IV

TRANSPORT PROPERTIES OF GASES

EXPERIMENTS

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KINETIC THEORY OF TRANSPORT PHENOMENA

In this section we shall be concerned with a molecular theory of the transport properties of gases. The molecules of a gas collide with each other frequently, and the velocity of a given molecule is usually changed by each collision that the molecule undergoes. However, when a one-component gas is in thermal and statistical equilibrium, there is a definite distribution of molecular velocities—the well-known Maxwellian distribution.[1] Figure 1 shows how molecular velocities are distributed in such a gas. This distribution is isotropic (the same in all directions) and can be characterized by a *root-mean-square velocity u,* which is given by

$$u = \left(\frac{3kT}{m}\right)^{1/2} = \left(\frac{3RT}{M}\right)^{1/2} \tag{1}$$

where k is Boltzmann's constant, R is the gas constant, m is the mass of one molecule, and M is the molecular weight. Sometimes it is more convenient to use the *mean speed* $\bar{c}$:

$$\bar{c} = \left(\frac{8kT}{\pi m}\right)^{1/2} = \left(\frac{8}{3\pi}\right)^{1/2} u \tag{2}$$

Another very important concept in kinetic theory is the average distance a molecule travels between collisions—the so-called *mean free path.* On the basis of a very simple conception of molecular collisions, the following equation for the mean free path can be derived:

$$\bar{l} = \frac{1}{\pi \bar{n} d^2}$$

where d is the "molecular diameter," or center-to-center collision distance, and $\bar{n}$ is the number of molecules per unit volume. When the fact is properly taken into

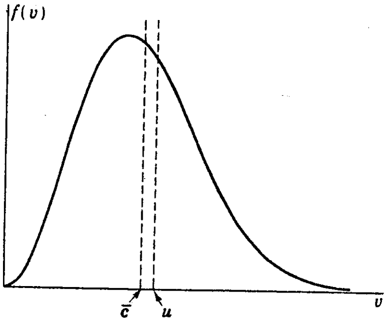

FIGURE 1
Schematic Maxwellian velocity distribution: $f(v)\,dv$ is the fraction of the molecules with velocities between v and $v + dv$. Values of the rms velocity u and the mean speed $\bar{c}$ are shown.

account that molecules do not all have the same velocities, a different numerical coefficient is obtained:[1]

$$\bar{l} = \frac{1}{\sqrt{2}\,\pi \bar{n} d^2} = 3.72 \times 10^{-25} \frac{RT}{pd^2} \tag{3}$$

In this equation the perfect-gas law has been used, and the numerical coefficient assumes that d, the molecular diameter, is in centimeters. Some typical values of $\bar{l}$ are given in Table 1.

We shall here consider in detail the viscosity, thermal conductivity, and diffusion of gases; indeed, the kinetic theory treatment of these three transport properties is very similar. But first let us consider the simpler problem of molecular effusion.

Effusion of gases The theory of effusion (Knudsen flow) is quite straightforward, since only molecular flow is involved; i.e., in the process of effusing, the molecules

Table 1 MEAN FREE PATHS OF VARIOUS GASES[a] AT 25°C

Gas	Mean free path, cm	
	At 1 atm	At 0.1 Torr
He	19.4×10^{-6}	14.7×10^{-2}
Ar	7.0×10^{-6}	5.3×10^{-2}
O_2	7.1×10^{-6}	5.4×10^{-2}
N_2	6.6×10^{-6}	5.0×10^{-2}
Air	6.7×10^{-6}	5.1×10^{-2}
CO_2	4.4×10^{-6}	3.3×10^{-2}

[a] E. H. Kennard, "Kinetic Theory of Gases," McGraw-Hill, New York (1938).

act independently of one another. For a Maxwellian distribution of velocities it can be shown[1, 2] that the number z of molecular impacts on a unit area of wall surface in unit time is

$$z = \frac{1}{\sqrt{6\pi}} u\bar{n} \tag{4}$$

where u is the rms velocity and $\bar{n}$ is the molecular concentration. Combining Eqs. (1) and (4) we obtain

$$z = \left(\frac{RT}{2\pi M}\right)^{1/2} \bar{n}$$

The number Z of *moles* colliding with 1 cm^2 of wall surface per second is

$$Z = \left(\frac{RT}{2\pi M}\right)^{1/2} \frac{N}{V} \tag{5}$$

where N/V is the number of moles per unit volume. For a perfect gas Eq. (5) becomes

$$Z = \frac{p}{\sqrt{2\pi MRT}} \tag{6}$$

Let two bodies of the same gas, at the same temperature but at two different pressures (p and p'), communicate through a small hole of area A, all dimensions of which are *small* in comparison with the mean free path of the gas molecules. It can then be assumed that the Maxwellian distribution of velocities is essentially undisturbed and that the same number of molecules will enter the hole as would otherwise have collided with the corresponding area of wall surface. It will also be assumed that all molecules entering the hole will pass through to the other side. The *net* rate of effusion through the hole will be the difference between the numbers of moles flowing through the hole in unit time in the two directions:

$$\frac{dN_{\text{eff}}}{dt} = \frac{A(p - p')}{\sqrt{2\pi MRT}} \tag{7}$$

This equation assumes that the gas is perfect, but it should be emphasized that the rate of effusion calculated from it is independent of the size and shape of the molecules provided only that these are such as to give a sufficiently long mean free path at the given temperature and pressure.

Gas viscosity Consider a body of gas under shear as shown in Fig. 4-1 and discussed in the introduction to Exp. 4. Assume that all the molecules in the gas are of one kind and that the gas undergoes laminar flow. By the mass velocity of the gas at each point, we understand the (vectorial) average velocity of all molecules passing through an infinitesimal region at that point. If the velocity gradient is substantially

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constant within one or a few mean free paths, we may also say that the mass velocity of the gas at a given point is the (vectorial) average velocity of all molecules that have suffered their most recent collision in an infinitesimal region at that point. We shall assume that, with respect to a system of coordinates moving at the mass velocity at a given point, the distribution of velocities of gas molecules which underwent their most recent collisions at that point is the same as it would be if the gas were not under shear (i.e., that the distribution is Maxwellian and therefore isotropic). We shall also assume, for simplicity, that all molecules travel the same distance $\bar{\ell}$ between collisions.

Let us focus our attention on a laminar plane $x = x'$, with $v = v'$. Molecules coming from below and colliding with molecules on this layer may be assumed (in a rough approximation) to have suffered their most recent previous collision on a plane at a distance $\bar{\ell}$ below the plane in question. The average momentum component in the shear direction parallel to the lamina (call it the y direction) for one of these molecules is therefore

$$mv(x - \bar{\ell}) = mv' - m\frac{dv}{dx}\bar{\ell}$$

where m is the mass of a molecule. Since by hypothesis the molecules have average momentum mv' after collision, an average amount of momentum

$$-m\frac{dv}{dx}\bar{\ell}$$

is transferred to the laminar plane x' from below, per collision. The number of molecules reaching a unit area of the plane from below per unit time is

$$\tfrac{1}{6}\bar{n}u$$

where $\bar{n}$ is the number of molecules per unit volume and u is their rms molecular velocity. Therefore, the rate of upward transfer of momentum to a unit area of the plane from below is

$$-\tfrac{1}{6}\bar{n}um\bar{\ell}\frac{dv}{dx}$$

Similarly it can be shown that the rate of downward transfer of momentum from a unit area of the plane x' to the plane at $(x' - \bar{\ell})$ is

$$+\tfrac{1}{6}\bar{n}um\bar{\ell}\frac{dv}{dx}$$

A downward flow of momentum is equivalent to an upward flow of momentum of the opposite sign. Thus the net rate of *upward* flow of momentum through any given plane, per unit area, is

$$-\tfrac{1}{3}\bar{n}um\bar{\ell}\frac{dv}{dx}$$

This rate of change of momentum must be balanced by a force in accordance with Newton's second law:

$$\frac{f}{A} = \tfrac{1}{3}\bar{n}um\bar{l}\,\frac{dv}{dx} \tag{8}$$

We can write Eq. (4-1), the defining equation for the viscosity coefficient η, as

$$\frac{f}{A} = \eta\,\frac{dv}{dx} \tag{9}$$

Combining Eqs. (8) and (9) we obtain an expression for η:

$$\eta = \tfrac{1}{3}m\bar{n}u\bar{l} \tag{10}$$

Since $m\bar{n}$ is the density of the gas, we have on the perfect-gas assumption

$$m\bar{n} = \rho = \frac{NM}{V} = \frac{pM}{RT}$$

and we obtain

$$\eta = \tfrac{1}{3}\sqrt{3}\,p\bar{l}\sqrt{\frac{M}{RT}} \tag{11}$$

where Eq. (1) has been used for u. Equation (11) can be rearranged to give

$$\bar{l} = \sqrt{3}\,\frac{\eta}{p}\left(\frac{RT}{M}\right)^{1/2} \tag{12}$$

This "mean-free-path treatment" involves several rough approximations; a more sophisticated derivation[1] gives a result identical with Eq. (12) except for the numerical factor:

$$\bar{l} = 1.256\,\frac{\eta}{p}\left(\frac{RT}{M}\right)^{1/2} \tag{13}$$

This equation can be used to calculate the mean free path in a gas from the experimentally observed viscosity.

If we combine Eqs. (3) and (13), a theoretical expression for the coefficient of gas viscosity is obtained:

$$\eta = 2.96 \times 10^{-25}\,\frac{\sqrt{MRT}}{d^2} \tag{14}$$

According to this equation, the gas viscosity coefficient should be independent of pressure and should increase with the square root of the absolute temperature. The viscosities of gases are, in fact, found to be substantially independent of pressure over a wide range. The temperature dependence generally differs to some extent from $T^{1/2}$ because the effective molecular diameter may be dependent on how hard the molecules collide and therefore may depend somewhat on temperature. Deviation from ideal behavior in the case of air (diatomic molecules, N_2 and O_2) is demonstrated by Eq. (4-19).

Equation (14) can also be used for the calculation of molecular diameters from experimental viscosity data. These can be compared with molecular diameters as determined by other experimental methods (molecular beams, diffusion, thermal conductivity, x-ray crystallographic determination of molecular packing in the solid state, etc.).

Thermal conductivity The mechanism of thermal conduction is analogous to that of viscous resistance to fluid flow. In the case of fluid flow, where a velocity gradient exists momentum is transported from point to point by gas molecules; in thermal conduction, where a temperature gradient exists, it is kinetic energy that is transported from point to point by gas molecules. If in the mean-free-path treatment of viscosity the momentum is replaced by the average kinetic energy $\bar{\varepsilon}$ of a molecule, we obtain for one-dimensional heat flow in the x direction an equation analogous to Eq. (8):

$$\dot{q} = \tfrac{1}{3}\bar{n}u\bar{l}\left(\frac{-d\bar{\varepsilon}}{dx}\right) \tag{15}$$

where $\dot{q}$ is rate of heat flow per unit area, $\bar{n}$ is the number of molecules per unit volume (in cubic centimeters), u is the rms molecular velocity, and $\bar{l}$ is the mean free path. Now

$$\frac{d\bar{\varepsilon}}{dx} = \frac{d\bar{\varepsilon}}{dT}\frac{dT}{dx} = m\bar{C}_v\frac{dT}{dx}$$

where m is the mass of a molecule and $\bar{C}_v$ is the constant-volume specific-heat capacity (i.e., per gram) of the gas; thus we obtain

$$\dot{q} = \tfrac{1}{3}m\bar{n}u\bar{l}\bar{C}_v\left(\frac{-dT}{dx}\right) \tag{16}$$

By comparison with $\dot{q} = -K(dT/dx)$, the defining equation for the coefficient of thermal conductivity K, we find that

$$K = \tfrac{1}{3}m\bar{n}u\bar{l}\bar{C}_v \tag{17}$$

Using the expression [Eq. (10)] derived with the mean-free-path treatment for the coefficient of viscosity of a gas, we obtain the following relationship between coefficients of thermal conductivity and of viscosity:

$$\frac{K}{\eta} = \bar{C}_v \tag{18}$$

This simple expression is correct in form but requires a numerical coefficient different from unity; it must be remembered that the mean-free-path treatment is a simple treatment with several rough approximations. More advanced treatments[1] yield a modified relation

$$\frac{K}{\eta} = \frac{5}{2}\bar{C}_v \tag{19}$$

This result holds well only for monatomic gases. Interactions between diatomic and polyatomic molecules, involving transfer of rotational and vibrational energy, are difficult to treat theoretically and will not be discussed here. For monatomic gases, we can write

$$\frac{K}{\eta} = \frac{15}{4}\frac{R}{M} \tag{20}$$

where R is the gas constant and M is the molecular weight.

Diffusion The theory of the diffusion of a gas is related to the theory of viscosity and of thermal conductivity in the sense that all three are concerned with a transport of some quantity from one point to another by the thermal motion of gas molecules. For diffusion, where a concentration gradient exists, chemical identity is transported.

Let there be two kinds of perfect gases, designated 1 and 2, present in a closed system of fixed total volume at concentrations of $\bar{n}_1$ and $\bar{n}_2$ molecules per cubic centimeter or $\bar{N}_1$ and $\bar{N}_2$ moles per cubic centimeter, respectively. These gases will have mean free paths of $\bar{l}_1$ and $\bar{l}_2$, respectively.

Let it be assumed that there is a concentration gradient in the x direction only. Consider a plane x_0, parallel to the y and z axes, and consider for a moment those molecules of kind 1 that pass through a small area $dA = dy\,dz$ on that plane. Assume for simplicity that these molecules suffered their most recent collision at or near the surface of an imaginary sphere of radius $\bar{l}_1$ with its center at dA. Now the mean distance from the plane x_0 up or down to the sphere is $2\bar{l}_1/3$. Therefore the mean concentration of these molecules, in the regions below the plane where they suffered their most recent collisions, is

$$\bar{n}_- = \bar{n}_1(x_0) - \frac{2\bar{l}_1}{3}\frac{d\bar{n}_1}{dx}$$

and the mean concentration similarly defined above the plane is

$$\bar{n}_+ = \bar{n}_1(x_0) + \frac{2\bar{l}_1}{3}\frac{d\bar{n}_1}{dx}$$

The number of molecules passing through a unit area of a given plane surface depends on the concentration of the molecules;

$$z = \tfrac{1}{4}\bar{c}\bar{n} \tag{21}$$

where $\bar{c}$ is the mean speed [see Eqs. (2) and (4)]. The *net* number of molecules of kind 1 crossing the x_0 plane in the upward direction is therefore

$$z_1 = \tfrac{1}{4}\bar{c}_1(\bar{n}_- - \bar{n}_+) = -\tfrac{1}{3}\bar{c}_1\bar{\ell}_1 \frac{d\bar{n}_1}{dx} \tag{22}$$

So far we have neglected the mass flow, if any, that is needed for the maintenance of constant and uniform pressure. If there is mass flow with a given velocity w_0 (which will be taken as positive when the mass flow is upward), the molecular velocities will be Maxwellian only with respect to a set of coordinate axes moving with that velocity, since the diffusing molecules suffered their recent collisions with molecules moving upward at that *mean* velocity. Equation (22) therefore represents the number of molecules per second crossing a unit area on a plane (parallel to the y and z axes) that is moving upward at velocity w_0. The number of molecules per second crossing a unit area on a *fixed* plane is then

$$\begin{aligned} z_1 &= \bar{n}_1 w_0 - \tfrac{1}{3}\bar{c}_1\bar{\ell}_1 \frac{d\bar{n}_1}{dx} \\ z_2 &= \bar{n}_2 w_0 - \tfrac{1}{3}\bar{c}_2\bar{\ell}_2 \frac{d\bar{n}_2}{dx} \end{aligned} \tag{23}$$

Now for maintenance of constant pressure we must have $z_1 = -z_2$; thus we obtain

$$\begin{aligned} w_0 &= \frac{1}{3(\bar{n}_1 + \bar{n}_2)}\left(\bar{c}_1\bar{\ell}_1 \frac{d\bar{n}_1}{dx} + \bar{c}_2\bar{\ell}_2 \frac{d\bar{n}_2}{dx}\right) \\ &= \frac{1}{3\bar{n}}\frac{d\bar{n}_1}{dx}(\bar{c}_1\bar{\ell}_1 - \bar{c}_2\bar{\ell}_2) \end{aligned} \tag{24}$$

and

$$z_1 = -\frac{1}{3\bar{n}}(\bar{n}_1\bar{\ell}_2\bar{c}_2 + \bar{n}_2\bar{\ell}_1\bar{c}_1)\frac{d\bar{n}_1}{dx} = -z_2 \tag{25}$$

where, since the pressure is constant, we have used the relation

$$-\frac{d\bar{n}_1}{dx} = \frac{d\bar{n}_2}{dx} \tag{26}$$

We can also write, in terms of moles,

$$\begin{aligned} Z_1 &= -\frac{1}{3\bar{N}}(\bar{N}_1\bar{\ell}_2\bar{c}_2 + \bar{N}_2\bar{\ell}_1\bar{c}_1)\frac{d\bar{N}_1}{dx} = -Z_2 \\ &= -\tfrac{1}{3}(X_1\bar{\ell}_2\bar{c}_2 + X_2\bar{\ell}_1\bar{c}_1)\frac{d\bar{N}_1}{dx} \end{aligned} \tag{27}$$

where X_1 and X_2 are mole fractions ($X_1 = \bar{N}_1/\bar{N}$, $X_2 = \bar{N}_2/\bar{N}$; $\bar{N} = \bar{N}_1 + \bar{N}_2$). By comparison with Eq. (5-2), the defining equation for the diffusion constant D_{12}, we find that

$$D_{12} = \tfrac{1}{3}(X_1\bar{l}_2\bar{c}_2 + X_2\bar{l}_1\bar{c}_1) \tag{28}$$

This equation appears to predict that D_{12} will be a function of the composition of the gas, although experimentally the diffusion constant is almost independent of composition. However, we must be careful in our definition of $\bar{l}_1$ and $\bar{l}_2$. We must take account of the fact that collisions of molecules of one species with one another can have no significant effect on the diffusion; such collisions do not affect the total momentum possessed by all the molecules of that species and thus do not affect the mean mass velocity of the species in its diffusion. Thus the total number of molecules of that species crossing the reference plane in a given period of time is not affected by such collisions and is the same as if such collisions did not take place at all. We should define $\bar{l}_1$ for our present purpose as the mean free path of molecules of species 1 between successive collisions with molecules of species 2 and *vice versa*. Accordingly we write [see Eq. (3)]

$$\bar{l}_1 = \frac{1}{\sqrt{2}\pi\bar{n}_2 d_{12}^2} \tag{29}$$

where by d_{12} we mean the center-to-center collision distance (assuming the molecules to be "hard spheres"). Equation (28) then becomes

$$D_{12} = \frac{1}{3\sqrt{2}\pi d_{12}^2\bar{n}}(\bar{c}_1 + \bar{c}_2) \tag{30}$$

which is independent of the composition. If we now introduce the kinetic theory expressions for $\bar{c}_1$ and $\bar{c}_2$ as given by Eq. (2) and make use of the perfect-gas expression for $\bar{n}$, namely,

$$\bar{n} = N_0\bar{N} = N_0\frac{p}{RT} \tag{31}$$

where N_0 is Avogadro's number, we obtain for the diffusion constant

$$D_{12} = \frac{2}{3\pi^{3/2}N_0}\frac{(RT)^{3/2}}{p}\frac{\sqrt{1/M_1} + \sqrt{1/M_2}}{d_{12}^2} \tag{32}$$

and for the *self-diffusion constant* (see Exp. 5)

$$D_1 = \frac{4}{3\pi^{3/2}N_0}\frac{(RT)^{3/2}}{p}\frac{\sqrt{1/M_1}}{d_1^2} \tag{33}$$

More advanced treatments[1] lead to a slightly different form of expression for D_{12} and different numerical coefficients for both D_{12} and D_1:

$$D_{12} = \frac{3}{8\sqrt{2\pi}\,N_0}\frac{(RT)^{3/2}}{p}\frac{\sqrt{1/M_1 + 1/M_2}}{d_{12}^2} \tag{34}$$

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and
$$D_1 = \frac{3}{8\sqrt{\pi}\, N_0} \frac{(RT)^{3/2}}{p} \frac{\sqrt{1/M_1}}{d_1{}^2} \tag{35}$$

Equations (32) and (34), which are based on a "hard-sphere" model, are in agreement in predicting no dependence of the diffusion constant on gas composition. However, for real molecules a slight composition dependence should exist, which depends upon the form of the intermolecular potential.[1]

That Eqs. (32) and (34) differ in the dependence of D_{12} on the molecular weights should not be altogether surprising, since in our simple treatment we have assumed that the velocities of molecules after collisions are uncorrelated with their velocities before collisions, while, in fact, such correlations in general exist and are functions of the ratio of the masses of the colliding particles. To take this and other remaining factors properly into account would require a treatment that is beyond the scope of this book. It may suffice to point out here that the square-root quantity in Eq. (34) is equivalent to $\sqrt{1/\mu_{12}N_0}$, where

$$\mu_{12} = \frac{m_1 m_2}{m_1 + m_2}$$

is the "reduced mass" of a system comprising a molecule of kind 1 and a molecule of kind 2.

The diffusion constant is predicted by Eqs. (32) to (35) to be inversely proportional to the total pressure. Experimentally this is the case to roughly the degree to which the perfect-gas law applies. The equations appear to predict that the diffusion constant will be proportional to the three-halves power of the temperature; however, as in the case of viscosity, significant deviations from this behavior occur, as actual molecules are not truly "hard spheres" and have collision diameters that depend on the relative speeds with which molecules collide with one another.

By means of Eq. (34) it is possible to calculate center-to-center collision distances d_{12} from a measured diffusion constant D_{12}. If three diffusion constants D_{12}, D_{13}, and D_{23} can be measured, individual molecular diameters d_1, d_2, and d_3 can be obtained if it can be assumed that the collision distances are the arithmetic averages of the molecular diameters involved, as would be the case with hard spheres:

$$d_{ij} = \tfrac{1}{2}(d_i + d_j) \tag{36}$$

If a self-diffusion constant D_1 can be measured approximately through one of the approaches discussed in Exp. 5, a molecular diameter d_1 can be obtained directly from Eq. (35). Conversely, Eqs. (34) and (35) can be used to estimate a diffusion constant, if molecular diameters are known from some other source, or to calculate self-diffusion constants from binary diffusion constants (or vice versa) by calculating first the molecular diameters. In the latter case it can be argued that any remaining approximations in the treatment will largely cancel out.

As expected, the self-diffusion constant can be related to other transport coefficients. From Eq. (28) we can write for self-diffusion

$$D_1 = \frac{2}{3}\left(\frac{8}{3\pi}\right)^{1/2} u_1\bar{\ell}_1 \tag{37}$$

where we now interpret $\bar{\ell}_1$ as the mean free path as customarily defined. The simple mean-free-path treatment of gas viscosity gave Eq. (10), which can be written as

$$\eta = \tfrac{1}{3}\rho u\bar{\ell} \tag{38}$$

where ρ is the mass density of the gas. Thus we obtain

$$\frac{D}{\eta} = 1.8\,\frac{1}{\rho} \tag{39}$$

More exact treatments[1] have shown that the coefficient of $1/\rho$ in this expression should be 1.20 for hard spheres and about 1.5 for spherical molecules with an inverse fifth-power repulsion. Clearly D may also be related to K; for monatomic gases, we can use Eq. (20) and obtain

$$\frac{D}{K} \cong \frac{0.4M}{\rho R} \tag{40}$$

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EXPERIMENT 4. VISCOSITY OF GASES

It is a general property of fluids (liquids and gases) that an applied shearing force that produces flow in the fluid is resisted by a force that is proportional to the gradient of flow velocity in the fluid. This is the phenomenon known as *viscosity*.

Consider two parallel plates of area A, a distance D apart, as in Fig. 1. It is convenient to imagine that D is small in comparison with any dimension of the plates in order to avoid edge effects. Let there be a uniform fluid substance between the two plates. If one of the plates is held at rest while the other moves with uniform velocity v_0 in a direction parallel to its own plane, under ideal conditions the fluid undergoes a pure shearing motion and a flow velocity gradient of magnitude v_0/D exists throughout the fluid. This is the simplest example of *laminar flow*, or pure viscous flow, which takes place under such conditions that the inertia of the fluid plays no significant

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APPARATUS

Procedure A Diffusion cell (Loschmidt type) with sturdy support; clamping device for flexible closure; two one-hole rubber stoppers, with short bent tubes, for ends of cell; four 1-in. lengths of rubber tubing; four screw clamps; four short glass tubes; three glass U tubes with rubber stoppers and policemen; bubbler, containing dibutyl phthalate; three long and two short lengths of rubber tubing; needle valve; two ring stands; four clamps with clamp holders; 0 to 30°C thermometer; stopwatch; meter stick.

Cylinders of helium, argon, and carbon dioxide; source of compressed air; glass wool; Ascarite; drying agent (such as magnesium perchlorate).

Procedure B Vacuum system with mechanical pump and manifold having provision for two attachments via taper joints; Loschmidt diffusion cell with stopcocks attached at top and bottom; two standard taper joints to fit manifold; two ball-socket joints to fit diffusion cell; glass (or metal) T joint; five long and one short length of heavy-wall rubber pressure tubing; tightly wound copper coil; large Dewar flask; closed-tube manometer; 1-liter beaker; towel; stopwatch or electrical timer; meter stick; 0 to 30°C thermometer.

Liquid nitrogen; cylinders or lecture bottles of helium, argon, and carbon dioxide.

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EXPERIMENT 6. LOW-PRESSURE EFFUSION OF GASES

In Exp. 4 we were concerned with the viscous flow of gas through a capillary tube. One of the conditions for that experiment was that the mean free path of the gas must be small compared with the diameter of the tube. Actually, the flow ceases to be purely viscous and begins to assume some molecular character when the slip correction becomes significant. When the mean free path becomes very large in comparison with the diameter of a tube or hole, the flow is completely molecular in character.

At a given temperature, the mean free path $\bar{l}$ is inversely proportional to the pressure; for most gases, $\bar{l}$ is of the order of 10^{-5} cm at 1 atm and about 0.05 cm at a pressure 0.1 Torr (see Table IV-1). Clearly, it is difficult to obtain the necessary conditions for molecular flow at 1 atm pressure, since extremely small holes or pores are needed. Demonstrations of molecular flow at 1 atm with pinholes punched in foils are of no value, although they may appear to give correct flow time ratios for two gases if the choice of a pair of gases for study is fortuitously such that the molecular diameters are about the same. In general the results of such experiments show a dependence of flow time on molecular diameter, which is a property of viscous flow and not true of pure molecular flow. Valid molecular flow can be achieved, however, using holes with diameters of about 0.01 cm if the gas pressure is 0.10 Torr or less.[1] Such low-pressure effusion of helium, argon, and carbon dioxide will be studied in this experiment.

METHOD AND THEORY

Effusion will be studied for gas at low pressure flowing through a small pinhole into a vacuum. The experimental apparatus is shown in Fig. 1. The important features of this apparatus are: (1) a system for obtaining high vacuum; (2) a large bulb *B* (about 5 liters), to contain the gas to be studied, at an initial pressure of 0.1 to 0.2 Torr; (3) an orifice *O* in the form of a pinhole of the order of 0.1 mm in diameter in very thin platinum foil, through which the gas in bulb *B* may effuse into the high-vacuum part of the system; (4) a vacuum gauge for measuring periodically the pressure of the gas remaining in bulb *B*; and (5) an expansion system for filling bulb *B* with gas at the desired initial pressure.

For this method we can write Eq. (IV-7) as

$$-\frac{dN}{dt} = \frac{Ap}{\sqrt{2\pi MRT}} \tag{1}$$

where N is the number of moles of gas in the bulb B at pressure p and temperature T, A is the area of the pinhole, and M is the molecular weight of the gas. In Eq. (1) we have made use of the fact that the pressure outside the pinhole is essentially zero (10^{-5} Torr or less). Applying the perfect-gas law to the gas in the bulb B (volume V) we write

$$dN = \frac{V}{RT}\,dp \tag{2}$$

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Combining Eqs. (1) and (2) gives

$$\frac{dp}{p} = -\frac{A}{V}\sqrt{\frac{RT}{2\pi M}}\,dt = -\frac{dt}{\tau} \tag{3}$$

where τ is the "relaxation time" for the system and is

$$\tau = \frac{V}{A}\sqrt{\frac{2\pi M}{RT}} \tag{4}$$

For a given apparatus and choice of gas, τ is a constant if T does not vary; therefore, Eq. (3) can be integrated to give

$$\ln\frac{p}{p_0} = -\frac{1}{\tau}t$$

or

$$\log p = \log p_0 - \frac{t}{2.303\tau} \tag{5}$$

where p is the pressure in bulb B at time t and p_0 is the initial pressure (at $t = 0$).

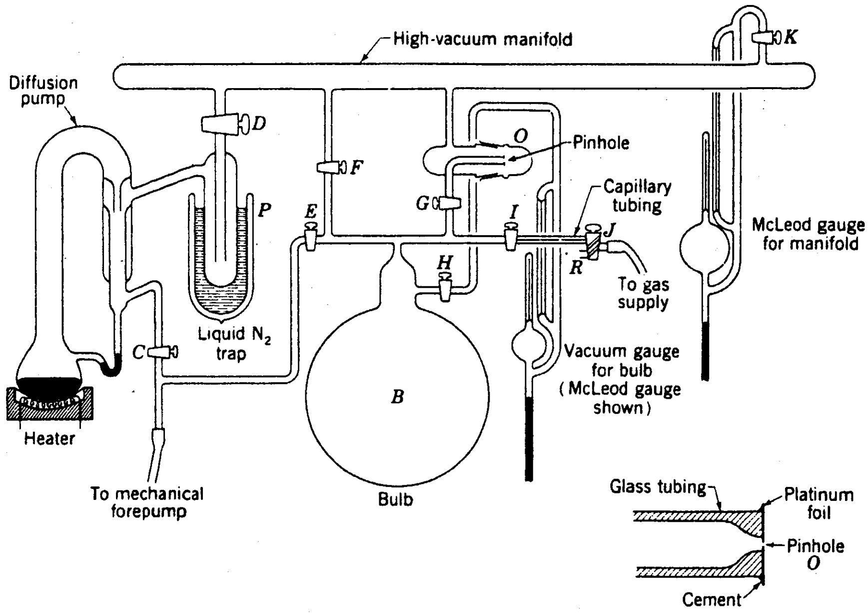

FIGURE 1
Apparatus for the low-pressure effusion of gases.

A plot of log p versus t should be a straight line. From the slope we can evaluate τ and then use Eq. (4) with known values of A, V, and T to calculate the molecular weight of the gas. Even if we do not know the value of A/V, if we obtain data for two different gases, we can determine the ratio of their molecular weights.

EXPERIMENTAL

Before the run is started, the entire system should be evacuated to a pressure of 10^{-5} Torr or less and liquid nitrogen should be placed in the Dewar flask around trap P. Either this will be done by an instructor before the period, or instructions will be issued for the proper procedure to be used. The pressure should be checked with the McLeod gauge which connects to the manifold through stopcock K. For a general discussion of high-vacuum systems and components see Chap. XVII.

The actual apparatus may differ from that shown in Fig. 1, in which case special operating instructions will be available. The procedure given here will refer to the system shown. When the system is completely evacuated, all stopcocks will be open except E and J.

The pressure gauge which is connected to the bulb by stopcock H will be either a small-volume McLeod gauge or a thermocouple gauge. If it is a McLeod gauge, readings during the run should be taken as quickly as possible, since a small amount of gas is cut off in the gauge during a pressure reading. If the gauge is a thermocouple gauge, this precaution is not necessary but the gauge must be calibrated against the manifold McLeod gauge with each gas used. This calibration can be done after the run by the following procedure: Close D and E; open H, F, and K; admit gas to the entire line at the highest required pressure through J and I. Now read both the McLeod and the thermocouple gauge. Reduce the pressure by opening D momentarily and repeat the measurements; continue until the desired range has been covered, and plot a calibration curve. (For precise calibration at very low pressures, one can insert a cold trap between the manifold and the McLeod gauge to eliminate mercury vapor.) A discussion of the thermocouple gauge is given in Chap. XVII.

Procedure Connect the gas inlet hose to a cylinder of helium, argon, or carbon dioxide which has a regulator valve, and adjust the pressure to about 2 psi above 1 atm. Carefully turn stopcock J so that the hose can be flushed out through outlet R of this stopcock. Close stopcock I and turn J so as to fill the short length of capillary tubing with the gas. Now close J, F, and G, and open I to allow the slug of gas to expand into the bulb B and its associated pressure gauge. Close I and measure the pressure in bulb B. If the pressure is between 100 to 150 μm (micrometers) (0.10 to 0.15 Torr), the run can be started; if above 150 μm, open stopcock E *momentarily* to reduce the pressure to the range 100 to 150 μm.

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To start the effusion, open stopcock *G* which connects the bulb *B* to the high-vacuum manifold through the pinhole at *O*. Take pressure readings on the gas in *B* at 5-min intervals. Continue readings until the pressure is down to about 5 percent of its initial value. Record the ambient temperature near bulb *B*. At least once during the run, check the manifold pressure (with the McLeod gauge at *K*) to verify that it is less than 10^{-4} Torr. Except for this measurement, keep stopcock *K* closed during the run.

To terminate a run, open *F* and *I* to allow the diffusion pump to evacuate the system to a high vacuum.

Repeat this procedure with one or both of the other gases. When this experiment has been completed, leave the apparatus evacuated unless otherwise instructed.

Record the necessary apparatus constants *A* and *V*.

CALCULATIONS

Convert all pressure-gauge readings obtained during a run to micrometers of mercury (p) and plot $\log p$ against the time in *seconds*. Alternatively, if a McLeod gauge was used, one can simplify the calculation by plotting $2 \log h$ versus t, since the pressure is proportional to h^2, where h is the gauge reading.

From each plot, determine τ from the slope and p_0 from the intercept at $t = 0$. Compare this p_0 value with the pressure prior to opening stopcock *G*. Using Eq. (4) compute the molecular weight M for each gas studied. Also compute the ratio of molecular weights from the ratio of τ values. The agreement with accepted values is expected to be better for the ratio than for the individual values because the effect of uncertainties in *A* and *V* has been eliminated.

DISCUSSION

Calculate the mean free path of each gas at pressure p_0. How does this compare with the pinhole diameter?

Estimate the effect of neglecting the back effusion from the manifold into the bulb.

For the highest effusion rates attained in this experiment, what is the minimum pumping speed required for the vacuum system to maintain a manifold pressure no higher than 10^{-4} Torr?

An alternative method employs effusion through a pinhole from one bulb to another of equal volume. How would you define a relaxation time τ' for this method, and what relationship would τ' bear to τ?

Suggest how an effusion experiment could be designed and carried out to measure a very low vapor pressure for a solid.

APPARATUS

High-vacuum system; effusion apparatus such as that shown in Fig. 1; heavy-wall rubber tubing; stopwatch; Dewar flask for cold trap.

Cylinders of helium, argon, and carbon dioxide; stopcock grease; liquid nitrogen (1 liter).

REFERENCE

1. M. Knudsen, *Ann. Physik*, **28,** 75 (1909).

GENERAL READING

E. H. Kennard, "Kinetic Theory of Gases," McGraw-Hill, New York (1938).

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