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An approximate expression for the flow of a binary gas mixture through a mass spectrometer "viscous" leak has been derived and compared with experimental data. The factors important in the design and use of the leak are determined from this result.

THE design of gas inlet systems for mass spectrometers must be such that the composition of the gas in the spectrometer bears a known relation to the composition of the sample to be analyzed. Two types of gas inlet systems which satisfy this criterion are commonly employed. The simplest of these employs a "molecular" leak. Its operation has been described by Honig.[1] The sample is placed in a large bulb at a pressure below 100 microns. Flow into the mass spectrometer is through a pinhole so small that the mean free path is much larger than the diameter of the hole. The flow through the hole is molecular. This is also true of the flow of gas out of the mass spectrometer tube. Hence the absolute pressure in the ionizing region of the mass spectrometer of any constituent of the gas sample is directly proportional to the absolute pressure of that constituent in the gas sample. The constant of proportionality is the same for all gases and all constituents regardless of the composition of the sample.

The second type of gas inlet system employs a "viscous" leak.[2] It has the virtue that the sample is admitted to the mass spectrometer from a high pressure region (several cm Hg, or more). This simplifies the inlet system and makes possible in a simple manner continuous gas analyses from, for example, a process stream.[3] Inghram[4] has discussed its use, but the literature contains no references on experimental tests or its performance. The present paper derives an approximate equation for the flow of a binary gas mixture through such a leak and compares it with experiment. Some general conclusions concerning the design and performance of viscous leak systems can be drawn from this result.

Figure 1 is a schematic diagram of a viscous leak gas flow system. For convenience in theoretical treatment, this system is divided into the three following flow regions: A. Flow through the spectrometer; B. Flow through the constriction; C. Flow through the capillary tubing on the high pressure side of the constriction. Equations are obtained for the flow of one component of a gas mixture through each of these regions. Since the gas flow through the system is continuous, these three flow equations may be equated. With suitable approxi-

mations one can then solve for the partial pressure of one component of a gas mixture in the mass spectrometer ion source in terms of its partial pressure in the sample. Finally, the ratio of the two such expressions obtained for a binary mixture gives one an expression for the variation in measured sample composition with sample pressure.

## A. Flow through the Spectrometer

The pressure in the spectrometer itself is so low that the mean free path of a molecule is much larger than spectrometer dimensions. Therefore, between two points in the vacuum system, such as 3 and 4, the flow is molecular and can be described by the equation

$$Q_{a34} = (k_{34}/M_a{}^{\frac{1}{2}})(P_{a3} - P_{a4}), \tag{1}$$

where $Q_{a34}$ = flow of component $a$ of a gas mixture between points 3 and 4 expressed as the time rate of change of pressure-volume product; $k_{34}$ = constant dependent upon the geometry and temperature in the region between points 3 and 4; $M_a$ = molecular weight of component $a$; and $P_{a3}$, $P_{a4}$ = partial pressures of component $a$ in regions 3 and 4, respectively.

## B. Flow through the Constriction

In the constriction the flow cannot be so simply described. If the pressure behind the constriction is lowered to the point where molecular mean free paths are much larger than constriction dimensions, the description must reduce to one of molecular flow. At high pressures the description should change to the form of Poiseuille's law for viscous flow. Knudsen[5] has given a rather complicated semi-empirical equation which meets
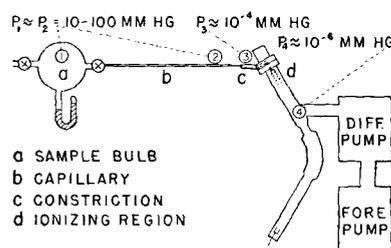


FIG. 1. Schematic diagram of spectrometer gas flow system with approximate pressure levels indicated.

[1] R. E. Honig, J. App. Phys. **16**, 646 (1945).
[2] A. O. Nier, Rev. Sci. Inst. **18**, 398 (1947).
[3] A. O. Nier *et al.*, An. Chem. **20**, 188 (1948).
[4] M. G. Inghram, *Advances in Electronics* (Academic Press, Inc., New York, 1948), Vol. I, p. 232.
[5] M. Knudsen, Ann. d. Physik [IV] **28**, 75 (1909).

these requirements and accurately describes the flow over the entire pressure range through cylindrical tubes. However, the geometry of the constriction is not so well defined. A simple sum of molecular and viscous flow terms is used here as an approximate form of the Knudsen equation. For the flow of one component of a gas mixture through the constriction

$$Q_{a23} = (k_{23}/M_a^{\frac{1}{2}})(P_{a2}-P_{a3}) + v(P_{a2}/P_2)\bar{P}(P_2-P_3), \quad (2)$$

where $k_{23}$ = constant dependent upon the geometry and temperature in the constriction; $\bar{P} = (P_2+P_3)/2$; $v$ = coefficient of viscous flow, proportional to $1/\eta$; and $\eta$ = coefficient of viscosity of gas mixture.

## C. Flow through Capillary Tubing

The variation of flow with mass, indicated by the first term of Eq. (2), would tend to change the composition of a gas mixture adjacent to the high pressure side of the constriction and establish concentration (or partial pressure) gradients along the capillary. The function of the capillary tubing is to create a mass flow of gas toward the constriction with a velocity sufficiently great to overcome any back diffusion which would result from such a gradient. The flow through the tubing is therefore described by competing mass flow and diffusion terms.

For one component one can write with fair approximation

$$Q_{a12} = VAP_{a1} - AD_{ab}[(P_{a2}-P_{a1})/L], \quad (3)$$

where $V$ = average velocity of mass flow along the capillary; $A$ = cross-sectional area of capillary; $D_{ab}$ = diffusion coefficient for a mixture containing two components $a$ and $b$, and $L$ = length of capillary behind the constriction.

In practice the pressure dependence of Eqs. (1) and (2) is simplified by the fact that $P_2 \gg P_3 \gg P_4$. Also the difference between $P_1$ and $P_2$, though finite to permit mass flow in the capillary, is sufficiently small to permit replacement of $P_2$ by $P_1$ in Eqs. (1) and (2). Equating the flow equations and solving for $P_{a3}$ in terms of $P_{a1}$.

$$k_{34}P_{a3} = P_{a1}\frac{[VA+(AD_{ab}/L)][k_{23}+(VM_a^{\frac{1}{2}}P_1/2)]}{(k_{23}/M_a^{\frac{1}{2}})+vP_1/2+(AD_{ab}/L)}. \quad (4)$$

The expression which would be obtained for the $b$ component is given by replacing the subscript $a$ by $b$ wherever it occurs alone. Noting that the ion current is in general directly proportional to the partial pressure of any particular gas in the ionizing region of the spectrometer (ionizing electron energy and intensity constant) one obtains for the ratio of ion currents

$$\frac{I_a}{I_b} = \frac{P_{a3}}{P_{b3}} = \frac{P_{a1}}{P_{b1}}\left\{\frac{[k_{23}+vM_a^{\frac{1}{2}}P_1/2][(k_{23}/M_b^{\frac{1}{2}})+v_1P_1/2+AD_{ab}/L]}{[k_{23}+vM_b^{\frac{1}{2}}P_1/2][(k_{23}/M_a^{\frac{1}{2}})+v_1P_1/2+AD_{ab}/L]}\right\}, \quad (5)$$

where $I_a$ and $I_b$ equal the ion currents from components $a$ and $b$ respectively.

Since $D_{ab}$ = constant/$P_1$; as $P_1 \to 0$, Eq. (5) reduces to

$$(I_a/I_b) \to (P_{a1}/P_{b1}). \quad (6)$$

Here the gas inlet system has introduced no mass discrimination and has behaved like a molecular leak. However, as $P_1$ gets large,

$$(I_a/I_b) \to (M_a/M_b)^{\frac{1}{2}}(P_{a1}/P_{b1}). \quad (7)$$

This situation results when there is viscous flow through the capillary and constriction, and separation of com-
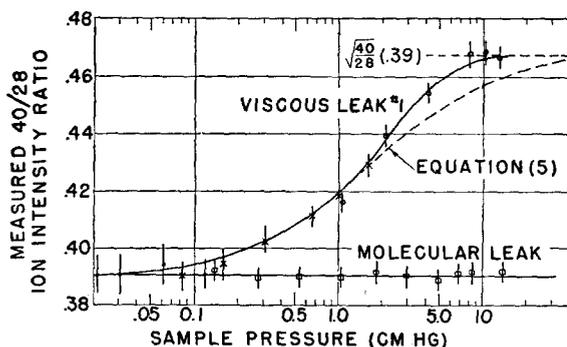


FIG. 2. Comparison of Eq. (5) with experiment for a mixture of argon and nitrogen (A/N$_2$ abundance ratio =0.39) using viscous leak No. 1. Molecular leak data is plotted such that points along abscissa indicate same total gas flow through both leaks.

ponents occurs only in the molecular flow through the source region.

Within the pressure range of transition between Eqs. (6) and (7), a viscous leak would introduce an uncertain mass discrimination. Therefore, it is important to know where this change occurs for any given leak, and to design the leak in a manner which will remove the transition from the desired sample pressure range.

In order to compare Eq. (5) with experiment the quantities $k_{23}$ and $v$ must be determined. At pressures low enough for the viscous flow term of Eq. (2) to be neglected, $k_{23} = M^{\frac{1}{2}}Q_{23}/P_1$ for pure gases. One can obtain the value of $k_{23}$, therefore, if the relationship between the gas flow, $Q$, and the ion current is known. This relationship can be determined from the rate of depletion of a known quantity of sample from a constant volume under molecular flow conditions, for, making use of a molecular flow equation and the fact that $I$ is proportional to $P_3$,

$$Q_{13}dt = (k_{13}/M^{\frac{1}{2}})P_1dt = -V_1dP_1.$$

Therefore,

$$Q_{13} = -(V_1P_1/\Delta t)\ln(P_{1t}/P_{1i})$$
$$= -(V_1P_1/\Delta t)\ln(I_t/I_i), \quad (8)$$

where $\Delta t$ is the time difference between initial and final ion current measurements $I_i$ and $I_t$, respectively.

The relationship between $v$ and $k_{23}$ for a given pure

gas is chosen to fit an experimental curve for the equation

$$(I/P_1) \propto (k_{34}P_3/P_1) = k_{23} + (vM^{\frac{1}{2}}P_1/2), \qquad (9)$$

obtained from Eqs. (1) and (2). For other gases $v$ can be calculated since it is inversely proportional to the coefficient of viscosity. Unfortunately, this coefficient for even a binary gas mixture is not simply related to the coefficients of its components, so an approximate value must be used where exact values are not available. It might be noted here that at pressures where the viscous flow term of Eq. (2) predominates, $Q \propto v \propto (1/\eta)$. Therefore the total flow of a gas mixture through the leak is subject to the same variations, often unpredictable, with composition as the coefficient of viscosity. Equation (7) shows, however, that relative abundance measurements are not affected by variations in $\eta$.

Figure 2 gives one example of the degree of agreement between Eq. (5) and experiment, a mean $v$ being used in this case. A consideration of the approximations involved in replacing $P_2$ with $P_1$ and assuming Eqs. (2) and (3) shows that a more elaborate treatment would improve the fit. The preceding development remains useful, however, for its simple physical picture of the gas flow.

Equation (5) suggests that the most feasible way of improving a leak of this design (i.e., extending the viscous flow portion of the curve to lower sample pressures) would be to decrease the cross-sectional area and/or increase the length of the capillary behind the leak. Figure 3 illustrates the effect of changing each in this manner by a factor of 2 for a frequently encountered type of isotope analysis. By changing each by the same factor the time response (i.e., transit time of gas through capillary) of the leak in the above example was essentially unchanged.
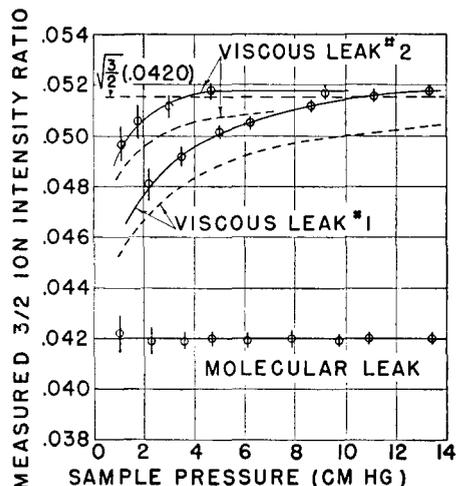


FIG. 3. Variation in measured $\frac{3}{2}$-ion intensity ratio as a function of sample pressure for several leaks. $HD/H_2$ abundance ratio for sample $=0.0420$. For viscous leak No. 1: $L=50$ cm; average i.d. $=0.010$ in. For viscous leak No. 2: $L=100$ cm; average i.d. $=0.007$ in. The constrictions were adjusted to give equal pumping speeds of $9 \times 10^{-5}$ cm$^3$ sec.$^{-1}$ for N$_2$. Broken curves give Eq. (5) for each leak. Molecular leak data are plotted such that points along abscissa indicate same total gas flow through all leaks.

In practice, area reduction is limited by the requirement that the diameter of the capillary must be sufficiently greater than the mean free path to obtain viscous flow. An increase in length, without a corresponding reduction in cross section, will increase the time response. Therefore the leak dimensions for optimum performance will vary somewhat with application.

## Erratum. Tektronix Advertisement

The Tektronix advertisement in the July issue, publicizing their Type 514-D Cathode Ray Oscilloscope, erroneously listed the sweep range as being ".01 usec/cm to .01 sec/cm." This should have read ".1 usec/cm to .01 sec/cm." They sincerely regret any inconvenience they might have caused to any of the readers of *The Review of Scientific Instruments*.