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On the Theory of Isotope Separation by Thermal Diffusion

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We here develop the theory of the processes in an apparatus with two concentric tubes, such as that used by Brewer and Bramley. In the first section we describe the process of thermal diffusion in general, and review the theoretical information on the subject. In Section II we set up the equations for the convection and diffusion processes, and obtain an expression for the net transport of a single isotope which is valid for arbitrary macroscopic properties of the gas. The assumption that the viscosity and heat conductivity of a gas are proportional to the absolute temperature is usually a good approximation; in this case the expression reduces to a simple form. In Section III we apply the transport equation to questions of separation factor and speed of operation. This is done both for the case of discontinuous operation, in which the approach to equilibrium is allowed to reach a certain stage and then the contents of an end-reservoir are removed, and for the case of operation with a continuous flow of gas through the tube. The advantages of the two methods are compared. In the last section we apply the formulas to a numerical example: the concentration of the C^{13} isotope by the use of methane, in an apparatus of moderate dimensions and power consumption.

I. Introduction

Recently Clusius and Dickel,[1] and subsequently Brewer and Bramley,[2] have reported the results of experimental work on the separation of isotopes by thermal diffusion. Their results suggest that this may become an important method. In this paper we discuss theoretically the problem of applying the process of thermal diffusion to isotope separation.

The phenomenon of thermal diffusion consists in the fact that a temperature gradient in a mixture of two gases gives rise to a gradient of the relative concentration of the two constituents. If the mixture as a whole is at rest, the equilibrium concentration gradient is such that the effect of thermal diffusion is just matched by the opposing effect of ordinary diffusion. The effect is by no means small; in some cases the coefficient of thermal diffusion may be as much as half of the ordinary coefficient.[3] A similar phenomenon is known in the case of liquids, where it is known as the Soret effect;[4] the theoretical explanation of the Soret effect has been signally unsuccessful.[5]

No simple theory can give an account of thermal diffusion; neither its existence nor its sign can be derived from elementary considerations.[6] Its presence can be understood only by a detailed consideration of the equations of transport in a gas. The phenomenon was completely overlooked by the classic workers in kinetic theory; it was first discovered theoretically by Enskog[7] in 1911, and independently by Chapman[8] six years later, and first demonstrated experimentally by Chapman and Dootson[9] in 1917.

The theory was fully and elegantly developed by Enskog,[10] and Chapman.[8] The more accessible treatment of Chapman is, however, unfortunately invalid because of algebraic errors.[11] Chapman's corrected result[12] may be shown to be identical with the result of Enskog. It is the result obtained by Enskog in his doctoral dissertation that is given in the well-known textbook of Müller-Pouillets.[13]

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[1] K. Clusius and G. Dickel, Naturwiss. **26**, 546 (1938).

[2] A. K. Brewer and A. Bramley, Phys. Rev. **55**, 590A (1939).

[3] S. Chapman, Phil. Trans. **A217**, 184 (1917).

[4] Ludwig, Wien. Akad. Ber. **20**, 539 (1856); Soret, Ann. Chim. Phys. **22**, 293 (1881).

[5] Wereide, Ann. de physique **2**, 67 (1914); Porter, Trans. Faraday Soc. **23**, 314 (1927). Also see comment by Chapman, Phil. Mag. **7**, 1 (1929).

[6] S. Chapman, reference 5.

[7] D. Enskog, Physik. Zeits. **12**, 56 and 533 (1911).

[8] Reference 3, p. 115.

[9] S. Chapman and F. W. Dootson, Phil. Mag. **33**, 248 (1917); for a complete list of the experimental literature on thermal diffusion, see T. L. Ibbs, Physica **4**, 1133 (1937).

[10] D. Enskog, Doctoral Dissertation, Upsala, 1917, published by Almqvist and Wiksells.

[11] D. Enskog, Arkiv. f. Mat., Astron., o. Fysik **16**, No. 16 (1921).

[12] S. Chapman and W. Hainsworth, Phil. Mag. **48**, 593 (1924); the presentation of the value of D_T in this paper does not become complete until it is stated that the matrix a_{ij} is *symmetrical*.

[13] Müller-Pouillets, *Lehrbuch der Physik*, eleventh edition, Vol. 3, Part 2, p. 110.

The coefficient of thermal diffusion vanishes for Maxwellian molecules (molecules which interact with a force which varies as the inverse fifth power of the separation). For molecules such that the force varies as an inverse power of the separation which is greater than five, the direction of the diffusion is such that the lighter molecules move toward the warmer part of the gas, in general, while for an inverse power less than five, the lighter molecules accumulate in the colder part of the gas. A general result of the theory is that the coefficient vanishes when the mode of interaction, the radii, and the masses of the two sets of molecules, are all equal;[3] this fact is also obvious from symmetry.

Even to the first approximation (the result comes out as an infinite determinant), the coefficient of thermal diffusion can be stated in closed form only for the case of rigid elastic spheres, in which case the effect is greatest. The experiments show a coefficient which is in general something less than half of the value predicted for elastic spheres.

The equation of diffusion, with thermal diffusion included, is

$$c_1(\mathbf{v}_1-\mathbf{v})=-D_{12}\text{ grad. }c_1+(D_T/T)\text{ grad. }T, \qquad (1)$$

where c_1 is the relative *particle* density of the lighter constituent, with $c_1+c_2=1$; $\mathbf{v}_1$ is the *convection* velocity of the lighter constituent alone, while $\mathbf{v}$ is the convection velocity of the gas as a whole ($\mathbf{v}=c_1\mathbf{v}_1+c_2\mathbf{v}_2$); D_{12} is the coefficient of ordinary diffusion, which in the case of isotopes may be replaced by D, the coefficient of self-diffusion, and D_T is the previously mentioned coefficient of thermal diffusion; T is the absolute temperature. In the corresponding equation for c_2, the D_T term has the opposite sign.

It can be shown rigorously, for the case of hard spheres, that the ratio $D_T/D_{12}=k_T$ depends only on the relative concentrations and on microscopic quantities, but not on the pressure or temperature. It is reasonable to suppose that for actual molecules this ratio does not vary with pressure or temperature to any significant extent.

For the separation of isotopes, we are interested in the case when the two sets of molecules in question are chemically identical, and differ only in mass. In this case, the expression for k_T becomes greatly simplified, because the modes of interaction and the radii of the two constituent molecules are then the same, since these properties are completely determined by the electronic configuration. For this special case, Enskog's result reduces to[14]

$$D_T/D=k_T=\alpha c_1c_2, \qquad (2)$$

where $\alpha=(105/118)(m_2-m_1)/(m_2+m_1)$, the m's being the relative masses of the two types of molecules. It is to be remembered that number 1 is the lighter species. This expression is the first approximation for the case of elastic spheres, in which furthermore we have retained only terms of the first order in $(m_2-m_1)/(m_2+m_1)$.

The experimental determinations of k_T for the case of *dissimilar* molecules yield values somewhat less than half of the theoretical result for elastic spheres.[9] Until experiment yields us values for k_T in the case of isotopes, therefore, we suggest that

$$\alpha=0.35(m_2-m_1)/(m_2+m_1) \qquad (3)$$

be used as a provisional value in the design of apparatus. The exact value of the numerical coefficient will vary from molecule to molecule, because of the different modes of interaction.

When values for k_T in the case of isotopes are determined experimentally, they may lead to valuable conclusions about the nature of the intermolecular forces in the gas in question. Thermal diffusion should be an excellent way to obtain this information, because it is one of the few phenomena in a gas that depend essentially on the peculiar characteristics of the molecules.[15] The knowledge of k_T for the case of isotopes is particularly valuable, because in this case there is no mixing of the characteristics of two dissimilar molecules.

The use of thermal diffusion for separating isotopes was first suggested by Chapman.[16] Its use was discussed by Mulliken,[17] on the basis of Chapman's first treatment. Mulliken concluded that it could not compete with other methods,

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[14] S. Chapman's earlier expression (reference 16) was

$$k_T=\frac{17}{3}\frac{m_2-m_1}{m_2+m_1}\frac{c_1c_2}{9.15-8.25\,c_1c_2}.$$

[15] S. Chapman, reference 3, p. 181; J. H. Jeans, *Dynamical Theory of Gases*, fourth edition (Cambridge, 1925), p. 325.

[16] S. Chapman, Phil. Mag. **38**, 182 (1919).

[17] R. S. Mulliken, J. Am. Chem. Soc. **44**, 1033 (1922).

but he did not consider the very effective method of fractionation employed by Clusius and Dickel.[1]

Clusius and Dickel ran a heated wire up the axis of a long vertical hollow tube, into which was put the gas whose isotopic constituents were to be separated. The combination of the effect of thermal diffusion and of the convection currents set up in the tube is such as to increase greatly the rather small separation caused directly by the radial temperature gradient. The light isotope collects at the top, while the heavier isotope goes to the bottom of the tube, as we shall discuss in detail in the next section.

The procedure of Brewer and Bramley[2] was very similar. They used two concentric tubes, of one and two centimeters diameter. The inner tube was heated.

In the following two sections we examine quantitatively what is occurring in this new method of separating isotopes. We find it possible to set up formulae showing the dependence of the performance characteristics on the dimensions of the apparatus, the temperature, the density, etc. These results should be useful in designing apparatus for isotope separation by this method.

II. THE CONVECTION FIELD AND THE TRANSPORT EQUATION

Description of apparatus and notation

The apparatus is supposed to consist of two concentric cylinders, the inner one heated and the outer one cooled, mounted in a vertical position, with reservoirs at the top and bottom communicating with the annular space between the cylinders, where convection and diffusion take place. The difference of the radii may be supposed small compared with either radius, so that we may proceed as if the convection were taking place in a thin flat slab, of breadth B equal to the mean circumference of the cylinders, thickness $2w$ equal to the difference of the radii, and length $2l$, the length of the tube.

In addition to the notation already introduced, we shall use the following: T_1, T_2 = absolute temperature of the outer, inner tube; $\Delta T = T_2 - T_1$; x = radial coordinate, $-w<x<w$; z = coordinate along the tube, $-l<z<l$; c = specific heat at constant pressure, in cal./gram-deg.; Q = heat flow, in cal./cm^2-sec.; λ = thermal conductivity, in cal./cm-deg.-sec.; p = pressure; η = viscosity; ρ = density; g = acceleration of gravity; $\mathbf{J}_1$, $\mathbf{J}_2$ = flux of species 1, 2 in grams/cm^2-sec.; τ = total upward transport, in grams/sec.; τ_1, τ_2 = upward transport of species 1, 2, in grams/sec. $\tau = \tau_1 + \tau_2$; $c_1{}^0$ = value of c_1 in the bottom reservoir; $c_1{}^1$ = value of c_1 in the top reservoir; κ_e = equilibrium value of $c_1{}^1$ with $\tau = 0$; κ_r = a specified value of $c_1{}^1$; m_t = mass of gas in the top reservoir; and t_r = relaxation time of the equilibrium. In all considerations subsequent to Eq. (29), the temperature dependent quantities are to be evaluated at the average temperature, $\frac{1}{2}(T_2+T_1)$.

General treatment of the convection and diffusion field

Throughout this section and the next it will be assumed that it is the lighter isotope, species 1, which one is interested in concentrating. The considerations will be completely symmetrical in respect to the interchange of 1 and 2, however, if we understand that the vertical coordinate changes sign when we apply our equations to the concentration of a heavy isotope—that is, $c_1{}^0$ becomes the concentration $c_2{}^0$ in the top reservoir, while the small collecting reservoir would be at the bottom; and so on, in an obvious manner.

In the immediately following presentation, we shall develop a mathematical description of the convection and diffusion processes in the tube, and derive the fundamental relations which yield the transport of species 1 along the tube. Having obtained these relations, we then proceed in the next section to determine the behavior of the apparatus in the large: to find what separation factors can be obtained, and at what speed a mixture of given concentration may be produced.

We shall calculate the convection by using the temperature distribution as determined by conduction only. Near each end of the tube, where gas at a different temperature is entering, the temperature distribution is of course different. On the basis of the treatment of the convection problem given below, one finds that the length over which this difference remains appreciable is of the order of

$$l_r = (w^4 c g \rho^2 / 48 \eta \lambda)(T_2 - T_1)/(T_2 + T_1), \qquad (4)$$

where here as in (5) the temperature dependent quantities ρ, η, λ are evaluated at the average temperature $(T_2+T_1)/2$. Our neglect of these regions depends on the condition $2l_r \ll 2l$, which will usually be strongly satisfied in practice.

The treatment of the convection flow as lamellar is justified, since the Reynolds number may be shown to be roughly

$$(w^3 g\rho^2/24\eta^2)(T_2-T_1)/(T_2+T_1), \tag{5}$$

which in practical cases will be very much smaller than the values at which turbulence occurs in flow through tubes or between plates.

In the region of the tube where the temperature gradient is determined by conduction alone, we have

$$Q=\lambda dT/dx,$$
$$2wQ=\int_{T_1}^{T_2}\lambda dT, \tag{6}$$
$$\partial/\partial x=(Q/\lambda)(\partial/\partial T).$$

We shall neglect the dependence of λ on the concentration c_1 and also the dependence on c_1 of ρ, η, and D. These dependences are not large when the fractional difference of molecular weight is small. Moreover, only transverse differences have any significant effect on the performance, and the transverse difference of concentration is very small. Thus only the temperature dependences of the various quantities is of any importance.

The hydrodynamical equation of steady, viscous flow is

$$(\text{div. }\eta\text{ grad.})\mathbf{v}=\text{grad. }p-\rho\mathbf{g}. \tag{7}$$

We assume that the velocity is entirely in the vertical direction, and that it is independent of z; this is a very close approximation since the pressure variation within the tube is negligible. Then we have from (6) and (7)

$$(Q^2/\lambda)(d/dT)(\eta/\lambda)(dv/dT)=(dp/dz)+\rho g \tag{8}$$

with the boundary conditions

$$v(T_1)=v(T_2)=0. \tag{9}$$

By (1), the equation for the flux of species 1 is

$$\mathbf{J}_1=\rho[\mathbf{v}c_1+D(-\text{grad. }c_1+\alpha c_1c_2\text{ grad. }\ln T)], \tag{10}$$

and a corresponding equation holds for $\mathbf{J}_2$.

We shall base our calculation of the transport of species 1 through the tube on the assumption that the time variation of the concentration c_1 at each point in the tube is negligible—that is, that the condition is either stationary or quasi-stationary. A stationary condition exists at final equilibrium in a closed apparatus, and also when there is a uniform output of the concentrated isotope. During the approach to equilibrium the condition will be essentially stationary provided each end-reservoir is sufficiently large. The volume of each reservoir must be larger than that of a length of tube in which the equilibrium concentration changes by a factor e.

Accordingly we proceed from the equations

$$\text{div. }\mathbf{J}_1=\text{div. }\mathbf{J}_2=0. \tag{11}$$

Eq. (10) then gives, on application of (6),

$$(\partial/\partial T)(\rho D/\lambda)[(\partial c_1/\partial T)-(\alpha c_1c_2/T)] = (\lambda\rho/Q^2)[v(\partial c_1/\partial z)-D(\partial^2 c_1/\partial z^2)]. \tag{12}$$

The term containing $(\partial^2 c_1/\partial z^2)$ is the one that introduces the effect of longitudinal diffusion. The retention of this term would make it impossible to carry out the analysis in any simple manner. Since the effect of diffusion along the tube can be calculated separately quite accurately, we shall omit the term in question, and calculate from

$$(\partial/\partial T)(\rho D/\lambda)[(\partial c_1/\partial T)-(\alpha c_1c_2/T)] = (\lambda\rho/Q^2)v(\partial c_1/\partial z). \tag{12'}$$

We now introduce a function $G(z, T)$ defined by

$$(\partial c_1/\partial z)G(z, T)=-(\lambda Q^3/\rho D)J_{1x} \tag{13a}$$
$$=Q^4[(\partial c_1/\partial T)-(\alpha c_1c_2/T)]. \tag{13b}$$

Then from (12′),

$$(\partial/\partial T)(\rho D/\lambda)(\partial c_1/\partial z)G(z, T) = \lambda\rho Q^2 v(\partial c_1/\partial z). \tag{14}$$

From this point on we shall assume that the dependence of $\partial c_1/\partial z$ on T can be neglected. This is equivalent to assuming that $\partial c_1/\partial T$ is independent of z, which is physically reasonable for a quasi-stationary condition. We shall at once establish two important consequences of this assumption: First, the total transport τ through the tube is zero; second, G is a function of T only.

Since div. $\mathbf{J}_1$ is zero, the flow of species 1 must be constant along the tube—that is,

$$\tau_1 = B\int_{-w}^{w} \rho c_1 v dx = \text{constant},$$

$$\tau_1 = (B/Q)\int_{T_1}^{T_2} \lambda \rho c_1 v dT, \qquad (15)$$

$$(d\tau_1/dz) = (\partial c_1/\partial z)(B/Q)\int_{T_1}^{T_2} \lambda \rho v dT$$

$$= (\partial c_1/\partial z)\cdot \tau = 0.$$

Then since $\partial c_1/\partial z$ is not identically zero, τ, the total transport, must vanish.

By (13a), we have

$$G(z, T_1) = G(z, T_2) = 0 \qquad (16)$$

since J_{1x} must vanish at the walls. The factor $(\partial c_1/\partial z)$ on each side of (14) cancels, and since the only remaining quantity that can be a function of z is $G(z, T)$, one finds, on integrating (14) that $(\rho D/\lambda)G$ can depend on z only through an additive function of z. Then, since (16) hold identically in z, we have

$$G(z, T) = G(T). \qquad (17)$$

We have now, canceling the $\partial c_1/\partial z$ in (14), and solving for v,

$$v(T) = (1/\lambda\rho Q^2)(d/dT)(\rho D G(T)/\lambda). \qquad (18)$$

Then from (18) and (16),

$$G'(T_1) = G'(T_2) = 0. \qquad (19)$$

If we now substitute (18) in (8), and differentiate with respect to T, we obtain as the differential equation for $G(T)$

$$\frac{d}{dT}\frac{1}{\lambda}\frac{d}{dT}\frac{\eta}{\lambda}\frac{d}{dT}\frac{1}{\lambda\rho}\frac{d}{dT}\left(\frac{\rho D}{\lambda}G(T)\right) = g\frac{d\rho}{dT} \qquad (20)$$

with the boundary conditions

$$G(T_1) = G(T_2) = G'(T_1) = G'(T_2) = 0. \qquad (21)$$

By the calculation of this single function one vas, by (18), a complete description of the convection process; and, within the limits of our approximations, one has, by (13), a description of the transverse diffusion, both thermal and ordinary. By the use of this same function we can proceed to obtain an expression for the transport of a single isotope along the tube.

According to (15) and (18) the net vertical transport of species 1 is

$$\tau_1 = (B/Q^3)\int_{T_1}^{T_2} c_1 (d/dT)(\rho D G(T)/\lambda) dT. \qquad (22)$$

Partial integration and substitution from (13b) and (21) lead to the expression

$$\tau_1 = H c_1 c_2 - K\partial c_1/\partial z, \qquad (23)$$

where H and K are positive constants defined by

$$H = -(B/Q^3)\int_{T_1}^{T_2} (\rho D\alpha/\lambda T) G(T) dT \qquad (24)$$

and

$$K = (B/Q^7)\int_{T_1}^{T_2} (\rho D/\lambda)\{G(T)\}^2 dT. \qquad (25)$$

We have removed c_1c_2 from under the integral sign of (24), because c_1c_2 varies only slightly with T. We could not consider c_1 as constant in (22), however, because it is only the slight variation of c_1 which prevents this integral from vanishing.

In Eq. (23) the term Hc_1c_2 gives the transport of species 1 caused by the existence, due to thermal diffusion, of a transverse flow of this isotope, which makes the concentration in the column of gas moving upward differ from that in the column moving downward. At the beginning of the process, when $\partial c_1/\partial z = 0$, this is the only cause of transport. After a longitudinal concentration gradient has been built up, the convection currents lead to a certain amount of remixing of the gas, represented by the term $-K\partial c_1/\partial z$. There is, however, another remixing effect which is not included in Eq. (23), because in replacing (12) by (12′) we omitted the term which corresponds to diffusion *along* the tube. Since the convection velocity will be small, however, the longitudinal diffusion will be practically independent of it. If we ignore the convection velocity, the transport of species 1 due to longitudinal diffusion is

$$\tau_{1d} = -K_d\, \partial c_1/\partial z,$$

$$K_d = (B/Q)\int_{T_1}^{T_2} \lambda \rho D dT. \qquad (26)$$

The total transport of species 1 is obtained by adding τ_{1d} to the τ_1 given by (23).

Specialization to the Maxwellian case

The treatment so far has been general, in the sense that the quantities D, λ and η might have an arbitrary temperature dependence. If, however, the mean free path varies as the $(n-\frac{1}{2})$th power of the temperature, and if c_v is independent of T, the following quantities should all be constant:

$$(\eta/T^n),\quad (\lambda/T^n),\quad (\rho D/T^n);\quad (\eta/\lambda),\quad (\rho D/\lambda).$$

Then (20) becomes

$$(d/dT)T^{-n}(d^2/dT^2)T^{1-n}(dG/dT) = -T^{-2}(\lambda^4\rho g)/(\eta D T^{2n-2}). \tag{27}$$

The general solution of (27) has been obtained, and there appears to be no bar to the explicit evaluation of H and K in this manner. The formulae would be awkward in practice, however, because of heavy cancellation of terms. The writers have worked out the cases of $n=\frac{1}{2}$ (hard spheres) and $n=1$ (Maxwellian molecules). Since the case $n=1$ is much simpler than any other, and corresponds fairly well to the temperature dependence of the properties of most gases, we suggest that the formulas for this case be used in practice. This simplification is particularly well justified because our knowledge of the all-important factor α itself is so inexact.

For $n=1$, integration of (27) and application of (21) gives

$$G(T) = -\{(\lambda^4 g\rho)/(24\eta D)\} \times (T_2-T)^2(T_1-T)^2/(T_2+T_1). \tag{28}$$

and (6) becomes

$$w = \lambda\Delta T/2Q, \tag{29}$$

where in this and all following formulae, ρ, D, λ, η and T are to be evaluated at $T=\frac{1}{2}(T_2+T_1)$. If (28) and (29) are used in (24), the result is

$$H = \{(w^3\rho^2\alpha g B)/(90\eta)\}(\Delta T/T)^2 f(\Delta T/T), \tag{30}$$

where

$$\begin{aligned} f(\Delta T/T) &= 30T^2(\Delta T)^{-4}\{(\Delta T)^2/6 - T_1T_2 \\ &\qquad + (T_1T_2)^2(T\Delta T)^{-1}\ln(T_2/T_1)\} \\ &= 15\textstyle\sum_k(\Delta T/2T)^{2k}/\{(2k+1)(2k+3) \\ &\qquad \times(2k+5)\} \\ &= 1+(15/3\cdot5\cdot7)(\Delta T/2T)^2+\cdots. \end{aligned}$$

$f(\Delta T/T)$ has the value unity for $\Delta T=0$, and the value 5/4 for the extreme case $T_1/T_2=0$, and lies between these two values for intermediate cases. For $T_2=2T_1$, $f=1.016$, while for $T_2=3T_1$, $f=1.039$.

From (25) and (29), we have

$$A = H/2K = (63/4) \times \{(\alpha\eta D)/(\rho g w^4)\} f(\Delta T/T), \tag{31}$$

and (26) gives

$$K_d/K = 1890(T_1^2+T_1T_2+T_2^2) \times \{D\eta/(w^3\rho g\Delta T)\}^2. \tag{32}$$

The corresponding relations for a gas consisting of hard spheres follow:

We introduce the abbreviations:

$$t=T^{\frac{1}{2}},\quad t_1=T_1^{\frac{1}{2}},\quad t_2=T_2^{\frac{1}{2}},$$
$$r=(t_2-t_1)/(t_2+t_1),$$
$$s(t)=(2t-t_2-t_1)/(t_2-t_1).$$

Then we find

$$G(t^2) = -\{(\lambda^4\rho g T)/(72\eta D)\}(t_2-t_1)^4\{1-(s(t))^2\}^2 \times\{(6-2r^2)(3+rs(t))^2-(3+r^2)^2\}(3+r^2)^{-1}(5-r^2)^{-1},$$

$$w=\{\lambda/(3QT^{\frac{1}{2}})\}(t_2^3-t_1^3),$$

$$H=\{(4\alpha\lambda^3\rho^2 gT)/(3Q^3\eta)\} \times\{(t_2-t_1)^5/(t_2+t_1)(3+r^2)(5-r^2)\}\psi(r),$$

$$\psi(r)=1-r^2/5-(30+2r^2) \times\{r^2/(1\cdot3\cdot5\cdot7)+r^4/(3\cdot5\cdot7\cdot9)+\cdots\},$$

$$\psi(0)=1,\quad \psi(1)=4/9,$$

$$K=\{(10\lambda^7 g^2T^2\rho^3)/(63Q^7\eta^2 D)\} \times\{(t_2-t_1)^9(t_2+t_1)/(3+r^2)^2(5-r^2)^2\}\varphi(r),$$

$$\varphi(r)=1-(692/825)r^2+(146/2475)r^4 +(4/75)r^6+(13/7425)r^8,$$

$$\varphi(0)=1,\quad \varphi(1)=(2044/7425),$$

$$K_d=\{(\lambda\rho D)/(2QT)\}(t_2^4-t_1^4).$$

In some cases the ratio (32) will be quite small, so that (23) gives essentially the total transport. For example, with fixed dimensions of apparatus this will be true provided the pressure is sufficiently high ($(\rho/D)\propto(\text{pressure})^2$). For the sake of simplicity we shall proceed with most of our considerations on the assumption that this condition $(K_d/K) \ll 1$, is satisfied. In cases where this is not true, it is only necessary to replace A in the following by

$$A_d = A/\{1+(K_d/K)\}. \tag{33}$$

III. Separation Factor and Speed of Operation

Discontinuous operation

We shall now apply the results we have just derived to the case of *discontinuous* operation, by which is meant that one waits until the upper reservoir has approached its equilibrium concentration, and then removes all of its contents, and starts over again. It is assumed that the reservoir is closed off from the tube during the removal of the gas; otherwise the mixing with gas drawn in from the tube would make it impossible to obtain the concentrations and amounts calculated here.

Our fundamental equation for these calculations is that for the total transport of species 1 up the tube. By (23) and (31) we have

$$\tau_1 = H\{c_1(1-c_1) - (2A)^{-1}(dc_1/dz)\}. \tag{34}$$

At the final equilibrium, when the concentration in the top reservoir has ceased to increase, $\tau_1 = 0$, and the solution of (34) is

$$c_1(z) = \tfrac{1}{2}\{1+\tanh A(z-z_0)\}, \tag{35}$$

where z_0 is determined by the condition that the total quantity of species 1 is conserved. If we set

$$c_1(-l) = c_1{}^0; \quad c_1(l) = \kappa_e, \tag{36}$$

we find for the equilibrium *separation factor:*

$$(\kappa_e/c_1{}^0)(1-c_1{}^0)/(1-\kappa_e) = e^{4Al}. \tag{37}$$

If κ_e is small with respect to unity, this becomes

$$(\kappa_e/c_1{}^0) \cong e^{4Al}. \tag{38}$$

When τ_1 is not zero, but has some constant value—that is, before the final equilibrium has been established—the solution of (34) is

$$c_1(z) = \tfrac{1}{2}\{1+q \tanh qA(z-z_0)\}, \tag{39}$$

where $\qquad q = (1-4\tau_1/H)^{\frac{1}{2}}.$

Under the boundary conditions $c_1(-l) = c_1{}^0$, $c_1(l) = c_1{}^1$ we have now

$$c_1{}^1 = \tfrac{1}{2} - (q/2)\{q \tanh 2qAl - q_0\}/ \\ \times\{q_0 \tanh 2qAl - q\}, \tag{40}$$

where $q_0 = 1-2c_1{}^0$.

In practice, it will be advantageous to make the lower reservoir sufficiently large that $c_1{}^0$ does not drop appreciably during the separation, since if it should drop, one would not realize all of the separation factor. If the reservoir is sufficiently large, then, $c_1{}^0$ is also the initial concentration of species 1. The constancy of $c_1{}^0$ may often be secured more conveniently by maintaining a continuous flow through the bottom reservoir. The quantity q_0 is then constant and equal to the initial value of q, and the equation for the time rate of change of $c_1{}^1$ is

$$(dc_1{}^1/dt) = \tau_1/m_t. \tag{41}$$

Let $t(\kappa_r)$ be the time for the concentration of the top reservoir to rise from its initial value $c_1{}^0$ to some required value κ_r. The integral of (41) may then be expressed as

$$t(\kappa_r) = m_t \int_{c_1{}^0}^{\kappa_r} dc_1{}^1/\tau_1. \tag{42}$$

The integral must be done numerically or graphically, by calculating $c_1{}^1$ from (40) for several values of τ_1.

In many cases, however, a close approximation can be used, which eliminates the necessity of numerical integration. We note that

$$c_1(1-c_1) \equiv c_1(1-2c_1{}') + (c_1{}')^2 - (c_1 - c_1{}')^2 \tag{43}$$

where $c_1{}'$ is arbitrary. If κ_r differs from $c_1{}^0$ by only a small amount, say not more than 0.2 or 0.3, one can select a value of $c_1{}'$ and a constant to replace the last term in (43) in such a way that the resulting linear expression is a good approximation to $c_1(1-c_1)$ throughout the range in question. If in (34) the quantity $c_1(1-c_1)$ is replaced by such a linear approximation, then (34) and (41) can be integrated explicitly, and the formula for $c_1{}^1$ so obtained represents a simple exponential approach to equilibrium, which can be characterized by a relaxation time. This gives us a useful way to describe the speed of operation for cases in which a linear approximation to (43) is valid. In the case that the range of c_1 is larger than about 0.3, the approach to equilibrium is of a more complicated type, which can not be characterized even approximately by a relaxation time.

A suitable value for c_1' is the mean value of c_1^0 and κ_r. In the present case, the constant value inserted in place of $(c_1-c_1')^2$ will not appear in the relaxation time; then by the procedure outlined, we find a relaxation time (time for $c_1^1-c_1^0$ to rise to $1-e^{-1}$ of its equilibrium value):

$$t_r=(m_t/H)\{e^{4Al(1-2c_1')}-1\}/(1-2c_1'). \quad (44)$$

There are several special cases of (44) worth mentioning: If c_1 is always small compared to unity,

$$t_r\cong(m_t/H)(e^{4Al}-1). \quad (45)$$

If the separation factor, which is e^{4Al} in this case, is much larger than one, we see that the relaxation time is directly proportional to the separation factor.

If, however, we are working in the middle region, where both c_1^0 and κ_e are approximately one-half,

$$t_r\cong 4Alm_t/H; \quad (46)$$

while if c_1 is always close to unity,

$$t_r\cong(m_t/H)(1-e^{-4Al}). \quad (47)$$

It may perhaps be possible in practice to reduce the equilibrium time to some extent by a suitable variation of the pressure during operation. From (30) and (31) we see that H and K vary, respectively, as the second and fourth powers of the pressure. According to (23) the transport of species 1 is determined essentially by H during the early part of the separation process, while $\partial c_1/\partial z$ is still small. Thus a high pressure at the beginning increases the transport. In order to reach a large concentration gradient finally, the pressure must be reduced again. By proper manipulation a considerable advantage might be obtained. Such a procedure, however, meets a considerable technical difficulty, since the volume of the upper reservoir would have to be varied along with the pressure in order to prevent the loss of a great deal of gas down the tube.

Continuous operation

So far we have been discussing operation with no total transport of gas through the tube. In such operation the concentrated material is obtained by waiting until the approach to equilibrium has reached a certain stage, and then removing the contents of the top reservoir. There is also available a continuous type of operation, in which a small steady flow of gas is removed from the top of the apparatus, so that there is a small total transport of gas along the tube.

The convection field with which we have been calculating, which is described by the function $G(T)$, provides no total transport along the tube. Because of the linearity of the hydrodynamical equation, however, we can superpose on the convection field an unidirectional velocity field corresponding to a very small additional pressure difference. Since the additional velocity field is unidirectional and c_1 varies only very slightly across the tube, we can omit all discussion of the details of the new field and the distribution of c_1 across the tube; we simply write for the transport of species 1 due to the new field the product of the mean value of c_1 at the given position along the tube and the total transport of gas. The *total* transport of species 1 is then

$$\begin{aligned}\tau_1'&=\tau_1+\tau c_1,\\&=Hc_1c_2-K(dc_1/dz)+\tau c_1,\end{aligned} \quad (48)$$

where τ_1' is now constant along the tube. The quantities H and K may still be taken as defined by (30) and (31), since, with attainable speeds of operation, the velocities in the superposed unidirectional field will in practice be extremely small.

As before we introduce $A=H/2K$, and as a convenient dimensionless parameter,

$$n=\tau/H. \quad (49)$$

We shall treat only the equilibrium case, where c_1^1 has a constant value, κ_r. There is little value in treating the approach to the new equilibrium, because the apparatus presumably would be operated with $\tau=0$ until c_1^1 rose to the value intended for continuous operation. Then we have $\tau_1'/\tau=\kappa_r$ and therefore

$$\tau_1'=nH\kappa_r. \quad (50)$$

The differential equation for c_1 is now

$$\{-c_1^2+(1+n)c_1-n\kappa_r\}^{-1}dc_1=2Adz, \quad (51)$$

whose solution is

$$c_1(z)=\tfrac{1}{2}\{1+n+q' \tanh q'A(z-z_0)\}, \quad (52)$$

where

$$q'=\{(1+n)^2-4n\kappa_r\}^{\frac{1}{2}}.$$

Eliminating z_0 by the condition $c_1(-l)=c_1^0$, $c_1(l)=\kappa_r$ we find

$$\tanh 2q'Al=q'(\kappa_r-c_1^0)\{(1-n)\kappa_r +(1+n)c_1^0-2\kappa_r c_1^0\}^{-1}. \quad (53)$$

This rather formidable equation gives the important relation between τ and κ_r. It must be solved in any given case by successive approximations. The procedure may usually be based on the assumption that n is small, since only for small values of n can a large separation factor be realized. If, for example, one replaces q' by unity in the left number, and by the linear approximation $1+n(1-2\kappa_r)$ in the right member, one obtains as a first approximation

$$n^{(1)}=\{(\kappa_r+c_1^0-2\kappa_r c_1^0) \tanh 2Al-(\kappa_r-c_1^0)\} \times(\kappa_r-c_1^0)^{-1}(1+\tanh 2Al-2\kappa_r)^{-1}. \quad (54)$$

The quantity q' can then be calculated with the value $n^{(1)}$ for n, and (53) can then be solved for the second approximation $n^{(2)}$, and so on. This particular procedure converges well if c_1^0 is small, but fails entirely if $c_1^0 \geqslant \frac{1}{2}$.

For cases in which the range of values of c_1 to be covered is small, one can simplify the analysis by replacing c_1c_2 in (48) by a linear expression in c_1, just as was done in obtaining Eqs. (44)–(47) for discontinuous operation. In the present case the resulting formula involves the parameters of the linear expression in a more complicated way than does (44). Simple formulas can be given, however, for each of the three special cases corresponding to (45)–(47). When c_1 remains fairly small throughout, we can replace c_1c_2 by c_1 in (48), and, remembering that n must be small, we obtain

$$(\kappa_r/c_1^0)\cong(e^{-4Al}+n)^{-1}. \quad (55)$$

For cases in which c_1 is throughout in a range of values of perhaps 0.3 to 0.7, we can replace c_1c_2 by $\frac{1}{4}$, and find

$$(\kappa_r-c_1^0)\cong(1-e^{-4nAl})/4n. \quad (56)$$

When $(1-c_1)$ remains fairly small, we can replace c_1c_2 by $1-c_1$ in (48), and obtain

$$(1-c_1^0)/(1-\kappa_r)\cong(e^{4Al(1-n)}-n)/(1-n). \quad (57)$$

These three formulas correspond precisely to (45), (46) and (47), respectively, and involve just the same linear approximations.

Continuous operation is the only practical method if we wish to use several stages in series, and the use of multi-stage apparatus seems distinctly desirable if we wish to combine a large separation factor with large speed of production. We have seen that if c_1^0 is small, the quantity $n=\tau/H$ must be small compared to unity. Therefore, in any stage, the transport is effectively limited by the quantity $Hc_1^0(1-c_1^0)$, where c_1^0 is the concentration at the bottom of the stage in question. If, now, c_1^0 is small, we see that in order to obtain a transport equal to that of a later stage, H must be larger for the first stage. A large H, however, means either a large K, and then the separation will be small, or a large B. A compromise would probably be used in practice.

The multi-stage apparatus should therefore consist of a series of vertical tubes; the first tube should be of large size and will produce a small change of concentration; subsequent tubes should be made progressively smaller.

Comparison of the two types of operation in single-stage apparatus

In the case of small c_1, formulas (45) and (55) make possible a simple direct comparison of the separations obtained by the two methods at a given effective speed, provided that $4Al$ is large enough so that e^{-4Al} can be neglected compared to unity. Eq. (55) can be written

$$(\kappa_r/c_1^0)\cong\{\theta/(1+\theta)\}e^{4Al}, \quad (58)$$

where

$$\theta=n^{-1}e^{-4Al}=(H/\tau)e^{-4Al} \quad (59)$$

is a parameter inversely proportional to the speed, and e^{4Al} is the equilibrium separation given by (38), which may also be obtained by setting $n=0$, or $\theta \rightarrow \infty$. In *discontinuous* operation the quantity which corresponds to τ is m_t/t_0, where t_0 is the time allowed for the separation to approach equilibrium before the reservoir is emptied. Then if we put

$$\theta' = Ht_0/(m_t e^{4Al}) \tag{59'}$$

equal values of θ and θ' correspond to equal effective speeds of production by the two methods. According to Eq. (45), the exponential approach to equilibrium now takes essentially the form

$$(\kappa_r/c_1{}^0) \cong (1-e^{-\theta'})e^{4Al}. \tag{60}$$

The expressions (58) and (60) show that at a given effective speed a greater fraction of the equilibrium separation ratio can be obtained by using discontinuous operation.

In the case of c_1 near one-half, we can introduce the parameters

$$\varphi = (4Aln)^{-1}; \qquad \varphi' = Ht_0/(4Alm_t), \tag{61}$$

equal values of which correspond to equal effective speeds. The equilibrium concentration difference, from (56) with $n=0$ is Al; and the realized concentration differences are, by (56) and (46),

$$(\kappa_r - c_1{}^0) \cong \varphi(1-e^{-1/\varphi})\cdot Al \tag{62}$$

for continuous operation, and

$$(\kappa_r - c_1{}^0) \cong (1-e^{-\varphi'})\cdot Al. \tag{63}$$

When less than a fraction $(1-e^{-1})$ of the equilibrium concentration difference is to be obtained, the continuous method works slightly better; otherwise, the discontinuous is better.

In the remaining case, c_1 nearly equal to one, it is not possible to introduce a single parameter characterizing the speed in such a way that a simple comparison of the two methods is possible. Rough computation from (47) and (57) shows that when large ratios $(1-c_1{}^0)/(1-\kappa_r)$ are required, continuous operation is decidedly faster.

General remarks on speed of operation

In the case of discontinuous operation, the quantity which characterizes the speed of operation in terms of the mass of the element with a given concentration, divided by the time required to produce it, is $m_t f/t_r$ where f is the fraction of the molecular weight contributed by the element in question. This characteristic quantity varies as Hf. In the continuous case, the corresponding quantity is τf, which, for a given concentration, also varies as Hf. Thus in either case the variation of the speed, s, is given by

$$s \propto Hf \propto (w^3\rho^2\alpha Bf/\eta)(\Delta T/T)^2. \tag{64}$$

Since Al must have a given value, and since $D \propto \eta/\rho$, we see from (31) that w must vary as

$$w \propto (\alpha l)^{\frac{1}{4}}(\eta/\rho)^{\frac{1}{2}}. \tag{65}$$

If we accept (3), α varies as f, and we have the significant relation

$$s \propto f^{2.75} l^{0.75}(\rho\eta)^{\frac{1}{2}} B(\Delta T/T)^2. \tag{66}$$

To get a large speed at the specified concentration, it is evident that one should choose as light a molecule as possible, because of the strong dependence on f. The factor B can be increased by using a larger tube, or several tubes in parallel. Since under ordinary conditions ρ is proportional to the pressure, the speed varies as the square root of the pressure and as the three-fourths power of the length, *provided* that $2w$, the difference of the radii, is readjusted for changes of pressure and length in accordance with (65).

It is assumed in the argument leading to (66) that the ratio K_d/K is very small compared with unity, since otherwise we should not be justified in using (31), and should use instead the modified value (33).

The power expended because of conduction is by (29)

$$P_c = 2lB(4.18Q) = 4.18\lambda lB\Delta T/w \tag{67}$$

in watts, and, by (65), is proportional to $l^{\frac{3}{4}}\rho^{\frac{1}{2}}B\Delta T$; the viscosity and heat conductivity are independent of the pressure. Thus so far as conduction is concerned, the speed and power are just proportional to one another, as long as a fixed concentration difference is demanded, and a fixed temperature difference is used. The advantage of a rather large ΔT is evident; but there is little use in going to extreme temperatures, since it is the ratio of ΔT to the *mean* temperature that is involved, and also since the radiation loss will be large if T_2 is made very high. The power consumption due to radiation between the walls is independent of w, and for nontransparent tubes is given by

$$P_r=2lB(1-R_1)(1-R_2)\times(1-R_1R_2)^{-1}\sigma(T_2^4-T_1^4), \quad (68)$$

where R_1 and R_2 are the average reflection coefficients of the walls of the tubes, and $\sigma=5.7\times10^{-12}$ watt/cm²-deg.⁴.

Effects of asymmetry; general constructional considerations

We shall here consider briefly the effect of asymmetry in the apparatus. Due to nonuniformity of heating or cooling of the tubes, it is possible that the temperature may vary around the tube. This will give rise to an additional convection, characterized by a slight upward flow at the hotter part of the annulus, and a corresponding downward flow at the colder part. For simplicity, we may suppose that the temperature field is still independent of z, but varies with the azimuthal angle, φ, in the simple manner:

$$T=f(r)+(\delta T/2)\cos\varphi. \quad (69)$$

One can then show that the essential effect is to introduce another contribution to the transport given by $-K_p dc_1/dz$, where

$$K_p/K=(315B^2/16\pi^2w^2)(\delta T/\Delta T)^2, \quad (70)$$

provided that $B\gg w$. Since K_p/K must be kept fairly small, Eq. (70) imposes rather strong conditions on the tolerable asymmetry of the temperature. In the apparatus to be discussed in the next section, K_p would become equal to K for $\delta T \leqq 5°$.

A lack of centering of the tubes would have a considerable direct effect on performance, because H and K depend on the third and seventh powers of w. The asymmetry in temperature brought about by the lack of centering would, if appreciable, be still more harmful. To minimize it, good conduction is essential. Thus metal tubes are to be preferred on several counts: for precision in construction, high conductivity, and large reflection coefficient to reduce radiation losses.

The importance of symmetry makes it evident that advantages in speed and concentration should be sought by increases in length rather than by the use of high pressures and small values of w. Also, both for accuracy of construction and because of the factor B^2 in (70), it is better to use several tubes in parallel rather than large tubes.

To avoid lack of symmetry in the temperature distribution, the water cooling must be efficient and the heating of the inner tube must be very uniform. Heating by condensation of a vapor rather than by resistance wire seems advisable.

IV. A NUMERICAL EXAMPLE: C^{13}

In order to illustrate the application of our formulas we shall apply them to the design of a single-stage apparatus for the concentration of C^{13}. Here we are concerned with the concentration of a *heavy* isotope at the *bottom* of the tube. Our equation for A and all our equations concerned with the speed of operation apply here with no change except the replacement of c_1 by c_2. A formal justification of this rule is provided by inspection of the fundamental equations (23) and (48). In these equations we must interchange c_1 and c_2; change the sign of the term in c_1c_2, since this term changes sign in rewriting (10) for species 2; and change the signs of the τ and τ_i' terms, because we are now concerned with transport *down* the tube. When this is done the equations are unchanged in form except for a change in sign of the term in $\partial/\partial z$. This is proper, since the concentration is now increasing downward instead of upward.

We take as the specifications of our apparatus: Length of tube, $2l=800$ cm; $B=2\pi\bar{r}=4\pi$; $T_1=300°K$; $T_2=600°K$; pressure, 1 atmosphere; and equilibrium concentration, $\kappa_e=0.30$. Since the carbon isotope of mass 13 occurs with a natural abundance[18] of one part in about 92, and therefore $c_1^0=0.0108$, it follows at once from (37) that we must have $e^{4Al}=39.3$, or $A=0.0023$/cm.

The required value of the difference in radii, $2w$, and the speed of operation are now determinate, once we have selected the molecule which is to carry the carbon.

Our general discussion of the speed shows

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[18] Vaughan, Williams and Tate, Phys. Rev. **46**, 327(A) (1934).

that one should use as light a molecule as possible (cf. Eq. (66)). Methane, CH_4, is therefore eminently suitable. Extrapolating to 450°K the data for CH_4 given in the *International Critical Tables*, we find

$$\begin{aligned} &\eta = 1.60\times 10^{-4}\text{ poise,}\\ &\rho = 0.433\times 10^{-3}\text{ g/cm}^3,\\ &D \cong 1.4\eta/\rho = 0.52\text{ cm}^2\text{/sec.,}\\ &\lambda = 1.20\times 10^{-4}\text{ cal./cm-sec.-deg.,}\end{aligned}\tag{71}$$

and by (3)

$$\alpha = 0.0106.$$

The conditions on the relaxation length l_r (Eq. (4)), and the Reynolds number (5) are strongly satisfied, as we shall verify after $2w$ has been evaluated. In the case under consideration, however, it is not true that $K_d/K \ll 1$, so that the effect of longitudinal diffusion cannot be ignored. Thus we must equate not A, but A_d to the value 0.0023/cm.

Putting the values (71) in (31) and (32), we find

$$A = (3.3\times 10^{-5})/w^4 \quad\text{and}\quad K_d/K = (5.1\times 10^{-4})/w^6.$$

Since A_d must have the value 0.0023, we have by (33),

$$w^6 - 1.45\times 10^{-2}w^2 + 5.1\times 10^{-4} = 0.$$

The larger of the two positive real roots gives the value $2w = 0.62$ cm. The ratio K_d/K is about 0.58, so that it certainly could not have been neglected.

In order to discuss the question of speed, we must know the value of H. We find by (30),

$$H = 2.3\times 10^{-5}\text{ g/sec.}$$

The range of c_1 in question, 0.01 to 0.30, is just within the range of validity of the linear approximation (44). If we wait a length of time of the order of the relaxation time, we shall reach a concentration in the bottom reservoir of only about 0.194. In this case, we are concerned only with the range 0.01 to 0.19, and a suitable value of c_1' is 0.10. If we suppose the bottom reservoir contains 5.0 grams of gas—or approximately 10^4 cc—the relaxation time given by (44) is

$$\begin{aligned} t_r &= [5.0/(2.3\times 10^{-5})]\times[(39.3)^{0.8}-1]/0.8\\ &= 4.9\times 10^6\text{ seconds} = 57\text{ days.}\end{aligned}$$

The speed of production by the discontinuous method is thus 88 mg/day of methane, or about 66 mg/day of carbon, with a concentration of 19 percent C^{13}.

A rough idea of the speed obtainable in continuous operation may be obtained from Eqs. (58) and (60). These formulae really apply only in the approximation $c_1' = 0$, but should be fairly reliable for purposes of comparison when a more accurate value has already been found for one method. The use of the time t_r between removals in discontinuous operation corresponds to $\theta' = 1$ in (60). Putting $\theta = 1$ in (58), we see that continuous operation at a speed of 88 mg of methane per day will give a concentration of roughly $\frac{1}{2}\kappa_e$, or about 15 percent C^{13}. To obtain an estimate of the speed at concentration 19 percent, we put

$$\theta/(\theta+1) = 1 - e^{-1}$$

and obtain $\theta = 1.72$. Since θ is inversely proportional to the speed, continuous operation will give roughly $88/1.72 = 51$ mg/day of methane at 19 percent C^{13}.

The speed of production at 19 percent C^{13} can be calculated exactly from (53). The estimated value just obtained corresponds to $\tau = 5.9\times 10^{-7}$ g/sec., or $n^{(1)} = \tau/H = 0.0259$. This can be used as a first approximation in solving (53). It gives $q' = 1.0161$, $\tanh 2q'Al = 0.95315$. The next approximation is now obtained by solving (53) for n as it occurs explicitly. The value obtained is $n^{(2)} = 0.0290$, and the value to which the approximations converge is $n = 0.0279$. This corresponds to a speed of 55 mg/day.

The power consumption due to conduction, by (66), is 2450 watts, while that due to radiation, by (67) would be 7000 watts if the tube walls were perfectly black ($R_1 = R_2 = 0$). If the walls were a polished metal, however, this value might well be cut down to less than 500 watts.

The Reynolds number, by (5), is of the order of 3. Since in the case of pure pressure flow through tubes or between plates this number must become of the order of several thousand before spontaneous turbulence occurs, it is difficult to believe that there could be any turbulence here.

By (4), the length of tube at each end in which the temperature gradient differs from that determined by conduction is of the order of 0.4 cm, and thus may certainly be neglected.

The calculations given above for C^{13} are based on the value $\alpha = 0.0106$ which is given by Eq. (3). This equation is, however, only a rough guess, albeit the best one possible. It may be found by experiment that the actual values of H and A for any given gas are distinctly different from those calculated from values of α given by (3), perhaps by as much as a factor 2. In practice, therefore, it will be necessary to do some preliminary work to find the actual value of α. It is suggested that this be done by running the apparatus at a fairly high pressure. For instance, in the example just discussed, the use of a pressure of two atmospheres instead of one will multiply H by 4, and divide A by approximately 4, so that the separation factor will be small, but so will also be the equilibrium time. If one now measures $c_1{}^1$ as a function of the time, one will obtain the values of both H and A. Either one will yield the value of α, by (30), or by (31), (32) and (33). We may now extrapolate A to the desired value by changing the pressure, since we know that H, A and K_d/K vary, respectively, as the second, inverse second, and inverse fourth power of the pressure.

Preliminary adjustments such as those just described will of course be necessary only in the first work on each gas. Once the correct value of α is known from experiment, our equations should make it possible to design apparatus which will perform in acceptable agreement with specifications.

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Calculation of the Second Virial Coefficient of Helium Gas for the Lowest Measured Temperature

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IN RECENT articles[1] an explicit and calculable expression has been derived for the second virial coefficient of a monatomic gas. This is the B in the equation of state,

$$pV/RT = (1 + B(T)/V + C(T)/V^2 + \cdots)$$

and, assuming the Einstein-Bose statistics, is given by the formula,

$$\begin{aligned} B_{\text{E.B.}} = -\frac{N\pi^{\frac{3}{2}}\lambda^3}{2} - 16N\pi^{\frac{3}{2}}\lambda^3 \sum_{n,\ \text{even}\ l} (l+\tfrac{1}{2}) \\ \times \exp\left[\lambda^2 k_0{}^2(n, l)/a_0{}^2\right] \\ -16\pi^{\frac{1}{2}} N\lambda^3 \sum_{\text{even}\ l} (l+\tfrac{1}{2}) \int_0^\infty dk_0 \\ \times \exp\left[-\lambda^2 k_0{}^2/a_0{}^2\right](d\eta_l/dk_0). \quad (1) \end{aligned}$$

Here, $\lambda^2 = \hbar^2/mkT$, η_l is the phase found from the wave equation for the relative motion of two radially interacting molecules,

$$\frac{d^2v}{d\rho^2} + \left(k_0{}^2 - \frac{m}{\hbar^2} a_0{}^2 V - \frac{l(l+1)}{\rho^2}\right) v = 0.$$

$k_0{}^2(\eta, l)$ are the discrete states for two such molecules, a_0 is the Bohr radius, and V is the interaction potential between the two molecules.

Extensive calculations have recently been made with formula (1) by Massey and Buckingham[2] on the inert gases, in particular, helium. These calculations are based on the use of the Slater-Kirkwood potential for the calculation of

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[1] E. Beth and G. E. Uhlenbeck, Physica **4**, 915 (1937); L. Gropper, Phys. Rev. **51**, 1108 (1937).

[2] H. S. W. Massey, and R. A. Buckingham, Proc. Roy. Soc. **168**, 378 (1938).