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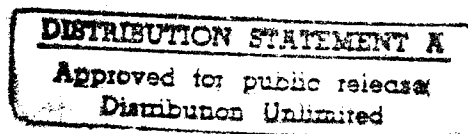
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SEPARATION OF A GAS MIXTURE FLOWING THROUGH A LONG TUBE AT LOW PRESSURE*

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ABSTRACT†

The separation of a binary gas mixture by diffusion through a capillary of radius r depends on the fact that the molecules have different masses m_i and mean speeds $\bar{v}_i$. When the inlet pressure is so low that the mean free path λ is much greater than r, the flow is diffusive and the separation factor (at zero outlet pressure) has its maximum value $(m_2/m_1)^{1/2}$. At high pressures ($\lambda \ll r$) no separation occurs.

This paper treats the intermediate case ($\lambda \approx r$) where the transfer of forward momentum from light to heavy molecules in unlike collisions equalizes the transport velocities and decreases the separation factor. As the inlet pressure rises, this effect makes the flow nonseparative before it becomes viscous. Flow equations are derived by equating the momentum acquired by the light component from the pressure gradient to the momentum lost to the wall plus that transferred to the other component. The viscous effects are treated as a small additive perturbation on the flow. The integrated flow equations express the separation factor as a function of the inlet and outlet pressures.

INTRODUCTION

For purposes of orientation, we consider first the effusion of a gas mixture through a circular orifice. The nature of the flow depends on the comparative magnitude of the mean free path λ and the radius r of the opening. When the opening is large ($r \gg \lambda$), many collisions occur in the vicinity of the orifice and, if two kinds of molecules are present, there is a continual transfer of momentum from the lighter, faster molecules to the heavier, slower molecules with the result that both kinds of molecules pass through the opening together with a common mass motion. Such a flow may be treated by the methods of hydrodynamics and the results are well-known. Since both components travel with the common drift velocity, the flow is nonseparative.

In the other limiting case ($r \ll \lambda$), a molecule traveling through the hole has very little chance of colliding with another molecule in the vicinity of the hole, i.e., the molecules effuse through the orifice independently with a velocity component proportional to the mean speed $\bar{v}$ of thermal agitation and inversely proportional to $m^{1/2}$, where m denotes the molecular mass. Hence the flow in this limit is separative.

If the molecular particle density in front of the orifice be denoted by n_F and behind the orifice by n_B, the net molecular flow per unit time per unit area of the opening is $(1/4)\bar{v}(n_F - n_B)$ according to elementary kinetic theory. The intermediate or transition region where λ and r are comparable is very difficult to treat. However, it is qualitatively clear that the nature of the flow and the amount

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*See Manhattan Project Report A-1289, Part I, June 8, 1944, and Part II, September 5, 1944.
†A preliminary abstract was published in Phys. Rev. 69:259 (1946).

of separation will depend essentially on the parameter r/λ. For a given hole size the separation can be improved by decreasing the pressures and thus increasing the mean free path, or conversely if the pressures are fixed the separation is improved by decreasing the size of the orifice.

We are primarily interested in the transition region where r and λ are comparable. The practical separation of gas mixtures by low pressure diffusion is accomplished through the use of some kind of a porous medium or "barrier."[1] It has been experimentally that the flow through a porous medium is in essential respects similar to the flow through a long capillary tube and quite unlike the flow through the orifices of a thin perforated membrane.[2] Thus, at high pressures, the pressure dependence of the flow through a porous medium is that of capillary viscous laminar flow and not that expected for orifice flow. At very low pressures the order of magnitude of the permeability of inverse flow resistance is compatible with the capillary flow value but not with the orifice flow model. The case of capillary flow at pressures in the transition region is, therefore, of greater practical interest and, in addition, is more amenable to theoretical treatment than the analogous problem for orifice flow.

The nature of the flow of a gas through a long circular capillary of radius r depends again on the comparative size of r and λ. If $\lambda \ll r$ the flow is given by the Poiseuille formula; in the case of a gas mixture both components are transported with the drift velocity and no separation takes place. In the other limit ($\lambda \gg r$) the flow obeys the well-known Knudsen formula,[3]

$$\overline{\varGamma} = -(16r/3\pi m\overline{v})dp/dx = -(2\overline{v}r/3)dn/dx \tag{1}$$

where $\overline{\varGamma}$ denotes the mean flow in molecules per unit area per unit time in the x-direction (axis of the capillary). The flow per unit area $\varGamma$ varies with the distance from the axis* and $\varGamma$ represents the total flow divided by the area of cross section πr^2. Formula (equation) 1 has been confirmed by both Knudsen[3] and Adzumi[4] in experiments with bundles of capillary tubes at very low pressures. Equation 1 will be referred to as the Knudsen or free-molecule flow formula and it is valid only when $\lambda \gg r$. It clearly represents a diffusive flow and the diffusion coefficient is $2\overline{v}r/3$. This corresponds to a mean random-walk step-size of 2r; i.e., the mean free path for intermolecular collisions (ordinary gaseous diffusion) is replaced by the mean free path for wall collisions (Knudsen diffusion). Since the molecules diffuse independently of each other, Equation 1 can be applied to both components of a gas mixture if the partial density gradients are used. We denote the concentration or mol fraction of the lighter gas at the inlet of the capillary by N and at the outlet by ν. The separation factor f is customarily defined by:

$$f = (\nu/1-\nu)/(N/1-N) \tag{2}$$

When $\lambda \gg r$ and the outlet pressure is zero, the separation factor has its maximum or "ideal" value f^+. It follows immediately from equation 1 that $f^+ = (m_2/m_1)^{1/2}$ where m_2 is the molecular mass of the heavier and m_1 of the lighter gas. According to equation 1, when the outlet or back pressure is zero, the composition of the flowing gas is constant down the length of the tube and changes discontinuously at the exit to the composition of the enriched outlet mixture. This may be understood as follows: the concentration ratio of the two components in the outlet mixture is the same as the flow ratio of the two components in the tube; however, the flow ratio is equal to the concentration-ratio times the ratio of transport velocities and the latter is constant and equal to $(m_2/m_1)^{1/2}$. When the back pressure is not zero the outlet mixture diffuses back into the tube and, according to equation 1, the concentration of light gas increases monotonically from the inlet to the outlet. In this case f obviously decreases as p_B/p_F, the back-pressure to fore-pressure ratio, increases.

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*$\varGamma = -1/2\overline{v}aE(r/a)dn/dx$ where "r" is the distance from the axis, "a" the tube radius, and E denotes the complete elliptic integral of the second kind, as shown by Pollard and Present, Phys. Rev. 73:762 (1948), Appendix II.

Knudsen,[3] Gaede,[5] and Adzumi[4] measured the flow of pure gases through capillaries over the entire pressure range from $\lambda \gg r$ to $\lambda \ll r$, and Gaede also made similar measurements of the flow between parallel plates. At high pressures their results can be represented in the usual way by the Poiseuille formula for viscous laminar flow plus a small correction term proportional to the pressure gradient. This correction term, which was originally attributed by Maxwell to "slip," has the same form as, but is smaller than, the free-molecule flow. When the specific flow (total flow/pressure drop) was plotted against the mean pressure, all three investigators found evidence of a slight minimum at low pressures when the mean free path was nearly equal to the tube diameter. Thus the specific flow initially decreases slightly (10 to 20 per cent) below the free-molecule value and then increases linearly with the pressure according to the Poiseuille law. A theoretical treatment of self-diffusion through a long capillary tube valid over the entire pressure range from $\lambda \gg r$ to $\lambda \ll r$ has been given by Pollard and Present.[6] Their work explains the existence of the minima observed by Knudsen, Gaede, and Adzumi; furthermore, it predicts the absence of such minima in the case of flow through porous media. Observations[7] on the flow of pure gases through many types of porous media have shown the relation between specific flow and average pressure to be accurately linear down to pressures for which the mean free path λ is of the order of several hundred times the mean pore radius $\bar{r}$. These results imply that the flow through a porous medium can be accurately represented over the entire pressure range from $\lambda \gg \bar{r}$ to $\lambda \ll \bar{r}$ by an expression of the form:

$$(c_1/m^{1/2})dp/dx + (c_2/\eta)p\, dp/dx \qquad (3)$$

i.e., by simply adding a laminar flow (viscosity η) to a free-molecule diffusive flow. Therefore, both theory and experiment have shown that the two types of flow, while not strictly additive in long capillary tubes, appear to be so in many porous media.

Further experiments performed at the SAM laboratories (mainly by Lagemann, Weil, Schleicher, Slack, Callihan, and Roberts) indicated that, in the case of a binary gas mixture flowing through a porous medium, the separation factor at intermediate pressures ($\lambda \sim \bar{r}$) could not be accounted for by assuming an equation of the form of equation 3 to hold for each component. At fore-pressures for which f (measured at zero back-pressure) was well below its ideal value f^+, flow measurements showed that the nonseparative viscous flow could be altogether negligible; i.e., the flow of the mixed gas was simply proportional to the pressure gradient. The experiments thus indicated the existence at intermediate pressures of a nonseparative nonviscous component of the flow which, when added to the separative free-molecule flow, gives rise to a total flow proportional to the pressure gradient as observed. Epstein[8] came to the same conclusion from a theoretical argument and Badger[9] made this the basis of a semi-empirical flow equation. Badger assumed that in a mixed flow the separative Knudsen diffusion should be weighted by a factor $1/1 + cp$ and he added to this a nonseparative diffusion term weighted by the factor $cp/1 + cp$. Apart from the effects of viscosity, which were neglected by Badger, his equations are very similar to, though not identical with, those to be derived in the following section.

MOMENTUM TRANSFER THEORY

Let us consider first the changes that take place in the character of the flow as λ decreases from an initially large value. In a long tube of length $L \gg r$ there will be no intermolecular collisions so long as $\lambda \gg L$. If $L \gg \lambda \gg r$, a molecule will make many intermolecular collisions before reaching the outlet, but for every collision that a molecule makes with another molecule, it will make many collisions with the wall. Now the flow is ideally separative as long as intermolecular collisions can be neglected; when these occur momentum is transferred on the average from the lighter to the heavier gas so that the flow rates tend to equalize. If $\lambda \gg r$, the effect of a momentum transfer in an intermolecular collision is effaced during the many subsequent collisions with the wall which precede another intermolecular collision, and in which the molecule comes into equilibrium

with the molecules of the wall. Thus the flow remains ideally separative Knudsen flow until the mean free path λ becomes comparable to the diameter of the tube. When $\lambda \approx r$ the effect of an intermolecular collision persists until the next intermolecular collision, and the cumulative effect of collisions between unlike molecules is to equalize the flow rates and diminish the separation efficiency. The transfer of forward momentum from the lighter to the heavier gas can take place in the absence of an appreciable gradient of the drift velocity normal to the tube axis, whereas the viscous transfer of momentum sets in only after the transverse velocity gradient has been established. We calculate first the nonseparative effect of collisions between unlike molecules on the free-molecule flow, neglecting viscous effects.

Consider the steady-state flow of a mixed gas through a long capillary of radius a extending in the x-direction. Regarding a cylindrical element of gas of length dx it is clear that the molecules of component 1 will receive a net forward momentum per unit time equal to $-\pi r^2 (dp_1/dx)dx$ where p_1 is the partial pressure of gas 1. If component 1 is the lighter gas, this momentum is transferred partly to the wall and partly to gas 2; on the other hand, gas 2 receives momentum from the pressure gradient and from collisions with gas 1 and transmits it to the wall of the tube. Consider first the momentum transfer to the wall and let us denote by u_1 the transport or mean x-component of velocity of gas 1. If the molecules leave the wall in completely random directions after a collision with the surface (an assumption well-confirmed by experiment[10]), they must on the average communicate their whole forward or x-component of momentum to the wall. The momentum transferred each second would then be expected to be $mu \cdot (n\bar{v}/4) \cdot 2\pi rdx$ for a pure gas. This is confirmed by a direct calculation using an approximate distribution function for a drifting gas (see reference 6, Appendix I). However, this result implies no variation of n, u and $\bar{\Gamma} = nu$ over the cross section of the tube and, as previously mentioned[4] (footnote on page 2), Γ varies with distance from the axis in free-molecule flow. From equation 1 we obtain:

$$dp/dx = -(3\pi m\bar{v}/16r)\,\bar{\Gamma} = -(3\pi m\bar{v}nu/16r) \tag{4}$$

where u represents the drift velocity averaged over the cross section. Multiplying both sides of equation 4 by $\pi r^2 dx$, the left-hand side becomes the resultant force on a cylindrical element due to the pressure gradient and the right side then represents the mean transfer of momentum from the gas to the wall per unit time: $(3\pi/8) \cdot m\,u \cdot (n\bar{v}/4) \cdot 2\pi rdx$. This result, which differs by a factor of $3\pi/8$ from that first given, will be used in the following presentation.

We come next to the calculation of the momentum exchange between the two components of the gas mixture in the cylindrical element. Assume $u_1 > u_2$ so that the molecules of gas 1 give up forward momentum on the average when colliding with molecules of gas 2. For purposes of orientation let us first assume, as in the hard elastic sphere model, that the scattering is isotropic in the center of mass system. Then the average momentum of molecule 1 in the x-direction after collision will be $m_1\bar{u}_c$ where $\bar{u}_c$ is the x-component of the mean velocity of the center of mass and is given by:

$$\bar{u}_c = (m_1 u_1 + m_2 u_2)/(m_1 + m_2)$$

The average momentum of molecule 1 before collision is $m_1 u_1$; therefore the average amount of forward momentum lost in one collision is $m_1(u_1 - \bar{u}_c)$ or $m^+(u_1 - u_2)$ in terms of the reduced mass. The number of collisions per second per unit volume between unlike molecules is:

$$n_1 n_2 \pi d_{12}^2 (\bar{v}_1^2 + \bar{v}_2^2)^{1/2}$$

where d_{12} is the collision diameter for unlike molecule encounters. Hence the momentum transferred per second from gas 1 to gas 2 per unit volume (M_{12}) would appear to be:

$$m^+(u_1 - u_2) \cdot n_1 n_2 \pi d_{12}^2 \cdot (\bar{v}_1^2 + \bar{v}_2^2)^{1/2}$$

on the average; however, the average momentum transferred is not quite the same as the average momentum loss per collision multiplied by the average number of collisions. Furthermore, the

assumption of "hard elastic sphere" molecules is unnecessarily restrictive. It is readily seen that the momentum exchange M_{12} can be expressed directly in terms of the coefficient for ordinary mutual diffusion D_{12} without special assumptions about the law of force or the distribution-in-angle of the scattering. Provided only that the drift velocities u_1 and u_2 are small in comparison with the thermal velocities $\bar{v}_1$ and $\bar{v}_2$, the momentum transfer M_{12} will be simply proportional to $u_1 - u_2$ and will not otherwise depend on the drift velocities (see Appendix I). Consider now a mutual diffusion of the same gas mixture at uniform total pressure with no total flow of molecules. Denoting the momentum transfer per unit volume per unit time from species 1 to species 2 by $M_{12}^{(D)}$ under the special conditions of mutual diffusion, we have:

$$M_{12}/M_{12}^{(D)} = (u_1 - u_2)/(u_1^{(D)} - u_2^{(D)}) = (u_1 - u_2)n_1 n_2/n\Gamma_1^{(D)} \qquad (5)$$

since $\Gamma_1^{(D)} + \Gamma_2^{(D)} = n_1 u_1^{(D)} + n_2 u_2^{(D)} = 0$. Considering now a steady mutual diffusion in the x-direction through an element of gas of unit area and thickness dx, it is evident that the momentum received by component 1 from its partial pressure gradient is transferred to component 2 giving:

$$(dp_1/dx)dx + M_{12}^{(D)} \, dx = 0$$

whence:

$$\Gamma_1^{(D)} = -D_{12}(dn_1/dx) = D_{12}M_{12}^{(D)}/kT$$

and therefore:

$$M_{12} = (u_1 - u_2)(n_1 n_2 kT/nD_{12}) \qquad (6)$$

Equation 6 is independent of the law of force acting between the molecules and for small drift velocities is practically independent of the distribution function. In the special case of "hard elastic sphere" molecules, the value obtained for D_{12} either by Stefan's momentum transfer method[13] or in the first approximation of the Enskog-Chapman theory[14] is:

$$D_{12} = \frac{3}{8} \left(\frac{\pi kT}{2m^+}\right)^{1/2} \cdot \frac{1}{n\pi d_{12}^2} \qquad (7)$$

Introducing equation 7 into equation 6 and replacing $8kT/\pi m^+$ by $\bar{v}_1^2 + \bar{v}_2^2$ we obtain:

$$M_{12} = (4/3)m^+(u_1 - u_2) \cdot n_1 n_2 \pi d_{12}^2 \cdot (\bar{v}_1^2 + \bar{v}_2^2)^{1/2} \qquad (6\text{-a})$$

which differs by a factor of 4/3 from our preliminary result. Formulae 6 and 6-a apply to any volume element in the flowing gas. The momentum transfer from gas 1 to gas 2 in the cylindrical element bounded by the wall of the capillary is then $M_{12}\pi r^2 dx$ provided that u_1 and u_2 are interpreted as the drift velocities averaged over the cross section. The following equations express the momentum balance in the cylindrical element*:

$$-\pi r^2 \cdot (dp_1/dx) = (3\pi/8) \cdot m_1 u_1 \cdot (n_1 \bar{v}_1/4) \cdot 2\pi r + (u_1 - u_2) \cdot (n_1 n_2 kT/nD_{12}) \cdot \pi r^2$$

$$-\pi r^2 \cdot (dp_2/dx) = (3\pi/8) \cdot m_2 u_2 \cdot (n_2 \bar{v}_2/4) \cdot 2\pi r - (u_1 - u_2) \cdot (n_1 n_2 kT/nD_{12}) \cdot \pi r^2 \qquad (8)$$

Adding and introducing the molecular flows per unit area G_1 and G_2 averaged over the cross section; i.e., $G_i = n_i u_i$, we find:

$$-r(dp/dx) = (3\pi/16)(m_1 \bar{v}_1 G_1 + m_2 \bar{v}_2 G_2) \qquad (9)$$

Since the right-hand side of equation 9 is a constant, the total pressure decreases linearly along the tube. Introducing the abbreviations:

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*It is readily seen that under the specified conditions of low pressure flow through long tubes the dynamical inertia term proportional to $u \, \delta u/\delta x$ can be neglected.

$$b(N) = \frac{8r}{3\pi} \cdot (\frac{\pi kT}{2m^+})^{1/2} \cdot \frac{\langle m^{1/2} \rangle_N}{(m_1 + m_2)^{1/2}} \cdot \frac{1}{pD_{12}}$$

$$\langle m^{1/2} \rangle_N = Nm_1^{1/2} + (1-N)m_2^{1/2}$$

where $N(x)$ denotes the mol fraction of gas 1 and using the Maxwellian value of $\bar{v}$, one finds from equation 8 that:

$$-G_1 = \frac{8}{3\pi}(\frac{\pi}{2kT})^{1/2} r \left\{ \frac{1}{m_1^{1/2}} \cdot \frac{1}{1+b(N)p} \cdot \frac{d(Np)}{dx} + \frac{N}{\langle m^{1/2} \rangle_N} \cdot \frac{b(N)p}{1+b(N)p} \cdot \frac{dp}{dx} \right\} \tag{11}$$

The first term, which is inversely proportional to $m^{1/2}$, is ideally separative. The second term is nonseparative, it vanishes as the pressure goes to zero ($\lambda \gg r$), and for large pressures ($\lambda \ll r$) it is negligible compared with viscous flow. In the case of a pure gas ($N = 1$) the two terms coalesce to give the free-molecule flow formula (equation 1). It is readily seen that if the capillary has a uniform noncircular cross section, the same expressions for b and G_1 are valid if r is interpreted as twice the cross sectional area divided by the perimeter. Badger's[9] semi-empirical equation is similar to equation 11; however, in his formulation $b(N)/\langle m^{1/2} \rangle_N$ was not independent of concentration. The second term of equation 11 representing a nonseparative diffusion becomes important when $b(N)p \approx 1$. In the case of an isotopic mixture it is evident that:

$$bp = \frac{2r}{3} \cdot (\frac{8kT}{\pi m})^{1/2} \cdot \frac{1}{D_{11}} = \frac{D_K}{D_{11}} = K(\frac{r}{\lambda}) \tag{12}$$

where D_{11} is the self-diffusion coefficient and D_K the Knudsen coefficient $2\bar{v}r/3$ for free molecule diffusion. The mean free path λ has been introduced in connection with the isotopic mixture and K denotes a numerical factor in the neighborhood of unity whose precise value depends on the relationship assumed between D_{11} and λ. It follows from equations 11 and 12 that the separation ceases to be ideal when λ becomes comparable to r.

CAPILLARY THEORY OF SEPARATION

In the preceding section it has been assumed that the effects of viscosity could be neglected in first approximation because of the small transverse gradient of the transport velocity. However, the transition to viscous flow takes place in the same range of pressures ($\lambda \approx r$) in which the non-separative diffusion becomes important. Consequently, although the effects of viscosity on separation are small in this range of pressure, they cannot be neglected. At higher pressures the entire diffusive flow equation 11 becomes negligible compared to the viscous flow. We now assume that the flow of a mixture of two gases at intermediate pressures can be represented by adding the viscous laminar flow to the diffusive flow of equation 11. In the case of pure gas flow through capillaries the transition region can be represented only approximately by adding the free-molecule and laminar flows: the minima found by Knudsen, Gaede, and Adzumi in the curve of specific flow versus mean pressure indicate that the flows are not strictly additive. Except at high pressures and low separation efficiencies, however, the effect of the viscous term is small and the error made by assuming exact additivity is of second order. The Poiseville term in the following formulae may be regarded as an additive perturbation on the main diffusive flow. As previously noted, the assumption of additivity is a better approximation for porous media than for capillary tubes.

Equation 11 is now rewritten for each component to include the viscous flow:

$$-\frac{G_1}{g} = \frac{f^+}{1 + b(N)p} \cdot \frac{d(Np)}{dx} + \frac{\overline{f}(N)b(N)p}{1 + b(N)p} \cdot N\frac{dp}{dx} + Na(N)p\frac{dp}{dx} \qquad (13)$$

$$-\frac{G_2}{g} = \frac{1}{1 + b(N)p} \cdot \frac{d(1-N)p}{dx} + \frac{\overline{f}(N)b(N)p}{1 + b(N)p} \cdot (1-N)\frac{dp}{dx} + (1-N)a(N)p\frac{dp}{dx}$$

where $g = (8/3\pi)(\pi/2kTm_2)^{1/2}r$

$$\overline{f}(N) = m_2^{1/2}/\left\langle m^{1/2}\right\rangle_N \qquad (14)$$

$$a(N) = 3r/16\,\eta(N)\overline{v}_2$$

The value of $\underline{a}$ is obtained from the Poiseuille flow through a circular capillary divided by the area of cross section: $(r^2p/8\eta)dn/dx$. All three terms in equation 13 represent averages over the cross section of the tube. The relative importance of the nonseparative diffusion and the viscous flow term is measured by the ratio $X(N) = b(N)/a(N)$. It follows from equations 10 and 14 that:

$$X(N) = \frac{256}{9\pi} \cdot \frac{\left\langle m^{1/2}\right\rangle_N \left\langle m\right\rangle_N}{m_2 m_1^{1/2}} \cdot \frac{\eta(N)}{\rho(N)D_{12}} \qquad (15)$$

where $\rho(N)$ is the mass density and $\left\langle m\right\rangle_N = Nm_1 + (1-N)m_2$. In the case of an isotopic mixture D_{12} reduces to the self-diffusion coefficient D_{11}. The dimensionless constant $\rho D_{11}/\eta$ may range in value from 1.20, corresponding to "rigid elastic sphere" molecules, up to about 1.5 for molecules repelling nearly as the inverse fifth power of the distance. In practice $\rho D_{11}/\eta$ lies usually between 1.30 and 1.40; hence, the value of X for an isotopic mixture is roughly independent of the gas. Experiments[13] indicate that the best value of $\rho D_{11}/\eta$ for the UF_6 isotopic mixture is in the neighborhood of 4/3, corresponding to $X = 64/3\pi$.

The differential equation of separation will now be obtained. Let ν denote the molar fraction of the first gas at the outlet; then $G_1/G_2 = \nu/1-\nu$, expressing the condition that the composition of the gas at the exit is determined entirely by the flow rates through the tube. By substituting equations 13 in this relation and writing $dN/dx = (dN/dp)(dp/dx)$ one obtains:

$$p\frac{dN}{dp}\left\{f^+(1-\nu) + \nu\right\} + (N-\nu)\left\{(\overline{f}b + a)p + abp^2\right\} + f^+N(1-\nu) - \nu(1-N) = 0 \qquad (16)$$

Let $y = N-\nu$ and $h(\nu) = 1 + (f^+-1)(1-\nu)$, then equation 16 becomes:

$$hp\frac{dy}{dp} + \left[h + \left\{\overline{f}b + a(y)\right\}p + a(y)b(y)p^2\right]y + (f^+-1)\nu(1-\nu) = 0 \qquad (17)$$

Evidently ν and $\overline{f}b$ are constants but the parameters a and b depend on the composition at every point through $\eta(N)$ and $\left\langle m^{1/2}\right\rangle_N$ respectively. Since $\left\langle m^{1/2}\right\rangle_N$ is a linear function of N and since $1/\eta(N)$ can be approximately represented by a linear function over not too large a range, we may rewrite equation 17 in the form (neglecting the small terms py^2 and p^2y^3):

$$p(dy/dp) + \left\{1 + cp + lp^2\right\}y + mp^2y^2 + s = 0 \qquad (18)$$

The solution of equation 18 can be obtained analytically in terms of confluent hypergeometric functions (See Appendix II) or more simply by numerical integration. However, even in the case of a gas mixture in which the molecular mass ratio and the change of composition are large and the coefficient of p^2 in equation 17 varies considerably, e.g., $H_2 - CO_2$, the solution of equation 17 is found to differ by only a few per cent at low and negligibly at high separation efficiencies from the solution in which a and b are treated as constants and given their values at the inlet. Since the composition of the gas in ideal Knudsen flow is constant at the inlet value throughout the length of the

tube, it is obviously preferable to use the inlet rather than the outlet values of a and b. Hence for all mixtures in which the molecular mass ratio of the components is not too large, we may replace equation 17 by:

$$h(\nu)p(dy/dp) + \left\{ h(\nu) + c_1 p + c_2 p^2 \right\} y + (f^+ - 1)\nu(1-\nu) = 0 \qquad (19)$$

where $c_1 = \bar{f}b + a$ and $c_2 = ab$. On integrating from the outlet to the inlet we obtain:

$$y(p_F) = N_0 - \nu = - \frac{(f^+ - 1)\nu(1-\nu)}{h(\nu)p_F} \cdot \frac{\int_{p_B}^{p_F} \exp\left\{ (c_1 p + (c_2/2)p^2)/h(\nu) \right\} dp}{\exp\left\{ (c_1 p_F + (c_2/2)p_F^2)/h(\nu) \right\}} \qquad (20)$$

where p_F and p_B denote fore- and back-pressures and N_0 the inlet concentration. We define the separation efficiency Z as the ratio of the actual enrichment to the ideal enrichment at constant back-composition. It is readily seen that:

$$Z = \frac{(\nu - N_0)h(\nu)}{(f^+ - 1)\nu(1-\nu)} = \frac{\int_{\phi_B}^{\phi_F} \exp\left\{ [(1 + X\bar{f})\phi + (X/2)\phi^2]/h(\nu) \right\} d\phi}{\phi_F \exp\left\{ [(1 + X\bar{f})\phi_F + (X/2)\phi_F^2]/h(\nu) \right\}} \qquad (21)$$

where the "reduced pressure" $\phi = ap = 3rp/16\eta\bar{v}_2$ has been introduced. A curve of Z versus ϕ_F for fixed ϕ_B/ϕ_F will be referred to as a "fore-pressure curve." It is apparent from equation 21 that there is no universal fore-pressure curve which would be independent of the gas mixture. However, since the X of an isotopic mixture is approximately independent of the gas, one may, to good approximation, use a universal fore-pressure curve for isotopic mixtures. In this case ($\bar{f} \approx 1$, $h(\nu) \approx 1$) equation 21 reduces to:

$$Z = \frac{\int_{\phi_B}^{\phi_F} \exp\left\{ (1 + X)\phi + (X/2)\phi^2 \right\} d\phi}{\phi_F \exp\left\{ (1 + X)\phi_F + (X/2)\phi_F^2 \right\}} \qquad (21\text{-a})$$

It is convenient for purposes of comparison with experiment to have the pressures expressed in terms of p_{50}, the fore-pressure at which $Z = 0.50$ when the back-pressure is zero. Using $X - 64/3\pi$, one finds that $Z = 0.50$ when $\phi_F = 0.1834$ and $\phi_B = 0$. Introducing the "relative pressure" $\pi = p/p_{50} = \phi/\phi_{50}$, equation 21-a becomes:

$$Z(\pi_F, \pi_B) = \frac{\int_{\pi_B}^{\pi_F} \exp\left\{ 1.430\pi + 0.1142\pi^2 \right\} d\pi}{\pi_F \exp\left\{ 1.430\pi_F + 0.1142\pi_F^2 \right\}} \qquad (21\text{-b})$$

Numerical results from equation 21-a are insensitive to variations in X arising from the slightly different values of $\rho D_{11}/\eta$ appropriate to different gases. When $\pi_B = 0$ a good approximation to equation 21-b is given by:

$$Z^{-1} = 1 + 0.662\pi_F + 0.338\pi_F^2 \qquad 0 \le \pi_F \le 2 \qquad (21\text{-c})$$

In the stated range of fore-pressures this formula is nowhere in error by more than 1 per cent.

In the case of a general binary gas mixture it is convenient to introduce the variable:

$$t = (X/2h)^{1/2}\phi + t_0$$
$$t_0 = (1 + X\bar{f})/(2hX)^{1/2}$$

Equation (21-b) was derived independently by C. H. Bosanquet from a quite different point of view. Bosanquet's results, which were communicated to R. Peierls in letters dated May 8 and 19, 1944, were obtained slightly earlier than those of the present authors. The considerations of Bosanquet were restricted to isotopic mixtures; however, it has been shown by Pollard (A-3813, November 23, 1945) that the method of Bosanquet can be generalized to an arbitrary gas mixture.

Equation 21 can then be written in a general form for all gas mixtures as the simple three-parameter function:

$$Z(t_F, t_B, t_0) = \int_{t_B}^{t_F} e^{t^2} dt / (t_F - t_0) e^{t_F^2} \tag{22}$$

The integrals are conveniently evaluated from the following formula* based on an approximation by Tschebyscheff polynomials and having in the range $2 \leq X < \infty$ an error nowhere exceeding 1 part in 2000:

$$\int_0^X e^{t^2} dt = (e^{x^2}/2x) \left\{ 0.9995 + 0.1489(2/x)^2 - 0.1361(2/x)^4 \right.$$
$$\left. + 0.4525(2/x)^6 - 0.2184(2/x)^8 \right\} - 0.56 \tag{23}$$

Graphs of Z vs t_F for selected values of t_B and t_0 can be simply prepared and applied to the separation of various binary gas mixtures for the two cases of constant fore-composition and constant back-composition.

The integration of equation 19 from the outlet of the capillary (at given back-pressure and back-composition) to a variable pressure p enables one to plot N as a function of p. Starting from the inlet value N_0, N is found to decrease monotonically along the tube when $p_B = 0$ and then jump discontinuously to the value ν at the exit; when p_B is small but finite the concentration of light component first decreases and then rises steeply but continuously near the exit. The explanation of the initial decrease in N is as follows: The ratio of the light component transport velocity to that of the heavy component is not constant as in free-molecule flow but increases as the lower pressure region of the tube is reached because of the decreasing frequency of collisions between unlike molecules. Since the ratio of concentrations is inversely proportional to the ratio of transport velocities, the light component concentration must decrease down the tube rising near the outlet because of back diffusion.

This article will be concluded with a brief consideration of the total flow of a mixed gas through the capillary tube. The total flow of the mixture is obtained by adding together the equations for the two components in equation 13 and eliminating the term in dN/dp by the use of equation 16. The result for $G = G_1 + G_2$ is simply:

$$-G/g = \bar{f}(\nu)dp/dx + \left\{ \bar{f}(\nu)/\bar{f}(N) \right\} a(N)p \, dp/dx \tag{24}$$

where $\bar{f}$ and $\underline{a}$ are defined by equations 14. Introducing $g' = gm_2^{1/2}$ and $a' = a(N)\eta(N)m_2^{-1/2} = 3r/16\bar{v}_2 m_2^{1/2}$ into equation 24, one obtains:

$$-G/g' = \frac{1}{\langle m^{1/2} \rangle_\nu} \cdot \left\{ 1 + \frac{a' \langle m^{1/2} \rangle_N p}{\eta(N)} \right\} \cdot \frac{dp}{dx} \tag{24-a}$$

which may be compared with the corresponding formula for a pure gas:

$$-G/g' = \frac{1}{m^{1/2}} \cdot \left\{ 1 + \frac{a' m^{1/2} p}{\eta} \right\} \cdot \frac{dp}{dx} \tag{24-b}$$

The first term of equation 24-a, which represents the free-molecule flow of a mixed gas, is seen to be inversely proportional to the average value of the square root of the molecular mass, the average being taken with respect to the outlet composition. The integration of equations 24 or 24-a is complicated by the fact that the coefficient of p dp/dx is a function of composition and the composition varies with the pressure as the gas flows from the inlet to the outlet. Details will not be given here.†

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*This formula was calculated for us by Dr. C. Lanczos.

†The calculations represented by equations 24, 24-a, and 24-b were made by Bethune and Pollard, A-2145, October 18, 1944.

APPENDIX I

MOMENTUM TRANSFER IN THE GAS

It will be shown here that for simple approximate distribution functions the momentum transfer is proportional to the difference in transport velocities $u_1 - u_2$. Since very similar derivations are to be found in the literature,[14] the discussion is abbreviated.

Let $\underset{\sim}{V} = \underset{\sim}{v}_1 - \underset{\sim}{v}_2$ be the relative velocity of two unlike molecules before an encounter and let ψ denote the angle between $\underset{\sim}{V}$ and the relative velocity after collision; i.e., ψ is the angle of deflection in the center of mass system. Assuming a spherically symmetrical interaction, the angle ψ evidently depends only on the relative speed $V = |\underset{\sim}{V}|$ and the impact parameter b. The number of unlike molecule collisions per unit volume per unit time between molecules with velocities in the range $\underset{\sim}{v}_1$ to $\underset{\sim}{v}_1 + d\underset{\sim}{v}_1$ and molecules of the other type with velocities between $\underset{\sim}{v}_2$ and $\underset{\sim}{v}_2 + d\underset{\sim}{v}_2$ is $dn_1 dn_2 V \cdot 2\pi b db$ for impact parameters between b and b + db. It is readily seen that the momentum transferred to molecule 2 in a single collision has a component $m^+ \underset{\sim}{V}(1 - \cos \psi)$ in the direction of $\underset{\sim}{V}$ and that the perpendicular component averages to zero. Hence the momentum transfer per unit volume per unit time from the group dn_1 to the group dn_2 is $dn_1 dn_2 m^+ \underset{\sim}{V} V \sigma(V)$ where:

$$\sigma(V) = \int_0^\infty 2\pi b db (1 - \cos \psi)$$

is the cross section for momentum transfer (in the case of hard elastic spheres $\sigma = \pi d_{12}^2$ where d_{12} is the mean diameter). Evidently, $dn_i = n_i f_i d\underset{\sim}{v}_i$ where f_i is the velocity distribution function for gas i drifting in the x-direction with velocity u_i. Provided that $u_i \ll \bar{v}_i$, a good approximation is obtained by taking:

$$f_i d\underset{\sim}{v}_i = (\beta_i/\pi)^{3/2} e^{-\beta_i(v_{ix} - u_i)^2} dv_{ix} e^{-\beta_i v_{iy}^2} dv_{iy} e^{-\beta_i v_{iz}^2} dv_{iz}$$

$$\cong (\beta_i/\pi)^{3/2} e^{-\beta_i v_i^2} (1 + 2\beta_i u_i v_{ix}) d\underset{\sim}{v}_i$$

where $\beta_i = m_i/2kT$. The total transfer of momentum per unit volume per unit time in the x-direction is then:

$$M_x = m^+ n_1 n_2 \int d\underset{\sim}{v}_1 \int d\underset{\sim}{v}_2 f_1^{(0)} f_2^{(0)} (1 + 2\beta_1 u_1 v_{1x})(1 + 2\beta_2 u_2 v_{2x}) V_x V \sigma(V)$$

$$= 2m^+ n_1 n_2 \int d\underset{\sim}{v}_1 \int d\underset{\sim}{v}_2 f_1^{(0)} f_2^{(0)} (\beta_1 u_1 v_{1x} + \beta_2 u_2 v_{2x}) V_x V \sigma(V)$$

using the abbreviation $f_i^{(0)} = (\beta_i/\pi)^{3/2} e^{-\beta_i v_i^2}$. The simplification of the foregoing equation follows from considerations of parity. We transform coordinates from $\underset{\sim}{v}_1, \underset{\sim}{v}_2$ to $\underset{\sim}{C}, \underset{\sim}{V}$ where $\underset{\sim}{C}$ is the velocity of the center of mass. It is readily found that:

$$M_x = \frac{m^+ n_1 n_2}{kT} \int d\underset{\sim}{C} \int d\underset{\sim}{V} f_C^{(0)} f_V^{(0)} V_x V \sigma(V) \left\{ (m_1 u_1 + m_2 u_2) C_x + m^+ (u_1 - u_2) V_x \right\}$$

where $f_C^{(0)} = (m_1 + m_2/2\pi kT)^{3/2} e^{-(m_1 + m_2/2kT)C^2}$

and $f_V^{(0)} = (m^+/2\pi kT)^{3/2} e^{-(m^+/2kT)V^2}$

The term in C_x vanishes since the integrand is odd. M_x is, therefore, proportional to $u_1 - u_2$.

APPENDIX 2

Equation 18 is rewritten:

$$p\,dy/dp + \left\{1 + cp + lp^2\right\} y + mp^2 y^2 + s = 0 \tag{A}$$

where c, l, m, and s are constants characteristic of the gas mixture. The solution is subject to the condition that $y = 0$ when $p = p_B$. Let $u = py$, then equation A becomes:

$$du/dp + (c + lp)u + mu^2 + s = 0$$

This is Riccati's equation. It can be transformed into a second-order linear equation by the substitution $u = (mw)^{-1}dw/dp$ and the resulting equation is:

$$d^2w/dp^2 + (c + lp)dw/dp + msw = 0$$

Let: $z = l^{-1/2}(c + lp)$ and $\alpha = ms/2l$

Then: $d^2w/dz^2 + z\,dw/dz + 2\alpha w = 0 \tag{B}$

The general solution of equation B can be written in terms of the confluent hypergeometric functions. In the notation of Jahnke-Emde and Webb-Airey the solution is:

$$w = AM(\alpha, \tfrac{1}{2}, \tfrac{z^2}{2}) + Bz^{1/2}M(\alpha + \tfrac{1}{2}, \tfrac{3}{2}, -\tfrac{z^2}{2}) \tag{C}$$

$$dw/dz = -2\alpha z AM(\alpha + 1, \tfrac{3}{2}, -\tfrac{z^2}{2}) + (B/2)z^{-1/2}M(\alpha + \tfrac{1}{2}, \tfrac{3}{2}, -\tfrac{z^2}{2})$$

$$-Bz^{3/2}\left[(2\alpha + 1)/3\right]M(\alpha + \tfrac{3}{2}, \tfrac{5}{2}, -\tfrac{z^2}{2})$$

where A and B are arbitrary constants, the ratio of which is fixed by the boundary condition: $y = 0$ at $p = p_B$. Hence $dw/dz = 0$ when $z = z_B = l^{1/2}p_B + cl^{-1/2}$.

$$\frac{B}{A} = \frac{12\alpha z_B^{3/2} M(\alpha + 1, \tfrac{3}{2}, -\tfrac{z_B^2}{2})}{3M(\alpha + \tfrac{1}{2}, \tfrac{3}{2}, -\tfrac{z_B^2}{2}) - (4\alpha + 2)z_B^2 M(\alpha + \tfrac{3}{2}, \tfrac{5}{2}, -\tfrac{z_B^2}{2})}$$

By using the asymptotic value of $M(\alpha, \gamma, x)$ for large x, the asymptotic solution for large fore-pressures is found to be:

$$w^{-1}dw/dz \to -2\alpha/z \qquad z \to \infty$$

$$y \to -s/lp^2 \qquad p \to \infty$$

The asymptotic form of the solution for large fore-pressures indicates that the separation efficiency falls off as the inverse square of the pressure. This is in agreement with the result for high-pressure differential diffusion based on the Chapman-Enskog diffusion formula.[15]

The formal solution (equation C) is inconvenient for numerical work. Actual calculations were carried out by two methods. In method I we made use of the fact that the solution of equation A was known for the case $m = 0$ from previous work in which the variation of C_2 with y was neglected. Since the term in p^2y^2 is initially small, the previous solution in terms of the tabulated integral $\int_0^x e^{t^2}\,dt$ was used for the first part of the interval and the Runge-Kutta method of numerical integration the remainder of the way. In method II, equation B was solved by power series after first changing the independent variable to $z - z_B$. This method cannot be used when $p_B = 0$.

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