivation of the slip correction term is not rigorous. Although this latter statement is true, it would seem also that for regions where the mean free path λ is approximately equal to the tube radius r even a simple kinetic theory should approximately describe the observed flow behavior. It is not apparent how the slip term could be reformulated even by a more sophisticated kinetic approach in such a way as to reconcile this qualitative disagreement. Certainly in formulating the slip term it would appear to be a justifiable assumption to say that in the region where $\lambda \approx r$, a zero value for the flow velocity at the wall is not a satisfactory approximation. Therefore it would seem to be more logical to suppose that the physical picture underlying Equation (1) is either essentially erroneous or incomplete.

It follows from the kinetic theory derivation of Equation (1) that it accounts for molecules undergoing intermolecular collisions, or those involved in a wall collision between two intermolecular collisions. However under conditions where $r \approx \lambda$, on the average, a considerable number of molecules do not suffer an intermolecular

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collision between two successive wall collisions. It would seem logical to exclude these latter molecules from the scope of the modified Poiseuille equation and to consider them separately. A plausible way to treat this group of molecules would be to assume that in the first approximation their flow can be described by the Knudsen flow formula.

Accordingly, the specific flow equation should have the form

$$G' = \left[1 - F\left(\frac{r}{\lambda}\right)\right](A\bar{p} + B) + F\left(\frac{r}{\lambda}\right)C \qquad (3)$$

where $F\left(\frac{r}{\lambda}\right)$ is the fraction of the molecules that, on the average, do not collide with other molecules between two wall collisions.

Considering the molecules that are leaving a surface element of the wall of a long capillary tube $(L >> \lambda)$, and assuming completely diffuse reflection, one can show that the fraction which strikes the wall again before undergoing an intermolecular collision is given by

$$F\left(\frac{r}{\lambda}\right) = \frac{4}{\pi}\int_0^{\frac{\pi}{2}}\int_0^{\frac{\pi}{2}} \sin\theta\cos\theta \; e^{-\left(\frac{\cos\phi}{\sin\theta}\right)\left(\frac{2r}{\lambda}\right)} d\theta d\varphi \qquad (4)$$

An approximate solution for this integral, obtained by numerical integration, can be expressed as

$$F\left(\frac{r}{\lambda}\right) = e^{-\sinh^{-1}\left(\frac{2r}{\lambda}\right)}$$

or for small values of r/λ

$$F\left(\frac{r}{\lambda}\right) = e^{-\left(\frac{2r}{\lambda}\right)} \qquad (5)$$

Therefore, for a long capillary tube of circular cross section, Equation (3) becomes

$$G' = \left[1 - e^{-\sinh^{-1}\left(\frac{2r}{\lambda}\right)}\right](A\bar{p} + B) + e^{-\sinh^{-1}\left(\frac{2r}{\lambda}\right)} C \qquad (6)$$

It is apparent that Equation (6) reduces to the Knudsen formula when $\lambda >> r$ and becomes the Poiseuille equation if $r >> \lambda$.

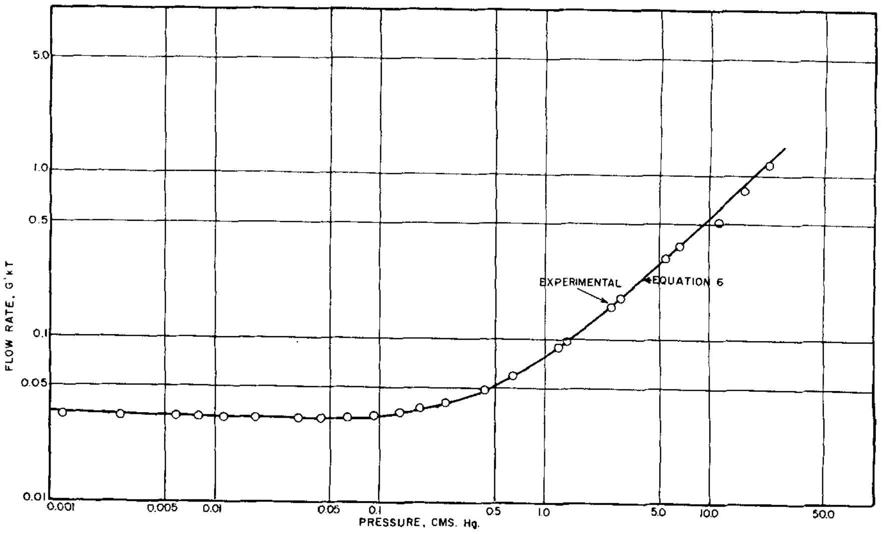

Fig. 1. Comparison of calculated and experimental flow rates for carbon dioxide in a glass capillary, experimental data from Knudsen (2).

The constant terms A, B, and C in the equation can be evaluated from simple kinetic theory. However the value of the slip term B is dependent on the extent of the region of slip velocity, which in turn is described in terms of the mean free path length. The elementary kinetic theory value for the mean free path $\eta = \frac{1}{3} nm\bar{v}\lambda$ has been used by Present (*1*) in formulating the slip term. It would seem to be logical however to make use of the more sophisticated kinetic equation of Chapman and Cowling; that is

$$\eta = \frac{1}{2} nm\bar{v}\lambda \qquad (7)$$

particularly as this equation applies much more rigorously for momentum transfer processes such as are being considered here.

Accordingly, then, if the constants of Equation (6) are evaluated, the following expressions can be written:

$$A = \frac{\pi r^4}{8\eta kTL} \qquad (8)$$

$$B = \frac{4\pi r^3}{3m\bar{v}L} \qquad (9)$$

$$C = \frac{16r^3}{3m\bar{v}L} \qquad (10)$$

As the mean free path is inversely proportional to pressure, one can write

$$\frac{2r}{\lambda} = a\bar{p} \qquad (11)$$

where a is a constant for a given capillary and a given gas at constant temperature. If this expression is now substituted into Equation (6), and the resulting equation differentiated, the condition at which the flow curve has a minimum is found to be determined by the equation

$$\frac{a(C-B)}{A} = \left[1 + \left(\frac{2r}{\lambda}\right)^2\right]^{\frac{1}{2}} \left[e^{\sinh^{-1}\left(\frac{2r}{\lambda}\right)} - 1\right] + \frac{2r}{\lambda} \qquad (12)$$

When one substitutes the foregoing kinetic expressions for A, B, C, and η, the term $\frac{a(C-B)}{A}$ should have a universal value equal to

$$\frac{a(C-B)}{A} = \left(\frac{16}{3} - \frac{4\pi}{3}\right)\frac{8}{\pi} = 2.91 \qquad (13)$$

and therefore $(r/\lambda)_{\min}$ should also have a single value given by Equation (12), from which

$$(r/\lambda)_{\min} = 0.49 \qquad (14)$$

It is of interest to compare this result with the flow minimum found by Knudsen in his experimental tests, which occurred at values of $(r/\lambda)_{\min} \approx 0.32$ to 0.48. It would appear that the value given by Equation (13) may be a little high, therefore, but it does fall very close to the experimentally found range.

A further check with experiment may be made by noting that the value of C, as given by Equation (10), gives quite close agreement with the actual limiting Knudsen flow as the pressure approaches zero. The ratio of the two constants C and B can be found from Equations (10) and (9):

$$\frac{C}{B} = \frac{4}{\pi} = 1.273 \qquad (15)$$

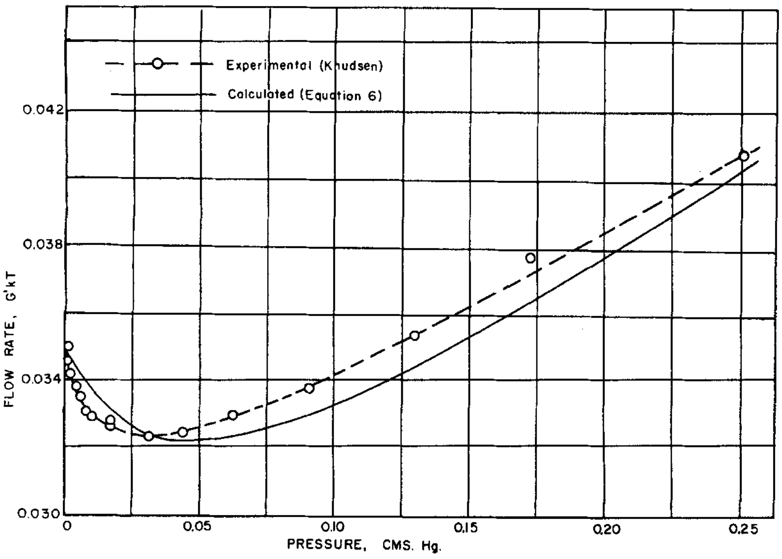

Fig. 2. Comparison of calculated and experimental flow rates for carbon dioxide in a glass capillary, low-pressure range.

A corresponding average value for this ratio taken from the experiments of Knudsen is 1.23, in good agreement with the above. If this empirical value of 1.23 is used for the ratio of the constants C/B, then the value of $(r/\lambda)_{min} = 0.44$ and falls within the experimental range.

It might be noted that use of the simpler kinetic equation relating viscosity and mean free path would result in the following equation for the slip term B:

$$B = \frac{\pi r^3}{m\bar{v}L} \qquad (16)$$

Use of this expression in Equation (13) results in a value for $(r/\lambda)_{min} = 0.60$ and also gives for the ratio C/B a value of 1.70. It may be concluded therefore that the region of slip velocity in terms of mean free path length is best described by the more rigorous kinetic expressions.

The experiments of Knudsen with carbon dioxide using his "Capillary No. 4" gave a value for the specific flow at the minimum of 0.0324. Putting Equation (6) in the same form as that employed by Knudsen, and using Equations (8), (9), and (10) for the values of A, B, and C respectively, one calculates the flow value as 0.0322, in excellent agreement with the experimental value.

In Figures 1 and 2 the solid line shows a plot of Equation (6) with values of the constants A, B, and C from kinetic theory, that is as given by Equations (8), (9), and (10). The points represent the data of Knudsen for the flow of carbon dioxide at 25°C. It can be seen that these values lie within 3% of those predicted by Equation (6). Additional calculations with Equation (6) agree equally well with data given by Knudsen for the flow of oxygen and hydrogen through tubes of varying length and radius.

The values for $(r/\lambda)_{min}$ calculated from (12) are somewhat on the high side in comparison with the values obtained by Knudsen and by Klose (5). These results showed an average value for $(r/\lambda)_{min}$ of about 0.40, with a scatter of 25%. The discrepancy may be partly explained by the fact that the experimental value of C, as found by Knudsen, is usually a little lower than the theoretical value used in the present calculations; that is Equation (12) shows that increasing B will decrease the value of $(r/\lambda)_{min}$, but from Equation (6) it will increase the value of the minimum flow. On the other hand a lower value of the constant C will both decrease the value of $(r/\lambda)_{min}$ and slightly decrease the value of the minimum flow. The form of Equation (12) suggests that it would be experimentally difficult to obtain a highly precise value for the ratio $(r/\lambda)_{min}$. However it appears to be true that the minimum flow rate in circular capillaries does occur at a universal value of the ratio r/λ, and this value is close to 0.40. The flow equation suggested here appears to reproduce experimental results within the accuracy of determination of values of the constants. Very close agreement with experiment can be obtained with Equation (6) by adjusting the values of the constants slightly. The magnitude of these adjustments is within the limits of error quoted by Knudsen. The success of Equation (6) would also appear to justify to a large extent the initial assumption of diffuse molecular reflection at the capillary walls.

GENERALIZED CORRELATION FOR FLOW IN DUCTS

When one considers the close agreement given by Equation (6) with experiment, it is of interest to generalize this equation as much as possible. Design equations for high vacuum systems used to the present have been of the type of Equations (1) or (2), including correction factors attributed to the fraction of diffuse or specular molecular reflection at the tube wall. In effect, these equations approximate the true shape of the flow curve with a best-fit straight line. This procedure

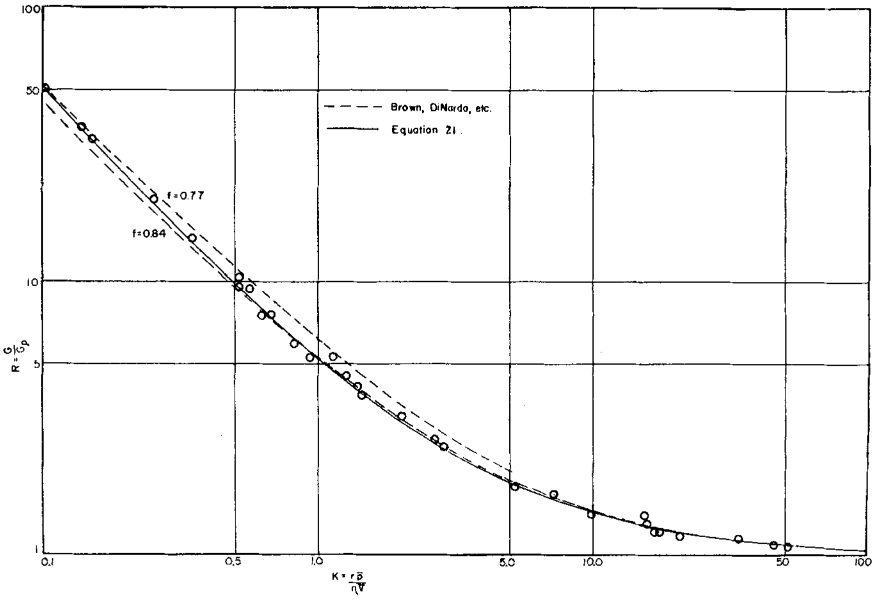

Fig. 3. Comparison of general flow equation with earlier correlations. Representative experimental data for carbon dioxide, oxygen, hydrogen, air from Knudsen (2).

TABLE 1. COMPARISON OF EQUIVALENT PORE SIZES BY MERCURY PENETRATION AND BY FLOW TESTS

Sample	Source and description	Pore radius, μ By mercury penetration	Pore radius, μ By flow tests
Filtros	Porous filter plate Filtros Corp.	16.4	14.7
Selas 015	Synthetic filter media Selas Corp.	1.17	1.02
Selas 03-1	Synthetic filter media Selas Corp.	0.65	0.67
Kaolin	Porous porcelain Coors Ltd.	0.16	0.13
Celite	Pelleted diatomaceous earth. Johns-Manville Co.	0.48	0.57
Limestone 36	Natural Alberta limestone	0.31	0.40
Limestone 63	Natural Alberta limestone	0.15	0.14

is probably satisfactory except at low pressures, that is if $r/\lambda < 1.0$. However Equation (6) should form the basis of a more exact design approach.

If Equation (6) is divided through by the term $A\bar{p}$, and the relationship $C = 1.273B$ is used, then

$$\frac{G'}{G_p'} = \frac{G}{G_p} = R = (1 - e^{-2r/\lambda}) \left(1 + \frac{C}{1.273A\bar{p}}\right) + e^{-2r/\lambda}\frac{C}{A\bar{p}} \quad (17)^*$$

where

$$G_p' = \frac{G_p}{\Delta p} = A\bar{p} = \frac{\pi r^4 \bar{p}}{8\eta kTL} \quad (18)$$

G_p is the fictitious flow that would occur *if* the Poiseuille equation above were used in calculations. The quantity R is the ratio of the true flow to that given by applying the Poiseuille equation. All groupings in Equation (17) are dimensionless. If now the kinetic expressions for A and C are introduced, with $\eta = \frac{1}{2} nm\bar{v}\lambda$, it can be found that

$$\frac{2r}{\lambda} = \frac{128}{3\pi}\frac{A\bar{p}}{C} = \frac{8}{\pi}\frac{r\bar{p}}{\eta\bar{v}} \quad (19)$$

It is convenient to define as the working dimensionless group the latter quantity in (19); that is

$$\frac{r\bar{p}}{\eta\bar{v}} = K \quad (20)$$

inasmuch as this group can be calculated directly from system properties and conditions. Rewriting Equation (18) with this group and rearranging one gets

$$\frac{G}{G_p} = R = e^{-\frac{8K}{\pi}}\left[\frac{1.144}{K} - 1\right] + \frac{4.189}{K} + 1 \quad (21)$$

All data for circular ducts when plotted as R vs. K should fall on a single curve.

A complete compilation of experimental data for flow in circular ducts has been given by Brown et al. (*6*), together with additional data from their own tests. These results were correlated by the equation

$$R = 1 + 4\left(\frac{\pi}{2}\right)^{\frac{1}{2}}\left(\frac{2}{f} - 1\right)X \quad (22)$$

where R has the same meaning as in Equation (21). The dimensionless parameter X can be shown to be related to the group K as follows:

$$X = \frac{1}{K}\sqrt{\frac{\pi}{8}} \quad (23)$$

The factor f is taken to be proportional to the degree of diffuse reflection occurring from the tube walls. Brown et al. found that experimental data could not be fitted equally well over the entire range of conditions by a single value of f. This result might have been expected. It is felt that the flow equation developed here [Equation (21)], which makes the more logical assumption of completely diffuse reflection, should fit experimental data equally well, over the entire range from laminar to free molecule flow. In Figure 3 the correlating curves of Brown et al. are reproduced as dashed lines, and Equation (21) is plotted as a solid line. At small values of r/λ (X large) the above authors fitted the experimental data by a straight line having the equation $R = 8.0X$. Equation (21) for the same range of values predicts a straight-line relationship equivalent to $R = 8.5X$, which appears to fit the data shown at least as well or somewhat better than the first relationship. For smaller values of X the form of Equation (21) fits all the data given with a smooth transition between the two curves proposed by Brown et al. The data for iron pipes given by these authors, which fell well below the curves of Figure 2, still cannot be explained. However the possibility of significant experimental error in these particular results is now much more likely in view of the theoretical nature of Equation (21).

PIPING DESIGN CONSIDERATIONS

The design chart given by Brown et al. (*6*) is based upon an adequate correlation and is therefore, of course, satisfactory for many design problems. Sofer and Weingartner (*7*) discussed the three particular solutions usually desired in the design of vacuum piping system. These three cases are listed below, together with the recommended procedure for design when employing Equation (21).

Case 1. Given exit and inlet pressures and pipe diameters, find throughput. Use Figure 2, Equation (21), or design charts of Brown et al.

Case 2. Given exit and inlet pressures and throughput, find required pipe diameter. Multiply Equation (21) × K^4, whence

$$RK^4 = \frac{Gm\,L\bar{p}^3}{\Delta p\,\eta^3\bar{v}^2} = e^{-\frac{8K}{\pi}} K^3 (1.144 - K) + K^3 (4.189 + K) \quad (24)$$

Case 3. Given exit presure (p_2), throughput, and pipe diameter, find pressure drop and inlet pressure (p_1). Modify Equation (21), and solve for p_1 by trial and error:

$$RK = \frac{Gm\,L\bar{v}}{r^3\,(p_1 - p_2)} = e^{\frac{-8K}{\pi}} (1.144 - K) + 4.189 + K$$

$$K = \frac{r(p_1 + p_2)}{2\eta\bar{v}} \quad (25)$$

It is believed that the above equations offer a design method which is theoretically satisfactory and which may be simpler and more accurate in some ranges than present methods.

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[*] Use of the simpler form $F = e^{-2r/\lambda}$ introduces an error in the calculated flow which never exceeds 2%.

The application of Equation (6) to gas flow through a porous solid is of considerable interest. Because of the unique and complex features of any given pore structure, such an application is bound to be approximate and to involve the use of averaged values.

The quantities of primary interest will be the equivalent circular radius and the length of the pores. Obviously, the pore channels may vary in shape from the circular, and they may vary in cross-sectional area along their length. The length of a pore, in general, will exceed the geometric sample length. For these reasons a certain number of experimental flow measurements are always necessary in order to evaluate the flow characteristics of a porous solid.

If flow measurements are available at relatively high pressures, that is such that $r > \lambda$, then Equation (6) to a close approximation becomes

$$G' = A\bar{p} + B = A^1 \bar{r}^4 \bar{p} + B^1 \bar{r}^3 \tag{26}$$

the usual form of the slip flow equation applied to porous solids. A plot of specific flow rate against the mean absolute pressure will give a straight-line relationship over this pressure range. If the resulting straight line is extrapolated to the zero pressure intercept, then this intercept gives a value for the slip term B, and the slope of the line is the value of A. The ratio of slope to intercept can be written for a spectrum of pore radii such as usually exists:

$$\frac{A}{B} = \frac{A^1 \sum_i n_i r_i^4}{B^1 \sum_i n_i r_i^3} \tag{27}$$

where i refers to the individual pore radius. Substituting from Equations (8) and (9) into the above one obtains

$$\frac{A}{B} = \left(\frac{3}{4\pi\eta\bar{v}}\right) \left[\frac{\sum_i n_i r_i^4}{\sum_i n_i r_i^3}\right] = \frac{3\bar{r}}{4\pi\eta\bar{v}} \tag{28}$$

The ratio of the summation terms given in Equation (28) has been set equal to an equivalent average pore radius $\bar{r}$. Because of the dependence of the flow rate on the pore radius to the fourth or third power, any constrictions in a pore channel will tend to have the effect of giving a minimum value for this equivalent radius. Therefore the value of $\bar{r}$ given by Equation (28) might be expected to agree fairly well with the volume average radius determined by mercury injection methods.

Flow rates as a function of total pressure were determined for a number of porous solids with the technique described by Arnell (*8*) and with pure nitrogen as the test gas. Such flow data gave good straight lines on plots of mean total pressure vs. flow rate. Some results for the equivalent pore radius calculated from these data and Equation (28) are given in Table 1 and are compared with the mean radius from mercury penetration experiments. It can be seen that the agreement is good.

If values of A and B are available from experiment, then L can be calculated from Equation (8), the expression for A, and C can be found from Equation (10), which is apparently correct to within about 3%.

As pointed out in another paper (*9*) the value of $\bar{r}$ calculated from diffusion measurements also agrees well with that obtained from mercury penetration experiments. Therefore permeability tests apparently will give a satisfactory value of an average true Knudsen diffusion coefficient by applying the relationship $D_k = 2/3\,\bar{r}\,\bar{v}$.

Also, since the value of C can be calculated from the known value of B, that is $C = (4B)/(\pi)$, it is possible to determine the limiting Knudsen flow from the slip flow intercept and to calculate therefore an average effective Knudsen diffusion coefficient based on the geometric proportions of the sample.

Wicke and Vollmer (*4*) have pointed out that no minimum is to be expected in the total flow rate-pressure plot for a porous solid because of the spectrum of pore radii present. At best, a flattening out of the curve at low pressures might be observed. Free molecule flow through porous solids has also been discussed in some detail by Hiby and Pahl (*10, 11*).

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NOTATION

All units used are in the absolute c.g.s. system.

A_s = geometric area of a porous solid sample
A = Poiseuille flow constant
B = slip flow constant
C = Knudsen flow constant
a = proportionality factor between mean pressure and mean free path
c_1, c_2 = constants in Knudsen flow equation
F = fraction of molecules undergoing successive wall collisions
f = fraction of molecules diffusely reflected
G = molecular flow per unit time
G' = specific molecular flow per unit time per unit pressure differential
G_p = molecular flow per unit time as given by the Poiseuille equation
k = Boltzmann constant
K = dimensionless group equal to $\bar{r}\bar{p}/\eta\bar{v}$
L = length of a capillary
L_s = geometric length of a porous solid sample
m = molecular mass
$\bar{p}$ = mean pressure
Δp = pressure differential causing flow
r = radius of a tube
$\bar{r}$ = equivalent circular radius defined by Equation (28)
R = flow ratio equal to G/G_p
$\bar{v}$ = average molecular velocity $\left(\frac{8kT}{\pi m}\right)^{\frac{1}{2}}$
X = dimensionless group by Equation (23)
λ = mean molecular free path
η = viscosity of the gas

LITERATURE CITED

1. Present, R. D., "The Kinetic Theory of Gases," McGraw-Hill, New York (1958).
2. Knudsen, M., *Ann. Phys.*, **28**, 75 (1909).
3. Pollard, W. G., and R. D. Present, *Phys. Rev.*, **73**, 762 (1948).
4. Wicke, E., and W. Vollmer, *Chem. Eng. Sci.*, **1**, 282 (1952).
5. Klose, W., *Ann. Phys.*, **2**, 73 (1931).
6. Brown, G. P., A. Di Nardo, G. K. Cheng, and T. H. Sherwood, *J. App. Phys.*, **17**, 802 (1946).
7. Sofer, G. A., and H. C. Weingartner, "Advances in Chemical Engineering," Vol. 2, Academic Press, New York (1958).
8. Arnell, J. C., *Can. J. Res.*, **25A**, 191 (1947).
9. Scott, D. S., and F. A. L. Dullien, *A.I.Ch.E. Journal*, **8**, No. 1, p. 113 (1962).
10. Hiby, J. W., and M. Pahl, *Phys. Rev.*, **88**, 414 (1952).
11. ——————, *Z. Naturforschg.*, **11a**, 80 (1956).

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