PHYSICS

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1957

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Abstract

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THEORY OF GAS FLOW

IN A POROUS BODY IN THE NEAR-KNUDSEN REGION.

PSEUDOMOLECULAR FLOW

Two regimes of gas flow in a porous body (or in individual capillaries) are known: molecular, when a—the ratio of the number of collisions of molecules with one another to the number of collisions with the pore walls—is small, and viscous, when $a \gg 1$ and a velocity profile is realized in the pores. It is generally accepted that, as the gas pressure p, and consequently a, increases, the molecular regime gradually passes into the viscous one, in accordance with which Q—the gas flow (in $\mathrm{mol} \cdot \mathrm{cm}^{-2} \cdot \mathrm{sec}^{-1}$)—will increase monotonically, and, to a first approximation, linearly.

This scheme is contradicted by experiment, which reveals, for round and, especially sharply, for slit-shaped capillaries, the presence of a minimum in the dependence of Q on p. Attempts to explain this minimum theoretically have been unsuccessful because the departure from the Knudsen regime is accompanied by the appearance of a convective component depending on the coordinates, i.e., by the appearance of a velocity profile. The calculations are then extremely complicated.

The situation is different for a highly porous body, for which

$$1 - \delta \ll 1, \tag{1}$$

where δ is the porosity. In this case the porous body is characterized by two scales that differ essentially in magnitude: the mean pore opening λ_c and the mean particle size D^*, equal to the mean values of the segments cut off on a "random" straight line by the points of its intersection with the walls and, respectively, located in the pores and in the particles. As follows from a lemma proved earlier (1):

$$\lambda_c = 4\frac{V}{S}, \qquad D = 4\frac{V_0}{S}, \tag{2}$$

where S is the surface of the walls; V is the volume of the particles; V_0 is the volume of the pores.

From (2) it follows that

$$\lambda_c = \frac{\delta}{1-\delta} D. \tag{3}$$

It is obvious that $a = \lambda_c/\lambda_g$, where λ_g is the ordinary mean free path of gas molecules at the given pressure p.

We see that, under condition (1), there will exist a region of gas pressures for which two conditions will be satisfied simultaneously:

$$\lambda_g \ll \lambda_c \quad (a \gg 1), \tag{4}$$

$$D \ll \lambda_g, \tag{4'}$$

of which the first means the absence of the Knudsen regime, while the second entails the absence of dependence of the convective component on the coordinates**.

* In a highly porous body one can simultaneously satisfy the still more stringent condition $D \ll a \ll \lambda_g \ll \lambda_c$, where a is the mean distance between neighboring particles.

** For circular cylinders D is equal to the diameter, and for spheres to 2/3 of the diameter.

Let us consider the flow of gas in this region, which we shall call pseudomolecular, and in the transition region between it and the Knudsen region, i.e., when only condition $(4')$ is satisfied. With the exception of the limiting case of a purely Knudsen regime ($\lambda_c \gg \lambda_g$), the motion of the molecules is characterized by a convective component u_z, equal to the mean value of the component v_z of the molecular velocity. Correspondingly, the distribution of molecular velocities becomes anisotropic.

The total gas flux Q, in moles/sec per 1 cm^2 of the porous body, is equal to

$$Q = Q_u + Q_D = Cu_z + Q_D, \tag{5}$$

where Q_u is the convective component of the flux; Q_D is the diffusion component; C is the gas concentration (per 1 cm^3 of the volume of the porous medium).

Similarly, the resistance of the flux per unit volume of the porous body, equal to the action of the flux on a unit volume of the body, is

$$W = W_u + W_D, \tag{6}$$

where $W_u \sim u_z$, $W_D \sim \operatorname{grad} p$.

For the case of a single sphere with radius $R \ll \lambda_g$, the formula (2) is known:

$$(W_u)_1 = \beta S_1 \frac{C u_z}{\delta} \sqrt{2\pi MRT}, \tag{7}$$

where S_1 is the surface of the sphere; β is a constant depending on the law of interaction with the surface of the molecules striking it.

Taking into account that, in deriving formula (7), the shape of the sphere played a role only insofar as it ensured an isotropic distribution in space of all elements of its surface S_1, and that C takes into account the dependence of the number of collisions on the concentration of molecules around the sphere, it is easy to generalize (7) to the case of particles of any (convex) shape, provided their aggregate is isotropic:

$$W_u = \beta S_0 \frac{C u_z}{\delta} \sqrt{2\pi MRT}, \tag{8}$$

where S_0 is the specific surface in square centimeters per 1 cm^3 of the porous body.

To find W_D, we shall use formula (3) for the velocity distribution function of gas molecules in the presence of a concentration gradient:

$$f^{(1)} = f^{(0)} \left(1 - \lambda_t \cos\vartheta \frac{\operatorname{grad} C}{C}\right), \tag{9}$$

where $f^{(0)}$ is the Maxwellian distribution function; λ_t is the transport mean free path of the molecules; ϑ is the polar angle of the molecular velocities relative to the direction $-\operatorname{grad} C$.

Formula (9), which is strictly valid for a purely Knudsen regime, will be assumed valid also in the pressure region under consideration, in a frame of reference moving with velocity u_z. In this case, as before,

$$\lambda_t = \frac{\lambda}{1 - \overline{\cos\gamma}}, \tag{10}$$

where $\overline{\cos\gamma}$ is the mean cosine of the angle of scattering of the molecules; λ and $\overline{\cos\gamma}$ are equal to

$$\frac{1}{\lambda} = \frac{1}{\lambda_c} + \frac{1}{\lambda_g}, \tag{11}$$

$$\overline{\cos\gamma} = \frac{\lambda}{\lambda_c}\overline{\cos\gamma_c} + \frac{\lambda}{\lambda_g}\overline{\cos\gamma_g}, \tag{11’}$$

where $\overline{\cos\gamma_c}$ and $\overline{\cos\gamma_g}$ refer to the scattering of a molecule upon collision with the wall and with another molecule. From (11) and (11′) it follows that

$$\frac{1}{\lambda_t} = \frac{1}{(\lambda_t)_c} + \frac{1}{(\lambda_t)_g}. \tag{12}$$

Knowing $f^{(1)}$, it is easy to compute W_D as the momentum transmitted by the molecules to the walls upon impacts, plus the recoil momentum upon reflections:

$$W_D = -\left[\mu\lambda_t\frac{S_0}{4} + (1-\delta)\right]\operatorname{grad} p. \tag{13}$$

Here the second term on the right expresses the “quasi-Archimedean” buoyant force on spheres located in the field of the pressure gradient p; μ is a parameter depending on the law of interaction of the molecules with the walls.

By Newton’ s third law, if inertial terms are neglected:

$$W = -\operatorname{grad} p. \tag{14}$$

Substituting (6), (8), and (13) into the left-hand side of (14), we obtain

$$Cu_z = \operatorname{grad} p\left(\mu\frac{\lambda_t}{\lambda_c} - 1\right)\frac{\delta^2}{\beta S_0\sqrt{2\pi MRT}}. \tag{15}$$

The diffusion flow rate Q_D is obtained by multiplying (9) by $Cv\cos\vartheta/\delta$ and integrating over all possible velocities:

$$Q_D = -\frac{4}{3}\frac{\delta}{\sqrt{2\pi MRT}}\lambda_t \operatorname{grad} p.$$

Thus, the total gas flow rate Q is equal to

$$Q = \frac{\delta^2}{S_0}\frac{\operatorname{grad} p}{\sqrt{2\pi MRT}}\left[\frac{1}{\beta}\left(\mu\frac{\lambda_t}{\lambda_c} - 1\right) - \frac{16}{3}\frac{\lambda_t}{\lambda_c}\right] = -k\operatorname{grad} p,$$

where it has also been taken into account that, according to (2), $\lambda_c = 4\delta/S_0$.

Hence the filtration coefficient k is equal to:

$$k = -\frac{\delta^2}{S_0}\frac{1}{\sqrt{2\pi MRT}}\left[\frac{1}{\beta}\left(\mu\frac{\lambda_t}{\lambda_c} - 1\right) - \frac{16}{3}\frac{\lambda_t}{\lambda_c}\right]. \tag{16}$$

From (10), (11), and (11′) it is seen that

$$\frac{\lambda_t}{\lambda_c} = \frac{1}{(1-\overline{\cos\gamma_c}) + \alpha(1-\overline{\cos\gamma_g})}. \tag{17}$$

In the Knudsen regime of gas flow $u_z = 0$, and consequently $Q_u = 0$; whence from formula (15) we have $\mu = 1 - \overline{\cos\gamma_c}$ and

$$k_{\text{kn}} = \frac{16}{3}\frac{\delta^2}{S_0}\frac{1}{\sqrt{2\pi MRT}}\frac{1}{1-\overline{\cos\gamma_c}}. \tag{18}$$

Substituting the value λ_t/λ_c (17) into (16), we obtain

$$k = \frac{\delta^2}{\beta S_0}\frac{1}{\sqrt{2\pi MRT}}\frac{{}^{16}\!/_3\beta + \alpha(1-\overline{\cos\gamma_g})}{\mu + \alpha(1-\overline{\cos\gamma_g})}.$$

In the pseudomolecular regime $(\alpha \to \infty,\ \lambda_t \to 0,\ W_D \to 0,\ Q_D \to 0)$

$$k = \frac{\delta^2}{\beta S_0}\frac{1}{\sqrt{2\pi MRT}}. \tag{19}$$

For diffuse and, respectively, specular reflection of molecules with preservation of speed, the calculation gives

$$\frac{1}{\beta} = \frac{27\pi}{26}; \qquad \frac{1}{\beta} = \frac{3\pi}{2}.$$

A simple calculation shows that the maximum decrease of k with increasing α occurs at $\sim 11.7\%$.

On the other hand, at pressures for which condition (4′) is violated, one may use the generalized Stokes law, empirically established by Millikan (^{4}), for the resistance encountered by a gas flowing with velocity u_z past a sphere of radius a:

$$W_1 = -\frac{6\pi\eta a u_z}{1 + A\frac{\lambda_g}{a} + B\frac{\lambda_g}{a}e^{-ca/\lambda_g}}. \tag{20}$$

where η is the viscosity coefficient; A, B, c are empirical constants.

Fig. 1

Figure 1: Fig. 1

Generalizing (20) to the case of a porous medium and using (14), we obtain (also taking into account the diffusion component of the resistance (13)):

$$Cu_z = -\frac{32}{15}\,\frac{\delta^2\,\mathrm{grad}\,p}{S_0\sqrt{2\pi MRT}}\left[\frac{3(1-\delta)}{4\delta}\alpha + A + Be^{-\frac{3c(1-\delta)}{4\delta}\alpha}\right]\frac{\alpha(1-\overline{\cos\gamma_g})}{\mu+\alpha(1-\overline{\cos\gamma_g})}.$$

The total gas flow rate Q is equal to

$$Q = -\frac{\delta^2\,\mathrm{grad}\,p}{S_0\sqrt{2\pi MRT}}\,\frac{16}{3}\,\frac{2\cdot\frac{2}{5}\left(\frac{3(1-\delta)}{4\delta}\alpha + A + Be^{-\frac{3c(1-\delta)}{4\delta}\alpha}\right)(1-\overline{\cos\gamma_g})\alpha + 1}{\mu+\alpha(1-\overline{\cos\gamma_g})}.$$

Hence the filtration coefficient is equal to

$$k = \frac{16}{3}\,\frac{\delta^2}{S_0\sqrt{2\pi MRT}}\,\frac{0.4\{[0.75(1-\delta)/\delta]\alpha + A + Be^{-[0.75c(1-\delta)/\delta]\alpha}\}(1-\overline{\cos\gamma_g})\alpha + 1}{1-\overline{\cos\gamma_c}+\alpha(1-\overline{\cos\gamma_g})}.$$

Figure 1 shows a family of curves $k(\alpha/\delta)/k_{\mathrm{Kn}}$ for the case $\overline{\cos\gamma_c} = -4/9$, $\overline{\cos\gamma_g} = 0.406$ (^{1,5}), $A = 1.0$; $B = 0.53$; $c = 1.62$ (^{4}) at various values of δ. On the curves a sharply expressed minimum is visible (especially at $\delta = 0.9$). In the region of high pressures the flow rate is directly proportional to the pressure. It is obvious that the physical cause of the minimum on the curve of gas flow rate as a function of pressure is analogous to that found in Knudsen' s experiments (^{7}), Gaede (^{8}), and others. Let us note, incidentally, that the coefficient of mutual diffusion of two gases also decreases with increasing pressure (^{5}).

Fig. 1. Upper curve for $\delta = 0.7$; middle–$\delta = 0.8$; lower–$\delta = 0.09$

In conclusion it should be noted that the derivation of W_D and Q_D assumed the validity of (9) and the independence of λ_t from the molecular velocity. These assumptions are apparently close to reality, since, as we have shown (^{6}), a calculation carried out quite rigorously leads to a similar dependence, differing only slightly in the coefficients. Since in deriving formula (19) it was assumed that $W_D = 0$ and $Q_D = 0$, the accuracy of formula (19), as well as the character of the pseudomolecular flow and the conclusion about the depth of the minimum on the flow-rate curve, do not depend on the accuracy of formula (9).

The closeness of the filtration coefficients for the Knudsen and pseudomolecular regimes, despite the substantial difference in their mechanisms, is a very unexpected and important result.

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Received
1 III 1957

REFERENCES

1. B. V. Deryagin, DAN, **53**, 627 (1946).
2. P. Epstein, Phys. Rev., **23**, 710 (1924).
3. S. P. Bakanov, ZhTF, No. 7 (1957).
4. R. Millikan, Phys. Rev., **22**, 1 (1923).
5. S. Chapman, J. G. Cowling, *The Mathematical Theory of Non-Uniform Gases*, Cambridge, 1939.
6. B. V. Deryagin, S. P. Bakanov, ZhTF, No. 9 (1957).
7. M. Knudsen, Ann. d. Phys., **28**, 75 (1909).
8. W. Gaede, Ann. d. Phys., **41**, 289 (1913).

Note: Figure translations are in progress. See original paper for figures.