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Measurement of the viscosities of He, Ne and Ar for the determination of their gas – kinetic diameters.

P.N. Ekemezie[1], E.E. Enekwechi[2] and Odinma S.C[3]
[1](*Pure & Industrial Chemistry, NnamdiAzikiwe University, AwkaNigeria*)
[2](*Natural Sciences, Federal Polytechnic, Oko Nigeria*)
[3](*Industrial Chemistry, Caritas University Amoji-Nike Enugu Nigeria*)

Abstract: *The viscosities of He, Ne and Ar gases were measured using pressure transducer to obtain the pressure, time data. Using the viscosity of dry air at the measured* 32^0C *ambient temperature, the evacuation data (pressure, time) were converted to viscosity values thus: He (1.03 x* 10^{-4} *poise), Ne (1.72 x* 10^{-4} *poise), and Ar (1.96 x* 10^{-4} *poise). Finally, the collision diameter of the gases were calculated using appropriate equations to obtain He (0.19nm), Ne (0.22nm), and Ar (0.33nm). The values obtained were compared with those of literature (He = 0.21nm, Ne = 0.24nm, Ar = 0.36nm). Since the values of collision diameter obtained in this experiment are in conformity with those obtained from literature, we can safely conclude that measurement of collision diameter can be used as a quality assay for gases.*

I. INTRODUCTION

In studying gas phase reaction dynamics, it is important to know the effective sizes, e.g., collision diameters, of the molecules involved in the elementary steps of the reaction. One of the ways that this fundamental information is obtained is through measurements of gas viscosity. From the application of gas kinetic theory to "hard sphere" molecules, the square of the collision diameter, σ, may be expressed as follows:

$$\sigma^2 = \frac{5(MRT/\pi)^{1/2}}{16N_A\eta} \qquad (\mathrm{cm}^2), \tag{1}$$

in which M is the molecular weight, η is the viscosity, $N_A$is Avogadro's number, and the other symbols have the usual meanings. This equation is derived from the relationship between the viscosity of a (hard sphere) gas and its density, D, mean speed, $<c>$, and mean free path, λ: (1)

$$\eta = \frac{5\pi}{32} D{<}c{>}\lambda \qquad (\mathrm{cm}). \tag{2}$$

Equation (1): which can be directly obtained from (2) may be rear-ranged to express the gas viscosity. Thus,

$$\eta = \frac{5(MRT/\pi)^{1/2}}{16N_A\sigma^2} \qquad (\mathrm{g\ s^{-1}\ cm^{-1}}). \tag{3}$$

The cgs units of η are called the *poise*, P. The interesting point about equation (3) is that it predicts that η should be independent of gas pressure [this is because the pressure dependence of the gas density in equation (2) cancels that of the mean free path], and that η should vary with temperature as $T^{1/2}$(from the temperature dependence of $<c>$). The first prediction seems counterintuitive, but it has been verified over a relatively wide range of pressures. The reasons that η becomes pressure-dependent at low and high pressures stem from departures from laminar flows. The $T^{1/2}$dependence has been confirmed experimentally and is unusual because gases demonstrate the opposite type of temperature dependence from liquids; that is, liquid viscosities decrease with increasing temperature.

We will now develop the physical and mathematical basis on which the viscosity of a gas is experimentally determined. The mass transport of a fluid (in this case, a gas) arising from a pressure gradient is represented by the general equation

$$J_x = -C\frac{dP}{dx} \qquad (\mathrm{g\ s^{-1}\ cm^{-2}}), \tag{4}$$

Where J_x is the flux (mass transported per unit cross section per unit time) of gas in the x direction as a result of the pressure gradient, dP/dx; C is a positive constant that is inversely proportional to the viscosity. Equation (4) is known as Poiseuille's law (1840) (or in other applications as Fick's first law). The minus sign reflects the fact that the flow direction opposes the pressure gradient (2,3).

The flux can be expressed as $J_x = (1/A)(dm/dt)$, where A is the unit cross section (normal to the flow direction) and dm is the (infinitesimal) mass transported in a time dt. To apply equation (4) to the case of a fluid flowing through a straight cylinder of radius r, we must consider Newton's law of viscosity. It states that the shear force, F_x, required to move an infinitesimally thin sheet of fluid having unit cross section, A, in a flow direction parallel to the plane of the sheet is proportional to the velocity gradient of the sheet taken in a direction normal to the flow (dv_x/dy). The mathematical statement is

$$\frac{1}{A}F_x = -\eta\frac{dv_x}{dy} \qquad (\mathrm{g\ s^{-2}\ cm^{-1}}). \tag{5}$$

The proportionality constant in equation (5) is the fluid viscosity. Another way of stating equation (5) is that the drag force exerted on a unit plate of flowing fluid is proportional to the change in velocity of adjacent plates. According to equation (5), a fluid flowing through a straight cylinder has the largest flow rate at the center of the cylinder (at the cylinder axis) and is zero at the walls. This particular fluid dynamic condition is known as laminar (or Newtonian) flow and is approached by many gases and (small molecule) liquids (called Newtonian fluids) as long as the flow rate (thus the pressure gradient) is not excessive. At very low pressures, gases deviate from Newtonian (or bulk) flow as the mean free path becomes comparable with the cylinder radius. In this situation, the gas flow is said to be in the molecular, or Knudsen flow regime, and viscosity, which is a bulk property, fails to have significance (4).

The application of Newton's law of viscosity to the flow of a fluid through a straight cylindrical tube of radius r leads to another statement of Poiseuille's law:

$$\frac{dV}{dt} = -\frac{\pi r^4}{8\eta}\frac{dP}{dx} \qquad (\mathrm{cm^3\ s^{-1}}). \tag{6}$$

In this equation, which is used in viscosity measurements of liquids, dV is the volume of gas transported through the tube in time dt, and dP/dx is the pressure gradient in the tube along the direction of flow.

The infinitesimals dV and dm are related through the density, D, as D = dm/dV; thus equation (6) becomes

$$\frac{dm}{dt} = -\frac{\pi r^4 D}{8\eta}\frac{dP}{dx}. \tag{7}$$

Because we are dealing with a gas at relatively low pressures (<1atm), the density can be expressed in terms of its pressure, P, temperature, T, and molecular weight, M, through the ideal gas law, i.e., D = PM/RT. Applying this result to equation (7), and recalling that n = m/M, we can write

(8)

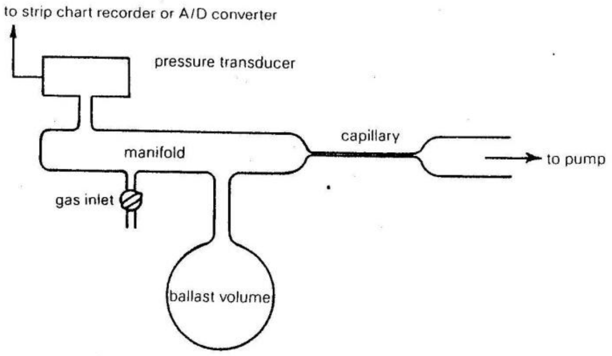

Figure 1: Schematic diagram of the evacuation apparatus.

Assuming the flow rate, *dn/dt*, to be independent of position *(x)* within the tube, the right-hand side of (8) containing the *x* dependence of *P* and the left-hand side of (8) can each be set equal to a constant. If we do this [or the right-hand side of (8) and then integrate [between $P_1(x_1)$ and $P_2(x_2)$], the following result is obtained:

$$\frac{dn}{dt} = \frac{\pi r^4(P_1^2 - P_2^2)}{16\eta RT(x_2 - x_1)}. \tag{9}$$

P_1 and P_2 are pressures at the beginning (x_1) and end (x_2) of the tube. Note that $P_1 > P_2$.

To clarify the rest of this development, a description of the experimental approach is presented. Refer to Figure 1. The gas is introduced to a manifold to which a large ballast volume (about 1 L), a pressure transducer (a device that converts the pressure to a voltage), and a capillary tube are connected. As the gas is evacuated through the capillary tube by a high-speed vacuum pump, the pressure of the system is continuously monitored by the transducer, whose output is displayed on a strip chart recorder. Alternatively, the transducer output is fed into the input port of a laboratory computer for direct data acquisition.

Because this experiment is carried out in such a way that $P_2 < P_1$, equation (9) simplifies to

$$\frac{dn}{dt} = \frac{\pi r^4[P_1(t)]^2}{16\eta RTL}, \tag{10}$$

in which the time dependence of the pressure at the beginning of the tube, P_1, (the manifold pressure) is explicitly indicated. L is the total length of the capillary tube (2,5).

By expressing the number of moles transported through the tube, dn, in terms of the manifold pressure, P_1, the ideal gas law furnishes this relationship: dn = (V/RT)dP. After rearrangement, equation (10) becomes

$$\frac{dP}{P^2} = \frac{\pi r^4 dt}{16\eta VL}. \tag{11}$$

V is the total volume of the manifold, ballast volume, etc. The integration of equation (11) with the boundary condition t = 0; P = P_0 furnishes

$$\frac{1}{P} = \frac{1}{P_0} + Kt, \tag{12}$$

in which the constant K is $\pi r^4/(16\eta VL)$. Thus, Poiseuille's law predicts that a plot of the reciprocal pressure of the system being evacuation vs. time should be linear. The slope can, in principle, provide an absolute value of the gas viscosity since r, V, and L can be determined. Note that the r^4 factor in K makes r a very sensitive characteristic. In practice, it is more satisfactory to obtain an empirical value of the constant K by calibrating the system using a gas of known viscosity, e.g., dry air. In this regard, the approach is similar to that followed in using the Ostwald viscometer in measuring liquid viscosities (6).

1.1 Corrections to Poiseuille's Law

Because equation (12) is based on the assumption of laminar, or streamline, flow, it is important to consider the conditions under which this condition is expected to apply. This understanding is vital to proper experimental design. As mentioned above, laminar flow fails to occur at high pressure (where turbulence sets in) and low pressure (when molecular flow and other complications arise). The goal is to identify the pressure regimes in which these two departures from Newtonian flow (hence Poiseuille's law) take place.

1.2 High Pressure:

Osborne Reynolds showed (1883) that if the average linear velocity of a fluid flowing through a straight tube exceeds a critical value, turbulent flow sets in; hence, Posieuille's law becomes invalid. The linear velocity is the speed with which an infinitesimal cross section of the fluid moves through the tube. The value of the linear velocity that approximately marks the transition between streamline and turbulent flow, v^1, is given by:

$$v' = \frac{1000\,\eta}{rD}, \tag{13}$$

where r is the tube radius and D and η are the density and viscosity of the fluid. Thus quantitative applications of Poiseuille's law should be made for fluids having flow velocities below v^1. Thequotient, 2rDv/η, which isdimensionless, is called the Reynolds number. When the Reynolds number exceeds 2000, fluid flow may not be laminar.

In the case where the fluid is an ideal gas of molecular weight M, equation (13) becomes.

$$v' = \frac{1000\ \eta RT}{rMP}. \qquad (14)$$

The linear velocity of a gas flowing through a tube can be obtained from equation by substituting – P/L for dP/dx and A dx/dt (where A = πr^2) for dV/dt. The linear velocity, v, is (dx/dt):

$$v = \frac{Pr^2}{8\eta L}. \qquad (15)$$

$$\frac{v}{v'} = \frac{Mr^3P^2}{8000\ RTL\eta^2} < 1. \qquad (16)$$

Although equation (16) cannot be used to determine whether laminar flow occurs without knowing the gas viscosity (the object of the experiment), ηcan be estimated for this purpose. Gas viscosities are generally 1 to 2 x 10^{-4}g cm-^{1}s^{-1}. In summary, the inequality in equation (16) places an upper limit on *P* for the application of Poiseuille's law (3,6).

1.3 Low Pressure:

If the pressure at which a gas being forced through a very narrow tube is decreased beyond a certain point, the flow rate of the fluid becomes *larger* than that predicted by Newtonian fluid mechanics. This is called the "slip condition," and it arises because the molecules adjacent to the tube walls do not move with zero velocity (as assumed in Newtonian flow); hence, the bulk gas "slips" through the tube. Poiseuille's law (6) can be written to include a slip correction *(dPldx*is again replaced by *- PIL):*

$$\frac{dV}{dt} = \frac{\pi r^4 P}{8\eta L}\left(1 + \frac{4S}{r}\right), \qquad (17)$$

S is known as the *slip coefficient* and has dimensions of length. Slip becomes important when the quantity *4SIr* approaches unity. It can be seen that this deviation becomes more important in tubes of narrow bore. It turns out that the slip coefficient depends on the pressure (as stated above). In one approximation [due to Maxwell (1879)], S ~ 2λ, where λis the mean free path of the flowing gas. From gas kinetic theory,

$$\lambda = \frac{RT}{\sqrt{2}\pi N_A \sigma^2 P}, \qquad (18)$$

where*σ* is the collision diameter. The inverse pressure dependence of S can be seen in (18). Actually, σis often determined from gas viscosity measurements. A can be alternatively expressed as

$$\lambda = \frac{1.25\eta(RT/M)^{1/2}}{P}. \qquad (19)$$

Thus to avoid slip conditions, which become significant when *4S/r* 1 [see equation *(17)]* the pressure must be *larger* than a value that can be obtained from equation (19) (using S = 2λ), i.e.:

$$P > \frac{10\eta(RT/M)^{1/2}}{r}. \qquad (20)$$

Equations (16) and (20) place upper and lower limits, respectively, on the pressure in the evacuation experiment such that equation (12) is valid (1,2,5).

1.4 Collision Diameters:

Once the gas viscosity is determined, its collision diameter can be obtained through equation (1). It is logical to compare *σ* obtained from gas viscosity with another experimental manifestation of molecular size, namely, the van der Waals *b* constant. *b,* having units of volume/mole, can be related to the gas collision diameter as follows. Figure 2 shows two identical spherical molecules in close contact during a collision. The center of molecule *B* cannot approach the center of molecule A by an amount less than the distance equal to σ. Therefore, molecule A effectively removes from the total container volume, V, an excluded volume, V_{excl}. This excluded volume is just $(4/3)\pi\sigma^3$, and the net available volume to molecule B is

$$V_{avail} = V - (4/3)\pi\sigma^3. \qquad (21)$$

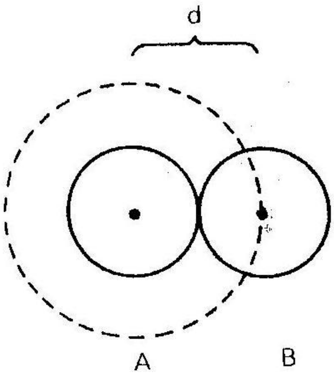

Fig 2: Two hard spheres in collisional contact. One Particle contributes an excluded volume of $4\pi\sigma^3/3$, where σ is the collision diameter.

Now if successive molecules are added to the container, the net available volume accessible to the added molecule is

$$V_{avail} = V - \sum(i - 1)V_{excel}, \tag{22}$$

and the average volume available to a total of N added molecules is

$$\langle V_{avail} \rangle = V - \frac{1}{N}\sum_{i=1}^{N}(i - 1)V_{excl}. \tag{23}$$

Because V_{excel} is a constant, the summation is simply

$$\frac{1}{N}V_{excl}\sum_{i=1}^{N}(i - 1).$$

The summation is equal to $N^2/2 - N/2$, and because N is large (on the order of N_A), this expression becomes $N^2/2$. Therefore, the average available volume is

$$\langle V_{avail} \rangle = V - \frac{N}{2}V_{excl}. \tag{24}$$

But $\langle V_{avail} \rangle$ is just the "net volume" term in the van der Waals equation, (V - nb), where n is the number moles of gas. We now have

$$V - nb = V - \frac{N}{2}V_{excl}. \tag{25}$$

Dividing by n, we get

$$V_m - b = V_m - 1/2V_{excl} \tag{26}$$

where V_m is the molar volume and V_{excl} is the excluded volume of the gas. Finally, the desired result is presented as

$$b = 1/2V_{excl} = 2/3N_A\pi\sigma^3 \tag{27}$$

This equation allows a comparison to be made between σ, the collision diameter, and b. Moreover, collision diameters can be estimated from van der Waals b constants (4,5).

II. MATERIALS AND METHOD

The output of the pressure transducer which produces 10V per 1000torr is connected to the strip chart recorder. The transducer power supply is turned on and the range switch, which indicates the maximum pressure for full-scale pen deflection, is in the proper position. Also, the zero position is set. The stopcock is used following the "two-hand rule" i.e. using one hand to counter-balance the torque exerted on the stopcock by the other. First, the system is calibrated using dry air by first pumping out the manifold, including the capillary tube and ballast bulb. As the pressure falls to a low value (below 1 torr), the recorder pen approaches the zero position and the ambient temperature is recorded.

The gas inlet line is evacuated and the system isolated by shutting off the main manifold stopcock. Gently the dry air valve is cracked open until the manifold pressure rises to an appropriate level. The chart pen should respond by indicating pressure, and it should be stable. The gas inlet line is isolated from the manifold. The recorder chart drive (about 5in/min) is started, and as the pen crosses a vertical line on the chart paper, the capillary stopcock is opened. The pressure falls immediately and after the pressure has dropped to about 5 to 10 percent of the initial value, the entire system is evacuated by opening the main stopcock. The gas inlet line is pumped out and the system filled with another gas. The above procedure is followed until all the gases to be studied are measured.

III. RESULTS AND DISCUSSION

For each of the evacuation, pressure, time data was obtained thus:

Table 1: He evacuation

P/(atm)	1.35	1.05	0.789	0.526	0.132
t/(s)	0	60	120	180	240

Table 2: Ne evacuation

P/(atm)	1.58	1.06	0.925	0.702	0.428
t/(s)	0	60	120	180	240

Table 3: Ar evacuation

P/(atm)	2.11	1.70	1.18	0.950	0.622
t/(s)	0	60	120	180	240

Using the viscosity of dry air at the measured ambient temperature of 32^0C (305K), the evacuation data are converted to viscosity values for each of the three gases after making the respective $T^{1/2}$ correction. This is done by the application of equations (14) and (16) with the following values obtained:He (1.03×10^{-4} poise), Ne (1.72×10^{-4} poise) and Ar (1.96×10^{-4} poise).

Finally, the collision diameters of the gases are calculated from their viscosities using equation (1) thus: He (0.19nm), Ne (0.22nm), Ar (0.33nm). The values obtained were then compared with those determined from van der waals b constants.

It is obvious from the evacuation tables 1 – 3 that the pressure increases from He Ne →→ Ar. This is expected since the molecular mass increases in that order. The values of viscosity obtained in this experiment are in conformity with those obtained from van der Waals b constant i.e. from literature. Again the values of collision diameter of the gases studied agree with those of literature, and we can therefore safely conclude that determination of gas collision diameter from its viscosity measurement can be used as quality control assay in analytical laboratories.

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