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The Separation of Isotopes by Thermal Diffusion†

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THERE are three main topics connected with the subject of this article: First, the fundamental theory of thermal diffusion itself; second, the phenomenological theory of the functioning of apparatus; and third, the discussion of experiments. The fundamental theory is still in need of much further detailed development; its foundations are well summarized in the recent book of Chapman and Cowling (C5). A general description of the effect is contained in Part I, together with an account of the predictions of the theory as they appear when specialized to the case of isotopic mixtures. The phenomenological theory of the functioning of apparatus is the main theme of this paper. It occupies Parts II and III, and its applications take up an important fraction of Part IV. Some discussion of experiments is also included in Part IV. An exhaustive account of the experimental material is not attempted, because the number of experiments which have been described in detail is so far not very large, and much of the existing experimental information is summarized in the long paper of Clusius and Dickel (C10).

A considerable part of the material on the theory of the functioning of apparatus is new. The derivation of the transport equation is one which has not been published previously, and places the emphasis on an understanding of the physical processes involved rather than on mathematical exactness. The most important new contribution is the complete analysis of the principles needed for the design and operation of efficient multi-stage (series-parallel) apparatus. This analysis should also be capable of application to any other separation processes for which the equations of transport have forms analogous to that used here.

The main limitation of the present treatment is its restriction to mixtures of two components only. Where additional components are present in extremely small amounts, the present results will very often be applicable; but there are undoubtedly many cases whose adequate discussion would require a general theory of the separation of many-component mixtures.

TABLE OF NOTATION

A number of symbols which occur only locally in short series of equations, and are suitably defined when used, are not included in this table. Most of the symbols listed are defined more fully at the point where they are introduced in the text.

$A = H/2K$.
$a = w^6 K_d / K_c$.
$B =$ mean circumference $= \pi(r_1 + r_2)$.
$c =$ either c_1 or c_2 (cf. remarks at beginning of Part III).
$\breve{c} = 1 - c$.
$c_1 =$ fractional molar concentration of the lighter isotope.
$c_2 =$ fractional molar concentration of the heavier isotope; $c_1 + c_2 = 1$.

$c_i = c_{z=0}$ = initial value of c.
$c_f = c_{z=L}$ = final value of c.
c_s = value of c in material rejected by scrubber.
c_{Nf} = final value of c in the Nth and last stage.
c_p = specific heat at constant pressure, per unit mass.
c_v = specific heat at constant volume, per unit mass.
C = Sutherland constant.
C_v = specific heat at constant volume, per mole.
D = coefficient of self-diffusion.
D_T = coefficient of thermal diffusion.
D_{12} = coefficient of ordinary diffusion.
$f(\nu)$ = cf. Eq. (12).
g = acceleration of gravity.
$G(T)$ = cf. Eqs. (61) and (98).
H = transport coefficient, cf. Eqs. (53)–(111).
H_I = value of H for a single column (cf. Eq. (286)).
H_p = cf. Eq. (136).
$\mathbf{J}_1 = \rho c_1 \mathbf{v}_1$ = flux of species 1, mass per unit area per unit time.
$\mathbf{J}_2 = \rho c_2 \mathbf{v}_2$ = flux of species 2.
$K = K_c + K_d + K_p$.
K_I = value of K for a single column (cf. Eq. (287)).
K_c, K_d, K_p = transport coefficients, cf. Eqs. (53)–(141).
l_r = relaxation length, cf. Eqs. (121)–(123).
L = length of column, $0 \leqslant z \leqslant L$.
$\mathcal{L}$ = total height of a multi-stage apparatus.
m = mass of gas in the positive reservoir.
m_+ = mass of gas in the positive reservoir.
m_- = mass of gas in the negative reservoir.
m_1 = mass of a molecule of species 1.
m_2 = mass of a molecule of species 2, $m_2 > m_1$.
M = molecular weight.
$\mathfrak{M}$ = the mass of isotope which must be transported into an apparatus to secure the operating condition.
$n = \sigma/H, \ = m/tH$.
n_b = most efficient value of n.
N = number of stages in a multi-stage apparatus.
$n_I = \sigma/H_I$.
$\mathfrak{N}$ = number of tubes in parallel in a given stage of a multi-stage apparatus.
$p = 1/q$ = reciprocal of separation factor.
$p_e = 1/q_e = e^{-2AL}$ = reciprocal of equilibrium separation factor.
P = pressure.
q = separation factor, cf. Eqs. (28) and (151).
$q_e = e^{2AL}$ = equilibrium separation factor.
Q = conductive heat flow, quantity per unit area per unit time.
$2\pi Q_1$ = conductive heat flow per unit length of tube, quantity per unit length per unit time.
r = radial coordinate, $r_2 \leqslant r \leqslant r_1$.
r_1 = radius of outer tube.
r_2 = radius of inner tube or of the hot wire.
R = Reynolds number, cf. Eq. (118).
R = reflection coefficient.
R = gas constant per mole.
R_T = ratio of actual value of α to the value (9) it would have for hard spherical molecules.
t = time.
t_b = most efficient value of the time t.
t_c = characteristic time for the approach to an operating condition.
t_r = relaxation time for the approach to equilibrium.
t = a reduced temperature, useful in discussing the extreme cylindrical case, and defined by Eq. (112).
t_1 = reduced temperature corresponding to T_1.
t_2 = reduced temperature corresponding to T_2.
T = absolute temperature.
T_1 = temperature of cold wall, or of the outer tube.
T_2 = temperature of hot wall, of the inner tube or of the hot wire, $T_2 > T_1$.
$\bar{T} = \frac{1}{2}(T_1 + T_2)$.
$\Delta T = T_2 - T_1$.
$u = (T_2 - T_1)/(T_2 + T_1) = \Delta T / 2\bar{T}$.
$\mathbf{v}$ = convection velocity of the gas as a whole $= c_1\mathbf{v}_1 + c_2\mathbf{v}_2$.
$\mathbf{v}_1$ = convection velocity of the molecules of species 1.
$\mathbf{v}_2$ = convection velocity of the molecules of species 2.
$w = \frac{1}{2}(r_1 - r_2)$ = one-half of the distance between the hot and cold walls, $-w \leqslant x \leqslant w$.
x = coordinate perpendicular to the walls, $-w \leqslant x \leqslant w$.
y = coordinate running around the mean circumference of the tube, $0 \leqslant y \leqslant B$ (used only in Part II).
$y = 2AL = HL/K$ (used in Parts III and IV).
y_b = most efficient value of $y = 2AL$.
z = coordinate along the column, $0 \leqslant z \leqslant L$.
α = thermal diffusion constant.
γ = stepping ratio (cf. Eq. (305)).
γ_n = roots of a transcendental equation (172).
$\Delta = c_f - c_i$.
η = viscosity.
Θ = cost per unit length of column.
λ = heat conductivity.
Λ = total length of tubing in a multi-stage apparatus.
Λ_s = total length of tubing in a scrubber.
μ = mass of gas per unit length of column.
ν = force index, (cf. Eq. (10)).
ξ = cf. Eqs. (214) and (215).
ρ = density, mass per unit volume.
σ = flow of gas through the column or stage in continuous operation, mass per unit time.
σ_s = continuous flow of gas through the scrubber.
τ = either τ_1 or τ_2 (cf. remarks at beginning of Part III).
τ_1 = transport of species 1 along the column, mass per unit time.
τ_2 = transport of species 2 along the column.
$\phi(u)$ = cf. Eqs. (79) and (84).

All quantities are in c.g.s. units, except that in practical calculations of heat flow the calorie is the unit of energy.

The subscript k on any of the quantities indicates that they refer to the kth stage of a multi-stage apparatus.

PART I. THERMAL DIFFUSION

Definition

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. Provided that 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 re-mixing effect of ordinary diffusion. Although the existence of thermal diffusion was not discovered until 1911, and was not demonstrated experimentally until 1917, a manifestation of thermal diffusion has been known since 1857—namely, the Thomson thermoelectric effect, which consists in a diffusion of the electron gas caused by the temperature gradient in the metal. The Thomson effect represents a very special case of thermal diffusion, however, and will not be treated further in this paper.

The equation of ordinary diffusion is

$$c_1(\mathbf{v}_1-\mathbf{v})=c_1c_2(\mathbf{v}_1-\mathbf{v}_2)=-D_{12}\,\mathrm{grad}\,c_1. \quad (1)$$

The existence of thermal diffusion makes it necessary to add another term to (1), so that it becomes

$$c_1(\mathbf{v}_1-\mathbf{v})=-D_{12}\,\mathrm{grad}\,c_1+(D_T/T)\,\mathrm{grad}\,T, \quad (2)$$

where D_T is the *coefficient of thermal diffusion.* Unlike the coefficient of ordinary diffusion, which to a first approximation is independent of the concentrations c_1 and c_2, the coefficient of thermal diffusion is proportional to the product c_1c_2. We are therefore led to introduce another quantity, the *thermal diffusion constant* α, which is related to D_T by

$$D_T=D_{12}c_1c_2\alpha. \quad (3)$$

The constant α is independent of the pressure. In the case of isotopes, it is to a first approximation independent of the relative concentrations. For certain particularly simple molecular models, α is independent of the temperature, but experiment and more general molecular models indicate that it does depend on the temperature.

Another quantity found in the literature is the *thermal diffusion ratio:*

$$k_T=D_T/D_{12}=\alpha c_1c_2. \quad (4)$$

It might at first be thought that the fact that D_T is proportional to c_1c_2 would drastically limit the effectiveness of thermal diffusion in concentrating isotopes with a small initial concentration. As will be seen in Part III, however, this form of the thermal diffusion term in (2) actually has the effect of making the logarithm of the separation factor proportional to the number of stages or the length of a separation column (Eqs. (147), (150) below). The problems of obtaining desired separation factors and yields are accordingly found to be of just the same type as those encountered in the various other methods of separating isotopes by progressive concentration.

History

The coefficient of thermal diffusion vanishes identically for Maxwellian molecules—that is, for point molecules which repel one another with a force which falls off as the inverse fifth power of the distance between them. It is perhaps for this reason that thermal diffusion was completely overlooked by the classical workers in kinetic theory. The phenomenon of thermal diffusion was discovered theoretically by Enskog (E1)* in 1911; and in 1912 he gave the exact value of its coefficient for a special case (E2, p. 750).

The theory of thermal diffusion appears as a by-product of any sufficiently complete and rigorous kinetic theory of the phenomena characteristic of a mixture of two or more gases. The great mathematical difficulties of such a theory were not surmounted by the classical workers in kinetic theory, and for our present detailed theory of gases we are indebted to two modern workers, Chapman and Enskog, whose work culminated in the second decade of this century. The work of these two men was done quite independently.

In 1917 Enskog (E3) published as his doctoral dissertation an elegant and rigorous derivation of the various gas coefficients, including that of thermal diffusion. The development was based on Boltzmann's integral equation for the velocity distribution function. The results obtained were expressed in terms of general integrals, however, and the reduction of the formulae to a usable form was sketched only briefly, although the results of the reduction were presented. The

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* References in parentheses are placed at the end of the article.

detailed presentation of the reduction was contained in a later article (E4).

In 1916 Chapman published a treatment (C1) of simple gases which was based on a general equation of transport. The method was more intuitive and less rigorous than Enskog's, but was equally effective. This treatment was followed in 1917 by an extension of the theory to a mixture of two gases (C2). Unfortunately, as was later pointed out by Enskog (E4, pp. 58–60), Chapman's treatment of a mixture of two gases contained algebraic and numerical errors in the working out of the important special case of the inverse power model (including the case of elastic spheres). These errors affected the coefficient of thermal diffusion, although the error was not serious as regards order of magnitude. The errors were corrected by Enskog (E4), and the results of Chapman were then found to agree with his own. The corrected results were later published by Chapman and Hainsworth (C3), and by Chapman (C4).

Although, as we have remarked, the existence of thermal diffusion was first demonstrated by Enskog in 1911 and 1912, the mention of it was so casual and brief that the existence of thermal diffusion remained essentially unknown until the appearance of Chapman's memoir in 1917 and until the experimental demonstration of its existence by Chapman and Dootson (C6) in 1917. Furthermore, the theory of thermal diffusion is much more fully developed from the physical point of view in Chapman's 1917 memoir than it is in Enskog's dissertation. For these reasons, it seems proper that the credit for the discovery and development of thermal diffusion should be shared equally by Chapman and Enskog.

There was no great progress in the development of the general theory of gaseous mixtures between 1917 and 1939, in which year the work of Enskog was generalized by Hellund and Uehling (H1) to include the effect of the quantum statistics. This generalization closely parallels the presentation in Enskog's dissertation, and is written in Enskog's notation. In the following year, the treatment of Hellund and Uehling was further generalized by Hellund (H2) to include the case of a mixture of more than two gases.

This discussion of the history of thermal diffusion is necessarily brief and sketchy. A much fuller account of the development of the kinetic theory of gases in general is contained in the book by Chapman and Cowling (C5, pp. 380–390).

A careful and detailed presentation of Enskog's general theory is contained in a recent book by Chapman and Cowling (C5). The reduction of the general expressions, however, is accomplished by a method different from that used by Enskog, although Enskog's method of integration is given in an appendix. The general reader will find this book easier reading than Enskog's dissertation, which is very abstract and difficult to read. On the other hand, the periodical literature will probably continue to utilize Enskog's notation because it is more concise and because so much of the literature is already written in this notation.

Qualitative Remarks

To a far greater extent than is the case with the three elementary gas coefficients, the coefficient of thermal diffusion is sensitive to the type of interaction between the molecules forming the gas. It has already been remarked that the coefficient is zero for a Maxwellian gas. For a composite gas whose molecules all repel one another with a force which varies as the inverse νth power of the distance, the constant α is positive for $\nu > 5$, whereas it is negative for $\nu < 5$. This statement depends upon the convention that the subscript 1 refers to the lighter molecules, and the subscript 2 to the heavier molecules; this convention will be used throughout this article. If the molecules behave as elastic spheres, both the ratio of the radii and the ratio of the masses of the two types of molecules are important in determining the value and the sign of α The lighter particles will in general become more concentrated in the hotter part of the gas ($\alpha > 0$), but if the masses are nearly equal, the relative size of the molecules may be more important, in which case the smaller molecules will become more concentrated in the hotter region ($\alpha > 0$ if the subscript 1 refers to the smaller molecules).

The fact that the value of the thermal diffusion coefficient depends so critically on the nature of the intermolecular forces means that the illuminating free-path arguments of elementary kinetic theory are quite inadequate for the treatment of thermal diffusion. Chapman (C4, pp. 1–3) has dwelt on the difficulties which beset any attempt to explain the effect on elementary grounds. Recently, however, Frankel (F2) has been able to derive by an elementary dimensional argument the most interesting features of the result for molecules which repel one another with a force which varies as the inverse νth power of the distance of separation. Frankel's argument shows that α must be zero for $\nu=5$, that it must be positive for ν greater than 5, and negative for ν less than 5. His argument runs as follows.

Thermal diffusion tends to establish a partial pressure gradient of the lighter constituent which is parallel or anti-parallel to the temperature gradient. In order to support such a partial pressure gradient, there must be a constant force on the lighter particles which restrains them from diffusing back toward the colder (or warmer) part of the enclosure. Such a force can come only from collisions between molecules of species 1 (the lighter molecules) and those of species 2; there must be a steady transfer of momentum from particles of one species to those of another. The transfer of momentum from species 2 to species 1 is proportional to

$$\langle(\mathbf{p}_2-\mathbf{p}_1)V\sigma\rangle_{\text{Av}}, \qquad (5)$$

where V is the relative velocity of two molecules, one of each species, the $\mathbf{p}$'s are the momenta of the molecules before the collision, and the average is to be taken over the velocity distributions of the two species of molecules. The quantity σ is the cross section for momentum transfer between molecules of the two species. Now in the case in which the molecules interact according to a law of the type $F=\kappa/r^\nu$, there is only one quantity with the dimensions of a cross section which may be obtained from the relative velocity V, the reduced mass μ of the collision, and the force constant κ—namely, $(\kappa/\mu V^2)^{2/(\nu-1)}$. Putting this expression for σ in (5), we find that the momentum transfer is proportional to

$$\langle(\mathbf{p}_2-\mathbf{p}_1)V^{(\nu-5)/(\nu-1)}\rangle_{\text{Av}}. \qquad (6)$$

For $\nu=5$, this expression reduces to the difference of the average velocities of the two species considered separately. Since we are considering the equilibrium case, these average velocities are both zero, and thus for $\nu=5$ the transfer of momentum is zero, and thermal diffusion cannot exist.

When ν is greater than 5, it is clear that collisions of high relative velocity are more important in contributing to the average (6). All of the molecules which are coming from the warmer part of the gas have, on the average, a higher velocity than those coming from the colder part, but the increase is greater for the lighter molecules than for the heavier ones. Thus the collisions of highest relative velocity are predominantly those in which the lighter molecule is coming from the hotter region, and the heavier from the colder region. Thus the average momentum transfer from species 2 to species 1 is directed toward the warmer part of the gas; this means that α is positive.

For ν less than 5, we find by exactly similar considerations that α is negative.

The weakness of Frankel's argument is that it cannot take into consideration the details of the asymmetry of the velocity distribution function itself. In the theory of Enskog, the vanishing of α for $\nu=5$ occurs because the expression for α is proportional to, among other quantities, the integral

$$\int_0^\infty \exp(-\gamma^2)\gamma^{-4/(\nu-1)}(2\gamma^7-5\gamma^5)d\gamma, \qquad (7)$$

where γ is a quantity proportional to the relative velocity V. It is difficult to see the relation between this integral and the average (6).

For the majority of gaseous mixtures which are not merely isotopic mixtures, the value of the constant α lies between 0.2 and 0.02. Larger values are occasionally obtained when the ratio of masses of the two constituents is large—for example, with mixtures of hydrogen and nitrogen, or helium and radon. A review of the experimental literature is given by Ibbs (I1), and a list of references by Chapman and Cowling (C5, p. 258). Since we are here concerned primarily with isotopes, we shall from this point on restrict ourselves to the case of isotopic mixtures.

Thermal Diffusion of Isotopes

Chapman (C7) was the first to suggest the use of thermal diffusion for separating isotopes. Before Clusius and Dickel (C9) devised their method for greatly enhancing its effect, however, thermal diffusion had no advantage over other methods of isotope separation, as was shown by Mulliken (M1).

The general theory of Enskog is developed on the assumption that the force fields of the molecules are spherically symmetrical. He finds general expressions for quantities which he indicates by μ, λ, κ, and ν. The quantities μ and λ are the ordinary coefficients of viscosity and thermal conductivity; κ is simply related to the coefficient of diffusion, and ν is related to the thermal diffusion constant α by

$$\nu = -nk\alpha c_1 c_2, \tag{8}$$

where k is the gas constant per molecule, and n is the number of molecules per unit volume.

The general expressions for these quantities involve ratios of infinite determinants, the elements of which are integrals over the velocity spaces of the two types of particles. Only the first approximation to ν has been worked out up to the present time.

The theory of the thermal diffusion constant is somewhat simpler for a mixture of two isotopes than it is for a mixture of two dissimilar molecules. This simplification occurs because the intermolecular forces are determined entirely by the electronic configurations of the atoms or molecules. If we are willing to disregard the quantum-mechanical distinction between identical and non-identical particles, we may consider an isotopic mixture as a mixture of two species of particles which are identical except for the fact that the particles of species 2 are slightly heavier than those of species 1. It is then possible to develop the general expression for α which is is given by Enskog (E3) and by Chapman and Cowling (C5) in ascending powers of $(m_2-m_1)/(m_2+m_1)$. Only the first term of this expansion is important for most pairs of isotopes.

It was first shown by Furry, Jones, and Onsager (F1) that for molecules which behave as elastic spheres, this procedure leads to

ELASTIC SPHERES

$$\alpha = \frac{105}{118} \cdot \frac{m_2-m_1}{m_2+m_1}. \tag{9}$$

It was later shown by Jones and Furry (J1) that for molecules which repel one another with a force which varies as the inverse νth power of the distance, the first term of this expansion is

FORCE $\propto R^{-\nu}$

$$\alpha = \frac{105}{118} \cdot \frac{m_2-m_1}{m_2+m_1} \cdot \frac{\nu-5}{\nu-1} \cdot C(\nu). \tag{10}$$

In this expression, $C(\nu)$ is given by the relation

$$C(\nu) = \frac{59}{21} \frac{(15/f)+6}{43+16\{f-1/(\nu-1)+1/(\nu-1)^2\}}, \tag{11}$$

where $f(\nu)$ is defined by

$$f(\nu) = \{1-2/[3(\nu-1)]\} A_2^{(\nu)}/A_1^{(\nu)}, \tag{12}$$

and where $A_1^{(\nu)}$ and $A_2^{(\nu)}$ are certain cross-section integrals which must be evaluated by numerical integration for each value of ν. Chapman (C8) has evaluated these integrals for $\nu = 3$, 5, 7, 9, 11, 15, and ∞. The quantities $A_1^{(\nu)}$, $A_2^{(\nu)}$, $f(\nu)$, and $C(\nu)$ are tabulated in Table I.* The quantity $6/5 \cdot f(\nu)$ is also tabulated because, as we shall see shortly, it is useful in connection with the coefficient of self-diffusion. It will be noted that (10) reduces to (9) for $\nu = \infty$, and that (10)

Table I. Quantities for the inverse power model.

ν	$A_1^{(\nu)}$	$A_2^{(\nu)}$	$f(\nu)$	$6f(\nu)/5$	$C(\nu)$
3	0.796	1.584	1.327	1.592	0.807
4				1.575	0.809
5	0.4220	0.6541	1.2918	1.5501	0.8156
6				1.514	0.828
7	0.3855	0.5349	1.2335	1.4802	0.8431
8				1.454	0.854
9	0.3808	0.4956	1.1930	1.4316	0.8648
10				1.412	0.874
11	0.3835	0.4778	1.1631	1.3957	0.8823
12				1.382	0.890
13				1.370	0.896
14				1.359	0.901
15	0.3931	0.4642	1.1248	1.3498	0.9064
∞	0.5000	0.5000	1.0000	1.2000	1.0000

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* This table differs from a similar table in (J2) in that the entries for $\nu = 3$ have been modified in accordance with a redetermination of $A_1^{(3)}$ and $A_2^{(3)}$ by Chapman, Proc. Roy. Soc. **A177**, 38–62 (1940).

TABLE II. R_T as a function of n according to the inverse power model.

n	$\nu=\frac{2n+3}{2n-1}$	$R_T= 2(1-n)C(\nu)$	n	$\nu=\frac{2n+3}{2n-1}$	$R_T= 2(1-n)C(\nu)$
1.1	4.33	−0.159	0.85	6.71	0.252
1.075	4.48	−0.120	0.8	7.67	0.340
1.05	4.65	−0.081	0.75	9	0.432
1.025	4.81	−0.040	0.7	11	0.529
1.0	5	zero	0.675	12.42	0.580
0.975	5.21	0.041	0.65	14.32	0.632
0.950	5.44	0.082	0.6	21	0.74
0.925	5.71	0.124	0.55	41	0.86
0.9	6	0.166	0.5	∞	1.000

changes sign at $\nu=5$. Very few non-ionized gases correspond to values of ν less than 5, however, so that we may expect α to be positive in almost all cases of isotopic mixtures.

Estimation of α from Viscosity Data

Equation (10) is very useful, because it is possible to obtain an estimate of ν from the equation of state of the gas, or from the temperature variation of the elementary gas coefficients. It was first shown by Lord Rayleigh (R1) that the relation between the temperature variation of viscosity and the force index ν could be obtained by a simple dimensional argument. He found in this manner that the coefficient of viscosity should vary as T^n, where n is related to ν by

$$\nu=(2n+3)/(2n-1). \tag{13}$$

This result is confirmed by the precise theories of Chapman and Enskog.

The substitution of (13) in (10) yields α as a function of n. The inverse power model thus gives us a means of predicting α from the observed temperature variation of viscosity. Instead of talking about α, however, it is simpler to talk about R_T, where R_T is the ratio of α as predicted or as found experimentally, to the value of α which is predicted by the theory for a gas consisting of hard spheres. From (9) and (10), we have

$$R_T=\frac{\nu-5}{\nu-1}C(\nu), \tag{14}$$

and then from (13),

$$R_T=2(1-n)C\left(\frac{2n+3}{2n-1}\right). \tag{15}$$

Now, since nearly all gases correspond to values of ν between 3 and 15, and since $C(\nu)$ varies between 0.8 and 0.9 for this range of ν, we have rather closely the simple approximate relation

$$R_T \cong 1.7(1-n). \tag{16}$$

The more precise relation (15) is tabulated in Table II.

By using the values of n which have been determined experimentally by Trautz and his co-workers, Brown (B1) has given in this manner an estimate of R_T for a number of gases. Brown's table, with rather extensive changes and additions, is reproduced as Table III. Caution should be observed in the use of this table, however, particularly in those cases where very small values of R_T are predicted. These very small values are due to the heavy cancellation which occurs in the general expression for values of ν near 5. The actual force law, however, is now believed to depart considerably from a simple inverse power repulsion; for the inert gases it is thought to be an inverse 7th power *attraction* at large distances, and an exponential repulsion at short distances; see Fowler and Guggenheim (F3, pp. 278–295). The cancellation required for very small values of R_T will probably not occur, therefore, and we may expect that Table III is unduly pessimistic in some of its predictions.

A formula corresponding to (9) was given by Chapman (C7) in 1919. This formula

WRONG

$$\alpha=\frac{17}{3}\frac{m_2-m_1}{m_2+m_1}\cdot\frac{1}{9.15-8.25c_1c_2} \tag{17}$$

was derived on the basis of his theory, which, as we have already remarked, was afflicted with algebraic errors. The writers have been surprised to find this incorrect formula still being quoted; it is given by Clusius and Dickel (C10) as being an alternative formula to (9), and it is the only formula given by Walcher (W1) in his review article on isotope separation. We should like to stress, therefore, that (17) is clearly wrong, and cannot be justified on any ground whatever.

The Coefficient of Self-Diffusion

The inverse power model is also useful in another connection. In Part II, where we develop the theory of the separation column, we shall find that the coefficient of diffusion of the one isotope into the other enters importantly into the results. This coefficient is not known experimentally, but it is clear that the coefficient must be nearly equal to the coefficient of self-diffusion of either isotope separately. It follows by simple division of the formulae given for D and η by Enskog (E3, pp. 94 and 102) and Chapman and Cowling (C5, pp. 218 and 245) for the inverse power model that

$$D=6f(\nu)\eta/5\rho, \qquad (18)$$

where $f(\nu)$ is the function defined by (12) and tabulated in Table I. The coefficient of self-diffusion may thus be determined fairly accurately from a knowledge of the coefficient of viscosity and its temperature variation, or from the coefficient of viscosity and some other means of estimating ν.

Temperature Dependence of α; Molecular Models

It will be noted that (9) and (10) indicate that α is independent of the temperature and pressure. The independence of temperature is due to the over-simplification of the inverse power model, and is not confirmed by experiment. The independence of pressure, however, is a general result of the theory, and may be expected to

TABLE III. Values for various gases of n, of R_T according to the inverse power model, and of the Sutherland constant C.

Gas	Reference	T°K	n	$R_T(n)$	C
A	*a*	221	0.89	0.18	138
		333	0.80	0.34	147
		423	0.76	0.41	142
		498	0.71	0.51	150
		979	0.62	0.70	140
He	*a*	48	0.644	0.64	6
		123	0.646	0.64	21
		210	0.652	0.63	37
		333	0.669	0.59	66
		423	0.667	0.59	83
		1022	0.645	0.64	173
Ne	*a*	244	0.668	0.59	34
		333	0.657	0.62	61
		423	0.644	0.64	70
		498	0.644	0.64	82
		1030	0.623	0.69	128
Xe	*b*	347	0.92	0.13	250
		425	0.91	0.15	303
		525	0.83	0.29	254
Br_2	*c*	330	0.833	0.28	162
		475	0.985	0.02	496
Cl_2	*c*	293–523	~1.0	~0	~400
I_2	*c*	420	0.92	0.13	301
		482	1.04	−0.06	590
HCl	*a*	293–523	~1.0	~0	~350
HI	*c*	294–524	~1.0	~0	~400
O_2	*d*	333	0.775	0.38	126
		398	0.735	0.46	122
		448	0.731	0.47	132
		498	0.655	0.62	91
H_2	*d*	333	0.666	0.60	66
		398	0.694	0.54	96
		448	0.667	0.60	90
		498	0.679	0.57	108
N_2	*d*	333	0.737	0.46	102
		398	0.713	0.50	107
		448	0.687	0.55	103
		498	0.645	0.64	85
NH_3	*d*	291–573	~1.0	~0	~550
NO	*g*	308	0.79	0.36	128
		498	0.64	0.66	121
N_2O	*f*	325	0.97	0.05	277
		349–551	~0.87	~0.22	~255
CH_4	*e*	308	0.860	0.23	174
		348	0.825	0.30	168
		398	0.795	0.35	166
		448	0.769	0.40	165
		498	0.728	0.48	146
C_2H_6	*e*	308	0.958	0.07	260
		498	0.801	0.34	213
C_3H_8	*e*	308	0.965	0.06	267
		498	0.830	0.29	244
CO_2	*f*	325	0.92	0.13	240
		525	0.85	0.25	281
CO	*h*	347	0.72	0.49	96
		450	0.69	0.55	103
		525	0.63	0.68	98
SO_2	*i*	287–472	~1	~0	~425

a M. Trautz and H. Binkele, Ann. d. Physik **5**, 561 (1930).
b M. Trautz and R. Heberling, Ann. d. Physik **20**, 118 (1934).
c M. Trautz and H. Winterkorn, Ann. d. Physik **10**, 511 (1931).
d M. Trautz and R. Heberling, Ann. d. Physik **10**, 155 (1931).
e M. Trautz and K. Sorg, Ann. d. Physik **10**, 81 (1931).
f M. Trautz and F. Kurtz, Ann. d. Physik **9**, 981 (1931).
g M. Trautz and E. Gabriel, Ann. d. Physik **11**, 606 (1931).
h M. Trautz and A. Melster, Ann. d. Physik **7**, 409 (1930).
i M. Trautz and W. Weizel, Ann. d. Physik **78**, 305 (1925).

TABLE IV. Values of α determined experimentally by Nier.

Species 1	Species 2	Temp. range	α	R_T
$C^{12}H_4$	$C^{13}H_4$	296°–728°K	0.0080±~5%	0.30
		296°–573°K	0.0074±~5%	0.27
Ne^{20}	Ne^{22}	283°–617°K	0.0302± 2%	0.71
		90°–294°K	0.0188± 2%	0.44
		90°–195°K	0.0165± 8%	0.39

hold to the same high degree that the coefficient of viscosity is independent of the pressure. Nier (N1 and N2) has pointed out that we may expect α to increase with temperature because as the molecules penetrate closer to one another, the effective hardness of the molecules will increase. This tendency is evident in the viscosity data presented in Table III, where n usually decreases and R_T increases as the temperature rises. Nier (N2) has found that in the temperature range 140° to 450°K, the constant α for neon varies approximately as the square root of the absolute temperature (Table IV). In the theory of the separation column which is presented in Part II, cognizance will be taken of the fact that α may depend on the temperature

A temperature dependence for α is predicted by the molecular model that was first considered by Sutherland (S1 and S2), which considers the molecules as elastic spheres surrounded by an attractive field of force which falls off as the inverse νth power of the distance. It has been shown by Jones (J2) that for the case in which ν is taken equal to 7, the expression for α is

SUTHERLAND MODEL

$$\alpha=\frac{105}{118}\,\frac{m_2-m_1}{m_2+m_1}\,\frac{1-0.9679C/T}{1+C/T}\cdot\frac{1+0.9771C/T}{1+0.9110C/T} \tag{19}$$

$$\cong\frac{105}{118}\,\frac{m_2-m_1}{m_2+m_1}\,\frac{1-0.98C/T}{1+0.92C/T} \tag{20}$$

where C is the constant which appears in the Sutherland equation for the variation of viscosity with temperature:

$$\eta\propto T^{\frac{1}{2}}/(1+C/T). \tag{21}$$

For a more detailed discussion of this case, and for a derivation of the value of α for the Lennard-Jones model (L1), the reader is referred to the paper by Jones. In this paper will also be found a derivation of (9) and (10) from the general theory of Enskog.

Equations[*] (20) and (21) are derived by assuming that C/T is small and ignoring all terms of higher order in $1/T$. Equation (21) is frequently used to approximate experimental viscosity data even when C/T is not small compared with unity, but there is no theoretical justification for such usage, and therefore no reason to suppose that α will be correctly predicted by (20) when the value of C is obtained from viscosity data which require a value of C which is not small compared with T.

Jones[1] has determined α as a function of temperature for the Lennard-Jones 9,5 model, in which the law of intermolecular force is

$$F=\kappa/r^9-\kappa'/r^5.$$

The constants κ and κ' are positive, and a positive value of F corresponds to a repulsive force. The results indicate that R_T rises slightly as T decreases from a high temperature, and then decreases, passing through zero when kT has dropped to a value equal to about twice the potential minimum ϵ of the force law. R_T continues to drop as the temperature decreases, and reaches a minimum of about -0.63 when kT is about one-half of ϵ. R_T then rises and approaches zero as T decreases to zero.

Limitations of the Theory

Use of the First Approximation

It has already been stated that the theoretical results which we have been quoting are derived from the first approximation to the exact result as given by the ratio of infinite determinants. The first approximation to the exact expression for the coefficients of viscosity, conductivity, and self-diffusion of a simple gas are increased only one or two percent by the higher approximations. The error of the first approximation to the thermal diffusion coefficient, however, may be much greater than one or two percent. This is shown by a discussion of a Lorentzian gas.

A Lorentzian gas is a gas in which the lighter

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[*] This paragraph and the following one were added in February, 1946.

[1] R. Clark Jones, Phys. Rev. 59, 1019–1033 (1941).

particles have a mass which is only a small fraction of the mass of the heavier particles, and in which furthermore either the number or the size of the heavier particles is much greater (C5, p. 187). The kinetic theory for such a gas was first developed by Lorentz (L2). The mathematical machinery for the study of this gas is much simpler than it is in the general case, and results may be obtained which are exact in the limit in which the concentration and mass of the lighter particles approaches zero.

It is shown by Enskog (E2, p. 750) in 1912 that for a Lorentzian gas in which the particles interact with an inverse power field of index ν, the constant α has the value

$$\alpha=\tfrac{1}{2}(\nu-5)/(\nu-1). \tag{22}$$

This result is exact in the limit $m_1/m_2=0$, $c_1=0$. On the other hand, according to Chapman and Cowling (C5, p. 254), the first approximation to α in the same limit is

$$\alpha=\frac{1}{2}\frac{\nu-5}{\nu-1}\bigg/\left\{\frac{5}{2}-\frac{2}{5}\frac{(3\nu-5)(\nu+1)}{(\nu-1)^2}\right\}. \tag{23}$$

Thus in this limiting case, the first approximation gives 10/13 of the exact value for elastic spheres ($\nu=\infty$), and 8/9 of the exact value for $\nu=9$. The ratio of (22) and (23) approaches unity as ν approaches 5.

All of the coefficients which relate to a mixture of two gases are given rather poorly by the first approximation in the Lorentz case, however. For the elastic sphere model, the coefficients of diffusion, viscosity, and conductivity are given with an error (C5, pp. 196–7) of 12, 8, and 15 percent, respectively, by the first approximation, whereas these coefficients are given with an error of only one or two percent in the case of a gas mixture in which the molecules are nearly identical. It appears likely, therefore, that the value of α as given by the first approximation is in error by considerably less than 23 percent for the case of isotopes. It is not possible to say anything more definite until the theory of α has been more completely developed.

Use of Classical Theory

The theory of Enskog is, of course, purely classical, as are all the theoretical results which we have been quoting. It is of interest to inquire into the changes that are involved in a quantum-mechanical treatment, such as that of Hellund and Uehling (H1). In the first place, the zeroth approximation to the velocity distribution function is not a Maxwell-Boltzmann distribution, but is a Fermi-Dirac or Bose-Einstein distribution, as the case may be. Secondly, the occupation number of a state enters into the probability of a molecule's being scattered into it (a change in the "*Stosszahlansatz*"). Thirdly, the scattering cross sections must be computed quantum-mechanically rather than classically. The quantum-mechanical cross sections will differ from the classical ones not only because of the ordinary diffraction effects, but also because of the symmetry effect between identical particles, which will remain effective even for particles which are sufficiently massive that the diffraction effects are negligible.

The first two effects can scarcely be important for gases at ordinary pressures and temperatures. The third effect is undoubtedly appreciable under these conditions, although the diffraction effect is not large; its negligibility depends upon the smallness of the ratio of the de Broglie wavelength to the diameter of the molecule. For hydrogen at room temperature the ratio $\lambdabar/d$ has the value 0.2, and for heavier molecules this ratio is given very roughly by $0.2M^{-\frac{1}{2}}$, where M is the molecular weight.

Because of the different symmetry of the wave functions involved, the interaction between two molecules of the same species and between a molecule of species 1 and one of species 2 will differ by an amount which does not depend on the mass difference of species 1 and 2. The details of this effect have been worked out by Mott-Smith ($M2$). For the case of elastic spheres, it is found that the effect introduces another term into the right member of Eq. (9); the additional term is

$$\frac{25}{472}\cdot\frac{\hbar}{d}\cdot\left(\frac{\pi}{mkT}\right)^{\frac{1}{2}}(c_2-c_1), \tag{24}$$

where d is the diameter of the molecules, and m is their average mass. The sign of this term is such that if it were the only term, the rarer constituent would be more concentrated in the hotter part of the gas. In the case of neon, Mott-Smith finds that the magnitude of this term is so small that it can account for only a small part of the observed temperature variation of α. The effect is less for other molecular models.

Comparison with Experiment

Very few direct determinations of α for isotopic mixtures have been made. Nier (N1 and N2) has measured the constant α over two temperature ranges for methane, and three temperature ranges for neon. His results are shown in Table IV. These experimental results have been compared with theory by one of the present authors (J2). The comparison indicates that the customary molecular models of kinetic theory are hardly adequate to give a satisfactory account of thermal diffusion. These models are quite satisfactory for the free-path phenomena to which they have been applied in the past, but they are not sufficiently precise to meet the test of thermal diffusion. The best check between experiment and theory is obtained for neon with the Sutherland model. The use of this model, however, places the entire burden of accounting for the decrease of α with temperature on the attractive part of the intermolecular force, whereas in view of the smallness of this attractive force as determined by other methods, it can hardly be doubted that the decrease is actually due to the increased "softness" of the *repulsive* force at low temperatures.

Stier[2] has measured* R_T for neon and argon over the temperature range 129° to 720°K. The experimental points all lie very close to the lines represented by the following empirical relations:

$$\begin{array}{ll} \text{Neon} & R_T=0.25 \log_e T/26.6, \\ \text{Argon} & R_T=0.25 \log_e T/86.9. \end{array}$$

The experimental data are all within 0.01 of the values predicted by these equations.

The results are in approximate accord with the predictions of the Lennard-Jones 9,5 model, but there are important differences. The extrapolation of the experimental results to zero values of R_T yields temperatures, 26.6° and 86.9°K, which are in rough agreement with the theory, but the linear dependence on the logarithm of the temperature is not predicted by the theory. Furthermore, the coefficient 0.25, which occurs in both of the empirical equations, should be perhaps 50 percent larger according to the theory, although the comparison is difficult to make because the theoretical curves are not linear in the logarithm of the temperature.

The experimental values of R_T for both neon and argon are all within 25 percent of the values predicted from (16) on the basis of the viscosity data for these two gases.

II. DERIVATION OF THE TRANSPORT EQUATION

In this part we discuss first the functioning of a single-stage, convection-free apparatus ("two-bulb" apparatus). We then consider the Clusius-Dickel apparatus, in which convection plays an essential part. The transport equation is derived by a simplified argument which brings out clearly the nature of the physical processes occurring in the apparatus. The results of more precise calculations for gases of different properties and for different geometrical conditions are then summarized. The assumptions used in the derivation are discussed, and the effects of asymmetries in the apparatus are estimated.

Separation Factor of a Convection-Free Unit

Before proceeding to a discussion of the separation column itself, we shall first examine the separation that thermal diffusion can bring about in the absence of convection currents. Equation (2), when written in terms of α rather than D_T, becomes

$$c_1(\mathbf{v}_1-\mathbf{v})=D_{12}(\alpha c_1 c_2 \text{ grad} \log T-\text{grad } c_1). \quad (25)$$

In the final equilibrium state, we have not only $\mathbf{v}=0$ (no convection currents), but also $\mathbf{v}_1=0$ (steady state), so that (25) reduces to

$$\text{grad } c_1=\alpha c_1 c_2 \text{ grad} \log T. \quad (26)$$

This equation is easily integrated, if we remember that $c_1+c_2=1$, and if we assume that α is independent of the temperature. The integral of (26) is then

$$c_1/c_2=\text{constant}\cdot T^\alpha. \quad (27)$$

In order to evaluate the constant of integration, we shall let the subscript 1 refer to one given

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[2] Louis Stier, Phys. Rev. **62**, 548–551 (1942).

* This paragraph and the following two were added in February, 1946.

point in the gas, and the subscript 2 to another. (This use of subscripts should not be confused with the use of the subscripts 1 and 2 on the concentrations, where they refer to the lighter and heavier isotope, respectively.) We then have

$$q \equiv \frac{(c_1/c_2)_2}{(c_1/c_2)_1} = \left(\frac{T_2}{T_1}\right)^\alpha = \exp\left[\alpha \log (T_2/T_1)\right]$$

$$\cong 1 + \alpha \log \frac{T_2}{T_1} \sim 1 + \alpha \frac{\Delta T}{\bar{T}}. \quad (28)$$

The quantity on the left, which we have indicated by q, is known as the *separation factor*, and is much used to indicate the degree of separation that is obtainable with the various methods of isotope separation.

If we accept the value of R_T given in Table III for N_2, we then find from (10) that the value of α for the mixture of $N_2{}^{14}$ and $N^{14}N^{15}$—the concentration of $N_2{}^{15}$, since N^{15} is rare, is about $\frac{1}{2}c_2{}^2$, and may therefore be neglected—is .0089, and thus q is 1.0062 for a temperature ratio of two. This value of q is to be compared with the typical separation factors obtainable with single-stage apparatus of other kinds, as given in Table V. One sees that the separation factor obtainable from a single stage by thermal diffusion is somewhat less than that obtainable by other methods.

TABLE V. Typical separation factors obtainable in a single stage by several methods of isotope separation, for the mixture $N^{14}{}_2$ and $N^{14}N^{15}$. With the exception of the case of thermal diffusion, the values are those given by Walcher (W1).

Method	q
Hertz pump	1.10
Centrifuge	1.05
Distillation	1.02
Chemical exchange reaction	1.02
Thermal diffusion	1.006

The relation (27) holds for the final equilibrium in the general case of an enclosure in which the temperature varies from point to point, *provided* that the left side of (25) can be set equal to zero, that is, provided that there are no convection currents in the enclosure. Equation (27) thus holds also for the case in which a tube connects a hot and cold reservoir with the respective temperatures T_2 and T_1. It is interesting to compute for this case the time required for the concentrations in the reservoirs to approach their equilibrium values.

Equilibrium Time of a Convection-Free Unit

Now, in order to calculate the equilibrium time in any simple manner, it is necessary to make a restricting assumption which, since it is also involved in the theory of the separation column itself, we shall give a special name: *The Quasi-Stationary Assumption.* In order to determine the equilibrium time, it is first necessary to compute the rate of transport of, say, the lighter isotope to the warmer reservoir, and then to compute the rate of change of the concentration in the reservoir from this transport. The quasi-stationary assumption consists in assuming that the time rate of change of the processes occurring within the connecting tube is sufficiently small that the transport between the two reservoirs at any given time during the separation does not differ significantly from the *steady-state* transport that would be obtained if the concentrations of the reservoirs were *held constant* at the values in question. This condition is obviously satisfied if the volume of each of the reservoirs is much larger than the volume of the tube itself.

Throughout this article we shall neglect the dependence of ρ on c_1. Not only is this dependence slight in the case of nearly all isotopic mixtures, but also the change in c_1 within any given unit of apparatus will usually not be very large.

We proceed with the calculation. Since the gas as a whole is at rest, $\mathbf{v}=0$. We assume for simplicity that the temperature gradient is constant along the connecting tube, and is therefore $dT/dz=\Delta T/L$, where z is the coordinate along the tube, and where L is the length of the tube; this assumption also permits us to change the independent variable from z to T. Finally, we replace the factor c_1c_2 which occurs in the middle term of (25) by its average value. This approximation is permissible since the variation of c_1c_2 will be small if α is small, as we assume to be the case. Then (25) becomes

$$c_1v_1 = \frac{D\Delta T}{L}\left\{\frac{\alpha\langle c_1c_2\rangle_{\text{Av}}}{T} - \frac{dc_1}{dT}\right\}. \quad (29)$$

The equation of continuity of species 1 by itself is

$$\operatorname{div} \rho c_1 \mathbf{v}_1 = -\partial \rho c_1/\partial t. \quad (30)$$

Since we are here concerned with a steady-state problem, by virtue of the quasi-stationary assumption, we have that $\rho c_1 v_1$ is independent of x, and therefore of T. In a gas, ρ varies inversely as T, and it is a fair approximation to assume that D varies as T^2. Multiplying both sides of (29) by ρ, we have

$$\rho c_1 v_1 = \frac{\rho D}{T}\frac{\Delta T}{L}\left(\alpha\langle c_1 c_2\rangle_{\text{Av}} - T\frac{dc_1}{dT}\right). \tag{31}$$

This equation can be integrated easily, since $\rho c_1 v_1$ and $(\rho D/T)$ are constants. Integrating and applying the boundary conditions at the two ends, we find

$$\rho c_1 v_1 = \frac{\rho D}{T}\frac{\Delta T}{L}\left(\alpha\langle c_1 c_2\rangle_{\text{Av}} - \Delta c_1 \Big/ \log\frac{T_2}{T_1}\right), \tag{32}$$

where Δc_1 is the difference of c_1 in the hot and cold reservoirs. Now the product of the quantity on the left and S, the cross section of the tube, is clearly the rate at which species 1 is being delivered to the hotter reservoir, in grams per second. Since the gas as a whole is at rest, an equal quantity of species 2 is being delivered to the cold reservoir. Let the masses of gas in the hot and cold reservoirs be indicated by m_h and m_c, respectively. Then clearly we have in the hot reservoir

$$m_c\left(\frac{dc_1}{dt}\right)_1 = \rho c_1 v_1 S, \tag{33}$$

and in the cold reservoir

$$m_h\left(\frac{dc_2}{dt}\right)_2 = -m_h\left(\frac{dc_1}{dt}\right)_2 = \rho c_1 v_1 S, \tag{34}$$

from which we find

$$\frac{d\Delta c_1}{dt} = \rho c_1 v_1 S\left(\frac{1}{m_c} + \frac{1}{m_h}\right). \tag{35}$$

Putting in the expression (32) for $\rho c_1 v_1$, we have an equation of the form

$$d\Delta c_1/dt = a - b\Delta c_1, \tag{36}$$

which indicates a simple exponential approach to equilibrium. If we let $t=0$ when the concentration difference is zero, the solution of (36) is

$$\Delta c_1 = (\Delta c_1)_{\text{equil}}(1 - e^{-t/t_r}). \tag{37}$$

Here

$$t_r = \frac{L}{\rho D S}\cdot\frac{m_c m_h}{m_c + m_h}\cdot\frac{T}{\Delta T}\cdot\log\frac{T_2}{T_1} \tag{38}$$

is the time required for the concentration difference to rise to a fraction $(1-1/e)$ of its equilibrium value. Such a time is often called a "relaxation time." The value of $(\Delta c_1)_{\text{equil}}$ in this approximation is obtained by setting equal to zero the left side of (32):

$$(\Delta c_1)_{\text{equil}} = \alpha c_1 c_2 \log\frac{T_2}{T_1} \sim \alpha c_1 c_2 \frac{\Delta T}{T}. \tag{39}$$

It is seen that t_r is independent of the temperature difference ΔT if ΔT is small compared with T. The relaxation time is proportional to the pressure if the volume of the reservoirs is constant, whereas it is independent of the pressure if the volumes are varied so that the mass contained is constant.

A knowledge of t_r is important in the experimental measurement of α, for which Nier (N1 and N2) has used a single-stage apparatus of the type just discussed.

We have gone into some detail in the treatment of this simple case because the methods used are similar to those which we shall use in treating the separation column. In the separation column, also, we shall find that our formulae appear more complicated than they are because of a large accumulation of physical constants which do not influence the nature of the mathematical treatment.

The Separation Column of Clusius and Dickel

It might at first be thought that the addition of convection currents would always serve to reduce the separation below the amount indicated by (28). Indeed, this seems to have been assumed tacitly, and sometimes explicitly, by many of the earlier writers on thermal diffusion. It was the great achievement of Clusius and Dickel (C9), however, to point out that convection currents could be utilized to secure relatively enormous separation factors. Using 36 meters of separation column, they obtained a separation factor of 4000 in separating HCl^{35} from HCl^{37}, whereas the q obtainable in a single-stage apparatus of the type considered at the beginning of this section would be about 1.01. The 36 meters of column were thus very roughly equivalent to 800 single stages, or about 20 stages per meter.

The apparatus used by Clusius and Dickel was surprisingly simple. It consisted essentially of a long vertical tube, closed at both ends, and containing a gas at approximately atmospheric pressure; along the axis of the tube was passed a wire which could be heated to a high temperature by an electric current. The effect of thermal diffusion is to drive the lighter molecules toward the hot wire, so that they enter the rising convection current which exists near the wire. The lighter molecules are thus carried upward, and the heavier ones downward, so that a concentration gradient is set up along the tube. On the other hand, the two convection currents, one rising near the wire, and the other descending near the cooled wall of the tube, are essentially mixing processes, which tend to neutralize any concentration gradient along the tube. The final equilibrium concentration gradient along the tube will therefore result from a compromise among these two effects and a third, the remixing effect of ordinary diffusion along the tube.

This situation has received quantitative treatment at the hands of Waldmann (W2, with a preliminary announcement W3, which, however, contains numerical errors), van der Grinten (G1), and Furry, Jones, and Onsager (F1). All of these treatments ignore the cylindrical aspect of the apparatus, however, and treat the processes as though they occurred in the space between two plane and parallel walls, one of which is warmer than the other. The treatments of Waldmann and of van der Grinten are further restricted to the case in which the temperature difference of the walls is small, inasmuch as their treatments ignore the temperature dependences of the relevant properties ρ, λ, η, and D. Furry, Jones, and Onsager obtain the solution for a fluid whose properties have any given temperature dependence in terms of certain definite integrals (Eqs. (57)–(62) below), and present explicit solutions for a gas in which λ, η, and D have the temperature dependences of a Maxwellian gas, and also for a gas whose properties have the temperature dependences characteristic of a gas consisting of hard elastic spheres (Eqs. (78)–(94) below).

The treatment of Furry, Jones, and Onsager was later extended by Furry and Jones (F4) to cover the cylindrical case. General solutions are obtained, and an explicit solution is obtained for the Maxwellian case (Eqs. (100)–(117) below).

The treatment chosen for presentation here is not one of those mentioned above, however, but is one which the authors have found suitable for presentation at seminars and colloquia during the past year. It was chosen not because of its exactness, for it is less precise than any of the treatments mentioned above, but rather because of its mathematical simplicity and because of the clarity with which it brings out the nature of the processes occurring in the separation column. The more precise treatments all suffer from the disadvantage that they are somewhat long and involved, with the result that the reader is likely to get lost in the mathematics while trying to understand the purely physical aspects of the situation.

Elementary Derivation of the Transport Equation

The derivation presented below breaks naturally into two parts. We shall first consider the purely hydrodynamical problem of the convection current set up between the hot and cold walls. We shall then rather simply derive an expression giving the total transport of the lighter isotope up the tube.

Two important approximations are used in the derivation. First, we shall follow Waldmann in ignoring the temperature dependence of ρ, η, λ, and D, except that in the computation of the convection velocity the density ρ is represented rather more accurately by a linear function of T. Second, we shall use a highly schematized model to represent the convection process. In this model each of the two columns of gas, one moving upward and the other downward, has a velocity constant across its cross section. Thus the only result of the hydrodynamical calculation which is required in the further considerations is a suitable value for the velocity $\bar{v}$ of each column.

In the actual apparatus, the processes of convection and diffusion take place in the annular space between the two concentric cylinders, the inner one hot, and the outer cold. We shall not, however, consider the cylindrical aspect of the apparatus, but rather we shall consider that the apparatus consists of a hot plane wall, with a cold wall parallel to it at a distance of $2w$. The walls are to have a height L and a breadth B. The coordinate along the length of the column is z; the coordinate along the breadth is y; and the coordinate perpendicular to the walls we shall call x. We shall assign to x the value w at the hot wall, and the value $-w$ at the cold wall.

The Hydrodynamical Problem

As we shall show later on in this section, the convective flow may be assumed to be free from turbulence. It will also be shown that the temperature distribution is that determined by conduction alone. The hydrodynamical equation for steady non-turbulent flow under the influence of gravity is

$$\begin{aligned}(\operatorname{div} \eta \operatorname{grad})\mathbf{v} &= -(\text{body force}) \\ &= \operatorname{grad} P - \rho \mathbf{g}, \qquad (40)\end{aligned}$$

which in the present case reduces to

$$\eta \frac{d^2 v_z(x)}{dx^2} = (\rho - \bar{\rho})g. \qquad (41)$$

Everywhere else in the calculations we shall identify ρ with its mean value $\bar{\rho}$. Here, however, in order to calculate a non-vanishing value of v_z, we must use a better approximation for ρ. The best linear approximation is

$$\rho = \bar{\rho}(1 - (T - \bar{T})/\bar{T}). \qquad (42)$$

The approximation $\lambda = \text{constant}$ makes the temperature a linear function of x:

$$T = \bar{T} + x\Delta T/2w. \qquad (43)$$

Substituting these values into (41), we obtain

$$\eta \frac{d^2 v}{dx^2} = -\rho g \frac{x\Delta T}{2w\bar{T}}, \qquad (44)$$

where we write ρ rather than $\bar{\rho}$, since from now on ρ is to be regarded as a constant.

Integrating (44) and using the fact that v vanishes for $x = \pm w$, we have

$$v = \frac{\rho g \Delta T}{12\eta w \bar{T}} x(w^2 - x^2). \qquad (45)$$

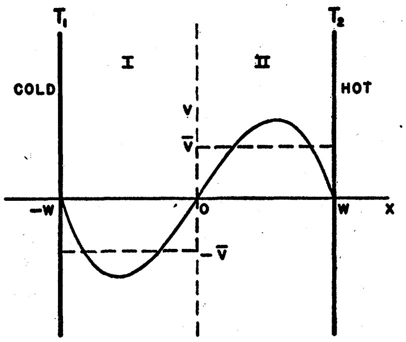

FIG. 1. Showing the form of the convection currents between the hot and cold walls of the separation column. The form indicated by the solid curve is correct only when the temperature difference is small; for larger temperature differences, the curve is no longer symmetrical. The simple treatment described in the text involves replacing the solid curve by the dashed curve.

One sees that this represents an upward flow in the space on the hotter side of the median plane, and a downward flow of gas on the colder side. In order to find the velocity $\bar{v}$ which a column of width w and breadth B must have in our simplified model in order that it shall represent the same flow as one of the actual columns, we must average v over half of the space between the walls:

$$\begin{aligned}\bar{v} = w^{-1}\int_0^w v dx &= -w^{-1}\int_{-w}^0 v dx \\ &= (\rho g w^2/48\eta)(\Delta T/\bar{T}). \qquad (46)\end{aligned}$$

The schematized model which we shall use from now on corresponds to replacing the actual flow by that indicated by the dashed lines in Fig. 1.

Determination of the Transport

The total transport of gas up the tube is zero, since the cross sections and densities of the two columns are equal, whereas the velocities are equal and opposite. If, however, the average value of c_1 is larger in the hotter column than it is in the colder, there will be a net transport of the lighter molecules up the tube; the effect of thermal diffusion is just such as to produce this variation in c_1. Since there will also be a transport down the tube because of ordinary diffusion, we may write for the total transport of the lighter isotope up the tube

$$\tau_1 = \rho(c_1^{II} - c_1^{I})\bar{v}wB - 2wB\rho D(\partial c_1/\partial z), \qquad (47)$$

where c_1^{II} and c_1^{I} are the mean values of c_1 in the hotter and colder columns, respectively, and c_1 as used in the last term means the average of these two values, which differ from each other by a very small amount.

The time has now come when we must use the quasi-stationary assumption. A more drastic form of this assumption than is needed here has already been used in the computation of the equilibrium time of a single-stage apparatus. We assume here that the transport at any point along the tube depends only on the values of c_1 and $\partial c_1/\partial z$ at that point, and does not depend appreciably on the time rates of change of c_1 and $\partial c_1/\partial z$. This is not really an assumption, but is a theorem which can be proved, as we shall discuss in detail later on in this section. The consequence of this assumption is that the result of a computation of the transport for a steady-state condition holds also for the non-equilibrium state. We shall not impede the derivation by dwelling further on this point here, but we shall return to it later.

Since we have reduced the problem to one involving only a steady state, it is clear that the effects which tend to change the value of $c_1^{II}-c_1^{I}$ must add to zero. There are two such effects; the movement of the columns causes c_1^{II} to decrease by the amount $\bar{v}(\partial c_1/\partial z)$ per second, and c_1^{I} to increase by the same amount. The effect of the convection is thus to increase $c_1^{II}-c_1^{I}$ at the rate $-2\bar{v}(\partial c_1/\partial z)$. The other effect is the transverse flow of the lighter molecules which is caused by diffusion and thermal diffusion. Since the distance between the centers of the columns is w, we may take $(c_1^{II}-c_1^{I})/w$ as an approximate expression for the transverse concentration gradient $\partial c_1/\partial x$. A corresponding approximate value for $\partial \log T/\partial x$ is $\Delta T/(2w\bar{T})$. Substitution in Eq. (25) gives

$$\rho c_1 v_{1x} = \rho D\left(\alpha c_1 c_2 \frac{\Delta T}{2w\bar{T}} - \frac{c_1^{II}-c_1^{I}}{w}\right), \tag{48}$$

and $\rho c_1 v_{1x}$ expresses directly the transverse flow of the lighter constituent in grams per unit area per second. Since the thickness of each column is w, we see that $c_1^{II}\rho$ is increased at the rate $\rho c_1 v_{1x}/w$, while $c_1^{I}\rho$ is decreased at the same rate. The total rate of change of $c_1^{II}-c_1^{I}$, which must be zero, is thus

$$(2c_1 v_{1x}/w) - 2\bar{v}(\partial c_1/\partial z) = 0, \tag{49}$$

or by (48)

$$(D/w^2)\cdot\{\alpha c_1 c_2(\Delta T/2\bar{T}) - (c_1^{II}-c_1^{I})\} - \bar{v}(\partial c_1/\partial z) = 0. \tag{50}$$

Equation (50) may now be solved for $c_1^{II}-c_1^{I}$:

$$c_1^{II}-c_1^{I} = \alpha c_1 c_2(\Delta T/2\bar{T}) - (\bar{v}w^2/D)(\partial c_1/\partial z). \tag{51}$$

Substitution of this value in (47) then gives

$$\tau_1 = wB\rho\bar{v}\cdot(\alpha\Delta T/2\bar{T})c_1 c_2 - \{wB\rho\bar{v}\cdot(\bar{v}w^2/D) + 2wB\cdot\rho D\}(\partial c_1/\partial z). \tag{52}$$

Substituting in (52) the expression (46) for $\bar{v}$, we obtain the following explicit formula for the transport of the lighter constituent up the tube:

$$\tau_1 = Hc_1(1-c_1) - (K_c+K_d)(dc_1/dz), \tag{53}$$

where H, K_c, and K_d are constants defined by

$$H = \frac{\alpha\rho^2 g w^3 B}{96\eta}\left(\frac{\Delta T}{\bar{T}}\right)^2, \tag{54}$$

$$K_c = \frac{\rho^3 g^2 w^7 B}{2304\eta^2 D}\left(\frac{\Delta T}{\bar{T}}\right)^2, \tag{55}$$

$$K_d = 2wB\rho D. \tag{56}$$

In Eq. (53), dc_1/dz is written as a total derivative in order to stress the fact that the variation of c_1 with x need not be considered in any of the applications of the transport equation (53). It is not that the small transverse variation of c is not important, but rather that its effect is taken into account by the coefficients H and K_c, and need not be considered further.

The three terms in the transport equation all have simple interpretations: the first and positive term represents the flow contributed by thermal diffusion; the last two terms represent remixing due to the convection currents, and to ordinary diffusion along the tube, respectively. The physical meaning of the terms may be seen most clearly from the way they are written in Eq. (52). The factor $wB\rho\bar{v}$ is the total convective transport in a column; $(\alpha\Delta T/2\bar{T})c_1c_2$ is the difference between the mean concentrations in the columns caused by thermal diffusion, as limited by the equalizing effect of ordinary diffusion; and

$-(\bar{v}w^2/D)(\partial c_1/\partial z)$ is the difference between the concentrations in the columns brought about by convection, limited by diffusion. In the last term the factor $2wB$ is the cross-sectional area of the tube, and $-\rho D(\partial c_1/\partial z)$ is the longitudinal flow per unit area caused by diffusion.

The transport coefficients which have just been derived become identical with the $H^{(0)}$, $K_c^{(0)}$, and $K_d^{(0)}$ of Eqs. (70)–(72) below when they are multiplied by the respective numerical factors 16/15, 256/315, and unity. The discrepancy is due entirely to the use of a simplified picture of the convection process.

The transport equation (53) will be discussed in detail in Part III. The remainder of this section will be devoted to the presentation of the results obtained by more precise calculations for the plane and for the cylindrical case, to a discussion of the assumptions involved in this sort of treatment of the problem, and to considerations on the effects of asymmetry in the apparatus.

More Accurate Treatment of the Plane Case

The derivation of the transport equation which has just been presented can be improved in two major respects. In the first place, the sums over the columns should be replaced by integrations with respect to x, and secondly, the properties α, ρ, λ, η, and D should be treated as temperature dependent quantities. Both of these steps were taken by Furry, Jones, and Onsager (F1) in their treatment. The following expressions were found for H, K_c, and K_d:

$$H=(B/Q^3)\int_{T_1}^{T_2}(\rho D\alpha/\lambda T)G(T)dT, \qquad (57)$$

$$K_c=(B/Q^7)\int_{T_1}^{T_2}(\rho D/\lambda)\{G(T)\}^2dT, \qquad (58)$$

$$K_d=(B/Q)\int_{T_1}^{T_2}\lambda\rho DdT, \qquad (59)$$

where Q is defined by

$$Q=(2w)^{-1}\int_{T_1}^{T_2}\lambda dT; \qquad (60)$$

the function $G(T)$ is the solution of

$$\frac{d}{dT}\frac{1}{\lambda}\frac{d}{dT}\frac{\eta}{\lambda}\frac{d}{dT}\frac{1}{\lambda\rho}\frac{d}{dT}\left(\frac{\rho D}{\lambda}G(T)\right)=-g\frac{d\rho}{dT}, \qquad (61)$$

which satisfies the boundary conditions

$$G(T_1)=G(T_2)=G'(T_1)=G'(T_2)=0; \qquad (62)$$

and T_2 and T_1 are the temperatures of the hot and cold wall. Equation (61) for $G(T)$ is a very simple differential equation, since it can always be solved by quadratures. Without specifying the manner in which ρ, λ, η, and D depend on T, the solution cannot be given in any more explicit form, except in the case in which the difference of the temperatures of the walls is so small that the variation in these quantities is negligible and may be ignored. In this case, the solution of (61) and (62) is

$$G(T)=(\lambda^4 g\beta/24\eta D)(T_2-T)^2(T-T_1)^2, \qquad (63)$$

where β is the temperature coefficient of the density:

$$\beta=-d\rho/dT. \qquad (64)$$

Equation (60) reduces to

$$w=\lambda\Delta T/2Q. \qquad (65)$$

The substitution of (63) and (65) in (57)–(59) now leads to the explicit expressions

$$H^{(0)}=\frac{(2w)^3\rho\alpha\beta gB(\Delta T)^2}{6!\eta T}, \qquad (66)$$

$$K_c^{(0)}=\frac{(2w)^7g^2\beta^2\rho B(\Delta T)^2}{9!\eta^2 D}, \qquad (67)$$

$$K_d^{(0)}=2w\rho DB. \qquad (68)$$

These are the expressions for H, K_c, and K_d for any gas or liquid, provided that the temperature range in question is sufficiently small, so that the variations of α, ρ, λ, η, β, and D are small. They are usually fair approximations even in the case that ΔT is not small, if one uses mean values for the temperature dependent quantities in (66)–(68).

Specialization of the Formulae for Gases

In the case of a gas,

$$\beta=\rho/T, \qquad (69)$$

so that (66)–(68) become

$$H^{(0)}=\frac{(2w)^3\rho^2\alpha gB}{6!\eta}\left(\frac{\Delta T}{T}\right)^2, \tag{70}$$

$$K_c^{(0)}=\frac{(2w)^7\rho^3g^2B}{9!\eta^2D}\left(\frac{\Delta T}{T}\right)^2, \tag{71}$$

$$K_d^{(0)}=2w\rho DB. \tag{72}$$

A molecular model whose predictions with respect to the temperature dependences of η, λ, and D are in good agreement with experiment is the inverse power model which was discussed in Part I. If all the molecules in the gas repel one another with a force which varies as the inverse νth power of the distance of separation, and if c_v is independent of the temperature (a condition which holds very well for monatomic gases), then the following five quantities should be independent of the temperature and pressure:

$$(\eta/T^n),\ (\lambda/T^n),\ (\rho D/T^n);\ (\eta/\lambda),\ (\rho D/\lambda), \tag{73}$$

where n is related to ν by Eq. (13). The number n is unity for a Maxwellian gas, and one-half for a gas consisting of hard spheres. The experimental values of n for nearly all gases lie between 0.6 and 1.0, as may be seen from Table III.

Although the inverse power model predicts that α is zero in the Maxwellian case, gases such as HCl may follow the Maxwellian behavior quite closely with respect to the temperature dependence of η, λ, and D, but in spite of this have a non-vanishing α. This behavior is traceable to the fact that the inverse power model is inadequate for an accurate description of the phenomenon of thermal diffusion, even though it is quite satisfactory for the simple free path phenomena of viscosity, heat conduction, and ordinary diffusion; this matter has already been discussed in Part I. The assumption that η, λ, and D have a Maxwellian dependence on temperature leads to much simpler results than any other assumption, and is in general a better approximation than the hard sphere model.

The constancy of the quantities in (73) brings about a great simplification in the differential equation (61) for $G(T)$; it reduces to

$$\frac{d}{dT}\frac{1}{T^n}\frac{d^2}{dT^2}\frac{1}{T^{n-1}}\frac{dG}{dT}=-\frac{1}{T^2}\left\{\frac{\lambda^4\rho g}{\eta DT^{2n-2}}\right\}, \tag{74}$$

where the bracketed factor in the right member is independent of T. The solution of (61) which satisfies the boundary conditions is easily written as the ratio of a five-rowed determinant to one of its minors, and there would be no difficulty except great algebraic complexity in obtaining the explicit expressions for H and K_c for any value of n. We shall present here only the solutions for $n=1$, and $n=\frac{1}{2}$.

For $n=1$, the solution of (61) and (62) is simple in form:[3]

$$G(T)=-\left\{\frac{\lambda^4g\rho}{12\eta D}\right\}\frac{(T_2-T)^2(T-T_1)^2}{T_2+T_1} \tag{75}$$

and the relation between w and Q is also simple:

$$w=\lambda\Delta T/2Q, \tag{76}$$

where λ is to be evaluated at the mean temperature.

The substitution of (75) in (57) and (58), and the elimination of Q by means of (76) then lead to explicit expressions for H and K_c. The transport coefficient K_d is of course determined by direct integration in the light of the constancy of the expressions (73).

When the various indicated substitutions, integrations, and eliminations are performed, it is found possible to express the results in terms of correction factors to be applied to $H^{(0)}$, $K_c^{(0)}$, and $K_d^{(0)}$ as defined by (70)–(72). We introduce the abbreviation

$$u=(T_2-T_1)/(T_2+T_1). \tag{77}$$

If now the quantities α, ρ, η, λ, T, and D which occur in H, K_c, and K_d are evaluated at the mean temperature $\bar{T}=\frac{1}{2}(T_2+T_1)$, we have for $n=1$ (Maxwellian case):

$$H=H^{(0)}\phi(u) \tag{78}$$

$$=H^{(0)}\left(1+\frac{1\cdot3\cdot5}{3\cdot5\cdot7}u^2+\frac{1\cdot3\cdot5}{5\cdot7\cdot9}u^4+\cdots\right) \tag{79}$$

if α is independent of T;

$$H=H^{(0)}\left(1+\frac{1\cdot3\cdot5}{3\cdot5\cdot7}\cdot\frac{1\cdot3}{2\cdot4}u^2+\frac{1\cdot3\cdot5}{5\cdot7\cdot9}\cdot\frac{1\cdot3\cdot5\cdot7}{2\cdot4\cdot6\cdot8}u^4+\cdots\right) \tag{80}$$

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[3] Equation (75) was in error by a factor of two in F1. The error was one of copying, and does not invalidate any of the following equations in F1.

if α varies as $T^{\frac{1}{2}}$; and

$$H=H^{(0)} \tag{81}$$

if α is proportional to T;

$$K_c=K_c^{(0)}, \tag{82}$$

$$K_d=K_d^{(0)}(1+\tfrac{1}{3}u^2). \tag{83}$$

In these expressions, $H^{(0)}$, $K_c^{(0)}$, and $K_d(^0)$ as defined by (70)–(72) are to be evaluated at the mean temperature $\bar{T}$. The function[4]

$$\phi(u)=(5/16u^5)\{10u^3-6u +3(1-u^2)^2\log[(1+u)/(1-u)]\} \tag{84}$$

which enters into H has the value 1.016 for a temperature ratio of two, the value 1.039 for a temperature ratio of three, and the value 5/4 for an infinite temperature ratio ($u=1$).

The case in which η, λ, and D have a temperature dependence corresponding to $n=\frac{1}{2}$ is less simple. We introduce the abbreviation

$$r=\frac{T_2^{\frac{1}{2}}-T_1^{\frac{1}{2}}}{T_2^{\frac{1}{2}}+T_1^{\frac{1}{2}}}=\frac{u}{1+(1-u^2)^{\frac{1}{2}}}. \tag{85}$$

If now $H^{(0)}$, $K_c^{(0)}$, and $K_d^{(0)}$ are evaluated at the mean temperature $\bar{T}$, we find for $n=\frac{1}{2}$ (gas of hard spheres):

$$H=H^{(0)}\frac{(1+r^2)^{9/2}\psi(r)}{(1+\frac{1}{3}r^2)^4(1-\frac{1}{5}r^2)}. \tag{86}$$

Here $\psi(r)$ is given by

$$\psi(r)=1-\frac{17}{35}r^2-\frac{16}{315}r^4-\frac{16}{1485}r^6-\cdots \tag{87}$$

if α is independent of T; then

$$H=H^{(0)}(1+2.8810r^2+1.9734r^4+\cdots). \tag{88}$$

The cases $\alpha\propto T^{\frac{1}{2}}$ and $\alpha\propto T$ have also been worked out. One obtains

$$\psi(r)=1-\frac{18}{35}r^2-\frac{1}{35}r^4 \tag{89}$$

for $\alpha\propto T^{\frac{1}{2}}$, and

$$\psi(r)=1-\frac{2}{5}r^2-\frac{1}{15}r^4 \tag{90}$$

for $\alpha\propto T$. For ratios $(T_2/T_1)<4$, neither of these differs from the values for constant α by more than one percent. The coefficients K_c and K_d are given by[5]

$$K_c=K_c^{(0)}\frac{(1+r^2)^{15/2}\varphi(r)}{(1+\frac{1}{3}r^2)^9(1-\frac{1}{5}r^2)^2}, \tag{91}$$

$$\varphi(r)=1-(692/825)r^2+(146/2475)r^4 +(4/75)r^6+(17/7425)r^8, \tag{92}$$

$$K_c=K_c^{(0)}(1+4.0612r^2+4.7439r^4+\cdots), \tag{93}$$

and

$$K_d=K_d^{(0)}(1+r^2)^{\frac{1}{2}}/(1+\tfrac{1}{3}r^2) =K_d^{(0)}(1+\tfrac{1}{6}r^2-(13/72)r^4+\cdots). \tag{94}$$

For $(T_2/T_1)=2$, the values of H, K, and K_d for $n=\frac{1}{2}$ are, respectively, 1.069, 1.124, and 0.968 as great as their values for the $n=1$ case.

The relations presented here for $n=1$ and $n=\frac{1}{2}$ represent an extension and simplification of the results derived by Furry, Jones, and Onsager (F1).

The Cylindrical Case

All of the considerations so far have applied to the plane-parallel type of apparatus. The extension of the theory to take account of the cylindrical shape of the actual apparatus is simple in principle, but is much more complicated in execution. The extension has been carried out by Furry and Jones (F4), who find as the general solution

$$H=(2\pi/Q_1^3)\int_{T_1}^{T_2}(\rho D\alpha/\lambda T)G(T)dT, \tag{95}$$

$$K_c=(2\pi/Q_1^7)\int_{T_1}^{T_2}(\rho D/\lambda)G^2(T)dT, \tag{96}$$

$$K_d=(2\pi/Q_1)\int_{T_1}^{T_2}r^2\lambda\rho D dT, \tag{97}$$

where $G(T)$ is now the solution of

$$\frac{d}{dT}\frac{1}{\lambda r^2}\frac{d}{dT}\frac{\eta}{\lambda}\frac{d}{dT}\frac{1}{\lambda\rho r^2}\frac{d}{dT}\left(\frac{\rho D}{\lambda}G(T)\right)=-g\frac{d\rho}{dT}, \tag{98}$$

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[4] The function $\phi(u)$ is the same as the $f(2u)$ of Furry, Jones, and Onsager (F1).

[5] The coefficient of r^8 in Eq. (92) was incorrectly stated as 13/7425 in F1.

which satisfies the boundary conditions (62), and where $2\pi Q_1$ is the heat flow per centimeter of tube length per second. The following relation holds between Q_1 and the radii of the inner and outer tubes:

$$Q_1 \log \frac{r_1}{r_2} = \int_{T_1}^{T_2} \lambda dT. \tag{99}$$

The equation (98) for $G(T)$ is formally very similar to the equation (61) for $G(T)$ in the plane case, but the presence of the variable r, which must be considered as a function of T, complicates the nature of the solution to such an extent that only the Maxwellian case has been treated. The Waldmann approximation leads to a slightly simpler solution, but this approximation is particularly bad in the cylindrical case, where the range of temperature that may readily be used is much greater than in the plane case.

The exact solution of (98) for the Maxwellian case has been obtained. It will not be given here because it is very complicated in form, involving exponentials and error functions of two different arguments. Unfortunately, the integral in (95) which yields H cannot be evaluated analytically, but must be performed by numerical quadrature. This restriction is particularly unfortunate because the cylindrical case involves two independent parameters, the ratio of the radii r_1/r_2 and the ratio of the temperatures T_1/T_2, so that many numerical integrations would be required to cover the range of possible types of apparatus.

The Nearly Plane Case

Fortunately, however, approximate solutions are available for the cases which are of chief interest in practice. For the case in which the ratio of the radii is not large ($r_1/r_2 \lesssim e = 2.718$), the coefficients of the transport equation may be expressed as ascending power series in $\log r_1/r_2$. The derivation is tedious and will not be given here. The result is

$$H = H^{(0)}\{\phi(u) + h_1(u) \log (r_1/r_2) + h_2(u)\{\log (r_1/r_2)\}^2 + \cdots\}, \tag{100}$$

$$K_c = K_c^{(0)}\{1 + k_{c1}(u) \log (r_1/r_2) + k_{c2}(u)\{\log (r_1/r_2)\}^2 + \cdots\}, \tag{101}$$

$$K_d = K_d^{(0)}\{1 + \tfrac{1}{3}u^2 + k_{d1}(u) \log (r_1/r_2) + k_{d2}(u)\{\log (r_1/r_2)\}^2 + \cdots\}, \tag{102}$$

$$h_1(u) = 1.010u + 0.165u^3 + 0.059u^5 + \cdots, \tag{103}$$

$$h_2(u) = -0.174 + 0.496u^2 + 0.088u^4 + \cdots, \tag{104}$$

$$k_{c1}(u) = 1.721u, \tag{105}$$

$$k_{c2}(u) = -0.213 + 1.505u^2, \tag{106}$$

$$k_{d1}(u) = -0.333u + 0.067u^3, \tag{107}$$

$$k_{d2}(u) = -0.022u^2 + 0.010u^4. \tag{108}$$

Here $H^{(0)}$, $K_c^{(0)}$, and $K_d^{(0)}$ are as given by (70)–(72), with α, ρ, η, λ, T, and D evaluated at the mean temperature, and with $2w = r_1 - r_2$, $B = \pi(r_1 + r_2)$; $\phi(u)$ is the function defined by (79) and (84).

The formula for H given above is that for α independent of T. For $\alpha \propto T$ one obtains instead

$$H = H^{(0)}\{1 + h_1(u) \log (r_1/r_2) + h_2(u)\{\log (r_1/r_2)\}^2 + \cdots\}, \tag{109}$$

$$h_1(u) = 0.838u, \tag{110}$$

$$h_2(u) = -0.174 + 0.363u^2, \tag{111}$$

if α is evaluated at the mean temperature. The remarkable lack of sensitivity to the temperature dependence of α, which is shown by the results for the plane case, is not retained in the cylindrical case.

The Extreme Cylindrical Case

The case in which r_1/r_2 is large is conveniently discussed with the assistance of a reduced temperature, defined by

$$t = (\lambda/Q_1 T)^{\frac{1}{2}} \cdot T. \tag{112}$$

The specification of t_1 and t_2 is equivalent to the specification of r_1/r_2 and T_1/T_2, as is evident from the following two relations

$$\log (r_1/r_2) = \tfrac{1}{2}(t_2^2 - t_1^2), \tag{113}$$

$$t_2/t_1 = T_2/T_1. \tag{114}$$

If the ratio of the radii is larger than about ten or fifteen, another approximate method is possible. For a given value of t_1, five numerical integrations suffice to determine H and K_c for all values of t_2 which correspond to a ratio of

TABLE VI. Values of h (Maxwellian gas, $n=1$).

T_2/T_1 \ r_1/r_2	15	25	40	60	100
2	0.059	0.059	—	—	—
3	0.091	0.098	0.100	0.101	0.100
4	0.092	0.103	0.109	0.113	0.116
5	0.075	0.092	0.103	0.108	0.114
6	—	—	0.085	0.093	0.102

radii greater than ten or fifteen. In case of large cylindricity, therefore, the problem has been reduced to one involving only one parameter so far as the numerical integration is concerned.

In the extreme cylindrical case, a large part of the gas is at a temperature not very much greater than T_1. In writing down our defining equations for the "shape factors" of the transport coefficients H, K_c, K_d we accordingly specify that the quantities η, ρ, λ, D shall be evaluated at the temperature T_1 of the outer tube. We write

$$H=(2\pi/6!)(\alpha\rho^2g/\eta)_1\cdot r_1^4\cdot h(T_2/T_1;r_1/r_2), \quad (115)$$

$$K_c=(2\pi/9!)(\rho^3g^2/\eta^2D)_1\cdot r_1^8 \cdot k_c(T_2/T_1;r_1/r_2), \quad (116)$$

$$K_d=2\pi(\rho D)_1\cdot r_1^2\cdot k_d(T_2/T_1;r_1/r_2). \quad (117)$$

The subscript 1 emphasizes that the quantities in question are to be evaluated at T_1.

Tables VI–VIII were obtained by graphical interpolation from the results of numerical integrations which have been carried out. They are for the "Maxwellian case," $n=1$, and for α independent of temperature.

A rather surprising feature of these results is the great difference between the dependences of H and K_c on T_2/T_1 in the extreme cylindrical case and in the plane case. Whereas in the plane case both coefficients increase (as $(\Delta T/\bar{T})^2$) with increasing T_2/T_1, in the extreme cylindrical case H is rather insensitive to this ratio and K_c *decreases* strongly as T_2/T_1 increases. In both cases there is an increase with increasing T_2/T_1 of the ratio H^2/K_c, which may be taken as a measure of the effectiveness of the separation process (cf. Eq. (333)).

The nature of the results found for the highly cylindrical case would scarcely be expected without calculation, but can be made plausible by physical considerations. For high values of T_2 the gas near the hot wire becomes highly conductive of heat and very viscous. This has the effect of reducing the convective flow. Now H depends on both the convective flow, which is decreased, and on the effectiveness of thermal diffusion, which is increased; K_c, on the other hand, depends only on the convective flow, and indeed quadratically (cf. Eq. (52)).

This behavior of H and K_c should be of considerable importance in practice. It seems likely that it depends rather strongly on the temperature dependences of the gas coefficients, and for this reason numerical calculations for the case $n=\frac{1}{2}$, which is in a sense the other limiting case, would be desirable.

It seems likely that the value of H would be rather strongly influenced by any marked temperature dependence which the factor α might have. Since the assumptions $\alpha\propto T^{\frac{1}{2}}$ and $\alpha\propto T$ are quite artificial and probably decidedly lacking in verisimilitude, numerical integrations were not carried through for such cases. Whenever a temperature dependence of α for a given gas may become reasonably well known empirically, it can be used together with tabulated results (F4) to carry out an *ad hoc* numerical integration for the value of H.

Discussion of the Assumptions Used in the Treatment

The Question of Turbulence

All of the results derived or presented so far in this section have depended upon the assumption of non-turbulent convective flow. The characteristic quantity which is involved in questions of turbulence is the Reynolds number, $R=v\rho l/\eta$, where v is a velocity and l a length characteristic of the problem in question. If on the basis of our simplified derivation, we take

TABLE VII. Values of k_c (Maxwellian gas, $n=1$).

T_2/T_1 \ r_1/r_2	15	25	40	60	100
2	0.0144	0.0184	—	—	—
3	0.0095	0.0130	0.0162	0.0183	0.0207
4	0.0045	0.0068	0.0088	0.0105	0.0128
5	0.0022	0.0034	0.0046	0.0056	0.0072
6	—	—	0.0025	0.0031	0.0040

$v=\bar{v}$, and $l=w$, we have for the Reynolds number[6]

$$R=\frac{w^3 g\rho^2}{48\eta^2}\frac{\Delta T}{\bar{T}}. \tag{118}$$

In view of the relation $D=(6/5)f(\nu)\eta/\rho$ (Eq. (18) of Part I), we have the simple relation

$$R=1.57(6f(\nu)/5)(K_c^{(0)}/K_d^{(0)})^{\frac{1}{2}} \tag{119}$$

$$\cong 2(K_c^{(0)}/K_d^{(0)})^{\frac{1}{2}}. \tag{120}$$

Onsager and Watson (O1), who first pointed out the existence of a relation of the form (119), have shown experimentally that with apparatus of the plane type, spontaneous turbulence occurs for R greater than about 25. The relation (119) thus puts an upper limit on the ratio of K_c to K_d; in fact, in order to insure that any disturbances caused by slight irregularities in the tube are quickly damped out, R should be substantially less than its critical value. If we take 10 as the maximum permissible value of R, it follows from (120) that K_d must not be made less than $(K_c/25)$. Since the maximum separation factor for a given length of tube is obtained for K_d equal to $2K_c$ (Part III, Eq. (155)), this restriction is unimportant when one is interested in obtaining a maximum separation factor. We are usually, however, not interested in getting a given separation factor in as short a length as possible, but are rather interested in obtaining the most efficient production of concentrated material. As we shall see in Part III, efficient operation demands that K_d be made *small* compared with K_c. Equation (120) permits us to satisfy this condition.

The limitation on the smallness of K_d/K_c is also important in another respect. For a given ratio B/w or r_1/r_2, K_d/K_c is inversely proportional to w^6 or r_1^6. The limitation on K_d/K_c thus puts an upper limit on w or r_1, and therefore also puts an upper limit on the value of H, which is proportional to w^3 or r_1^4. This limitation on H will often make it necessary to use several tubes in parallel for some of the stages of efficient multi-stage apparatus.

TABLE VIII. Values of k_d (Maxwellian gas, $n=1$).

T_2/T_1 \ r_1/r_2	15	25	40	60	100
2	0.61	0.60	—	—	—
3	0.75	0.73	0.70	0.68	0.67
4	0.91	0.87	0.83	0.81	0.78
5	1.08	1.01	0.97	0.94	0.90
6	—	—	1.11	1.07	1.03

The arguments given above apply directly to the plane case, or, in practice, to the "nearly plane" cylindrical case, in which the hot and cold walls are the surfaces of cylinders of nearly the same radius. For the extreme cylindrical case, that of a hot wire along the axis of a tube, it is evident on dimensional grounds that the Reynolds number R may be taken to be defined by (119). There are at present, however, no direct experimental determinations of the values of R at which turbulence occurs in extreme cylindrical cases. It seems highly desirable that experiments similar to those of Onsager and Watson should be performed for such cases.

The Temperature Distribution

All of the results so far presented or derived have also depended upon the assumption that the temperature distribution is that determined by conduction alone. A crude argument on the basis of the simple two-column model is sufficient to show that the length of tube at either end of the column, in which the temperature distribution differs from that determined by conduction, is of the order

$$l_r=\frac{w\eta c_p}{2\lambda}R. \tag{121}$$

The relation

$$\eta c_v/\lambda=\tfrac{2}{5} \tag{122}$$

holds very closely for monatomic gases, and fairly well for polyatomic gases (C5, p. 241). We thus find the very simple relation

$$l_r=wR/5. \tag{123}$$

This "relaxation length" may be compared with the length of tube necessary to give a separation factor $1+\alpha(\Delta T/\bar{T})$, which is roughly that of a single stage apparatus (cf. Eq. (28)). According

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[6] The definition (118) of the Reynolds number is that given in F1. Onsager and Watson (O1) employ a different definition of the Reynolds number, with the result that all of the values of R given by them should be divided by 6.16 to agree with ours. It does not matter, of course, which definition is used as long as it is used consistently.

to Eq. (150) this "length per stage" is given by

$$l_1=(\alpha\Delta T/\bar{T})\cdot(K_c^{(0)}+K_d^{(0)})/H^{(0)}, \quad (124)$$

$$=(2/63)\{(\rho g w^4\Delta T)/(\eta D\bar{T})\}\cdot\{1+(K_d^{(0)}/K_c^{(0)})\}, \quad (125)$$

$$=(32/21)(\eta/\rho D)\cdot Rw\{1+(K_d^{(0)}/K_c^{(0)})\}, \quad (126)$$

$$\cong\{1+(K_d^{(0)}/K_c^{(0)})\}Rw. \quad (127)$$

Thus l_r is only a rather small fraction of l_1. It is reasonable to suppose that this conclusion is also valid for the extreme cylindrical case.

The Quasi-Stationary Assumption

This assumption is of decisive importance in the elementary approximate argument by which we have derived the transport equation. It is also involved in the work of Furry, Jones, and Onsager on which are based the more accurate results which have been quoted. Indeed, these writers used the assumption in its strongest possible form: they based their calculation on the equation

$$\operatorname{div}\mathbf{J}_1\equiv\operatorname{div}\mathbf{J}_2\equiv 0, \quad (128)$$

which says that the concentration at each point in the tube is precisely constant in time. They also used two other assumptions for which no rigorous justification was provided. The first of these was that the effect of diffusion along the tube could be ignored in making the calculations, and taken into account by simply adding the term $-K_d(\partial c_1/\partial z)$ to the transport equation after it had been obtained. The second was that, with the neglect of longitudinal diffusion and in the absence of any net flow of the gas as a whole along the tube, the derivative $(\partial^2 c_1/\partial z\partial t)$ could be set equal to zero.

A derivation of the transport equation which is independent of these assumptions has been given by Bardeen (B3). Using instead of (128) the equation of continuity

$$\operatorname{div}\mathbf{J}_1+\partial\rho c_1/\partial t=0, \quad (129)$$

he proves that the transport equation is that obtained by Furry, Jones, and Onsager, except that the coefficients are slightly different; the differences are small, since they amount to a fractional correction of the order of $\alpha\Delta T/\bar{T}$. Bardeen's work shows that the transport equation possesses this accuracy even when applied to the case of a tube which is not connected to any reservoirs, but is closed at both ends.

Effects of Asymmetry

In practice, there will be other remixing effects besides those so far discussed, because of inevitable parasitic convection currents, caused by small irregularities and asymmetries. In general, these parasitic currents will add other terms of the K type to the transport equation, except that the new terms will involve K's which, in general, are functions of z. It is, of course, very difficult to evaluate the effect of such irregularities. A conception of their possible importance, however, is given by the consideration of a very special kind of asymmetry: that in which there is in addition to the radial temperature gradient (in a concentric tube apparatus) also an azimuthal variation of amount δT:

$$T=f(r)+\tfrac{1}{2}\delta T\cos\varphi, \quad (130)$$

where

$$\varphi=2\pi y/B. \quad (131)$$

As a consequence of this azimuthal variation of temperature there will be superposed on the convection currents already calculated a parasitic current which travels upward on one side of the tube (φ near 0) and downward on the other (φ near π). The parasitic current thus consists of two columns, A and B, and the parasitic transport can be calculated in a way similar to that used for the simple calculation of the main transport.

So far as the hydrodynamical problem is concerned, we observe from Fig. 2 that for the parasitic currents the surfaces on which the velocity must vanish are separated by a distance $2w$, whereas for the main currents this distance is w. On the other hand, the driving temperature difference is δT instead of ΔT. By noting the way in which $\bar{v}$ depends on w and ΔT (cf. Eq. (46)) we obtain as an estimate of the mean velocity of the parasitic currents

$$\bar{v}_p\cong 4(\delta T/\Delta T)\bar{v}. \quad (132)$$

The parasitic transport of the lighter isotope up the tube is given by

$$\tau_{1p}=\rho(c_1^B-c_1^A)\bar{v}_p wB. \quad (133)$$

The value of $c_1^B - c_1^A$ may be calculated in the same way as that of $c_1^{II} - c_1^I$. From Fig. 2 it is evident that in computing the diffusion between the columns we have to use $B/2$ as the value for width of a column and distance between columns, instead of w. Also, there are *two* diffusive connections between columns A and B. Then, replacing w by $B/2$, ΔT by δT, $\bar{v}$ by $\bar{v}_p$, and D by $2D$ in Eq. (51), we obtain

$$c_1^B - c_1^A = \alpha c_1 c_2(\delta T/2\bar{T}) - (\bar{v}_p B^2/8D)(\partial c_1/\partial z). \quad (134)$$

Then from (133) and (134) we get for the parasitic transport

$$\tau_{1p} = H_p c_1 c_2 - K_p dc_1/dz, \quad (135)$$

where

$$H_p = \alpha\rho\bar{v}_p wB(\delta T/2\bar{T}) = 4(\delta T/\Delta T)^2\cdot H, \quad (136)$$

$$K_p = \rho\bar{v}_p^2 wB^3/(8D) = 2(B/w)^2(\delta T/\Delta T)^2\cdot K_c. \quad (137)$$

Furry, Jones, and Onsager (F1) use a somewhat more detailed calculation and obtain the more precise result

$$K_p/K_c = (315/16\pi^2)(B/w)^2(\delta T/\Delta T)^2. \quad (138)$$

This more accurate relation differs from (137) only very slightly, since $315/16\pi^2 = 1.995$.

In practice, δT will always be much smaller than ΔT, so that H_p will never be important. Because of the presence of the factor $(B/w)^2$, however, the ratio K_p/K_c may rise to very appreciable values even when $\delta T/\Delta T$ is small compared with unity. The relation (138) puts an upper limit on the values of B/w which may be used in practice.

In the extreme cylindrical (hot wire) case a distinction must be made between the effects of asymmetries in the cooling of the outer tube and those of improper centering of the wire. As an example of the former type, we can calculate the temperature distribution with the boundary condition

$$T(r_1, \varphi) = T_1 + (\delta T/2)\cos\varphi, \quad (139)$$

ignoring the effect of the hot wire and taking η, λ, and D as constants evaluated at T_1. We obtain

$$K_p/K_c = (441/64k_c)(\delta T/T_1)^2. \quad (140)$$

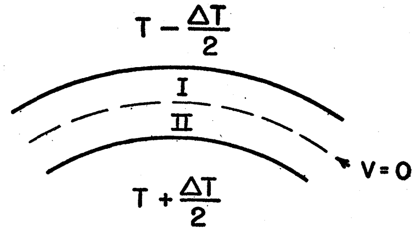

FIG. 2a. Showing the main convection currents, rising in the region II and descending in the region I. The diagram represents a horizontal cross section of the separation column.

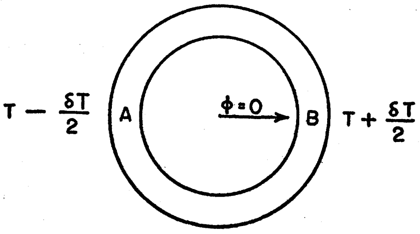

FIG. 2b. Showing the parasitic convection currents, rising in the region B and descending in the region A, which would be caused by the particular type of temperature asymmetry which is indicated by Eq. (130).

Since by Table VII the values of k_c which may occur are of the order of magnitude 10^{-2}, it is evident that the restrictions on δT are roughly the same as would be obtained by using (138) with $(B/w) \cong 20$. This must, however, be much too high an estimate for K_p in this case, because of the evaluation of λ, η, and D at the temperature T_1. The presence of a central region of high conductivity, viscosity, and diffusivity, and low density, will decidedly reduce the true value of K_p.

The effect of inexact centering of the wire can be estimated by using a linear dipole distribution —a linear source of heat parallel to and very near to a linear sink—on the axis of the tube. If λ, ρ, η, and D are again given their constant values at T_1, one obtains

$$\frac{K_p}{K_c} = \frac{8169}{64k_c}\left(\frac{\Delta T}{T_1}\right)^2\left(\frac{\delta x}{r_1 \log(r_1/r_2)}\right)^2, \quad (141)$$

where δx is the displacement of the wire from the axis of the tube. Then $K_p \cong K_c$ would occur for $(\delta x/r_1) \cong 1/30$. Again, however, the estimate for K_p is surely much too high. In this case it might be more reasonable to use the values of ρ, η, and D at T_2. This would, for a Maxwellian gas, introduce a factor $(T_1/T_2)^7$ in the right member of (141).

If Eqs. (140) and (141) were taken literally, one would have to suppose that parasitic currents are about as serious a consideration in the extreme cylindrical case as in the plane case. Actually both these equations certainly overestimate the parasitic effects by large factors. It seems likely that, if reasonable care is taken in construction, parasitics will be of no appreciable importance in the performance of hot wire apparatus.

III. CONSEQUENCES OF THE TRANSPORT EQUATION

By applying the transport equation we now discuss the various types of operation: discontinuous operation, continuous operation of single-stage apparatus, and continuous operation of multi-stage (series-parallel) apparatus. For each type of operation the relation between length, separation factor, and yield is obtained in exact general form, and also in simple approximate forms for various special cases. These formulae, together with the formulae for H and K which were obtained in Part II, complete the description of the performance of an apparatus of given dimensions and temperatures, run at a given pressure.

This part also includes a description of the problems of choosing dimensions, temperatures, and pressure in such a way as to obtain the greatest efficiency in operation. These problems can be placed in two mutually exclusive categories. The problems of the first category are concerned with fixing the lengths and arrangement of columns, which have prescribed values of H and K, in such a way as to obtain the best efficiency. These problems are discussed by using the formulae developed in this part. In the second category we place the problem of choosing the radii and temperatures used in a column to obtain the most advantageous values of the coefficients H and K. This second sort of problems is discussed in the section on entropy efficiency, the discussion being based on the material of Part II.

Generalized Notation

The transport equation which was derived in Part II may be written in the simple form

$$\tau_1 = Hc_1c_2 - Kdc_1/dz, \qquad (142)$$

where K is the sum of the coefficients which account for the various re-mixing effects:

$$K = K_c + K_d + K_p. \qquad (143)$$

In this equation τ_1 is the transport of species 1 up the tube in grams per second, c_1 is the fractional particle density of species 1, $c_2 = 1 - c_1$ is the corresponding density of the heavier constituent, and z is a coordinate whose positive direction is up the tube. The transport coefficients H and K are constants which, as we have shown in detail in Part II, depend on the nature of the gas or liquid, on the pressure in the case of a gas, on the dimensions and shape of the apparatus, and on the temperature difference maintained in the column; they do not depend on τ_1, c_1 or z. The transport τ_1 and the concentrations depend only on z and the time.

In deriving Eq. (142) we have always focused our attention upon what happens to the lighter isotope. It is clear, however, that the physical situation is symmetrical with respect to the species 1 and 2. The equation for the transport of the heavier constituent down the tube is precisely similar to (142):

$$\tau_2 = Hc_1c_2 - Kdc_2/dz, \qquad (144)$$

where the coordinate z is now considered to increase *down* the tube.

The considerations to be developed in the present section will apply equally well to cases in which one is concentrating either the heavier or the lighter isotope. In order to simplify the language used in discussing the transport equation, we shall accordingly introduce the symbol c without a numerical subscript to refer to the concentration of the constituent we are interested in concentrating, and we shall refer to the direction in which c tends to increase as the *positive* direction. We shall further refer to the end of the tube at which c is greater as the *positive end* of the column, and to the reservoir, if any, which is connected to the positive end as the *positive reservoir*. The terms *negative end* and *negative reservoir* have corresponding meanings. The coordinate z is assumed to increase in the same direction as c, so that the positive direction may equally well be considered as the direction in which z increases. We also introduce the quantity

$\bar{c}=1-c$. Thus in the case in which we are concentrating the lighter isotope, c is identified with c_1, $\bar{c}$ with c_2, and the positive direction is upward. Correspondingly, if we wish to concentrate the heavier isotope, we identify c with c_2, $\bar{c}$ with c_1, and the positive direction is downward.

In either of these two cases, the transport equation is now

$$\tau=Hc\bar{c}-Kdc/dz, \tag{145}$$

where τ is the transport in the positive direction of the species we are interested in concentrating.

In the event that the separation column is to be used for the separation of chemically dissimilar gases, the gas which tends to concentrate in the hotter regions of the gas (in the absence of convection currents) should be identified with species 1. In this case, however, we may have the additional complication that H will depend on c to an appreciable extent because α is not independent of the concentrations in the case of mixtures of greatly dissimilar molecules.

The Two Types of Operation

The type of operation which was contemplated during the derivation of (145) was that in which one places the gas in the separation column, which may or may not connect with reservoirs at the ends, and then waits until the concentration difference has reached a suitable value, at which time the contents of the apparatus are removed; the performance is repeated if more material is desired. This type of operation we shall term discontinuous. There is also available a continuous type of operation, in which the gas is removed at a small steady rate from the positive end of the column. Continuous operation will be more important in practice than discontinuous operation, and the mathematical discussion of continuous operation is slightly less complicated.[7] Even with continuous operation, however, the apparatus must first reach a suitable condition before we can begin to withdraw concentrated material from the positive end, and the discussion of the approach to this condition is the same as in the case of discontinuous operation.

Our discussion of continuous operation is more complete than the corresponding discussion of discontinuous operation, because of the greater importance of the former. Because of considerations of logical order, however, the treatment of discontinuous operation is given first.

DISCONTINUOUS OPERATION

Discontinuous operation may be defined as operation in which the total transport of gas through the tube is zero. This condition is already written into Eq. (145).

Equilibrium Separation Factor

The final equilibrium state is that in which τ is zero all along the tube. Putting $\tau=0$ in (145), we have

$$\frac{dc}{c\bar{c}}=d\log\frac{c}{\bar{c}}=\frac{H}{K}dz=2Adz, \tag{146}$$

the integral of which is

$$c/\bar{c}=\exp\left[2A(z-z_0)\right], \tag{147}$$

or equivalently

$$c(z)=\tfrac{1}{2}\{1+\tanh A(z-z_0)\}. \tag{148}$$

The quantity A defined by

$$A=H/2K \tag{149}$$

is important in all that follows. If we use the subscript f to refer to the positive end of the

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[7] For the case of continuous operation Clusius and Dickel (C10) describe an extremely simple procedure for the complete design of apparatus. Like the treatment given here, it is based on the characterization of a separation tube by two parameters. Our two parameters are H and $y=2AL=HL/K$; Clusius and Dickel use the initial transport ($=Hc_i\bar{c}_i$) and the equilibrium separation factor ($=e^y$). Unfortunately their very simple discussion is based essentially on the false assumption that the equilibrium separation factor can be realized while *at the same time* one removes concentrated material at a rate corresponding to the full initial transport. Thus they ignore the fundamental question as to *how much the equilibrium is disturbed* by the removal of the material one is interested in producing, so that their treatment, though simple, can be of no use in practice.

The criticism just given applies directly to the discussion of the numerical example (C10, p. 436). The same error shows up in a rather different form in the abstract discussion (pp. 432–435). Here (Eq. (35)) it is assumed that the difference between the concentrations of the two columns (cf. our Fig. 1, or Fig. 16 of C10) is determined by diffusion and thermal diffusion only, and is *not affected by the presence of a concentration gradient or by a net transport of gas along the tube.* This is equivalent to setting $K=0$, which means, if one is to be consistent, an infinite equilibrium separation factor.

column (the end where c is greater), and the subscript i to refer to the other end, we have from (147)

$$q_e = e^{2AL}, \tag{150}$$

where L is the length of the separation column, and where q_e is the equilibrium value of the separation factor

$$q = \frac{(c/\bar{c})_f}{(c/\bar{c})_i}. \tag{151}$$

We shall find it convenient to introduce also the reciprocals of q and q_e:

$$p = q^{-1}, \tag{152}$$

$$p_e = q_e^{-1} = e^{-2AL}. \tag{153}$$

In order to secure the largest equilibrium separation factor with a given length of tube, it is clear that we must make A as large as possible. If K_p is set equal to zero, A is given, as we have seen in Part II, rather closely for the plane case by the expression

$$A = H^{(0)}/2(K_c^{(0)} + K_d^{(0)}). \tag{154}$$

It is easily shown that A is maximized with respect to a variation of w, if w is adjusted so that $K_d^{(0)} = 2K_c^{(0)}$ (see Eqs. (70)–(72)). We then find that the maximum value of A is given by

$$A_{\max} = \frac{(105)^{1/3}}{180} \alpha \left(\frac{\Delta T}{\bar{T}}\right)^{4/3} \left(\frac{\rho g}{\eta D}\right)^{1/3}. \tag{155}$$

Since $(\rho/\eta D)$ is proportional to the square of the pressure, there is no limit in principle to the value of A which may be attained. For pressures which amount to more than a few atmospheres, however, the values of w required may become so small that serious constructional difficulties arise.

For the separation of He^3 from He^4, we note that $\alpha = 0.076$, $\rho/\eta D = 0.127$, at atmospheric pressure and $\bar{T} = 450°K$ (see Part IV); therefore the value of $A_{\max}$ in an apparatus with $T_2 = 2T_1$ is about 0.0058 cm^{-1} so that in all those parts of the separation column in which c is less than say 0.2, the concentration of He^3 will double every 60 cm. With such a large value of A, a column working at atmospheric pressure with a length of only 14 meters would suffice to raise the concentration of He^3 from its natural value of 10^{-7} to 50 percent. On the other hand, the equilibrium time of the single tube just described may be estimated from Eq. (174), and is about 350 years. We shall see in Part IV how to design an apparatus which can be made to yield results within a more reasonable time.

Equilibrium Time in Columns with One or Both Ends Closed Off

These cases have been treated by Bardeen (B2), some of whose results we quote here. The case of a tube closed at both ends has also been treated by Debye (D1).

Tube Closed at Both Ends

In this case c is a function of both z and the time t, so that the derivative in (145) should be replaced by a partial derivative. The conservation of the species whose concentration is c requires that

$$\mu \partial c/\partial t = -\partial \tau/\partial z \tag{156}$$

or, by substitution from (145), that

$$\mu \partial c/\partial t = -H\partial(c\bar{c})/\partial z + K\partial^2 c/\partial z^2, \tag{157}$$

where μ is the mass of gas in unit length of the tube. The treatments of Bardeen and Debye apply only in the case that c is everywhere small compared with unity, so that $\bar{c}$ in (157) may be set equal to unity. This approximation has the merit of making the equations linear so that superposition may be used. The general case is much more difficult and has not been solved.

Equation (157) must be solved subject to the boundary conditions that

$$\tau = 0 \quad \text{at} \quad z = 0 \quad \text{and} \quad z = L, \tag{158}$$

and that

$$\tau = Hc_0 \quad \text{at} \quad t = 0 \tag{159}$$

where c_0 is the constant initial concentration. By using the standard theory of linear equations, Bardeen finds that the solution of (157)–(159) is

$$c(z) = ke^{2Az} + e^{Az} \sum_n b_n \{\cos(n\pi z/L) + (AL/n\pi)\sin(n\pi z/L)\} \cdot e^{-t/t_n}, \tag{160}$$
$$n = 1, 2, \cdots$$

in which the constants k, b_n, and t_n are defined by

$$k=2ALc_0/(e^{2AL}-1),$$
$$b_n=4c_0(n^2\pi^2/A^3L^3)(1-(-1)^n e^{-AL})/(1+n^2\pi^2/A^2L^2)^2, \tag{161}$$
$$t_n=2(\mu/AH)/(1+n^2\pi^2/A^2L^2).$$

From (160) we have for the separation factor which is actually realized at the time t:

$$q=\frac{c_f}{c_i}=e^{2AL}\left(\frac{1+k^{-1}\sum_n b_n(-1)^n e^{-AL-t/t_n}}{1+k^{-1}\sum_n b_n e^{-t/t_n}}\right). \tag{162}$$

The first term of (160) represents the equilibrium concentration distribution, and the remaining terms are the transient terms, each of them decaying with a characteristic time t_n. For cases in which AL is rather small ($\lesssim 2$), t_1 will be much longer than any of the remaining t_n's; after a time of the order t_2, which is only a fraction of t_1, the only important transient term in (160) will be the first. Thus if AL is not too large, the approach to equilibrium is characterized by a relaxation time

$$t_r=t_1=(2\mu/AH)/\{1+\pi^2/(AL)^2\}. \tag{163}$$

For large values of AL, it is necessary to use more than one term of the series (160).

The case in which AL is small compared with unity has been considered in more detail by Debye (D1). In this approximation, the quantities k, b_n, and t_n take on the simple form

$$\begin{gathered} k\cong c_0 \\ b_n\cong 4c_0AL(1-(-1)^n)/(n\pi)^2 \\ t_n\cong(\mu L^2/\pi^2K)/n^2. \end{gathered} \tag{164}$$

With the use of the approximation

$$e^{2AL}\cong 1+2AL, \tag{165}$$

the expression (162) now reduces to the form

$$c_f/c_i=1+2AL\{1-(8/\pi^2)\times\textstyle\sum_k \exp[-(2k+1)^2t/t_1]/(2k+1)^2\}, \tag{166}$$
$$k=0,1,2,\cdots.$$

For values of t large compared with t_1, the expression on the right clearly reduces to $1+2AL$, whereas for $t=0$, the well-known series (special case of the zeta function)

$$1+3^{-2}+5^{-2}+\cdots=\pi^2/8 \tag{167}$$

indicates that the value of the curly bracket is zero.

For small values of $x=t/t_1$, Debye has shown that

$$(8/\pi^2)\textstyle\sum_k \exp[-(2k+1)^2x]/(2k+1)^2 =1-(4/\pi^{\frac{3}{2}})x^{\frac{1}{2}} +(32/\pi^5)x^{\frac{3}{2}}\exp(-\pi^2/4x)+\cdots. \tag{168}$$

If we retain only the first two terms of (168), and insert the specific value of t_1, (166) may now be written:

$$c_f/c_i=1+4H(t/\pi\mu K)^{\frac{1}{2}}+\cdots. \tag{169}$$

This result is striking in two respects. In the first place, it indicates that the concentration difference increases initially as the *square root of the time.* This result is of special importance in application to liquids; in such apparatus the equilibrium time is very long, of the order of a year. The result (168) indicates that a period of operation as short as ten hours would nevertheless achieve 1/40 of the equilibrium concentration difference. In practice, this relation will break down for extremely small values of t, since the space at the end of the column in which the convection current turns around will constitute a small reservoir.

Secondly, the result indicates that the initial rise of the concentration difference is *independent of the length of the column.* This result seems more plausible when we consider that the rapid increase in the concentration difference occurs only in a small length near each end. The length of the column does enter into the result in the sense that (169) holds only as long as t/t_1 is suitably small, and t_1 is proportional to the square of the length L. The fact that the rapid changes in c are restricted to a small space near the ends, moreover, means that the result (169) must hold even when AL is not restricted to small values. In this case, however, it is not so easy to say for how long a time the relation (169) will be valid.

In an apparatus of this type, closed at both ends, the concentration cannot rise at one end without its falling at the other. Thus only a part of the equilibrium separation factor can be realized as a displacement of the concentration from its original value. If, however, the negative end of the column (the end where c is smaller) is connected with a reservoir whose value of c is maintained at its original value, then *all* of the equilibrium separation factor may be realized as an increase of c above its original value. This case is treated next.

Tube Closed at One End and Connected with an Infinite Reservoir at the Other

The equivalent of an infinite reservoir, as far as the maintenance of c_i at a constant value is concerned, is obtained by running a stream of fresh gas past the negative end of the column, or more efficiently by means of a short scrubbing column, as we shall discuss in detail later on.

The treatment of Bardeen shows that for this case, with the restriction that c be everywhere small,

$$q=(c_f/c_i)=e^{2AL}-\sum\nolimits_n C_n e^{-t/t_n}. \tag{170}$$

Here, C_n, t_n are defined by

$$\begin{aligned} C_n &= \{4\gamma_n{}^2/(1-\gamma_n{}^2)\}/\{1-AL(1-\gamma_n{}^2)\}, \\ t_n &= (2\mu/AH)/(1-\gamma_n{}^2), \quad t_1>t_2>t_3>\cdots, \end{aligned} \tag{171}$$

and the γ_n are solutions of

$$\tanh \gamma AL=\gamma, \tag{172}$$

where, however, the root $\gamma=0$ is not to be included unless it is a multiple root. These relations may be obtained from the results given by Bardeen by taking the limit as $R\rightarrow 0$, $M\rightarrow\infty$. (Bardeen's Eq. (49) contains misprints which have been corrected (B3).) As in the previous case, the derivation is subject to the restriction that c must remain small.

For all values of AL which are not extremely small, C_1 is much larger than any other C_n, and is nearly equal to $e^{2AL}-1$; also t_1 is much larger than any other t_n. Thus, for AL not too small, the main part of the approach to equilibrium follows rather closely a simple exponential law, of the form

$$(q-1)=(q_e-1)(1-e^{-t/t_r}) \tag{173}$$

with $t_r=t_1$. Now, if one assumes a law of the form (173), it is physically reasonable to take as an approximate value for the relaxation time t_r the quotient of the total mass of the isotope which must be transported into the tube, divided by the initial transport from the reservoir into the tube. The value estimated in this way is

$$\begin{aligned} t_r' &= (Hc_i)^{-1}\cdot \mu Lc_i\left\{\int_0^L e^{2Az}dz-1\right\} \\ &= (\mu L/H)\{((e^{2AL}-1)/(2AL))-1\}. \end{aligned} \tag{174}$$

TABLE IX. Quantities for a separation column which is closed at one end and is connected with an infinite reservoir at the other.

AL	γ_1	γ_2	θ_r'	θ_1	θ_2	$e^{2AL}-1$	C_1	C_2
0.50	$2.33i$	$9.20i$	0.718	0.621	0.05	1.72	1.53	0.09
0.75	$1.125i$	$6.07i$	1.321	1.177	0.07	3.48	3.20	0.14
1.00	0	$4.50i$	2.19	2.00	0.09	6.39	6.00	0.19
1.50	0.8586	$2.92i$	5.36	5.07	0.14	19.09	18.52	0.27
2.00	0.9575	$2.14i$	12.40	12.03	0.18	53.6	52.8	0.32
2.50	0.98560	$1.67i$	28.5	28.0	0.21	147.4	146.4	0.35

For purposes of comparison we introduce the numbers

$$\theta_n=(H/\mu L)t_n, \quad \theta_r'=(H/\mu L)t_r'. \tag{175}$$

Table IX shows that even for quite small AL the estimate t_r' obtained by physical reasoning is in rough agreement with t_1, and for larger AL the agreement becomes good. We see also that θ_1 is much larger than θ_2, and C_1 is much larger than C_2. Moreover, C_1 is only slightly smaller than $e^{2AL}-1$, so that all but a small fraction of the concentration change takes place according to the simple law (173). The fact that very simple physical considerations enable us to give a quite good account of the approach to equilibrium is of importance: it justifies us in applying similar considerations when c is not everywhere small, and also in the case of multi-stage apparatus,[8] where precise treatment would entail many complications.

Since $\sum C_n/t_n$ diverges, the initial rise of concentration at the closed end again has a vertical slope. We see, however, from the seventh and eighth columns of Table IX, that this sharp initial rise cannot cover more than a small fraction of the total shift of concentration, if $AL\geq 0.50$. For $AL\ll 1$, the series (170) can be put

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[8] In Part II the term *single-stage* was used to refer to the type of apparatus in which there was no compounding of the fundamental separating effect. Henceforth, however, we shall use the term single stage to refer to a single length of separating column. By *multi-stage* apparatus, we shall understand the type in which several single stages are connected in series or series-parallel.

in the form (166), with a value of t_1 four times as large as in the previous case. Debye's result (168) for the value of the series then gives

$$c_f/c_i = 1 + 2H(t/\pi\mu K)^{\frac{1}{2}} + \cdots. \tag{176}$$

The physical reason for the factor one-half in the coefficient of the second term of (176) as compared with (169) is that in the present case c_i remains fixed, and only c_f changes.

The reason that the initial change of concentration at any closed end of a separation column is proportional to the square root of the time, may be seen from very elementary considerations. As long as there is no concentration gradient, the transport equation (145) indicates that there will be a transport of isotope to the very end of the column. The material collecting at the end will bring about an equilibrium concentration gradient in a short length of column adjacent to the end. The additional amount of isotope required is proportional to this length and to the increase in concentration at the end, and therefore to the square of the increase of concentration. Thus the square of the increase of the concentration is proportional to the time, or the increase of concentration is proportional to the square root of the time. This method of argument is adequate to yield a derivation of (169) and (176), apart from a numerical constant factor in the term proportional to $t^{\frac{1}{2}}$.

Equilibrium Time in Columns with Both Ends Connected with Reservoirs

This case is not so important in practice as the case in which the positive end of the column is closed off and does not connect with a reservoir. The present case, however, may be treated much more completely in a theoretical way, since we need not restrict ourselves to the case in which c is everywhere small compared with unity. This case also possesses considerable theoretical interest, as we shall show in the section on entropy efficiency.

We shall here, as in the previous case, suppose that the reservoir at the negative end of the column is effectively infinite, although the generalization to the case in which it is large but finite is often very simple (cf., e.g., Eq. (186)).

We shall further suppose—and this is the restricting assumption which makes the present treatment so much simpler than the previous case—that the volume of the reservoir at the positive end of the column is large compared with the volume of the tube, or equivalently that the mass of gas m in the positive reservoir is large compared with the mass of gas μL in the separating column. In this case it is clear on physical grounds that at any given time during the approach to equilibrium the transport of the desired isotope between the two reservoirs will not differ appreciably from the transport which would be obtained if the concentrations in the reservoirs were held constant at the values which they have at the given moment. The present treatment will thus hold rigorously in the limit in which the harmonic mean of the volumes of the reservoirs becomes infinite compared with the volume of the separation column, but will hold quite well in the case in which this ratio is only several times unity.

The reader will recognize the restriction made in the last paragraph as a strong form of the quasi-stationary assumption, which was used in a weaker form in the derivation given above for the transport equation itself, but which Bardeen has shown to be actually unnecessary for the derivation of the transport equation.

Exact General Solution

The mathematical significance of the assumption that m is large compared with μL is that we may take the transport τ to be independent of z, and to depend only on the time t. The solution of the transport equation (145) with τ constant is

$$c(z) = \tfrac{1}{2}\{1 + b \tanh bA(z - z_0)\}, \tag{177}$$

where

$$b = (1 - 4\tau/H)^{\frac{1}{2}}. \tag{178}$$

Eliminating z_0 by the boundary conditions

$$c(0) = c_i, \qquad c(L) = c_f, \tag{179}$$

we have

$$c_f = \frac{1}{2}\left\{1 - b\frac{(b \tanh bAL) - b_0}{(b_0 \tanh bAL) - b}\right\}, \tag{180}$$

where

$$b_0 = 1 - 2c_i. \tag{181}$$

By the same argument which led to Eq. (33) of Part II, the time variation of c_f is given by

$$dc_f/dt = \tau/m. \tag{182}$$

If the reservoir at the negative end of the column is effectively infinite, c_i will not vary in time, and the time required for the concentration in the positive reservoir to rise from c_i to any required value c_r is given by

$$t(c_r) = m\int_{c_i}^{c_r} dc_f/\tau, \tag{183}$$

where the relation between c_f and τ is given by (180).

If the mass of gas m_- in the negative reservoir is not effectively infinite, the time variation of c_i and c_f is given by the simultaneous equations

$$dc_f/dt = \tau/m_+, \tag{184}$$

$$dc_i/dt = -\tau/m_-, \tag{185}$$

whence

$$d\Delta/dt = \tau/\{m_+m_-/(m_+ + m_-)\}, \tag{186}$$

where

$$\Delta = c_f - c_i. \tag{187}$$

The integration indicated in (183) and the one resulting from (186) cannot be done analytically, but must be done numerically. In nearly all of the cases which will arise in practice, however, some approximate treatment will suffice. The remainder of this section on discontinuous operation will be devoted to a statement of various approximate solutions, and to a discussion of the most efficient mode of operation.

Solution for $c\bar{c} \cong$ constant

In those cases where the equilibrium separation is sufficiently small that $c\bar{c} = c(1-c)$ does not change appreciably along the column, the approach to equilibrium may be treated simply. With τ and $c\bar{c}$ constant, the solution of (145) which satisfies (179) is

$$\tau = H(c\bar{c} - (c_f - c_i)/2AL), \tag{188}$$

and the integral of (182) which satisfies the initial condition

$$t = 0, \qquad c_f = c_i \tag{189}$$

is

$$t(c_f) = -(my/H)\log(1 - \Delta/yc\bar{c}). \tag{190}$$

We have here introduced the abbreviation

$$y = 2AL = HL/K. \tag{191}$$

Equation (190) represents a simple exponential approach to equilibrium, as may be seen most easily by writing it in the form

$$\Delta = \Delta_e(1 - e^{-t/t_r}) \tag{192}$$

where

$$\Delta_e = yc\bar{c} \tag{193}$$

is the equilibrium value of Δ, and

$$t_r = my/H \tag{194}$$

is the relaxation time for the separation.

If the negative reservoir is of finite volume, the only change to be made in (190)–(194) is to replace m by the quantity $m_+m_-/(m_+ + m_-)$.

The chief practical value of this result lies in the case in which c varies within the range 0.3 to 0.7. In this range $c\bar{c}$ is never far from $\frac{1}{4}$. This result will also be useful in connection with the discussion of entropy efficiency.

Solution for $c \ll 1$

For the case in which c is everywhere much less than unity, so that $\bar{c}$ may be set equal to unity, we find the same procedure as that used in the previous section, that[9]

$$(q-1) = (q_e - 1)(1 - e^{-t/t_r}), \tag{195}$$

where

$$q_e = e^y \tag{196}$$

is the equilibrium separation factor, and

$$q = c_f/c_i \tag{197}$$

is the separation factor which is realized at the time t. For this case,

$$t_r = (m/H)(e^y - 1). \tag{198}$$

Solution for $\bar{c} \ll 1$

For the case in which c may be set equal to unity, we have

$$(1-p) = (1-p_e)(1 - e^{-t/t_r}), \tag{199}$$

where

$$p = \bar{c}_f/\bar{c}_i \tag{200}$$

and

$$t_r = (m/H)(1 - e^{-y}). \tag{201}$$

The General Linear Approximation

The fact that $c\bar{c}$ is quadratic in c is the difficulty that leads to the complication of the

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[9] Equation (60) of F1, which corresponds to (195), was subject to the unstated condition that q and q_e were large compared with unity.

general treatment. In many of the cases which arise in practice, however, the increase of c along the column will not be greater than about 0.2. In such cases, the function $c(1-c)$ can be closely approximated in the range of c in question by an expression linear in c. A linear expression which is never greater than $c\bar{c}$ in the range $c=r$ to $c=s$, and which is exact at r and s, may be obtained by using the chord drawn between $c=r$ and $c=s$ on the parabola $c(1-c)$. This procedure means replacing c by

$$rs+(1-r-s)c. \tag{202}$$

By the same procedure as that used in the previous sections, we find that the approach to equilibrium is of the type (192), where the relaxation time is now given by

$$t_r=(m/H)(q_e^{1-r-s}-1)/(1-r-s). \tag{203}$$

The results derived in the three previous paragraphs are all special cases of this result. In this case also, the generalization to the case in which both reservoirs are finite is accomplished by replacing m by $m_+m_-/(m_++m_-)$.

It is clear that the result is not sensitive to the values chosen for r and s as long as the range of c to be covered is small.

Solution for $c_i \ll 1$ and c_f Unrestricted

In cases in which the range of c is larger than about 0.2 or 0.3 the approach to equilibrium is of a more complicated type, which cannot be characterized even approximately by a relaxation time. This may be shown by a treatment of the case in which c_i is small compared with unity, but c_f is not so restricted.

It is clear from Eq. (145) that τ/H can never be larger than c_i. For $c_i \ll 1$

$$b=1-2\tau/H \tag{204}$$

is accordingly a good approximation. A slightly more stringent assumption about the smallness of c_i, namely

$$4ALc_i \ll 1 \tag{205}$$

enables us to set

$$\tanh bAL \cong \tanh AL=(q_e-1)/(q_e+1). \tag{206}$$

The substitution of (204) and (206) into (180) leads to the result

$$\frac{H}{\tau}=\frac{q_e(1+c_i-c_f)-(1-c_i+c_f)}{q_ec_i(1-c_f)-c_f(1-c_i)}. \tag{207}$$

This expression may now be substituted in (183) and the integration can be performed. We obtain

$$t(c_f)=\frac{m}{H}\cdot\frac{q_e+1}{1+c_i(q_e-1)}\left\{c_f-c_i\right.$$
$$\left.+\frac{(q_ec_i^2+\bar{c}_i^2)(q_e-1)}{(1+c_i(q_e-1))(q_e+1)}\log\frac{c_i\bar{c}_i(q_e-1)}{c_i\bar{c}_fq_e-c_f\bar{c}_i}\right\}. \tag{208}$$

We see that this approach to equilibrium is not of the form (192), since the quantity c_f appears outside the argument of the logarithm. If $c_iq_e \ll 1$, however, then the term c_f-c_i can be neglected in comparison with the logarithmic term, and (208) gives the results (195) and (198) which were obtained for $c \ll 1$.

The Most Efficient Mode of Operation

The questions of efficiency may be placed in two distinct categories. Suppose first that the constants of the column, H and K, are given. One may then obtain the same amount of material concentrated to the same extent, either by using a shorter column and running close to equilibrium, or by using a longer column and removing the contents of the positive reservoir long before the apparatus has approached equilibrium. The problem immediately arises, what is the most efficient length of a given type of tube for the obtaining of a given change of concentration? This problem belongs to the first category.

There is the further question of how to choose the most efficient values of the constants H and K. This problem in turn involves the question of choosing the most efficient values of the temperature T_1 and T_2 and the best value of w in the plane case, or the best values of r_1 and r_2 in the cylindrical case. We place these problems in the second category. Such questions are independent of those in the first category, and are independent of the type of operation, whether it be continuous or discontinuous, and are also independent of whether the apparatus is of the single- or multi-stage type. The independence of the problems in the two categories has been given a formal proof by Krasny-Ergen (K1). Krasny-Ergen has also obtained independently a number of the considerations we shall present. His discussion is much less detailed than ours, and, in the case of multi-stage apparatus, is confined to what we shall call the ideal multi-stage apparatus.

The questions of efficiency which fall into the first category are treated in this section and in the following section on continuous operation. Problems in the second category are treated in the section on entropy efficiency.

Throughout the discussion of efficiency in this and the following section, it will thus be assumed that H and K are given constants, and that the only variables are the lengths of the columns, the rate at which concentrated material is obtained, and in the case of multi-stage apparatus, also the numbers of tubes which are used in parallel in the various stages.

Both the initial cost and the cost of operation of a separation column of given dimensions and given temperature difference will be approximately proportional to the length, and therefore to $y=2AL$. The rate of production of material with a given concentration is just m/t, where t is the time allowed for the apparatus to approach equilibrium. With a given type of tube, the rate of production is proportional to the dimensionless quantity

$$n=m/tH. \tag{209}$$

It would appear that a suitable measure of the efficiency when the final concentration and the type of tube are already chosen, is the quantity n/y. Under these conditions, the larger n/y is made, the greater is the yield per unit cost of production.

For the case previously discussed in which $c\bar{c}$ may be considered constant, we have from (190)

$$n^{-1}=-y\log(1-\Delta/yc\bar{c}), \tag{210}$$

or upon multiplication by y,

$$y/n=-y^2\log(1-\Delta/yc\bar{c}). \tag{211}$$

The condition that y/n be stationary with Δ held constant is

$$(\Delta/yc\bar{c})/(1-\Delta/yc\bar{c})=-2\log(1-\Delta/yc\bar{c}). \tag{212}$$

The substitution

$$\xi=(1-\Delta/yc\bar{c})^{-1} \tag{213}$$

carries (212) into the simple form:

$$\tfrac{1}{2}(\xi-1)=\log\xi. \tag{214}$$

This transcendental equation for ξ will also be met in the corresponding discussion for continuous operation. Its solution is

$$\begin{aligned}\xi&=3.51286\\ \log\xi&=1.25643,\end{aligned} \tag{215}$$

from which we find that the "best" values of y, n, and t are

$$y_b=(\xi/2\log\xi)(\Delta/c\bar{c})=1.39795(\Delta/c\bar{c}), \tag{216}$$

$$n_b=(2/\xi)(c\bar{c}/\Delta)=0.56934(c\bar{c}/\Delta), \tag{217}$$

$$t_b=t_r\log\xi=1.25643t_r, \tag{218}$$

$$n_b/y_b=(4\log\xi/\xi^2)(c\bar{c}/\Delta)^2=0.40726(c\bar{c}/\Delta)^2. \tag{219}$$

For the cases in which $c\ll 1$, and in which $\bar{c}\ll 1$, we have, respectively,

$$y/n=-y(e^y-1)\log\left(1-\frac{q-1}{e^y-1}\right), \tag{220}$$

and

$$y/n=-y(1-e^{-y})\log\left(1-\frac{1-p}{1-e^{-y}}\right). \tag{221}$$

The conditions that n/y be stationary are easily obtainable for these cases, but the conditions take such a form that they are not easily usable. Because of the small practical importance of these cases with relatively large reservoirs, it was not thought worth while to prepare a table of the best values of n and y as functions of q, as will be done for the corresponding cases in continuous operation.

For purposes of comparison, however, the maximum values of n/y as given by (220) and (221) have been determined for two special values of q—namely 10 and 50. The results will be presented in the section on continuous operation.

CONTINUOUS OPERATION

The distinction between continuous and discontinuous operation was made in the introduction to this part. In continuous operation the apparatus is operated as in discontinuous operation until the concentration at the positive end of the column has risen to a suitable and usually predetermined value. After this time, concentrated material is removed from the end of the column at such a rate that the concentration rises no further. In practice the concentrated material will probably not be withdrawn in a truly continuous manner, but will more likely be withdrawn in small amounts at frequent intervals. If the time between withdrawals is short compared with the characteristic time of the apparatus, (cf. Eq. (300)), the yields and concentrations obtained will not differ significantly from those which would be obtained in truly continuous operation.

Generalization of the Transport Equation

The initial increase of concentration is that of the case in which the positive end of the column is closed off, and has already been treated. A more practical discussion of this preliminary phase of the operation will be given later. In this section we shall treat the steady-state situation in which concentrated material is being drawn off at the constant rate σ, in grams per second.

The transport equation (145) which has been used up to now provides for no such transport of the gas as a whole through the tube. It was shown by Furry, Jones, and Onsager (F1) that the presence of a total transport σ introduces the term σc into the transport equation (145), so that in the case of continuous operation it becomes:

$$\tau = Hc\bar{c} + \sigma c - Kdc/dz. \qquad (222)$$

It is clear that at the positive end of the column, the relation between τ and σ must be simply

$$\tau/\sigma = c_f. \qquad (223)$$

We are here concerned with a steady-state problem, however, so that τ and σ are constants independent of both t and z. The boundary condition (223) thus holds not only at the end, but also defines the ratio τ/σ all along the tube. This boundary condition may be substituted right into the transport equation itself, so that it becomes

$$H(c\bar{c} - n(c_f - c)) = Kdc/dz, \qquad (224)$$

where

$$n = \sigma/H \qquad (225)$$

has the same physical interpretation as the quantity introduced in Eq. (209). The concentration c_f which appears in (224) is the value of c at the end where the material is being withdrawn, and is not to be confused with the value at the positive end of one of the intermediate tubes in a multi-stage apparatus.

The Scrubber

Both in the section on discontinuous operation, and in the present section on continuous operation, it is assumed that the concentration at the negative end of the column remains at a fixed value c_i. Such a fixed value may be secured by continuous flushing of a small reservoir with fresh gas; this method is wasteful, however, and it is much more economical with respect to the amount of gas used to employ a scrubbing column. A scrubbing column, or "scrubber," is simply an additional column used in such a way that the gas leaving it is *reduced* in its concentration of the isotope in question. For convenience of description, the scrubbing column and the separation column itself may be considered as a single column, with the gas entering somewhere in the middle of the tube and flowing toward both ends. The gas will leave the positive end enriched in the desired isotope, and it will leave the other end with a concentration c_s which is smaller than c_i.

The conservation of the mass of each isotope means that we must have in the steady state

$$(\sigma + \sigma_s)c_n = \sigma c_f + \sigma_s c_s, \qquad (225.1)$$

where c_n is the concentration of the entering gas, and where σ_s is the rate of flow of gas, considered to be positive, through the scrubber. Now in general, the concentration of the gas in the column at the point of entry, c_i, will not be equal to the concentration c_n of the entering gas. It will usually be desirable, however, to adjust the rates of flow in the separating column and in the scrubber so that c_i is equal to c_n. That is to say, it will be desirable to adjust σ_s so that it satisfies the relation

$$\sigma_s = \sigma \frac{c_f - c_i}{c_i - c_s}, \qquad (225.2)$$

which follows from (225.1) upon setting c_n equal to c_i. This adjustment may be accomplished in a straightforward manner: the separating column should first be completely designed on the basis that c_i is equal to the concentration of the gas that will be introduced, so that c_i, c_f, and σ are determined. One should next decide upon a suitable value of c_s. The relation (225.2) then determines σ_s uniquely. The length of the scrubber is now determinate.

The scrubber is a device for concentrating the *undesired* isotope. In applying to the scrubber the formulae to be derived in the following sections, it is therefore necessary to remember that c and $\bar{c}$ exchange their identity as we pass from a consideration of the separating column to a consideration of the scrubber. In order that the following formulae apply to the scrubber, it is necessary only to substitute c_i for $\bar{c}_i$, c_s for $\bar{c}_f$, and σ_s for σ.

Because this change is easily made, we shall not give any specific formulae for the scrubber, except in the single instance of the ideal multistage apparatus.

A scrubber can also be used in discontinuous operation, but even in this case the scrubber itself would probably be operated continuously.

Single-Stage Apparatus

We shall first treat the case in which all of the separation takes place in a single stage; the formulae for multi-stage apparatus will be developed in the next section.

Exact General Solution

The integral of (224) which satisfies the boundary conditions

$$c(0)=c_i, \qquad c(L)=c_f, \tag{226}$$

is

$$\tanh \tfrac{1}{2}b'y=\frac{b'(c_f-c_i)}{c_f+c_i-n(c_f-c_i)-2c_fc_i}, \tag{227}$$

where

$$b'=\{(1+n)^2-4nc_f\}^{\frac{1}{2}}=\{(1-n)^2+4n\bar{c}_f\}^{\frac{1}{2}}. \tag{228}$$

This equation gives the important relation between n and c_f; it tells us what final concentration may be obtained at a rate of withdrawal of $\sigma=nH$. Its form is too complicated to be very helpful or illuminating, however, and we shall therefore, as in the case of discontinuous operation, have recourse to a rather large number of different kinds of approximate solutions.

Solution for $c\bar{c}\cong$ constant

The integral of (224) with $c\bar{c}$ held constant which satisfies (226) is

$$\Delta=c\bar{c}(1-e^{-ny})/n. \tag{229}$$

For the important case in which c is everywhere within the range 0.3 to 0.7, and in which therefore $c\bar{c}$ is never far from $\frac{1}{4}$, this becomes

$$\Delta=(1-e^{-ny})/4n. \tag{230}$$

Solution for $c\ll 1$

For the case in which $c\bar{c}$ may be replaced by c, we have[10]

$$p=c_i/c_f=(e^{-y(1+n)}+n)/(1+n). \tag{231}$$

Solution for $\bar{c}\ll 1$

For the case in which $c\bar{c}$ may be replaced by $\bar{c}$, we have

$$q=\bar{c}_i/\bar{c}_f=(e^{y(1-n)}-n)/(1-n). \tag{232}$$

The General Linear Approximation

The last three approximate solutions are all special cases of the treatment in which $c\bar{c}$ is replaced by the linear approximation (202) in the manner there discussed. The solution for this case is

$$c_f=\frac{(1-r-s+n)c_i+rs(1-e^{-y(1-r-s+n)})}{n+(1-r-s)e^{-y(1-r-s+n)}}. \tag{233}$$

The approximations so far treated are such that the validity of the result is restricted only by the condition that the range of c must be small. The results are otherwise exact; in particular, n is arbitrary.

Solution for $c_i\ll c_f$

The approximate solution for this case will be obtained by making suitable approximations

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[10] Equation (231) was simplified to an unwarranted extent in F1 (Eq. (55) of that paper). We are indebted to Professors A. O. Nier and J. Bardeen (University of Minnesota) for pointing out this fact.

in the exact solution (227), rather than by starting anew from the transport equation (224) as in the previous cases.

It follows directly from the transport equation (224) that

$$n \leqslant c_i(1-c_i)/(c_f-c_i), \qquad (234)$$

where the equality holds only when dc/dz is zero. The condition

$$c_i/c_f \ll 1 \qquad (235)$$

therefore has a consequence that

$$n \ll 1. \qquad (236)$$

The right member of (227) may now be reduced to the form

$$1-2(p-n\bar{c}_f). \qquad (237)$$

It also follows from (235) that $p \ll 1$, and *a fortiori*

$$p_e = e^{-y} \ll 1 \qquad (238)$$

so that the left member of (227) may be written

$$1-2p_e^{1+n(1-2c_f)}. \qquad (239)$$

The equating of (237) and (239) now yields

$$p = p_e^{1+n(1-2c_f)} + n\bar{c}_f \qquad (240)$$

subject only to the restriction (235).

A Solution for $\bar{c}_f \ll \bar{c}_i$

No decided simplification is possible without further restrictions on the quantities involved. The restriction

$$4\bar{c}_f n/(1-n)^2 \ll 1 \qquad (241)$$

enables us to write

$$b' = 1-n+2n\bar{c}_f/(1-n). \qquad (242)$$

We must also require

$$p_e^{b'} \ll 1. \qquad (243)$$

The left member of (227) can be written

$$\tanh b'AL = (1-p_e^{b'})/(1+p_e^{b'}). \qquad (244)$$

If we substitute (242) and (244) into (227), clear fractions, and use (241), (243), and $\bar{c}_f/\bar{c}_i \ll 1$ to justify the omission of certain terms, we obtain

$$\frac{\bar{c}_f}{\bar{c}_i} = p_e^{b'} - \frac{n\bar{c}_f}{(1-n)\bar{c}_i} + \frac{\bar{c}_f}{(1-n)^2}. \qquad (245)$$

This can be written in the form

$$p = (1-n)p_e^{1-n+2nc_f/(1-n)} + \bar{c}_f n/(1-n). \qquad (246)$$

The validity of this result is subject not only to the restriction $\bar{c}_f/\bar{c}_i \ll 1$, but also to the restrictions (241) and (243).

The Most Efficient Mode of Operation; Comparison of Efficiencies in the Two Types of Operation

It is clear from the results which have been presented that there is no unique choice of n and y for the obtaining of a given separation factor q. The yield factor n and the length factor y may be varied simultaneously in such a way that q remains constant. The question then arises, is there any "best" value of y for a given separation problem? If the apparatus constants H and K are already fixed, we may give a simple answer to this question.

Just as in discontinuous operation, both the cost of construction and that of operation will be roughly proportional to L, and therefore to y, whereas the yield of concentrated material is proportional to σ, and therefore to n. From this point of view, the best choices of n and y are those values which maximize n/y. The quotient n/y we call the efficiency.

The condition that n/y be a maximum is easily written down for the general solution (227), but it is of so complicated a form that it is useless in practice.

For the case in which the entire change of c along the column is sufficiently small that $c\bar{c}$ may be considered constant, we have from (229)

$$y/n = -n^{-2}\log(1-n\Delta/c\bar{c}). \qquad (247)$$

The condition that y/n be stationary is

$$(n\Delta/c\bar{c})/(1-n\Delta/c\bar{c}) = -2\log(1-n\Delta/c\bar{c}). \qquad (248)$$

The substitution

$$\xi = (1-n\Delta/c\bar{c})^{-1} \qquad (249)$$

now reduces (248) to the same transcendental equation that occurred for the corresponding case in discontinuous operation, namely Eq. (214). The relations among ξ, n_b and y_b are quite different in the two cases, however. From (215), (247), and (249) we have

$$y_b = \tfrac{1}{2}\xi(\Delta/c\bar{c}) = 1{,}75643(\Delta/c\bar{c}), \qquad (250)$$

TABLE X. The most efficient values of n and y in continuous operation for a single stage with $c \ll 1$ throughout.

q	y_b	n_b
1	0	∞
1.25	0.39	3.0
1.5	0.70	1.5
2.0	1.18	0.74
2.5	1.54	0.50
3.0	1.83	0.38
4.0	2.29	0.26
5.0	2.63	0.195
6.0	2.90	0.158
8.0	3.32	0.113
10.0	3.64	0.090
12.0	3.90	0.074
15.0	4.21	0.058
20.0	4.59	0.043
25.0	4.89	0.035
30.0	5.10	0.029
35.0	5.30	0.025
40.0	5.49	0.022
50.0	5.75	0.0175
∞	∞	0

$$n_b=(2\log \xi/\xi)(c\bar{c}/\Delta)=0.71533(c\bar{c}/\Delta), \qquad (251)$$

$$n_b/y_b=(4\log \xi/\xi^2)(c\bar{c}/\Delta)^2=0.40726(c\bar{c}/\Delta)^2. \qquad (252)$$

Comparing these results with (216)–(219), we have the important result that although n_b and y_b are somewhat different in the two cases, *the maximum efficiency n_b/y_b is the same in continuous and discontinuous operation.* This result, of course, applies only to the cases in which $c\bar{c}$ may be considered constant.

For the case in which c is everywhere small, we have from (231)

$$\frac{y}{n}=-\frac{1}{n(1+n)}\log\{p-n(1-p)\}. \qquad (253)$$

The condition that y/n be stationary cannot be expressed so simply as in the previous case. The best values of n and y are given by the following relations involving the parameter x

$$n_b=xe^{-x}/(1-(1+2x)e^{-x}), \qquad (254)$$

$$y_b=x/(1+n_b), \qquad (255)$$

$$q=(1+n_b)/(e^{-x}+n_b). \qquad (256)$$

As x varies from $\log \xi$ to plus infinity, q varies from unity to plus infinity. A plot of n_b and y_b as functions of q was prepared by the use of the above parametric relations; the values of n_b and y_b in Table X were then read off this plot. For values of q greater than 50, the following simple relations determine n_b and y_b with sufficient accuracy.

$$q=e^{y_b}/(1+y_b), \qquad (257)$$

$$n_b=y_be^{-y_b}. \qquad (258)$$

The case in which $\bar{c}$ is everywhere small is formally very similar to the case just treated. From (232) the value of y/n is given by

$$\frac{y}{n}=\frac{1}{n(1-n)}\log\{q-n(q-1)\} \qquad (259)$$

and the values of n and y which minimize y/n may be related by the parameter x, where now

$$n_b=xe^{x}/((2x-1)e^{x}+1), \qquad (260)$$

$$y_b=x/(1-n_b), \qquad (261)$$

$$q=(e^{x}-n_b)/(1-n_b). \qquad (262)$$

As x is varied from $-\log \xi$ to plus infinity, q varies from unity to plus infinity. Just as in the previous case, a table of n_b and y_b as functions of q has been prepared (Table XI). For values of q greater than those given in the table, the following relations are quite accurate

$$n_b=\tfrac{1}{2}+\tfrac{1}{4}/(\log \tfrac{1}{2}q), \qquad (263)$$

$$y_b=2(\log \tfrac{1}{2}q)+1. \qquad (264)$$

For $q=10$ and $q=50$, the best values of n and y in discontinuous operation have been obtained from (220) and (221). The results are given in

TABLE XI. The most efficient values of n and y in continuous operation for a single stage with $\bar{c} \ll 1$ throughout.

q	y_b	n_b
1	0	∞
1.25	0.39	3.55
1.5	0.73	2.06
2.0	1.26	1.40
2.5	1.66	1.14
3	2	1
4.0	2.53	0.87
5.0	2.95	0.81
6.0	3.30	0.77
8.0	3.86	0.72
10.0	4.30	0.69
12.0	4.65	0.67
15.0	5.10	0.65
20.0	5.65	0.63
25.0	6.10	0.62
30.0	6.47	0.61
35.0	6.77	0.60
40.0	7.03	0.60
50.0	7.50	0.59
∞	∞	0.5

TABLE XII. The most efficient values of n and y in discontinuous operation.

	q	n_b/y_b	y_b
$c\ll 1$	10	2.75×10^{-2}	3.1
	50	3.36×10^{-3}	5.1
$\bar{c}\ll 1$	10	1.20×10^{-1}	2.9
	50	4.77×10^{-2}	4.6

Table XII. These values were obtained by the elementary procedure of trying a few values of y in (220) and (221) and looking for the maximum of n/y. The values of n_b/y_b are thus quite accurate, whereas the corresponding values of y_b are only approximate.

Exactly the same data obtained from Tables X and XI for continuous operation are collected for convenience in Table XIII. A comparison of these two tables shows at once that for the case in which c is small, discontinuous operation is slightly more efficient. When $\bar{c}$ is small, on the other hand, we see that continuous operation is more efficient, and that the advantage is quite appreciable. We have already seen that when q is not far from unity, the efficiencies of continuous and discontinuous operation are equal.

We may thus conclude that the only case so far discussed in which discontinuous operation is more efficient, is that in which c is everywhere small. Even in this case, the advantage is not very large. Inasmuch as the sort of discontinuous operation we have been considering has the serious practical disadvantage that a much longer time must elapse before one may begin to obtain concentrated material, the writers feel that few occasions will occur in which it will be preferable. If the total production envisaged is very small, an apparatus without reservoirs can be operated discontinuously.

By far the most important conclusions which may be drawn from the numerical relations presented above, is the fact that in continuous operation the *ratio of y_b to log q is nearly constant in all of those cases in which q does not become greater than, say, ten.* The value of this ratio is 1.756 when q is very near unity, and for $q=10$ is 1.58 when c is small, and 1.86 when $\bar{c}$ is small. The ratio $y_b/\log q$ approaches unity in the former case, and two in the latter case, as q becomes infinite.

As we shall see in the next section, it will almost never be desirable to obtain a separation factor of as much as ten in a single stage when c is small. We shall also see in the next section that even in the case in which a length of column is only part of a multi-stage apparatus, the best ratio of the y of that stage to the $\log q$ of that stage will be near two if the q in question is not larger than about ten.

We thus find that under widely varying conditions, the most efficient value of y is about twice the logarithm of the separation factor obtained with the stage in question. We shall call this guiding principle the "two-log-q" rule, for convenience of reference.

This rule has an interesting physical interpretation. By (196), the relation between y and the equilibrium value of q is

$$y=\log q_e.$$

Thus when a short column is operated according to the two-log-q rule, the average concentration gradient is just one-half of the equilibrium concentration gradient, or, equivalently, the separation factor obtained is just the square root of the equilibrium separation factor. In the section on entropy efficiency, it will become apparent that the two-log-q rule is a special case of a general theorem due to Onsager, cf. Eq. (323).

As we shall see in the section which follows immediately, on multi-stage apparatus, the two-log-q rule is the foundation upon which the design of multi-stage apparatus will be built.

Multi-Stage Apparatus

In order to stress the fact that the c_f which appears in the transport equation (224) is the

TABLE XIII. The most efficient values of n and y in continuous operation.

	q	n_b/y_b	y_b
$c\ll 1$	10	2.48×10^{-2}	3.63
	50	3.04×10^{-3}	5.75
$\bar{c}\ll 1$	10	1.61×10^{-1}	4.29
	50	$7.9\ \times 10^{-2}$	7.50

final value of c in the *last* stage, we shall here rewrite this equation in the form

$$H_k(c\bar{c}-n_k(c_{Nf}-c))=K_k dc/dz. \tag{265}$$

Here the k's indicate that the quantities are those of the kth stage, and c_{Nf} is the final value of c in the Nth (and last) stage; correspondingly, the initial and final values of c in the kth stage will be denoted by c_{ki} and c_{kf}. The quantity n_k is, of course, defined by

$$n_k=\sigma/H_k. \tag{266}$$

The only boundary condition needed is that c must vary continuously from one stage to the next—that is,

$$c_{kf}=c_{k+1,\,i}, \quad k=1,2,\ldots,N-1. \tag{267}$$

The relations between separation factor and transport which were presented in the last section are easily generalized to cover the case in which c_{kf} and c_{Nf} are not identical. The solutions which we present below without comment are the solutions of (265) which satisfy the boundary conditions

$$c(0)=c_{ki}, \quad c(L_k)=c_{kf}. \tag{268}$$

The approximations involved in each case are the same as those previously described. In those cases where there are restrictions on the value of c, the restrictions apply only to the values of c lying between c_{ki} and c_{kf}; for example, in the "Solution for $c\ll 1$," both c_{ki} and c_{kf} must be small, but c_{Nf} is not so restricted.

The expressions given below will often admit a considerable simplification in application to specific cases. The simplification to be used will always become apparent as soon as one begins to use the expressions, however, and we do not feel that it would be worth while to indicate all of the special cases of these formulae.

Exact General Solution

$$\tanh \tfrac{1}{2}b_k'y_k=\frac{b_k'(c_{kf}-c_{ki})}{c_{kf}+c_{ki}+n_k(c_{kf}+c_{ki}-2c_{Nf})-2c_{ki}c_{kf}}, \tag{269}$$

where

$$b_k'=\{(1+n_k)^2-4n_kc_{Nf}\}^{\frac{1}{2}}=\{(1-n_k)^2+4n_k\bar{c}_{Nf}\}^{\frac{1}{2}}. \tag{270}$$

Solution for $c\bar{c}\cong$ Constant

$$c_{kf}=(c\bar{c}/n_k+c_{ki}-c_{Nf})\exp(y_kn_k)+c_{Nf}-c\bar{c}/n_k. \tag{271}$$

Solution for $c\ll 1$

$$(1+n_k)c_{kf}=\{(1+n_k)c_{ki}-n_kc_{Nf}\}\exp[y_k(1+n_k)]+n_kc_{Nf}. \tag{272}$$

Solution for $\bar{c}\ll 1$

$$(1-n_k)\bar{c}_{kf}=\{(1-n_k)\bar{c}_{ki}+n_k\bar{c}_{Nf}\}\exp[-y_k(1-n_k)]-n_k\bar{c}_{Nf}. \tag{273}$$

The General Linear Approximation

$$(1-r-s+n_k)c_{kf}=\{(1-r-s+n_k)c_{ki}+rs-n_kc_{Nf}\}\exp[(1-r-s+n_k)y_k]-rs+n_kc_{Nf}. \tag{274}$$

It is understood that the values of r and s are those appropriate to the kth stage.

Solution for $c_{ki}\ll c_{kf}$

$$p_k=p_{ek}{}^{1+n_k(1-2c_{Nf})}+n_k\bar{c}_{kf}(c_{Nf}/c_{kf}). \tag{275}$$

A Solution for $\bar{c}_{kf}\ll\bar{c}_{ki}$

It is not possible to get a simple formula without other restrictions in addition to $\bar{c}_{kf}\ll\bar{c}_{ki}$. If we require

$$4\bar{c}_{Nf}n_k/(1-n_k)^2\ll 1 \tag{276}$$

and

$$\exp[-y_k(1-n_k+2n_k\bar{c}_{Nf}/(1-n_k))]\ll 1, \tag{277}$$

we can show that

$$p_k=(1-n_k)\exp\left[-y_k(1-n_k+2n_k\bar{c}_{Nf}/(1-n_k))\right]+n_k(\bar{c}_{kf}-\bar{c}_{Nf})/\bar{c}_{ki}+n_k\bar{c}_{Nf}/(1-n_k). \qquad (278)$$

Considerations on Efficiency in Multi-Stage Apparatus

The Two-log-q Rule

In the section on single-stage apparatus it was found possible to present tables giving the best values of n and y for various q's and under various conditions on the order of magnitude of c. In multi-stage apparatus, however, there is the additional complication that the best values of n_k and y_k depend not only on the desired separation factor q_k, but also on the value of c_{Nf}. We thus have a two-parameter problem (q_k and c_{Nf}) in place of the previous one-parameter problem (only q). Because of the large amount of labor that would be involved, no tables have been prepared for this more general case. We shall therefore content ourselves with a general proof of the two-log-q rule for a short stage which is part of a multi-stage apparatus, and with a few numerical examples to indicate the greater generality of the principle.

Suppose that the kth stage is sufficiently short that the gradient of the concentration may be approximated by

$$\frac{dc}{dz}\cong\frac{(\Delta c)_k}{L_k}=2A_k\frac{(\Delta c)_k}{y_k}. \qquad (279)$$

The transport equation (265) then takes the form

$$c\bar{c}-(\Delta c)_k/y_k-n_k(c_{Nf}-c)=0. \qquad (280)$$

We assume further that (Δc_k) is so small that the fractional changes in $c\bar{c}$ and in $(c_{Nf}-c)$ within the stage are small. The last condition means of course that the stage in question must not be too near the positive end of the apparatus. From (280), we have

$$n_k/y_k=\{c\bar{c}/y_k-(\Delta c)_k/y_k^2\}/(c_{Nf}-c). \qquad (281)$$

If $c\bar{c}$ and $(c_{Nf}-c)$ are considered constant, the condition that n_k/y_k be stationary is just

$$y_k=2(\Delta c)_k/c\bar{c}=2\log q_k \qquad (282)$$

which is the two-log-q rule.

A completely general proof of the two-log-q rule cannot be given, because it is only an approximate rule. Indeed, we know that in the case of a single stage apparatus in which c is everywhere small and in which q is large, the rule does break down (cf. Table X). This is just the case *par excellence*, however, in which single-stage apparatus is inefficient, and in which multi-stage apparatus must be used in order to secure good efficiency and short equilibrium times.

The following numerical examples are given to indicate the validity of the two-log-q rule in cases which are not included in the proof just given.

I Given:

$$c_{ki}=10^{-3},\quad c_{kf}=10^{-2},\quad c_{Nf}=0.5.$$

Then:

$$\begin{aligned} q_k&=10, \qquad (283)\\ (n_k/y_k)_{\max}&=4.19\times10^{-4},\\ y_{kb}&=3.79\\ &=1.65\log q_k. \end{aligned}$$

II Given:

$$c_{ki}=0.4,\quad c_{kf}=0.6,\quad c_{Nf}=1.0.$$

Then:

$$\begin{aligned} q_k&=2.25, \qquad (284)\\ (n_k/y_k)_{\max}&=0.1542,\\ y_{kb}&=1.58\\ &=1.95\log q_k. \end{aligned}$$

III Given:

$$\bar{c}_{ki}=10^{-1},\quad \bar{c}_{kf}=10^{-2},\quad \bar{c}_{Nf}=0.$$

Then:

$$\begin{aligned} q_k&=11, \qquad (285)\\ (n_k/y_k)_{\max}&=0.1085,\\ y_{kb}&=4.60\\ &=1.92\log q_k. \end{aligned}$$

The maximum value of n_k/y_k was determined from (272), (271), and (273), respectively.

It becomes obvious after a certain amount of numerical manipulation of the formulae for n/y that the efficiency n/y decreases quite slowly as $y/\log q$ rises above its optimum value near two, but that on the other hand it decreases rapidly to zero as $y/\log q$ falls toward unity. This means that in practice it will be advisable to "play safe" by designing the apparatus with a value of $y/\log q$ which is greater than two, until a certain amount of experience with the gas and with the column has been obtained. If then it turns out that A is less than expected, because of uncertainties in the values of α and the gas coefficients, or because of an unexpectedly large value of K_p, the efficiency will not suffer. If no such margin of safety is allowed, the efficiency will suffer badly in such a case. It might at first be thought that one could compensate for a smaller A by operating the apparatus with a smaller c_{Nf}; this is not a real remedy, however, because a multi-stage apparatus is efficient only when the concentrations are those contemplated in the design.

The considerations just presented mean that in the design of multi-stage apparatus, one should always use a pessimistic value of A until a reliable value of A becomes known experimentally.

The Ideal Multi-Stage Apparatus

The advantage of multi-stage apparatus over that of the single-stage type is that in the former the value of H may be varied along the column in such a way that the two-log-q rule is satisfied not only by the column as a whole, but also by every short section of it. The value of H may, of course, be varied in a large variety of ways. Because there will usually be a type of column which is most efficient for a given gas, however, it will usually be best to vary H by varying the number of columns which are used in parallel. We shall suppose therefore that the entire apparatus is to be constructed of separation columns with the same values of H_I and K_I; the subscript I is added in order to indicate that the values are those of a single tube. In terms of $\mathfrak{N}_k$, the number of tubes in parallel in the kth stage, we now have

$$H_k = \mathfrak{N}_k H_I, \tag{286}$$

$$K_k = \mathfrak{N}_k K_I, \tag{287}$$

$$n_k = n_I/\mathfrak{N}_k = \sigma/\mathfrak{N}_k H_I, \tag{288}$$

$$n_I = \sigma/H_I = n_k \mathfrak{N}_k. \tag{289}$$

The quantity n_I which is introduced in (288) is a particularly useful quantity, because it provides a measure of the total flow σ which has the same value in every stage. The parameter $n_k = \sigma/H_k$ is also useful because it is exactly inversely proportional to the number of tubes in each stage.

The two idealizations involved in the apparatus now to be discussed are as follows: (1) Each stage is to be so short that the two-log-q rule is equivalent to the condition that the concentration gradient is one-half of the equilibrium concentration gradient; this requirement is equivalent to the requirement that the fractional change in $c\bar{c}$ within the stage be small compared with unity. On the other hand, the length of each stage must be long compared with twice the relaxation length defined by (121). There will always be a large range of lengths over which these two conditions on the length are compatible. (2) The value of $\mathfrak{N}_k$ for every stage is to be large compared with unity.

Since both of these idealizations may be very closely realized in large scale apparatus, the ideal multi-stage apparatus is of considerable practical interest.

By (265) the equilibrium value of $K_k dc/dz$ is $H_k c\bar{c}$. Setting $K_k dc/dz$ equal to half of this value, we have from (265)

$$H_k = 2\sigma(c_{Nf} - c)/c\bar{c} \tag{290}$$

or

$$\mathfrak{N}_k = 2n_I(c_{Nf} - c)/c\bar{c}. \tag{291}$$

This formula shows the manner in which $\mathfrak{N}_k$ should vary with c in order that the two-log-q rule be satisfied in each stage.

Since the concentration gradient is everywhere just one-half of the equilibrium concentration gradient, the total length of the apparatus is of course just twice that of a column whose equilibrium separation factor is equal to the separation factor obtained in the ideal apparatus. Thus the total length is given by

$$\mathfrak{L} = \sum_k L_k = (\log q)/A \tag{292}$$

where q is the total separation factor.

The total length of tubing in the apparatus is

$$\Lambda = \sum_k \mathfrak{N}_k L_k. \tag{293}$$

Since $\mathfrak{N}_k$ is a large number and there are many stages, the summation may be replaced by an integral:

$$\Lambda=\int_0^{\mathcal{L}}\mathfrak{N}_k dz=\frac{4\sigma K_I}{H_I^2}\int_{c_{1i}}^{c_{Nf}}\frac{c_{Nf}-c}{[c(1-c)]^2}dc, \tag{294}$$

$$=\frac{4\sigma K_I}{H_I^2}\left\{\frac{(1-2c_{1i})(c_{Nf}-c_{1i})}{c_{1i}(1-c_{1i})}-(1-2c_{Nf})\log q\right\}. \tag{295}$$

This is a very important formula. It shows that the total length of tubing required is proportional to the rate of production of concentrated material σ and to a factor which depends only on the initial and final concentrations, and is inversely proportional to H_I^2/K_I. The quantity H_I^2/K_I is accordingly the measure of the effectiveness of a unit length of column.

If we assume also that the scrubbing column is an ideal multi-stage apparatus, we find from (295) for the total length of tubing in it,

$$\Lambda_s=\frac{4\sigma_s K_I}{H_I^2}\left\{\frac{(1-2c_{1i})(c_s-c_{1i})}{c_{1i}(1-c_{1i})}+(1-2c_s)\log q_s\right\}, \tag{296}$$

where q_s is the separation factor obtained in the scrubber. Adding (295) and (296), we have for the total length of tubing in the multi-stage apparatus and in the scrubber

$$\Lambda+\Lambda_s=\frac{4\sigma K_I}{H_I^2}\left\{\frac{(1-2c_s)(c_{Nf}-c_{1i})}{(c_{1i}-c_s)}\log q_s-(1-2c_{Nf})\log q\right\}, \tag{297}$$

where σ_s has been eliminated by means of (225.2).

It is easily shown that the number of tubes at the beginning of the scrubber is the same as the number at the beginning of the actual separation apparatus. There is usually very little advantage in operating the scrubber as a multi-stage apparatus, however. If a single-stage scrubber is used, it is very convenient to use the same number of tubes in the scrubber as in the first stage of the separation apparatus. In this case, the use of a scrubber means in practice that the length of the first stage is increased somewhat, and that the fresh gas is introduced at a point somewhere between the ends of the columns.

Equation (295) may also be written in the form

$$\frac{2A\Lambda}{n_I}=4\{\text{as in (295)}\}, \tag{298}$$

where $2A\Lambda/n_I$ has the same significance in relation to efficiency as the y/n which was used in the discussion of single-stage apparatus. The last equation permits us to make a direct comparison of the efficiencies of single-stage and multi-stage apparatus. Suppose that both c_{1i} and c_{Nf} are much less than unity, and that we desire a separation factor of ten. From Table X, we find that the maximum value of n/y in a single-stage apparatus is 1/40.5, whereas, according to (298), a value of $n_I/2A\Lambda$ of 1/26.8 may be secured with an ideal multi-stage apparatus. The multi-stage apparatus thus increases the efficiency by a factor 1.51. The corresponding increase in efficiency for a separation factor of 50, with c everywhere small, is 1.82, and for a separation factor of 10^5, which would be needed to raise the concentration of He^3 from 10^{-7} to 10^{-2}, the multi-stage apparatus is 3.6 times as efficient as the single stage apparatus.

These increases in efficiency, although very worth while, are not striking. The real advantage of multi-stage apparatus is that the time required before continuous operation may begin will in many cases be very much shorter than the corresponding time for a single-stage apparatus. This is true, as may be seen from (291), because the number of tubes in parallel decreases as the concentration increases. Thus in the multi-stage apparatus, a smaller amount of the desired isotope will have to be concentrated inside the apparatus to bring it to the point at which continuous operation may begin.

We may easily obtain a simple expression for the mass of desired isotope which must be transported into the column in order to secure the concentration distribution required for continuous operation. This mass is clearly given by

$$\begin{aligned}\mathfrak{M}&=\mu\textstyle\sum_k(c_k-c_{1i})\mathfrak{N}_kL_k\\&=\mu\frac{4\sigma K_I}{H_I^2}\int_{c_{1i}}^{c_{Nf}}\frac{(c-c_{1i})(c_{Nf}-c)}{[c(1-c)]^2}dc\\&=\mu\frac{4\sigma K_I}{H_I^2}[(c_{1i}+c_{Nf}-2c_{1i}c_{Nf})\log q\\&\qquad\qquad-2(c_{Nf}-c_{1i})].\end{aligned}\tag{299}$$

When the apparatus is first put into operation, the desired isotope will be transported into the column at the rate $\mathfrak{N}_1H_Ic_{1i}\bar{c}_{1i}$, since there is no concentration gradient. As the apparatus approaches the time at which continuous operation may begin, however, the transport will be reduced to one-half of this value. The time required before continuous operation can begin is therefore greater than

$$t_c=\mathfrak{M}/(\mathfrak{N}_1H_Ic_{1i}\bar{c}_{1i})\tag{300}$$

and less than $2t_c$. Because of the Debye effect (cf. Eqs. (169) and (176)) the concentration at the positive end will probably rise to the desired value before the characteristic time t_c has elapsed, but it will not be possible to obtain concentrated material at the full computed rate until a time somewhat greater than t_c has elapsed.

Equation (300) is very similar in appearance to (174), which is the equation for the relaxation time of the approach to true equilibrium. The physical meaning of (300) is quite different, however, because there the mass in question is the mass to be transported into the column in order to secure equilibrium, whereas $\mathfrak{M}$ is the mass computed for a state which is very far from equilibrium. Indeed, the separation factor obtained in the ideal multi-stage apparatus is just the square root of the equilibrium separation factor. The characteristic time t_c will usually be very much shorter than the relaxation time of the approach to true equilibrium.

We may now also compare the characteristic times of single- and multi-stage apparatus. Since the initial transport of both types of apparatus will be approximately the same if they are designed for the same rate of production σ, we may compare these times by comparing the values of $\mathfrak{M}$ for the two types of apparatus. (In extreme cases, the initial transport for the ideal apparatus will be as much as twice that of the single-stage apparatus.) For simplicity, we examine only the case in which c is everywhere small. Then it is easily shown the value of $\mathfrak{M}$ for the single-stage apparatus is β times the value of $\mathfrak{M}$ for the ideal multi-stage apparatus, where β is given by

$$\beta=\frac{\{(q-1)(1+ny)-y\}/\{n(1+n)\}}{4\{(q+1)\log q-2(q-1)\}}.\tag{301}$$

In this expression, n and y refer to the single-stage apparatus, and are related by the condition (231) that the separation factor must be q. If we use the values of n and y given in Table X, which maximize the ratio n/y, we find that for separation factors of ten and fifty, respectively, the values of β are about three and seven; for values of q so large that $\log q\gg 1$, we find from (257)–(258) that β has the approximate value $q/(4\log q)$, so that for a separation factor of 10^5, the single-stage apparatus will have a characteristic time about 2000 times that of the ideal multi-stage apparatus!

The Design of Practical Multi-Stage Apparatus

In this section we develop formulae for the design of actual multi-stage apparatus which will approximate very closely the behavior of the ideal apparatus discussed in the previous section.

In practice, the number of tubes in parallel cannot be varied continuously, nor can the separation effect of each stage be infinitely small. We shall therefore examine the questions of efficiency and equilibrium time in multi-stage apparatus in which the number of tubes in parallel changes discontinuously, and in which the stages are of finite length.

This examination falls into two rather distinct parts. We shall first give a complete treatment, based on the two-log-q rule, but one which holds only for stages in which the restricting conditions

$$c_{ki},\ c_{kf}\ll c_{Nf}\tag{302}$$

are satisfied. We shall then give a treatment which is not subject to any restriction of the type (302), but which on the other hand is incomplete in one respect and must fall back on the first treatment for completion. The second treatment does not invoke the two-log-q rule, although a modification of it is implicitly contained in the treatment.

We proceed with the first treatment; we select for consideration the kth stage, and postulate that

$$\begin{aligned} \mathfrak{N}_{k-1}=\gamma\mathfrak{N}_k;\quad \mathfrak{N}_k=\gamma\mathfrak{N}_{k+1}\quad &(k>1)\\ \mathfrak{N}_1=\gamma\mathfrak{N}_2\quad &(k=1)\end{aligned} \tag{303}$$

where γ is a number, the stepping ratio, which will usually be between one and ten. The restriction (302) makes it possible to use Eq. (272), and to simplify the latter equation, so that we obtain

$$\frac{c_{kf}-n_kc_{Nf}}{c_{ki}-n_kc_{Nf}}=\exp\,(y_k). \tag{304}$$

The assumption used here, that n_k is a small quantity of the order of c_{kf}/c_{Nf}, is verified explicitly by Eq. (307) below.

Application of the two-log q rule now gives, by Eqs. (302) and (304):

$$\frac{c_{kf}-n_kc_{Nf}}{c_{ki}-n_kc_{Nf}}=\left(\frac{c_{kf}}{c_{ki}}\right)^2. \tag{304.1}$$

This leads to the result

$$c_{Nf}n_k=\frac{c_{ki}c_{kf}}{c_{ki}+c_{kf}}=\frac{c_{kf}}{1+q_k}. \tag{305}$$

Equation (303) is equivalent to

$$\begin{aligned} \gamma n_{k-1}=n_k=n_{k+1}/\gamma\quad &(k>1),\\ n_1=n_2/\gamma\quad &(k=1).\end{aligned} \tag{306}$$

Relations similar to (305) can also be written for the $(k+1)$th stage, and the $(k-1)$th (if $k>1$). These relations, together with Eqs. (267) and (306), make it evident that in order to obtain a simple treatment which takes the same form for all three stages—or for both the first two stages if $k=1$—we must give to all of the separation factors $q_{k-1}(k>1)$, q_k, q_{k+1}, the same value γ; accordingly

$$q_k=c_{kf}/c_{ki}=\gamma. \tag{306.1}$$

From Eqs. (305) and (306.1) we now obtain the result

$$\frac{1}{n_k}=\frac{\gamma+1}{\gamma}\frac{c_{Nf}}{c_{ki}}=(\gamma+1)\frac{c_{Nf}}{c_{kf}}. \tag{307}$$

TABLE XIV. Comparison of the stepped and ideal apparatus.

γ	$\Lambda_k/\Lambda_{\text{ideal}}$	$\mathfrak{M}_k/\mathfrak{M}_{\text{ideal}}$ $c_{1i}/c_{ki}=0$	 $c_{1i}/c_{ki}=1$
1	1.000	1.000	1.000
2	1.040	1.041	1.045
3	1.099	1.107	1.112
4	1.155	1.176	1.201
5	1.207	1.246	1.284
6	1.254	1.314	1.366
8	1.337	1.447	1.571
10	1.407	1.570	1.689

It is interesting that this value of $1/n_k$, obtained by using the two-log-q rule, is equal to that obtained by finding the values of $1/n$ in the ideal apparatus at the concentrations c_{ki} and c_{kf} and taking their average.

Correspondingly, the average value of $1/n$ in the ideal apparatus, obtained by averaging with respect to z between the points at which the concentration is c_{ki} and c_{kf}, is

$$\langle 1/n\rangle_{\text{Av}}=\frac{2(\gamma-1)}{\log\gamma}\frac{c_{Nf}}{c_{kf}}. \tag{308}$$

The quantities $1/n_k$ and $\langle 1/n\rangle_{\text{Av}}$ are proportional to the total length of tubing in the kth stage of the stepped apparatus and in the corresponding part of the ideal apparatus, respectively. The length of tubing in the stepped apparatus is thus greater than the length in the ideal apparatus by the factor

$$\frac{\Lambda_k}{\Lambda_{\text{ideal}}}=\frac{(\gamma+1)\log\gamma}{2(\gamma-1)}. \tag{309}$$

This factor is tabulated briefly in Table XIV.

From* (307), the number of tubes in parallel in the first stage is

$$\mathfrak{N}_1=\frac{n_I}{n_1}=n_I\frac{\gamma+1}{\gamma}\frac{c_{Nf}}{c_{1i}}, \tag{309.1}$$

whereas the number of tubes in parallel at the negative end of the ideal apparatus is

$$\mathfrak{N}_{1,\,\text{ideal}}=\frac{n_I}{n_{1,\,\text{ideal}}}=2n_I\frac{c_{Nf}}{c_{1i}}, \tag{309.2}$$

from (291) and (302). Thus the maximum

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* This paragraph was added in February, 1946, in order to provide a satisfactory reference for Eq. (376).

number of tubes in parallel is less in the stepped than in the ideal apparatus by the factor

$$\frac{\mathfrak{N}_1}{\mathfrak{N}_{1,\,\text{ideal}}}=\frac{n_{1,\,\text{ideal}}}{n_1}=\frac{\gamma+1}{2\gamma}. \tag{309.3}$$

If now we compute for the stepped and for the ideal apparatus the mass of the desired isotope which is present between the points at which the concentration is c_{ki} and c_{kf}, minus the mass present initially, we find that the mass in the stepped apparatus is greater by the factor

$$\frac{\mathfrak{M}_k}{\mathfrak{M}_{\text{ideal}}}=\frac{1}{4}\,\frac{\gamma^2-1+2(\gamma-(\gamma+1)c_{1i}/c_{ki})\log\gamma}{\gamma\log\gamma-(\gamma-1)c_{1i}/c_{ki}}. \tag{310}$$

This factor is also tabulated in Table XIV for c_{1i}/c_{ki} equal to unity and to zero.

It is evident from Table XIV that neither the efficiency nor the characteristic time is seriously affected when γ is not more than two or three.

Any number of stages of the type indicated by (307) may be used in series, and as long as the condition (302) is satisfied, they will satisfy the two-log-q rule exactly, provided that the stepping ratio γ is the same for each successive stage. Suppose, however, that we wish to change the stepping ratio after a certain number of stages. Specifically, we assume

$$\begin{aligned}\mathfrak{N}_{k-2}&=\gamma_1\mathfrak{N}_{k-1}, & \mathfrak{N}_{k-1}&=\gamma_1\mathfrak{N}_k;\\ \mathfrak{N}_k&=\gamma_2\mathfrak{N}_{k+1}, & \mathfrak{N}_{k+1}&=\gamma_2\mathfrak{N}_{k+2}.\end{aligned} \tag{311}$$

Since the $(k-1)$th and the $(k+1)$th stage satisfy the conditions (305) of the previous problem, we have by (307)

$$\frac{1}{n_{k-1}}=\frac{\gamma_1}{n_k}=(\gamma_1+1)\frac{c_{Nf}}{c_{ki}} \tag{312}$$

and

$$\frac{1}{n_{k+1}}=\frac{1}{\gamma_2 n_k}=\frac{\gamma_2+1}{\gamma_2}\,\frac{c_{Nf}}{c_{kf}}. \tag{313}$$

Solving the last two equations for c_{kf}/c_{ki}, we find

$$q_k=c_{kf}/c_{ki}=\frac{\gamma_1(\gamma_2+1)}{\gamma_1+1}. \tag{314}$$

According to the last three relations, the design of the kth stage is *uniquely determined* by the fact that the stages before and after are designed in accordance with Eq. (307). It is thus not possible to add the further condition that the kth stage satisfy the two-log-q rule. Instead, we find by further calculation

$$\frac{y_k}{\log q_k}=\frac{\log(\gamma_1\gamma_2)}{\log\{\gamma_1(\gamma_2+1)/(\gamma_1+1)\}}. \tag{315}$$

Provided that $\gamma_1>\gamma_2>1$, this expression has a value which is always greater than two. It is tabulated in Table XV.

We may also compare the efficiency of this stage with the efficiency of the corresponding part of an ideal apparatus. A short calculation gives:

$$\frac{y_k/n_k}{y_{\text{ideal}}\langle 1/n\rangle_{\text{Av}}}=\frac{\Lambda_k}{\Lambda_{\text{ideal}}}=\frac{(\gamma_1+1)(\gamma_2+1)\log\gamma_1\gamma_2}{4(\gamma_1\gamma_2-1)}. \tag{316}$$

This ratio is also tabulated in Table XV.

The design of stages of the type (307) is based on the two-log-q rule. For large values of γ, however, this rule is no longer valid. For example, we see from (283) that for $\gamma=10$, the most efficient operation is obtained for $y=1.65\log q$. Our detailed considerations on stepped apparatus are thus valid only when the γ's are small, say not greater than ten. The formulae are still correct for larger values, of course, but the stepped apparatus so designed will not be the most efficient one possible with the given stepping ratio.

The conditions (302), on which the present treatment is based, obviously break down in the last few stages of every apparatus. The formulae to be developed in the second treatment will hold for every stage of the apparatus.

We procede with the second treatment. It has already been pointed out that the ratio $2A\Lambda/n_I$ has the same significance with relation to efficiency as the y/n which was used in the discussion of single-stage apparatus. For the stepped multi-stage apparatus, this ratio takes the form

$$\begin{aligned}2A\Lambda/n_I&=(1/n_I)\textstyle\sum_k\mathfrak{N}_k y_k\\ &=\textstyle\sum_k(\mathfrak{N}_k/n_I)\\ &\quad\times\displaystyle\int_{c_{ki}}^{c_{kf}}\frac{dc}{c(1-c)-n_I(c-c_{Nf})/\mathfrak{N}_k}.\end{aligned} \tag{317}$$

We assume that the values of c_{1i} and c_{Nf} are pre-assigned, and also that the number of tubes in each stage, $\mathfrak{N}_k$, has been specified. That is to say, we assume that the initial concentration and the desired final concentration have been decided, and also that the type of stepping has been determined.

In order to obtain the maximum efficiency with such an apparatus, it is now necessary to maximize (317) with respect to a variation of n_I and of each of the c_{kf}'s. It is apparent at the outset that the maximization with respect to n_I will not lead to any simple relations, and this is the respect in which this second treatment is incomplete. On the other hand, the maximization with respect to each of the c_{kf}'s may be performed very simply. Let $\gamma = \mathfrak{N}_k/\mathfrak{N}_{k+1}$ be the stepping ratio between the kth and the $(k+1)$th stage. Then (317) may be written in the form

$$2A\Lambda/n_I = \cdots + \frac{\mathfrak{N}_k}{n_I}\int_{c_{ki}}^{c_{kf}} \frac{dc}{c(1-c)-n_k(c-c_{Nf})} + \frac{\mathfrak{N}_k}{\gamma n_I}\int_{c_{kf}}^{c_{k+1,f}} \frac{dc}{c(1-c)-\gamma n_k(c-c_{Nf})} + \cdots, \quad (318)$$

where have been included only those terms in (317) which depend on c_{kf}. Setting the derivative of (318) with respect to c_{kf} equal to zero, we find the important relation

$$c_{kf}\bar{c}_{kf} + (\gamma+1)n_k(c_{Nf}-c_{kf}) = 0. \quad (319)$$

Solved explicitly for c_{kf}, this equation becomes

$$c_{kf} = \tfrac{1}{2}\{1 + [(\gamma+1)n_k] - (1 + 2(1-2c_{Nf})[(\gamma+1)n_k] + [(\gamma+1)n_k]^2)^{\frac{1}{2}}\}. \quad (320)$$

Equation (319) may be looked upon as a generalization of (307), but the interpretation of these two equations is quite different. Whereas (307) was considered as an equation giving n_k in terms of γ and c_{kf}, Eq. (319) must be considered as an equation giving c_{kf} in terms of γ and n_k.

Let us suppose for the moment that the value of n_I, which of course determines the values of all of the n_k's, has been determined in some manner. The values of c_{ki} and c_{kf} for every stage is then determined by (320), and the value of each of the y_k's may then be determined from (269) or one of its approximate forms. The design of the multi-stage apparatus is thus complete except for the determination of the most efficient value of n_I.

TABLE XV. Comparison of the stepped and ideal apparatus for a stage of the type (311).

γ_1	γ_2	q_k	$y_k/\log q_k$	$\Lambda_k/\Lambda_{\text{ideal}}$
3	2	2.25	2.210	1.075
4	2	2.40	2.375	1.119
5	2	2.50	2.513	1.151
6	2	2.57	2.631	1.186
8	2	2.67	2.827	1.248
10	2	2.73	2.986	1.301
4	3	3.20	2.135	1.129
5	3	3.33	2.249	1.161
6	3	3.43	2.346	1.190
8	3	3.56	2.505	1.244
10	3	3.64	2.635	1.290
10	5	5.45	2.306	1.317

Probably the safest way to determine the best value of n_I is to design the apparatus for several different values of n_I, and then to determine by graphical interpolation the value of n_I which maximizes $n_I/2A\Lambda$. This maximum is not at all critical, as we shall see in the numerical examples of Part IV. A very good first guess for n_I may be obtained by operating the first stage, which contains the largest number of tubes in parallel, according to the two-log-q rule. When the value of c in the first stage is everywhere small compared with c_{Nf}, this may be done very simply by giving n_1 the value (307). When the conditions (302) do not hold for the first stage, however, it will be necessary to determine n_1, c_{1f}, and y_1 so that they simultaneously satisfy (269), (319), and the condition $y_1 = 2\log q_1$, in order that the first stage obey the two-log-q rule.

When, as often happens in practice, the conditions (302) hold in several of the first stages of the apparatus, the first guess obtained in the above manner will be very close to the best value of n_I, because in such a case a large part of the tubing will actually be operating according to the two-log-q rule.

It is easily shown that the mass of the desired isotope which must be transported into the stepped multi-stage apparatus in order that it reach its continuously operating condition, is given by

$$\begin{aligned}\mathfrak{M}&=\frac{\mu}{2A}\sum_k \mathfrak{N}_k\int_{c_{ki}}^{c_{kf}}\frac{(c-c_{1i})dc}{c\bar{c}-n_k(c-c_{Nf})},\\ &=\frac{\mu}{4A}\sum_k \mathfrak{N}_k\biggl\{(1-n_k-2c_{1i})y_k\\ &\qquad -\log\frac{(c\bar{c})_{kf}-n_k(c_{kf}-c_{Nf})}{(c\bar{c})_{ki}-n_k(c_{ki}-c_{Nf})}\biggr\},\end{aligned}\qquad(321)$$

where y_k is defined by (269).

In using this value of $\mathfrak{M}$ in order to obtain a value of t_c to compare with the ideal characteristic time, one must be careful, however. We have already pointed out that the transport of the desired isotope drops to half of its initial value in the ideal apparatus. It is clear that this behavior cannot hold for the stepped apparatus, because, since the initial number of tubes is less for the stepped apparatus, the initial transport of the stepped apparatus will be less than that of the corresponding ideal apparatus; on the other hand, the steady-state transport of both apparatuses is the same, namely, equal to σc_{Nf}.

In order to obtain a value of t_c which may be compared with the value (300) for an ideal apparatus, we should thus divide $\mathfrak{M}$ by a transport which is somewhere between the initial transport of the stepped apparatus, and the initial transport of the corresponding ideal apparatus. Because of our ignorance of the details of the approach to equilibrium in such apparatuses, the best that one can do is to use the average of the two initial transports. The exact choice is not of great importance, since one is interested mainly in finding out whether there is a *large* difference between the characteristic times, and this could come about only through a large difference between the values of $\mathfrak{M}$ for the stepped and for the ideal apparatus.

The use of the considerations presented in this section will be illustrated in Part IV, where we shall give numerical examples of the design of multi-stage apparatus.

ENTROPY EFFICIENCY

The Onsager Theorem

It has been shown by Onsager that for any small volume of gas the inequality

$$-\dot{S}_m/\dot{S}_c\leqslant\tfrac{1}{4}\alpha^2 c\bar{c}(PD/\lambda T)\qquad(322)$$

is valid. Here $\dot{S}_m$ is the rate of increase of entropy in the volume caused by mixing of the two constituents, and $\dot{S}_c$ is the rate of increase of entropy caused by the conduction of heat through the volume. The result (322) is a rigorous consequence of the general equation of transport (25) and the equation of continuity (30). The sign of equality holds in (322), if and only if

$$\mathbf{J}_{1D}=-\tfrac{1}{2}\mathbf{J}_{1\alpha},\qquad(323)$$

where $\mathbf{J}_{1D}$ is the contribution of the ordinary diffusion term to the flux vector $\mathbf{J}_1$, and $\mathbf{J}_{1\alpha}$ is the contribution of the term corresponding to thermal diffusion.

It is interesting to inquire what fraction of this theoretical upper limit may be obtained in actual thermal separation apparatus of the type we have been discussing. We first state an elementary thermodynamic relation. Consider two chambers A and B, each of which contains initially a mixture of gases with the same relative concentration; and then suppose that a small number of moles of species 1 is transferred from A to B, and that an equal number of moles of species 2 is transferred from B to A, with the result that the values of c in the two chambers now differ by the amount Δ. Then if $\Delta/c\bar{c}$ is small compared with unity, the total change of entropy is given by

$$\Delta S_m=-\tfrac{1}{2}R(\Delta/c\bar{c})\times(\text{no. of moles transferred}),\qquad(324)$$

where R is the gas constant per mole.

Consider now an infinite reservoir connected by a short separation column with a positive reservoir containing m grams of gas. Then we have

$$\text{no. of moles transferred}=m\Delta/M,\qquad(325)$$

where M is the molecular weight of the gas in question. Equation (324) may now be written

$$\Delta S_m=-\tfrac{1}{2}(R/M)m(\Delta^2/c\bar{c}),\qquad(326)$$

from which we find

$$-\dot{S}_m=(R/M)m(\Delta/c\bar{c})d\Delta/dt.\qquad(327)$$

The substitution of the value (192) for Δ yields finally

$$-\dot{S}_m=\frac{R}{M}\cdot\frac{H^2L}{K}\cdot c\bar{c}\{e^{-t/t_r}(1-e^{-t/t_r})\}.\qquad(328)$$

The rate of increase of entropy caused by the degradation of heat in the separation column is

$$\dot{S}_c = BL\cdot(\lambda\Delta T/2w)\cdot(\Delta T/T_1T_2) \qquad (329)$$

in the plane case. If now we insert in (328) the values of H and K for the plane Maxwellian case (Eqs. (78) and (82)), and note that the maximum value of the bracketed expression in (328) is $\frac{1}{4}$, we find

$$-\left(\frac{\dot{S}_m}{\dot{S}_c}\right)_{\max} = \frac{1}{4}\alpha^2 c\bar{c}\frac{PD}{\lambda T}\cdot\frac{7}{10} \cdot\left(1+\frac{K_d}{K_c}\right)^{-1}\cdot\phi^2(u)\cdot\frac{T_1T_2}{\bar{T}^2}. \qquad (330)$$

The last two factors in (330) approach unity as ΔT becomes small. The restriction (119) which prevents our making K_d/K_c as small as we wish is not a thermodynamic restriction. One thus sees that the ideal efficiency of the thermal separation column is 70 percent of the fundamental thermodynamic efficiency (322). This result was first stated by Onsager (O2). The factor 7/10 represents the best average fit that may be made to the relation (323) in the space between the walls of the separation column.

The entropy efficiency given by (330) is reached at only one time during the separation, at the time $t=(\log 2)t_r$. The greatest average efficiency which may be obtained in either continuous or discontinuous operation is easily shown to be that given by (330) with the additional factor

$$8\log\xi/\xi^2 = 0.81453. \qquad (331)$$

The factor $PD/\lambda T$ which occurs in (330) is independent of the pressure and temperature, and on the basis of the inverse power model is given by

$$PD/\lambda T = (4/15)\cdot(6/5)f(\nu) \qquad (332)$$

for a monatomic gas, where $(6/5)f(\nu)$ is the function tabulated in Table I, Part I.

Efficiency of the Column Itself

It was mentioned in the section on efficiency in discontinuous operation that the problems connected with efficiency could be placed in two categories. We here consider those in the second category, which are concerned with the efficiency of the column itself, without reference to the manner in which the column is used.

It was also mentioned in the same place that the problems in the two categories had been shown to be independent by Krasny-Ergen. Strictly speaking, his proof is valid only when one makes the same assumptions that are involved in defining the ideal multi-stage apparatus.

We have already pointed out that the value of H^2/K is the real measure of the effectiveness of a unit length of separation column. This may be seen from Eq. (295). It may also be seen in Eq. (328), where S_m/L is proportional to H^2/K, and to nothing else which depends on H or K. A third method of demonstrating this fact is illuminating. The fundamental problem of efficiency may be described as the problem of maximizing $\sigma/L\Theta$, where σ is the rate of production of concentrated material, L is the length of column required, and Θ is the cost of construction and operation per unit length of column. We may write

$$\frac{\sigma}{L\Theta} = \frac{H^2}{K\Theta}\cdot\frac{n}{y}. \qquad (333)$$

The problem of maximizing n/y has already been treated, and we have seen that the solution is independent of the values of H and K. In order to maximize $\sigma/L\Theta$, therefore, we must maximize the ratio of H^2/K to the cost per unit length.

The Plane Case

We shall first suppose that the temperatures T_1 and T_2 are held fast, and determine the best value of w. We have

$$H^2/(K\Theta) \propto 1/(w\Theta(1+a/w^6)), \qquad (334)$$

where a/w^6 is equal to K_d/K_c. According to (76), the power consumption Q due to conduction varies inversely as w. Thus if the cost is chiefly that of supplying power to maintain the conductive heat flow, the maximum value of $H^2/K\Theta$ is obtained by letting w increase without limit. The restriction imposed by turbulence, however, means that w^6/a may not be made greater than 25. We may obtain 96 percent of the efficiency which would be possible if longitudinal diffusion did not exist.

The cost of operation may, however, be mainly due to the transfer of heat by radiation. The transfer of heat per square centimeter per second by radiation is

$$Q_{\mathrm{rad}}=\sigma(T_2{}^4-T_1{}^4)\frac{(1-R_1)(1-R_2)}{(1-R_1R_2)}, \quad (335)$$

where R_1 and R_2 are the reflection coefficients of the cold and hot wall, respectively, suitably averaged over solid angle and the frequency spectrum involved, and where $\sigma=5.7\times10^{-12}$ watt/cm^2-deg.$^4=1.36\times10^{-12}$ calorie/cm^2-deg.^{4}-sec. is here the Stefan-Boltzmann radiation constant. Both Q_{rad} and the cost of construction are independent of w. If these factors form the chief contribution to Θ, it is easily found that $H^2/K\Theta$ is maximized when w is adjusted so that K_c/K_d is made equal to 5.

In the general case in which all of these factors are important in contributing to the cost, the optimum value of K_c/K_d will be somewhere between 5 and 25. Since a value of $K_c/K_d=10$ will always provide operation at very nearly the maximum of efficiency, it does not seem worth while to carry the maximization procedure further.

We now consider the dependence of efficiency on the temperatures T_1 and T_2. It follows from (70), (71), and (76) that for the plane Maxwellian case the value of H^2/K_cQ is proportional to $\Delta T/\bar{T}^2$, and for given T_1 is therefore maximized when $T_2/T_1=3$. (Since K_d is a small fraction of K_c, it is sufficient to consider only K_c in the present connection.) The consideration of the cost of construction would tend to raise this ratio above three, whereas the consideration of power consumption due to radiation would tend to reduce this ratio. The difficulty with radiation losses will almost certainly make it advisable to reduce the temperature ratio below three, at least in the usual case in which T_1 is about room temperature. The best value of T_2/T_1 should be determined by carrying out the maximization for each case as it is encountered; the general formulae are cumbersome.

The above procedure is an approximate one, of course. One should really write out Θ as a function of w, T_1, and T_2, and maximize $H^2/K\Theta$ with respect to a simultaneous variation of w, T_1, and T_2. This procedure, however, leads to very complicated and unilluminating formulae when carried through in general. In the above we have merely tried to pick out the simple conclusions which can be drawn.

The Cylindrical Case

We shall reverse the order of discussion used in the plane case, and treat the dependence on temperature first. We propose to show that in the extreme cylindrical case, the hot wire should always be operated at as high a temperature as possible in order to *minimize* the transfer of heat by radiation. The proof will actually be given only for the Maxwellian case, because this is the only case for which we have developed formulae, but it will be evident from the method of proof that the conclusion is also valid when the temperature dependences of the gas coefficients differ somewhat from those of the Maxwellian case.

We want to maximize $H^2/K(Q_1+Q_{1\,\mathrm{rad}})$, where $Q_{1\,\mathrm{rad}}$ is $1/2\pi$ times the radiative transfer of heat per unit length of column. The expression (335) for radiative transfer in the plane case was derived by considering the fate of the heat which left the two walls as it was reflected back and forth between them. Such a procedure is not easy to carry through in the cylindrical case, because of the much more complicated situation from the point of view of geometrical optics, particularly when the wire is displaced from the axis of the tube by even a small fraction of its radius. In the extreme cylindrical case, however, where the wire occupies only a small part of the solid angle as seen from the wall, it is a good approximation to assume that very little of the radiation ever gets back to the wire; it is effectively radiating into a nearly blackbody. We then have as an upper limit to $Q_{1\,\mathrm{rad}}$

$$Q_{1\,\mathrm{rad}}=\sigma r_2T_2{}^4(1-R_2). \quad (336)$$

This expression is probably a fair approximation when r_1/r_2 is greater than about ten, and when T_2/T_1 is greater than about two. The former condition we shall consider to be the definition of the extreme cylindrical case.

We shall now hold Q_1, r_1, and T_1 fast, and examine the behavior of $H^2/K(Q_1+Q_{1\,\mathrm{rad}})$ as T_2 is increased and as r_2 is correspondingly decreased. It follows from (112)–(113) that this procedure is equivalent to holding t_1 fast and increasing t_2. It then further follows from (113) that the upper limit (336) is proportional to

$$r_2T_2^4 \propto t_2^4 \exp(-\tfrac{1}{2}t_2^2). \qquad (337)$$

Since the expression (337) has a maximum at $t_2=2$, $Q_{1\,\mathrm{rad}}$ will always decrease as t_1 is held fast and t_2 is increased, provided that t_2 is greater than two; from (113), however, we find that for all apparatus for which r_1/r_2 is greater than ten, the value of t_2 must be greater than $(2 \log 10)^{\frac{1}{2}} = 2.14$. Thus $Q_{1\,\mathrm{rad}}$ will always decrease under the stated conditions because r_2 decreases more rapidly than T_2^4 increases.

Although the data given in Tables VI and VII are not in the best form to demonstrate the fact, it may be shown from them that the ratio H^2/K_c increases monotonically as t_1 is held fast and t_2 is increased. Indeed, we should always expect this to be the case, because under these conditions the ratio of $\dot{S}_c$ to Q_1 will always increase (cf. Eq. (322)).

We therefore see that the hot wire should always be operated at as high a temperature as the stability of the gas will permit, in order to minimize radiation losses. The fact that the reflection coefficient R_2 will in general decrease as T_2 is increased, will have the effect of making the advantage of a high T_2 somewhat less than is indicated by (337), but even so the exponential will always be the dominant factor.

If, however, we choose to ignore the existence of a transfer of heat by radiation, it is interesting to inquire what is the most efficient choice of r_1/r_2 and T_2/T_1. At the present time, we are able to answer this question only for the Maxwellian case. Let us suppose that we have a given gas, and that the lower temperature T_1 is fixed, as will usually be the case. Then according to Eqs. (115)–(117), the ratio H^2/K_c is proportional only to h^2/k_c. Furthermore, we see from (112) that under the same conditions the power consumption due to conduction, Q_1, is inversely proportional to t_1^2. The power efficiency of the column, as measured by H^2/K_cQ_1, is thus proportional to $h^2t_1^2/k_c$. The latter ratio is tabulated in Table XVI.

TABLE XVI. Values of $h^2t_1^2/k_c$ for the Maxwellian case.

T_2/T_1 \ r_1/r_2	1	15	25	40	60	100
2	0.46	0.44	0.41	—	—	—
3	0.54	0.59	0.59	0.57	0.57	0.56
4	0.54	0.68	0.67	0.66	0.66	0.64
5	0.51	0.58	0.67	0.71	0.71	0.69
6	0.48	—	—	0.61	0.65	0.68

Perhaps the most interesting feature of the results presented in Table XVI is the fact that the entries vary as little as they do; the largest entry is only 1.73 times the smallest. The table further indicates that with a small temperature ratio, the concentric tube type of construction is the more efficient, whereas for gases which permit a large temperature ratio, the hot wire type of construction is more efficient. The latter result is a pleasant one, since the difficulty with transfer of heat by radiation compels us to use the hot wire type of construction for large temperature ratios.

Suppose now that r_1/r_2, T_1, and T_2 have all been determined, so that the only quantity left to vary is the radius of the outer tube. Now whereas in the plane case the quantity Q was proportional to $1/w$, and Q_{rad} and the cost of construction were independent of w, in the cylindrical case Q_1 is independent of r_1, and $Q_{1\,\mathrm{rad}}$ and the cost of construction are proportional to r_1. On the other hand, however, in the plane case the ratio H^2/K_c was inversely proportional to w, whereas now the ratio H^2/K_c is independent of r_1. Just as in the plane case, therefore, the ratio K_c/K_d should be made as large as possible (namely, about 25) when the chief cost is that of supplying power to maintain the conductive transfer of heat, and should be made equal to five, if the radiative transfer and cost of construction are the chief cost. A value of K_c/K_d equal to ten will yield nearly the maximum of efficiency in all cases.

A comparison of the advantages of the concentric tube and the hot wire type of construction is given at the beginning of Part IV.

The Effect of Changing the Pressure

The pressure of the gas within the column may readily be varied within wide limits, so that it is interesting to inquire what changes may be produced by a variation in pressure.

Two remarks may be made at once. By (328), (330), and (332), the fundamental efficiency of a separation column, as measured by the ratio H^2/KQ, is independent of the pressure, so that we shall not expect any very large changes in the efficiency to be produced by a change in pressure. Secondly, as may be seen from (70)–(72) and (138), the constants H and K depend on the pressure always in the combination P^2g, so that any change in these coefficients which could be produced by a change in the effective value of g could also be produced by a change in the pressure.

In the following discussion, we shall assume that r_1/r_2 and T_2/T_1 have pre-determined values in the cylindrical case. For the plane case, we make the corresponding assumptions that B/w and T_2/T_1 have fixed values; it is desirable to make B/w large in order to obtain a large transport from a single tube, but on the other hand B/w may not be made too large or there will be difficulty with parasitic convection currents (cf. Eq. (138)); there will therefore be an optimum value of B/w. We shall consider as variable the total length of tubing Λ, the length of the apparatus $\mathfrak{L}$, the pressure P, and the radius r_1 of the outer tube.

According to (295), it is necessary that $\Lambda H_I^2/K_I$ have a given value in order to secure a given rate of yield with a given increase in concentration. Since the most efficient value of K_c/K_d is approximately a constant, we see from (70)–(72) that w or r_1 must be proportional to $(P^2g)^{-\frac{1}{3}}$. We then find that $\Lambda H_I^2/K_I$ is proportional only to Λ. Under the same conditions, the heat transferred by conduction in the entire apparatus is proportional only to Λ. We have thus confirmed that the fundamental efficiency is independent of the pressure. The cost of construction, as measured by the area of tubing, and the heat transferred by radiation are proportional to Λr_1 or Λw, however, and are therefore proportional to $\Lambda(P^2g)^{-\frac{1}{3}}$; they may accordingly be reduced by increasing the pressure above atmospheric pressure. This apparent advantage is more or less completely offset by other considerations, however.

The smaller value of w or r_1 will mean that it will be more difficult to obtain adequate precision in construction; the tubes will require more care in fabrication, and the cost will therefore not be proportional to the surface area. Furthermore, if a really appreciable increase of pressure is contemplated, it will be necessary to increase the wall thickness of the tubes. This will also add to the cost on construction. For these reasons it seems unlikely that the use of pressures much greater than one atmosphere will very often be profitable.

Although the ratio H_I^2/K_I is independent of the pressure when K_c/K_d is maintained at a constant value, the ratio $A=H_I/2K_I$ is proportional to $(P^2g)^{\frac{1}{3}}$. The length of the apparatus $\mathfrak{L}$ is therefore proportional to $(P^2g)^{-\frac{1}{3}}$, since the length is inversely proportional to A. The total length of tubing required Λ, is independent of the pressure, so that the number of tubes in parallel in each stage is proportional to $(P^2g)^{\frac{1}{3}}$. The characteristic time t_c is proportional to $\Lambda r_1^2P/H_1$, and thus varies as $(Pg^2)^{-\frac{1}{3}}$. This is the only case in which P and g occur otherwise than in the combination P^2g.

Minimization of the Characteristic Time t_c

We have seen that the best value of K_c/K_d from the point of view of efficiency is between 5 and 25 in every case. We shall show immediately, however, that in order to secure the shortest characteristic time, this ratio should be given the value 2.

It follows immediately from (299) and (300) that in order to minimize t_c, the ratio $H_I^2/K_I\mu$ should be maximized. With fixed r_1/r_2 or fixed B/w, μ is proportional to r_1^2 or w^2, so that we have

$$\frac{H_I^2}{K_I\mu}\propto\frac{1}{w^2(1+a/w^6)}, \tag{338}$$

where w may be considered to be either w or r_1, as the case may be. This expression is maximized when $K_c/K_d=2$.

The characteristic time does not depend strongly on this ratio, however. For example, when K_c/K_d has the value 10, which as we have already remarked provides nearly the maximum of efficiency in every case, the characteristic time has a value which is only 25.3 percent greater than its value for $K_c/K_d=2$.

PART IV. APPLICATIONS OF THE THEORY

Very little new theoretical material will be developed in this part, which is devoted to a comparison of the advantages of the concentric tube and hot wire type of separation column, constructional considerations, some numerical examples of the design of apparatus, and a discussion of the experimental literature.

Comparison of the Concentric Tube and Hot Wire Types of Column

Advantages of the Hot Wire Type

(1) The hot wire type of apparatus is less subject to difficulties with parasitic convection currents which serve no useful purpose and increase the value of K. Our computations on this matter (cf. Eqs. (139)–(141)) are not very apposite to the question, but it is clear that the parasitic currents must be of less importance in the hot wire type of apparatus.

(2) When very large separation factors are desired, the ideal multi-stage design will often demand an impossibly large number of tubes in parallel for the first stage, or else a number of tubes for the later stages which is less than unity. If the concentric tube type of column is considered as the unit tube, the hot wire type of column makes it possible to realize a "fractional" tube. This matter will be discussed in more detail in the design of the helium apparatus.

Less important advantages:

(3) The hot-wire type of construction permits one to obtain an appreciably greater H^2/K for a given power consumption per unit length. This is true because a much larger temperature difference may be obtained without incurring prohibitive radiation losses.

(4) The hot wire type of apparatus is simpler in construction, and requires less precision in its construction.

(5) Clusius and Dickel (C10, p. 449) have pointed out that in some cases desirable exchange reactions are facilitated by the hot wire. For example, in concentrating O^{18}, the reaction

$$2O^{16}O^{18} \rightleftarrows O_2^{16} + O_2^{18}$$

will occur in the gas near the wire, so that one may obtain nearly pure O_2^{18} instead of the nearly pure $O^{16}O^{18}$ that would be obtained with a concentric tube column.

(6) The thermal diffusion constant α will usually increase at high temperatures, and H^2/K is proportional to α^2.

Advantages of the Concentric Tube Type

(1) In the initial stages of multi-stage apparatus, it is often necessary to obtain very large values of H. The value of H which may be obtained from one column of the concentric tube type is several times the value obtainable from one hot wire column, so that the number of columns which it is necessary to use in parallel may be substantially reduced.

(2) In many (probably in the majority) of the cases which arise in practice, the possibility of undesirable chemical reactions will reduce drastically the value of T_2 which may be employed; the gas may decompose, or it may react with the material of the tube or wire if the temperature exceeds a certain limiting value, which may be quite low. In some cases also T_1 cannot be very low because the gas would condense. Now if the temperature difference is rather small, one simply cannot put much power into a hot wire apparatus because of the small area of the hot surface. Our discussion of entropy efficiency in Part III has shown us that in efficient apparatus, the output in terms of separation factor and yield is proportional to the increase of entropy due to conduction, and therefore to the power put in to maintain the conductive heat flow. The use of a hot wire column with a small temperature difference would therefore mean that very many columns would be required. This would mean elaborate and expensive construction, and would probably bring with it the attendant difficulty of long equilibrium times. In these cases, the concentric tube construction is indicated in order that one be able to put a satisfactory amount of power into the apparatus.

(3) When the inner cylinder is simply a wire, electrical heating is required. The concentric tube type of construction makes it possible to use other means of heating the inner cylinder, such as condensing vapor or circulating liquid. For large scale apparatus, concentric tube construction thus makes it possible to use an inexpensive kind of power.

Constructional Considerations

Under this heading we shall discuss some of the implications of the preceding theory with respect to the manner in which the apparatus should be constructed. The material is necessarily somewhat miscellaneous.

(1) Our considerations on the effect of a small azimuthal variation in temperature, and on the effect of a lack of perfect centering of the wire, show that these imperfections should be avoided as much as possible. To insure accurate alinement, the inner tube or wire should be held in position by spacers placed at frequent intervals along the tube. The wire, if heated by alternating current, will tend to vibrate in the earth's magnetic field, if it is not restrained.

Metal tubes are to be preferred, because their good conduction will minimize the azimuthal variation in temperature. Metal tubes are also advantageous because when properly polished, they will reduce radiation losses, and because greater precision in construction may be realized with them. In the case of concentric tubing, heating by condensation of a vapor or by rapidly circulating liquids is probably better than heating by resistance wire. The water cooling of the outer tube should also be efficient in order to minimize temperature asymmetries.

(2) We have seen that both the true equilibrium time (cf. Eq. (174)) and the characteristic time which one must wait before continuous operation may be begun (cf. Eq. (300)) are proportional to the mass of the desired isotope which must be transported into the column. Any dead space in the column or connecting tubes will increase this mass, and will thus increase the equilibrium or characteristic time.

In the operation of multi-stage apparatus, it is necessary to connect the bottom of one column to the top of the one following or preceding it. In order to prevent a reverse concentration gradient, it is essential that a good circulation be maintained in the connecting tubes. It has been customary, we understand, to maintain this circulation by the simple means of applying a heater to one of the two connecting tubes. Because of the small pressure difference obtainable by this method, however, it is necessary to use rather large connecting tubes to obtain adequate circulation, and this means that the tubes will contribute appreciably to the dead space. The writers recommend that a more effective method be used to secure the necessary circulation, so that smaller connecting tubes may be employed with a consequent reduction in the equilibrium time. Since the resistance to the flow of gas through a tube is by Poiseuille's law inversely proportional to the square of the cross-sectional area, it is clear that a large increase in the driving pressure will be necessary in order to realize a substantial decrease in the column of the connecting tubes. It is further necessary that the pumping device be inserted in such a way that it does not interfere with the pressure gradient which is causing the gas to flow through the separation columns at the rate σ.

When very large separation factors are to be obtained, it may be necessary to purify the gas at several points along the apparatus, because the impurities may be concentrated far more effectively than the isotope itself. In order to keep the dead space small, it is very important that the volume required by the purification apparatus be made as small as possible.

(3) When two or more separation columns are connected in parallel in such a way that the upper ends are connected freely together, and the lower ends likewise, the inevitable temperature differences among the columns will produce parasitic circulating currents rising in some of the columns and falling in others. These large circulating currents will more or less completely obliterate the concentration gradient that would otherwise be obtained. It is therefore vitally necessary that such circulating currents be suppressed.

Before we indicate how this may be accomplished, it will be convenient to clarify our language. We shall suppose the scrubber to be of the single-stage type, with the same number of tubes in parallel as in the first stage of the apparatus. The first stage and the scrubber together will then consist of a number of columns in parallel, with the fresh gas flowing in at a point somewhere between the ends of the columns, and flowing out at the rate σ and concentration c_{Nf} at the positive end of the last stage of the multi-stage apparatus. We shall refer to the point in each of the columns of the first stage where the fresh gas flows in as the *inlet* of that column. We shall further consider the end of the scrubber at the inlet as the negative end, so that the gas flows out of the positive end of the scrubber at the rate σ_s and with the concentration c_s, where σ and σ_s are related by (225.2).

Another way of saying that parasitic circulating currents of the type just described must be avoided, is to say that the flow of gas through the tubes in a given stage must be approximately the same in each tube. The equality of flow in the tubes of the last stage, and the equality of flow in the tubes of the scrubber, may be secured easily by connecting all the inlets together with a path of low resistance and by providing the positive end of each of the tubes in the scrubber with matched capillary tubes, through which the gas must flow as it leaves the scrubber; exactly similar remarks apply to the last stage. If the resistance of the capillaries is large compared with the resistance of the columns, and if further the pressure difference between the ends of the capillaries is large compared with any pressure difference which might be produced by differences in the mean temperature of the columns, then the flows in the separate tubes must be alike to the extent that the resistances of the capillaries are matched.

Unfortunately, this simple method of suppressing circulating currents cannot be used except in the last stage and in the scrubber, because the insertion of a capillary in one of the intermediate stages would very seriously interfere with the transport of the two isotopes in opposite directions which occurs at the point of juncture of two stages; a large reverse concentration gradient would build up in the capillaries which would largely offset the separation obtained in the columns. Rather, one needs something which will present a large resistance to convective flow, but which will nevertheless permit good diffusive equilibrium to be established across it. A plate of suitably chosen porous material seems well adapted to accomplish this task. One porous plug inserted at one end or the other of every column in the apparatus except those in the last stage and in the scrubber, would insure the equality of flow in all of the tubes of each of the intermediate stages, and would not interfere with the necessity of maintaining the concentration at the positive end of one stage equal to the concentration at the negative end of the next.

It is possible to connect the tubes in such a way that it is necessary to provide only the tubes of the first stage with porous plugs, in addition to the capillary tubes at the positive ends of each of the tubes in the scrubber and last stage. This is accomplished by using integral stepping ratios only; integral stepping ratios make it possible to connect each tube of the $(k+1)$ stage to the same number of tubes of the kth stage. If each tube is connected separately to the number of tubes in the preceding stage—that is to say, if there is no connection between the negative ends of the tubes in each of the stages (except the first), then it is clear that there will be no "loop" circuits in the apparatus except those which involve part of the first stage as part of the circuit. This method is practical, however, only for those apparatuses in which each stage is actually above the preceding one; in the usual type of multi-stage apparatus, in which the respective stages are beside one another and in which it is necessary to provide connecting tubes between the stages, this method would involve as many pairs of connecting tubes between the kth and $(k+1)$th stages as there are tubes in the $(k+1)$th stage. It is clear that it is usually simpler to provide every column with a porous plug.

It may at first be thought that in the apparatus described in the last paragraph, it would be possible to eliminate even the porous plugs in the first stage by providing also the inlets with matched capillaries. Closer examination shows, however, that in order to equalize the flows in the tubes of the first stage by this method, it is necessary that the fractional deviations in the resistances of the capillaries at the inlets (and also in the resistances of the capillaries at the outlets of the scrubbing tubes) be small compared with σ/σ_s (cf. Eq. (225.2)); since σ/σ_s will always be small compared with unity in multi-stage apparatus, it is clear that the capillaries would have to be matched with prohibitive accuracy.

Numerical Examples of the Design of Efficient Multi-Stage Apparatus

In this section we propose to design two multi-stage apparatuses on the basis of the theory which has been developed in the first three parts of this article. The first apparatus will be for the concentration of $C^{13}H_4$, and the second for the concentration of He^3.

The material in this section will be valuable in several respects. In the first place, it will serve to demonstrate the concrete meaning of the formulae which have been developed. Secondly, it will indicate how a rough estimate of the possibilities of the Clusius-Dickel method may be obtained for any given problem in a short time. Finally, it will illustrate how the formulae may be used to obtain the complete design of an efficient multi-stage apparatus for the accomplishing of a given task.

The Methane Apparatus

Since methane is not stable at very high temperatures, it is desirable to use a concentric tube type of column. We shall assume that the temperatures of the inner and of the outer tube are the same as in the apparatus of Nier (N3):

$$T_1 = 300^\circ, \quad T_2 = 573^\circ, \quad \therefore \quad \bar{T} = 436.5^\circ, \quad \Delta T = 273^\circ. \tag{339}$$

At the temperature 436.5°K we find from the recent work of Trautz and Sorg (reference *e* of Table III) that the coefficient of viscosity of methane is

$$\eta = 1.51 \times 10^{-4} \text{ poise}, \tag{340}$$

and either from this reference or from Table III we find that at this temperature the viscosity varies as $T^{0.78}$. We have further

$$\rho = 4.47 \times 10^{-4} \text{ g/cm}^3 \tag{341}$$

if we consider that methane is chiefly $C^{12}H_4$.

The value $n = 0.78$ corresponds to $\nu = 10.4$, according to Eq. (13) which is based on the inverse power model. From Eq. (18) and Table I, we then have

$$D = 1.406\eta/\rho = 0.474 \text{ cm}^2/\text{sec.}$$

If necessary, we could now obtain an estimate of α from Eq. (10) and Table I; this procedure gives the value $\alpha = 0.0104$. The value of α has, however, been determined experimentally by Nier (N1), who finds:

$$\alpha = 0.0077. \tag{342}$$

These data are all for a pressure of one atmosphere. To a very high degree of precision, η and α are independent of the pressure, ρ is proportional to the pressure, and D is inversely proportional to the pressure. Since it is convenient to work at a pressure near one atmosphere, and since the use of a pressure of one atmosphere leads to a column of reasonable dimensions, we shall base the design on a pressure of one atmosphere.

The carbon isotope of mass 13 occurs with a natural abundance of one part in 92 (V1):

$$c_{1i} = 0.0108. \tag{343}$$

We may now substitute these data in (70)–(72). For simplicity, we assume that the ratio $B/2w$ has the same value as in the apparatus used by Nier:

$$B/2w = 18.53. \tag{344}$$

We then have

$$H^{(0)} = 1.006 \times 10^{-4}(2w)^4 \text{ g/sec.}, \tag{345}$$

$$K_c^{(0)} = 1.575 \times 10^{-1}(2w)^8 \text{ g-cm/sec.}, \tag{346}$$

$$K_d^{(0)} = 3.94 \times 10^{-3}(2w)^2 \text{ g-cm/sec.} \tag{347}$$

In order to obtain a rough estimate of the possibilities of the thermal diffusion method, we need only to determine w so that $K_c/K_d = 10$, and then to substitute the resulting values of $(H^{(0)})^2/(K_c^{(0)} + K_d^{(0)})$ in (295), in order to determine how much tubing will be necessary in order to obtain material of concentration c_{Nf} at the rate of σ grams per second.

We shall proceed in a more precise manner, however, and determine the correction factors which are to be applied to (70)–(72) in order to take account of the finite temperature difference and the cylindrical shape of the column. From (77) and (339) we have

$$u = 0.3125, \tag{348}$$

and from (344) we have

$$\log r_1/r_2 = 0.342. \tag{349}$$

Substituting these values of u and $\log r_1/r_2$ in

(100)–(108), we find

$$H/H^{(0)}=1.109, \tag{350}$$

$$K_c/K_c^{(0)}=1.176, \tag{351}$$

$$K_d/K_d^{(0)}=0.998. \tag{352}$$

We then have finally

$$H=1.116\times 10^{-4}(2w)^4\text{ g/sec.}, \tag{353}$$

$$K_c=1.852\times 10^{-1}(2w)^8\text{ g-cm/sec.}, \tag{354}$$

$$K_d=3.93\times 10^{-3}(2w)^2\text{ g-cm/sec.} \tag{355}$$

We must now choose w so that the column operates with maximum efficiency. It has been shown (section on entropy efficiency, Part III) that the most efficient value of K_c/K_d always lies between 5 and 25, and that the value 10 always provides operation at nearly the maximum of efficiency. Setting $K_c/K_d=10$, we have

$$47.1(2w)^6=10 \tag{356}$$

or $2w=0.772$ cm. This is very near the value $2w=0.712$ cm which was actually used by Nier. Since the wall separation 0.712 cm is known to represent a practical type of construction, we shall assume

$$2w=0.712\text{ cm} \tag{357}$$

for the column which we are hypothetically designing. We then have from (353)–(355)

$$H=2.866\times 10^{-5}\text{ g/sec.}, \tag{358}$$

$$K_c=1.224\times 10^{-2}\text{ g-cm/sec.}, \tag{359}$$

$$K_d=1.992\times 10^{-3}\text{ g-cm/sec.} \tag{360}$$

As we shall see later on when we compare our theory with experiment, Nier's experimental results indicate that there was present in his column a parasitic convection current given by

$$K_p/K_c=0.283. \tag{361}$$

Whether such a large value is due to an avoidable asymmetry of Nier's column, or whether such a value is as low as can reasonably be obtained, can be determined only by future experimental work. In the latter case, it may be desirable to reduce the value of $B/2w$, since K_p/K_c is proportional to the square of this ratio.

We now have

$$\begin{aligned}K&=K_c+K_d+K_p\\&=1.771\times 10^{-2}\text{ g-cm/sec.},\end{aligned} \tag{362}$$

whence

$$A=H/2K=0.810\times 10^{-3}/\text{cm} \tag{363}$$

and

$$H^2/K=4.64\times 10^{-8}\text{ g/cm-sec.} \tag{364}$$

Nier's column required 3.77 watts per centimeter of length. Only 1.03 watts/cm were required when the apparatus was evacuated. The difference 2.74 watts/cm is to be attributed to conduction through the gas. Using the value

$$\lambda=1.20\times 10^{-4}\text{ cal./cm-sec.-deg.} \tag{365}$$

obtained by extrapolation from the *International Critical Tables*, we find

$$BQ=2.54\text{ watts/cm}, \tag{366}$$

which is in fair agreement with experiment. The discrepancy is perhaps to be attributed to the uncertainty in the value of λ, since this ought to be a good method of measuring the thermal conductivity.

The mass μ of gas in unit length of the column may be computed with fair accuracy from the formula

$$\mu\cong 2\rho wB \tag{367}$$

if we use the value (341) for ρ. In this manner we find

$$\mu\cong 4.21\times 10^{-3}\text{ g/cm.} \tag{368}$$

We have now completed the design of the column itself, and it remains only to determine how the tubes should be connected in series-parallel in order to realize efficient operation. We shall suppose that methane containing 20 percent $C^{13}H_4$ is desired:

$$c_{Nf}=0.20 \tag{369}$$

so that the total separation factor is 22.9.

We shall first determine what could be done with an ideal multi-stage apparatus. Substituting (343), (364), and (369) in (295), we find

$$\Lambda/\sigma=1.33\times 10^9\text{ cm-sec./g.} \tag{370}$$

If we require one gram of the 20 percent material per day ($\sigma=1.16\times 10^{-5}$ g/sec.), we find for the total length of tubing

$$\Lambda=154\text{ meters.} \tag{371}$$

Since the column requires 3.77 watts per centimeter, the total power consumption will be 58

TABLE XVII. Design of the methane apparatus for several values of n_I.

	(1)	(2)	(3)	(4)
σ (g/day)	0.634	0.694	0.746	0.793
n_I	0.2560	0.2800	0.3013	0.3200
$\mathfrak{N}_1$	8	8	8	8
$\mathfrak{N}_2$	4	4	4	4
$\mathfrak{N}_3$	2	2	2	2
$\mathfrak{N}_4$	1	1	1	1
n_1	0.0320	0.0350	0.0377	0.0400
n_2	0.0640	0.0700	0.0753	0.0800
n_3	0.1280	0.1400	0.1507	0.1600
n_4	0.2560	0.2800	0.3013	0.3200
c_{1i}	0.0108	0.01080	0.0108	0.0108
c_{1f}	0.0178	0.01934	0.0207	0.0219
c_{2f}	0.0331	0.03577	0.0380	0.0400
c_{3f}	0.0579	0.06185	0.0652	0.0680
c_{4f}	0.2000	0.20000	0.20000	0.2000
q_1	1.661	1.806	1.936	2.047
q_2	1.890	1.881	1.870	1.864
q_3	1.793	1.777	1.763	1.751
q_4	4.067	3.792	3.582	3.427
y_1	0.920	1.1285	1.324	1.506
y_2	1.278	1.2684	1.258	1.251
y_3	1.176	1.1635	1.143	1.129
y_4	2.080	1.9874	1.912	1.852
$y_1/\log q_1$	1.81	1.91	2.00	2.10
$y_2/\log q_2$	2.01	2.01	2.01	2.01
$y_3/\log q_3$	2.01	2.02	2.02	2.02
$y_4/\log q_4$	1.48	1.49	1.50	1.50
$n_I/\Sigma_k\mathfrak{N}_k y_k$	0.015146	0.015206	0.015202	0.015124
L_1 (meters)	5.68	6.96	8.17	9.30
L_2 (meters)	7.89	7.82	7.76	7.72
L_3 (meters)	7.26	7.19	7.06	6.96
L_4 (meters)	12.84	12.26	11.80	11.43
$\mathcal{L}$ (meters)	33.7	34.2	34.8	35.4
Λ (meters)	104.3	113.8	122.4	130.7

kilowatts. From (292) and (363), the length of the apparatus is

$$\mathcal{L}=38.6\text{ meters.} \tag{372}$$

By (291), the number of tubes in parallel in the first stage is

$$\mathfrak{N}_1=14.3. \tag{373}$$

Finally, the mass $\mathfrak{M}$ is

$$\mathfrak{M}=1.12\text{ g} \tag{374}$$

according to (299), so that by (300) and (358) the characteristic time for the approach to the operating condition is

$$t_c=2.96\text{ days.} \tag{375}$$

The performance of this ideal apparatus will serve as a standard of excellence with which to compare the performance of the following stepped apparatus.

The relation (309.3) suggests that for an apparatus with a stepping ratio of two, the value of n for the first stage should be 4/3 of the value for the first stage of the ideal apparatus, or

$$n_1=0.03767. \tag{376}$$

Correspondingly, the number of tubes in parallel in the first stage should be just $\frac{3}{4}$ the number in the first stage of the ideal apparatus, or $\mathfrak{N}_1=10.7$ if we require one gram per day as before. In order to use a stepping ratio of two, however, it is necessary that the number of tubes in each stage be an integral power of two. Accordingly, we choose

$$\mathfrak{N}_1=8. \tag{377}$$

With the value (376) for n_1, this means that σ is not one gram per day, but is rather only 0.75 gram per day.

The apparatus will thus have 8, 4, 2, and 1 tubes in parallel in the first, second, third, and fourth stage, respectively. The complete design of a multi-stage apparatus with the value (376) for n_1 is given in the third column of Table XVII. The values of the various c's were determined from (320), with $\gamma=2$, and the y's were obtained from (269). The q's were computed by Eq. (151). The L's were obtained from the relation $L_k=y_k/2A$, $\mathcal{L}$ is the sum of the L's, and Λ is the total length of the columns used $=\sum_k\mathfrak{N}_kL_k$. It is evident that the design is straightforward.

The design was then repeated for a value of n_1 slightly smaller than (376), and also for a slightly larger value. The result is given in the second and fourth columns of Table XVII. The quantity $n_I/\sum_k\mathfrak{N}_ky_k$ is a dimensionless measure of the efficiencies of the several designs. When it was observed that the efficiencies were substantially the same for the designs in the second and third columns, the design was repeated for a still smaller value of n_1; the result is presented in the first column.

It is interesting to compare the performance of these practical multi-stage apparatuses with the performance of the corresponding ideal apparatus as given by Eqs. (370)–(375). For the sake of definiteness, we shall base our further remarks upon the design in the second column of Table XVII. For this apparatus, we have

$$\Lambda/\sigma = 1.42 \times 10^9 \text{ cm-sec./g}, \tag{378}$$

which is to be compared with (370). It is evident that the stepped apparatus achieves 93 percent of the efficiency of the ideal apparatus. The mass $\mathfrak{M}$ has been computed from Eq. (321):

$$\mathfrak{M} = 1.02 \text{ g}. \tag{379}$$

The characteristic time is thus about 4 or 5 days; that is to say, perhaps 50 percent greater than the characteristic time (375) of the ideal apparatus. Since the power consumption as determined experimentally by Nier is 3.77 watts per centimeter, the apparatus will require 43 kilowatts.

Perhaps the most striking feature to be observed in Table XVII is the fact that the efficiency depends so slightly upon the initial choice of n_I; as n_I is varied from 0.256 to 0.320, the efficiency passes through a very flat maximum. It is pleasant that the maximum is so broad, because this means in practice that only a very few trial designs will have to be made in order to find one of nearly maximum efficiency. In fact the application of Eq. (307) to the first stage may be expected to give at once an acceptable design. Indeed, Eqs. (306.1), (307), (343), (369), and (377) give $n_1 = 0.036$, which lies between the values in the second and third columns of Table XVII.

It is interesting to note that all of Table XVII except the first row and the last six rows can be computed without knowing H and K. The design as given by the c's, n's, and y's is the most efficient design of any apparatus of the 8, 4, 2, 1 type of staging which is to raise the concentration of an isotope from 0.0108 to 0.200.

It remains to design a suitable scrubber for the apparatus. The ideal scrubber has the same number of tubes in parallel in the first stage of the scrubber as in the first stage of the separation apparatus. We shall therefore postulate eight tubes in parallel for the scrubber.

The value of c in the scrubber will be less than or equal to 0.0108, so that we are certainly justified in using the approximation $c \ll 1$. The concentrations c and $\bar{c}$ exchange their significance in the scrubber, however, as we pointed out in the section on the scrubber, so that the formula for the scrubber in the present case is Eq. (232). If we substitute c_{1i} for $\bar{c}_i$, c_s for $\bar{c}_f$, and n_s for n, we have from (232)

$$q_s = c_{1i}/c_s = (e^{y_s(1-n_s)} - n_s)/(1-n_s). \tag{380}$$

Since the value of H is the same for the scrubber and for the first stage, (225.2) may be written:

$$n_s = \frac{c_{Nf} - c_{1i}}{c_{1i} - c_s} n_1, \tag{381}$$

where of course $c_{Nf} = c_{4f}$ in the present apparatus. The specification of c_s now determines n_s by (381), and then y_s by (380).

We have computed a scrubber for two values of c_s, the first corresponding to removing $\frac{1}{3}$ of the $C^{13}H_4$ from the methane which is used, and the second to removing $\frac{2}{3}$ of the desired isotope. The multi-stage apparatus to which the scrubber is to be attached is taken to be that described by the second column of Table XVII ($n_1 = 0.0350$). By the method described in the last paragraph, we find for the first case

$$\begin{aligned} c_s &= \tfrac{2}{3} c_{1i} = 0.0072, \\ q_s &= 1.5, \\ n_s &= 1.839, \\ y_s &= 0.649, \\ \sigma_s &= 36.4 \text{ g/day}, \\ L_s &= 4.00 \text{ meters} \end{aligned} \tag{382}$$

and for the second case

$$\begin{aligned} c_s &= \tfrac{1}{3} c_{1i} = 0.0036, \\ q_s &= 3, \\ n_s &= 0.920, \\ y_s &= 1.85, \\ \sigma_s &= 18.2 \text{ g/day}, \\ L_s &= 11.41 \text{ meters}. \end{aligned} \tag{383}$$

In both cases, we find by comparing the values of n_s/y_s with those obtained from Table XI that the values of n_s/y_s are within one percent of the maximum. The use of eight tubes in parallel for the scrubber is thus very well justified.

It is apparent that the more efficient scrubbing of the second case is obtained at the expense of a much longer scrubber. Since methane is cheap, the first scrubber is probably the more practical.

The Helium Apparatus

It has recently been demonstrated that He^3 exists as a stable isotope with a natural concentration of the order of 10^{-7} or 10^{-8}, according to Alvarez and Cornog (A1). The concentrating of this isotope is a matter of considerable interest, because of the use which could be made of it as a cyclotron particle. Its precise atomic weight would be of theoretical interest.

The thermal separation column should be effective for the concentration of He^3 because of the relatively large value of α for the mixture He^3-He^4. We shall present here the design of an apparatus with very moderate dimensions which is to have a separation factor of 10^5; that is to say, it will raise the concentration of He^3 to somewhere between 10^{-2} and 10^{-3}, the exact value depending on the initial concentration.

An efficient multi-stage apparatus for the accomplishing of this task would require at least 10^4 tubes in parallel in the first stage. Such a construction is clearly out of the question. On the other hand, a single column used to obtain the entire separation would require several years to reach an operating condition. Some compromise is therefore necessary. As we shall see, the dimensions and power consumption of the apparatus will be so modest that the cost of construction and operation will be a rather small item. We shall accordingly direct our attention to the problem of securing a reasonably short characteristic time in a simple manner.

We have seen that the characteristic time required to put an apparatus into steady operation is equal to the mass of isotope which must be transported into the column divided by the initial transport. As long as we restrict the apparatus to have only a few tubes in parallel in the first stage, it is clear that the main contribution to $\mathfrak{M}$ will come from the positive end of the apparatus. Furthermore, in such an apparatus the transport $Hc\bar{c}$ near the positive end will always be so much greater than its value at the negative end, that the part of the column near the positive end will be running very close to equilibrium. Since c is everywhere small in the proposed apparatus, we may thus compute the mass $\mathfrak{M}$ very simply:

$$\begin{aligned}\mathfrak{M}&=\mu\int_0^{\mathcal{L}}(c-c_{1i})dz,\\&\cong\mu c_{Nf}\int_{-\infty}^{0}e^{2Az}dz,\\&\cong(\mu c/2A)_{Nf}.\end{aligned}\tag{384}$$

The characteristic time is then given by

$$t_c=\frac{(\mu c/2A)_{Nf}}{(Hc)_{1i}}.\tag{385}$$

We see from (385) that the simplest possible way of reducing the characteristic time is to use a two-stage apparatus, each stage of which comprises only one column; the column in the first stage is to have a value of H as large as possible, while the column in the second stage is to be designed to have the smallest possible value of μ/A. We shall find that this simple procedure is adequate to reduce the characteristic time to a reasonable value.

We now address ourselves to the task of designing the two kinds of column, the first with a large H, and the second with a small μ/A. In order to save space, we remark at the beginning that the use of a pressure of one atmosphere would involve columns of such large dimensions that the use of a higher pressure seems desirable. We accordingly base our design on a pressure of five atmospheres. In order to obtain a large H, we require the column for the first stage to be of the concentric tube variety;

$$\begin{aligned}B/2w&=20,\\T_1&=300°\mathrm{K},\\T_2&=600°\mathrm{K}.\end{aligned}\tag{386}$$

The viscosity data of Trautz and Binkele (reference *a* of Table III) yield for helium at the temperature 450°K,

$$\eta=2.60\times10^{-4}\ \text{poise},\tag{387}$$

and indicate that the viscosity varies rather closely as the $\frac{2}{3}$ power of the absolute temperature. From Table I and Eq. (10) we then have

$$\alpha=0.0758.\tag{388}$$

At five atmospheres and 450°K the density of helium is

$$\rho=5.40\times10^{-4}\ \mathrm{g/cm^3},\tag{389}$$

and then from Table I and Eq. (18) we have

$$D = 1.370\eta/\rho = 0.660 \text{ cm}^2/\text{sec.} \tag{390}$$

We may now determine $H^{(0)}$, $K_c^{(0)}$, and $K_d^{(0)}$ as functions of w, and w may then be evaluated by requiring that $K_c^{(0)}/K_d^{(0)} = 10$. The result of this procedure is

$$\begin{aligned} 2w &= 0.975 \text{ cm}; \quad B = 19.5 \text{ cm}, \\ H^{(0)} &= 0.928\times 10^{-3} \text{ g/sec.}, \\ K_c^{(0)} &= 0.677\times 10^{-1} \text{ g-cm/sec.}, \\ K_d^{(0)} &= 0.677\times 10^{-2} \text{ g-cm/sec.} \end{aligned} \tag{391}$$

If we assume a parasitic transport given by $K_p/K_c = 0.30$, we have

$$K = 0.947\times 10^{-1} \text{ g-cm/sec.} \tag{392}$$

We have omitted making any corrections for the fact that the walls are not plane. We know these corrections at present only for a Maxwellian gas, and the properties of helium differ rather greatly from those of a Maxwellian gas.

We have

$$\mu \cong 2\rho w B = 1.03\times 10^{-2} \text{ g/cm}, \tag{393}$$

so that if this column were used to obtain the entire separation factor of 10^5, we should have by (385)

$$t_c = \frac{c_{Nf}}{c_{1i}} \cdot \frac{\mu K}{H^2}, \tag{394}$$

$$\begin{aligned} &= 10^5 \times (1.13\times 10^3 \text{ sec.}), \\ &= 3.6 \text{ years.} \end{aligned} \tag{395}$$

Such a time is clearly out of the question.

On the basis of the concentric tube type of column, μ/A is proportional to B, so that we are led directly to the hot wire type of column in order to obtain a small μ/A. In attempting to give a theoretical design of a hot wire column for helium, however, we are met by the serious difficulty that we know the corrections only for a Maxwellian gas. The procedure which we shall follow is to pretend that helium is Maxwellian during the entire design; when we finish, we shall indicate how rough corrections may be applied to take into account the actual behavior of helium. The procedure will thus serve as an illustration of how apposite tables may be used when they become available, and in any event the design will not be too far removed from the correct design.

It is easily shown that for a Maxwellian gas, the mass of gas in unit length of the column is given by

$$\mu = \pi\rho_1 r_1^2 \cdot \left\{ 2t_1 \exp(t_1^2) \int_{t_1}^{t_2} \exp(-t^2) dt \right\}, \tag{396}$$

where the curly bracket is a factor analogous to h, k_c, and k_d which depends only on the ratios r_1/r_2 and T_2/T_1. For fixed values of these ratios, we have

$$\frac{\mu}{2A} = \frac{\mu K_d}{H}\left(1 + \frac{K_c}{K_d}\right), \tag{397}$$

where $\mu K_d/H$ is independent of r_1, and where K_c/K_d is proportional to r_1^6. In order to minimize μ/A, therefore, we should make K_c/K_d *small* compared with unity. There is little value in carrying the matter to extremes, however. $K_c/K_d = \frac{1}{5}$ is probably a good choice. Reducing this ratio to 1/40 would reduce μ/A by 15 percent, but would reduce A to half of the value it has if $K_c/K_d = \frac{1}{5}$, so that it would be necessary to use twice as long a column.

At $T = 300°\text{K}$ and five atmospheres, we have

$$\begin{aligned} \eta_1 &= 1.983\times 10^{-4} \text{ poise}, \\ \rho_1 &= 8.13\times 10^{-4} \text{ g/cm}^3, \\ D_1 &= 0.334 \text{ cm}^2/\text{sec.}, \\ \alpha &= 0.0758. \end{aligned} \tag{398}$$

The result of substituting (398) in (115)–(117) is

$$\begin{aligned} H/hr_1^4 &= 2.16\times 10^{-3} \text{ g/sec.-cm}^4, \\ K_c/k_c r_1^8 &= 0.679 \text{ g/sec.-cm}^7, \\ K_d/k_d r_1^2 &= 1.70\times 10^{-3} \text{ g/sec.-cm.} \end{aligned} \tag{399}$$

Inspection of Tables VI and VIII indicates that h/k_d has a very flat maximum at about

$$r_1/r_2 = 100, \quad T_2/T_1 = 4. \tag{400}$$

For these values we find from Tables VI, VII, and VIII:

$$h = 0.116, \quad k_c = 0.0128, \quad k_d = 0.78. \tag{401}$$

Substitution of these values in (399) and the determination of r_1 by the condition $K_c/K_d = \frac{1}{5}$ leads to

$$\begin{aligned} r_1 &= 0.560 \text{ cm}, \\ H &= 2.46\times 10^{-5} \text{ g/sec.}, \\ K_c &= 0.838\times 10^{-4} \text{ g-cm/sec.}, \\ K_d &= 0.417\times 10^{-3} \text{ g-cm/sec.}, \end{aligned} \tag{402}$$

whence

$$K = K_c + K_d = 0.501 \times 10^{-3}\ \text{g-cm/sec.} \qquad (403)$$

For the ratios (400), the curly bracket in (396) has the value 0.686, from which we find

$$\mu = 0.549 \times 10^{-3}\ \text{g/cm.} \qquad (404)$$

If a column with these specifications were used to obtain the entire separation factor of 10^5, we find according to (394)

$$t_c = 1.4\ \text{years.} \qquad (405)$$

Suppose now, however, that the latter column is used as a second stage, and that the column with the design (391) is used for the first stage. We then find according to (385)

$$t_c = 14\ \text{days.} \qquad (406)$$

This time is not an unreasonable one. It could, of course, be reduced still further by using several columns in parallel in the first stage in order to increase the initial value of H. If five tubes of the design (391) were used in the first stage, the characteristic time t_c would be reduced to less than three days.

It remains to determine what the lengths of the two columns should be. The value of H for the hot wire column is only 1/37.7 of the value of H for the column used in the first stage, so that if we match the initial transports of the two stages, we have as a first approximation

$$q_1 = 38, \quad q_2 = 2630. \qquad (407)$$

If now we use as our criterion that the values of n/y for each stage should be individually maximized, we find by a rough numerical examination that the values of n for the two stages should be

$$\begin{aligned} n_1 &= 0.845/q = 0.845 \times 10^{-5}, \\ n_2 &= 0.910/q_2. \end{aligned} \qquad (408)$$

The condition that the total flow σ be the same for each column then yields as a second approximation

$$q_1 = 35, \quad q_2 = 2860, \qquad (409)$$

$$\begin{aligned} n_1 &= 0.845 \times 10^{-5}, \\ n_2 &= 3.18 \times 10^{-4}, \\ y_1 &= 5.39, \\ y_2 &= 10.35, \\ L_1 &= 5.50\ \text{meters}, \\ L_2 &= 2.10\ \text{meters}, \\ \sigma &= 6.77 \times 10^{-4}\ \text{g/day.} \end{aligned} \qquad (410)$$

The value of σ corresponds to 3.80 cm^3/day of helium at N.T.P., with a concentration of He^3 between 10^{-2} and 10^{-3}.

In computing the power consumption it is necessary to consider only the heat transferred by conduction because of the high conductivity of helium. Helium, as well as the other noble gases, obeys the relation

$$\lambda = 15\eta R/4M \qquad (411)$$

with considerable precision (C5, p. 241), where R is the gas constant per mole, and M is the molecular weight. From (387) and (398) we have

$$\begin{aligned} \lambda &= 4.84 \times 10^{-4}\ \text{cal./cm-deg.-sec.}, \quad T = 450°\text{K}, \\ \lambda &= 3.69 \times 10^{-4}\ \text{cal./cm-deg.-sec.}, \quad T = 300°\text{K}; \end{aligned} \qquad (412)$$

and then according to (76) and (99) the power consumption of the concentric tube column is 12.1 watts per centimeter, and that of the hot wire column is 4.8 watts per centimeter. The total power consumption is then found to be 7.7 kilowatts, exclusive of the scrubber.

If the column used for the scrubber is of the same design as that used in the first stage, the relations (380)–(381) still hold, and we find by the same procedure as used for the methane scrubber:

$$\begin{aligned} c_s &= \tfrac{2}{3}c_{1i}, \\ q_s &= 1.5, \\ n_s &= 2.53, \\ y_s &= 0.951, \\ \sigma_s &= 203\ \text{g/day}, \\ L_s &= 0.97\ \text{meters}, \end{aligned} \qquad (413)$$

and for a scrubber which removes more of the He^3 from the gas which is passed through the apparatus:

$$\begin{aligned} c_s &= \tfrac{1}{3}c_{1i}, \\ q_s &= 3, \\ n_s &= 1.27, \\ y_s &= 2.77, \\ \sigma_s &= 102\ \text{g/day}, \\ L_s &= 2.83\ \text{meters}. \end{aligned} \qquad (414)$$

This completes the design of the apparatus.

The design of this apparatus, based on tables and formulae which are known not to be really applicable to the case of helium, has been given in full for two reasons. It provides an illustration of the use of the concepts and data of the theory, and also, we believe, provides a sufficient basis for proceeding with attempts to separate the helium isotopes even without any further theoretical information.

The helium problem is, in certain respects, a case *par excellence* in which trial and error construction of apparatus without the use of theoretical principles would have practically no chance of producing a successful result. This is true because the initial concentration is so small that, unless the apparatus at once produces a large separation factor after a reasonably short waiting time, one will have no way of measuring its effectiveness, or of determining the consequences of tentative changes in the conditions.

We believe that the design we have given can overcome this difficulty, and make possible the successful preparation of helium enriched in He^3. To make it suitable for this purpose the design must be changed in such ways as to allow roughly for the differences which we know exist between helium and a Maxwellian gas.

If suitable tables of h, k_c, and k_d for helium were available, we should of course construct the design *de novo*. Such a complete reconstruction could also be given on the basis of estimates of the differences between the behavior of helium ($n=\frac{2}{3}$) and a Maxwellian gas ($n=1$) in the apparatus. Because these estimates are uncertain, however, and also because changes may be necessary after experimental tests are made, we do not give such detailed considerations. It suffices to indicate certain general changes in the design as given.

First, *the lengths of both stages should be increased by about twenty percent.* This is enough to offset any differences between $H^{(0)}$, $K_c^{(0)}$, and $K_d^{(0)}$ and the correct coefficients for the concentric tube column; this is evident from the sizes of the Maxwellian cylindricity corrections and of the differences between Maxwellian ($n=1$) and hard-sphere ($n=\frac{1}{2}$) results for the plane case. For the hot wire column this increase in length provides a useful factor of safety, but the other changes which we describe next are of primary importance.

Second, *the diameter and temperature of the hot wire must be increased*, the radius of the tube for the hot wire column remaining the same. This is necessary in order to make the actual values of h, k_c, k_d, and μ roughly the same as were used in the design. The reasoning is as follows: In the theoretical model used, the quantities η, λ, D are, throughout the tube, taken to be larger than they actually would be. This is because they are given their correct values at r_1, T_1, and assumed to increase with the temperature more rapidly than they actually do. Throughout most of the volume the difference is not large, but in the immediate neighborhood of the hot wire it amounts to a factor of $4^{\frac{1}{3}}=1.59$. Both the temperature distribution and the convection currents are thus taken to be different from what they actually are.

The errors in the estimates of μ and k_d are not very great, because of the small volume involved. The same is true of h, since H varies only as η^{-1}. For k_c, however, the difference is probably quite large. Not only do the smaller values of η and D which actually occur mean obviously a great increase in K_c, but also it must be remembered that, owing to the smaller value of λ, the high temperature itself is confined to a smaller region. It is probable that k_c is larger by a sizable factor than the value taken from the table. The purpose of making the wire larger and hotter is to provide a more effective viscous, highly diffusive "core" to limit the remixing effect of convection.

The size of the changes required is hard to estimate precisely. It is reasonable to suppose that they are about the same as those which would make (Q_1/λ_1) take the same value as it has for the original Maxwellian design. Computations based on Eq. (99) indicate that this could be done either by increasing T_2/T_1 from 4.0 to 4.8, or by making r_2 four times as large. Since H, K_d, and μ are not very sensitive to these changes, they should be taken amply large. Thus, it seems reasonable to suggest that *the wire should be twice as large in diameter as previously indicated, and about 200° hotter.* Actually, the wire originally specified might be inconveniently small in diameter.

The design as given, with the changes indicated in italics, should form a satisfactory basis for the separation of the helium isotopes. Moderate readjustments of the pressure and of the temperature of the hot wire should suffice to adjust the apparatus for satisfactory routine operation.

Since the initial concentration of He^3, believed to be between 10^{-7} and 10^{-8}, is so very small, it is important to consider the effect of possible impurities. There is only one which can cause difficulty, namely, hydrogen, because this is the only molecule which is lighter than He^3.

The presence of hydrogen will not interfere with the concentration of the light helium isotope as long as the concentration of hydrogen is small compared with unity. The value of α for the H_2-He^4 mixture will be slightly more than twice that of the He^3-He^4 mixture, so that in continuous operation the ratio of the concentration of H_2 to that of He^3 at the top of the column will be several times, say about four times, the value of this ratio in the gas forming the starting material. We therefore see that the concentration of hydrogen in the original helium must be reduced to at least 2×10^{-7}. With this initial concentration, the concentration of H_2 at the top of the apparatus will be about 10 percent when a separation factor of 10^5 for He^3 has been obtained.

The usual method of removing hydrogen from a gas is to pass it over a hot metallic oxide, such as copper oxide. A temperature of 600°C is probably the best compromise between the opposing considerations of reaction velocity and the equilibrium concentration of H_2 in the reaction

$$2H_2+O_2\rightleftarrows 2H_2O.$$

The addition of a few percent of oxygen to the helium would displace the equilibrium further in the desired direction, and would eliminate the necessity of replacing the copper oxide at frequent intervals. The added oxygen could do no harm, since it would be eliminated by the scrubber along with all other heavy impurities.

It may well be, however, that the simple procedure just suggested will not reduce the concentration of H_2 to as low a value as 2×10^{-7}. In this case, two further methods of purification suggest themselves. One could insert a copper oxide purification tube between the first and second stage, where the concentration of the hydrogen will be much higher. Or after the hydrogen concentration is reduced by the method described in the last paragraph, one could add approximately one percent of D_2 to the helium and pass it through another heated tube containing copper oxide. The hydrogen concentration would then be reduced to its previous value, but almost all of the hydrogen remaining would be D_2, which would not be concentrated by the column because of its greater mass. The D_2O resulting from the oxidation in the second purifying tube could be recovered by a liquid air trap.

Comparison with Experiment

The most detailed experimental study of the operation of the thermal separation column which has yet been published is that of Clusius and Dickel (C10, C11). They have examined in considerable detail the dependence of initial transport and separation factor upon variations in the tube diameter, pressure, and temperature difference. The natural oxygen-nitrogen mixture found in the air was used in these measurements. The separation columns were all of the hot wire type, although unfortunately the authors do not state the diameters of the wires.

In the authors' Fig. 5 the initial transport is plotted against the pressure for columns of three different radii. The current through the hot wire was maintained at 2.3 amperes. The experimental points for the two smaller tubes fit very accurately a curve whose ordinate is proportional to the square of the pressure. The scattering of the points for the largest tube is to be attributed to errors in the measurement of the changes in the oxygen concentration, which were very small.

In Fig. 6 of their article Clusius and Dickel show that the experimental points for the dependence of the initial transport on tube radius can be fitted very well by a curve whose ordinate is proportional to r_1^4. The authors are thus able to conclude the empirical relation

$$\text{initial transport} \propto r_1^4 P^2 \qquad (415)$$

for a constant temperature of the hot wire. This relation is in good agreement with our theory; according to (145), the initial transport for a given initial concentration is proportional only to H, and by (115), the essential dependence of

H on r_1 and P is of the form (415). There is also a small dependence on r_1/r_2 through the factor h. For large ratios of radii this factor is insensitive to r_1/r_2, (cf. Table VI), and since we do not know r_2, the importance of this effect can not be estimated.

In Fig. 7 of C10 it is shown that the initial transport increases about 20 percent as the temperature of the hot wire is increased from 600° to 750°. The authors state neither the tube radius nor the pressure, so that the most we can conclude is that the observed insensitivity of the initial transport to changes in the temperature ratio is in accord with the predictions of Table VI, where the factor h actually passes through a maximum as the temperature ratio is increased.

The authors show in Figs. 8 and 9 that the equilibrium concentration *difference* is inversely proportional to r_1^4 for large values of r_1, but that for smaller values of r_1 the points fall under the r_1^{-4} curve. Our theory predicts a relation of the form

$$\log q_e = ar_1^{-4}/(1+br_1^{-6}) \tag{416}$$

(cf. Eqs. (115)–(117) and (150)), if we ignore the dependence of h, k_c, and k_d on r_1/r_2. It would thus appear that the experimental values for smaller values of r_1 are under the r_1^{-4} curve not only because of the presence of the second term in the denominator (which is just K_d/K_c), but also because the logarithm of the separation factor is not proportional to the concentration difference for larger values of the latter.

Perhaps the most exacting test of the theory is the prediction of the dependence of the equilibrium separation factor upon the pressure of the gas in the column. Our theory predicts that for any type of column, whether it be of the concentric tube or the hot wire variety, the dependence of q_e on P is exactly of the form

$$\log q_e = \frac{a/P^2}{1+b/P^4}, \tag{417}$$

where the ratio of a to b can be predicted from theory. This relation follows from (150) if we note that H, K_c, and K_d are proportional to P^2, P^4, and P^0, respectively. The coefficient K_p obviously must have the same pressure dependence as K_c, since they both represent convective phenomena. The values of a and b separately cannot be predicted theoretically because of our inability to predict K_p with any accuracy.

The most careful check which has been made of the relation (417) is that of Nier (N3), who used a column of the concentric tube type for the concentration of $C^{13}H_4$. The design of the column is exactly the same as that used in the preceding section for the methane multi-stage apparatus. The theoretical predictions for this column are given by (358)–(360). Using the fact that the column was 7.30 meters long, we have according to the theory

$$\log q_e = 2AL = \frac{1.710/P^2}{1+0.1628/P^4}, \tag{418}$$

where P is measured in atmospheres.

Nier found that his three experimental points could be fitted exactly by the formula

$$\log q_e = \frac{1.34/P^2}{1+0.126/P^4}. \tag{419}$$

If now we multiply numerator and denominator of this relation by 1.283, we have experimentally

$$\log q_e = \frac{1.72_0/P^2}{1.283+0.161_8/P^4}. \tag{420}$$

Comparison of (420) with (418) shows that the assumption of a parasitic remixing given by

$$K_p/K_c = 0.283 \tag{421}$$

leads to a discrepancy between experiment and theory of about 0.6 percent.[11] The excellence of this check is of course fortuitous, since the physical constants used are not known to such an accuracy; in particular, the probable error in the measurement of α is several percent. The excellence of the check may be taken to indicate, however, that all of the relevant properties of the column have been taken fully into account by the theory.

An experiment very similar to that of Nier has been performed by Taylor and Glockler. Their column was also of the concentric tube type and was used to concentrate $C^{13}H_4$. By the same procedure as was used to obtain (358)–

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[11] Nier's values for K_p/K_c and the difference between experimental and theoretical results were both considerably larger than those given here; his comparison was based on the formulae for the plane case.

TABLE XVIII. Comparison with theory of the pressure dependence of q_e as observed by Taylor and Glockler.

P (atmospheres)	$(\log q_e)_{\text{obs}}$	$(\log q_e)_{\text{l.sq.}}$	Difference	$(K_c/K_d)_{\text{l.sq.}}$
0.97	0.77	0.76	− 1%	39.
0.66	1.61	1.51	− 6%	8.4
0.37	2.22	2.44	+ 10%	0.82
0.25	1.85	1.74	− 6%	0.172

(360), we find for their column at atmospheric pressure:

$$\begin{aligned} H&=0.979\times10^{-4}\ \text{g/sec.},\\ K_c&=1.385\times10^{-1}\ \text{g}-\text{cm/sec.},\\ K_d&=2.75\ \ \times10^{-3}\ \text{g}-\text{cm/sec.} \end{aligned}\tag{422}$$

Since their column was 10.90 meters long, we have theoretically,

$$\log q_e=\frac{0.771/P^2}{1+0.0199/P^4}.\tag{423}$$

The four experimental points obtained by Taylor and Glockler do not fall exactly on a curve of the form (417). We have fitted a curve of the form (417) to their points by the method of least squares, with the result

$$\log q_e=\frac{0.739/P^2}{1+0.0227/P^4}.\tag{424}$$

The extent to which this curve fits the points is indicated in Table XVIII.

The reason for the scattering is suggested by Taylor and Glockler. The negative reservoir was not so large that the concentration of $C^{13}H_4$ in it did not fall considerably. It was thus necessary to measure also the reduced concentration of $C^{13}H_4$. We have been informed by Professor Nier, who made the measurements of the concentration of $C^{13}H_4$, that the mass spectrometer was not working properly at the time the measurements were made, and that the measurements are therefore of very questionable accuracy.

Clusius and Dickel also give data on the dependence of separation factor on pressure. In their Fig. 10 they show that with a tube of large diameter and for pressures greater than 40 cm, the concentration difference is inversely proportional to the square of the pressure, as is predicted by (417) when K_d/K_c is small, and in Fig. 11 they present several curves for tubes of smaller radius. We have fitted a curve of the form (417) to the curve in their Fig. 11 which covers the greatest range of pressure, that for a tube with a radius of 0.69 cm; the data for this curve are also given in their Table 9.

Table XIX shows the extent to which the data are fitted by the formula

$$\log q_e=\frac{0.378/P^2}{1+0.0657/P^4}.\tag{425}$$

This formula does not represent the best fit in the least squares sense, but is merely the result of a few trial formulae.

Additional comparisons between theory and experiment are given in the next section.

Discussion of the Experimental Literature

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

This is the letter in which Clusius and Dickel announced the discovery of their new method of separating isotopes. They present results in separating several gaseous mixtures, and also in the concentration of HCl^{37} and Ne^{22}.

2. K. Clusius and G. Dickel, Naturwiss. **27**, 148(L) (1939).

The authors describe the use of the thermal diffusion column with liquids. The apparatus consisted of two parallel plates, 2 cm wide and 1.5 meters long, separated by a distance of 0.1 cm. This apparatus produced a change in the concentration of a NaCl solution by a factor of 3.6 and a change in the concentration of an acetone-water solution by a factor of about seven.

The authors observed that with the acetone-water mixture, the water was concentrated at the *bottom* of the column, and interpret this behavior as evidence of the associated nature of water.

3. K. Clusius and G. Dickel, Naturwiss. **27**, 148(L) and 487(L) (1939).

These letters contain the advance report of the results with HCl which are described in detail in the following reference.

4. K. Clusius and G. Dickel, Zeits. f. physik. Chemie **44**, 397–473 (1939).

This article consists of two parts, the first of which is devoted to a detailed study of the operation of the thermal separation column with gaseous mixtures; in the second part the authors describe their work in separating the chlorine isotopes.

We have already discussed in some detail the general experimental results given in the first part, and have found that they are in good agreement with theory. The experimental work of Clusius and Dickel is of high quality and precision, and the results are reported in satisfying detail.

We have remarked in a footnote that the discussion of continuous operation given by the authors on pp. 431–438 is based on incorrect physical premises. It further contains algebraic errors. We have not been able to find any simple way of carrying through the procedure suggested so that it leads to a correct result; the difficulty probably lies in the fact that the correct result is rather complicated in form.

We should like to remark again that the expression for the thermal diffusion coefficient which is given in Eq. (22) of C10 and which is attributed to Chapman, is based on a treatment which Chapman has long since acknowledged to be incorrect. The Chapman-Enskog theory of thermal diffusion in gases leads to the result given in our Eq. (9) and in Eq. (23) of Clusius and Dickel.

In the second part of the paper the authors report in detail their work in separating the isotopes of chlorine. 500 cm^3 of HCl containing 99.6 percent of HCl^{35} and 600 cm^3 of HCl containing 99.4 percent of HCl^{37} were obtained. These results were obtained with a three-stage apparatus 20 meters long, and with a four-stage apparatus 29 meters long, respectively.

All of the columns (except one) which were used in the concentration of the chlorine isotopes had the specifications

$$r_1 = 0.42\text{ cm},\qquad r_2 = 0.02\text{ cm},\qquad (426)$$
$$T_1 = 300°\text{K},\qquad T_2 = 960°\text{K}$$

and the gas was at a pressure of one atmosphere.

The authors observed a very interesting phenomenon: the value of A depended upon the concentration of the gas to an easily measurable extent. The extent of the dependence is shown in Fig. 8 and Table 5 of the second part; for values of c equal to 0.05 or 0.95 the apparent value of A is 1.38 times the value of A for c equal to 0.50. The authors state that they have traced the effect to the platinum disks which were placed at intervals of 60 cm along the column for the purpose of centering the wire. In a note added in proof they further state that they have a theoretical explanation of the effect of the "*Scheibchen.*"

TABLE XIX. Comparison with theory of the pressure dependence of q_e as observed by Clusius and Dickel.

P (atmospheres)	$(\log q_e)_{\text{obs}}$	$(\log q_e)_{\text{calc}}$	Difference	$(K_c/K_d)_{\text{calc}}$
0.935	0.416	0.398	−4.5%	11.6
0.780	0.525	0.525		5.7
0.666	0.631	0.638	+1.1%	3.0
0.579	0.680	0.711	+4.5%	1.71
0.488	0.703	0.733	+4.3%	0.87
0.358	0.631	0.590	−6.3%	0.25

Now the spacers would certainly disturb the convective flow in their neighborhood, and would thus be expected to affect the values of H and K to some extent. But it is clear on the basis of the present theory that there is no way a disturbance of the convective flow could influence the coefficients H and K in a manner which would depend on the *concentrations*. We are therefore sceptical of the validity of the "*Scheibchen*" effect, and we believe the observed results are to be attributed to the apparatus' not being in equilibrium at the time the measurements were made. Our reasons are stated in the following seven paragraphs.

According to the results of Trautz and Narath (T1), the viscosity of HCl is very nearly proportional to the temperature in the range 294°–523°K; that is to say, the temperature dependence of η is very closely that of a Maxwellian gas in the given temperature range. We may therefore expect that our theory of the Maxwellian cylindrical case will apply to the apparatus of Clusius and Dickel with some precision.

Using the results of Trautz and Narath for the viscosity, we find the following data for HCl at $T = 300°$K:

$$\eta = 1.46\times 10^{-4}\text{ poise},$$
$$\rho = 1.48\times 10^{-3}\text{ g/cm}^3,\qquad (427)$$
$$D \cong 1.45\eta/\rho = 0.143\text{ cm}^2/\text{sec}.$$

From these data, (426) and (115)–(117) we find

$$H/h\alpha = 4.00\times 10^{-3}\text{ g/sec.},$$
$$K_c/k_c = 1.71\times 10^{-2}\text{ g-cm/sec.},\qquad (428)$$
$$K_d/k_d = 2.34\times 10^{-4}\text{ g-cm/sec.}$$

The form factors h, k_c, and k_d must be determined by interpolation in Tables VI, VII, and VIII. Using logarithmic interpolation, we find for $T_2/T_1=3.2$ and $r_1/r_2=21$

$$h=0.096,\quad k_c=0.0103,\quad k_d=0.77, \tag{429}$$

whence we have finally

$$H/\alpha=3.84\times10^{-4}\text{ g/sec.},\quad K_c=1.76\times10^{-4}\text{ g-cm/sec.},\quad K_d=1.80\times10^{-4}\text{ g-cm/sec.} \tag{430}$$

and

$$2A/\alpha=H/\alpha K=1.08/\text{cm}. \tag{431}$$

Clusius and Dickel base the exposition of the "*Scheibchen*" effect on their fourth experiment, in which the concentration of HCl^{37} was raised from its natural value 0.24 to 0.994. In this experiment, the concentration increased from 0.31 to 0.62 in the second stage of the apparatus. By (151), this increase corresponds to a separation factor of 3.63, so that since the stage was 6 meters long, we have experimentally

$$2A=\frac{\log 3.63}{600\text{ cm}}=2.15\times10^{-3}/\text{cm} \tag{432}$$

if we assume that the apparatus had reached its equilibrium. Comparing (431) with (432), we have

$$\alpha=1.99\times10^{-3} \tag{433}$$

or since the value of α for the elastic sphere model is 0.0247 (cf. Eq. (9)), we have

$$R_T=0.081. \tag{434}$$

This value of R_T is surprisingly low, and in itself would lead one to suspect that the apparatus was not in equilibrium.

We have just computed the value of α in the second stage of the apparatus by assuming that the observed concentration gradient was the equilibrium concentration gradient. This is not, however, the only way that we may obtain an estimate of α. We may obtain a lower limit to α by the observation that the initial transport must be sufficient to transport the observed amount of isotope into the column during the time that the apparatus was allowed to approach equilibrium.

The first stage of the apparatus consisted of a column with a higher transport than the other stages, so that the point of smallest initial transport occurred at the negative end of the second stage, where the concentration was 0.31 or less during the approach to equilibrium. Thus the transport past this point was never greater than

$$H\times0.31\times0.69=8.22\times10^{-5}\alpha\text{ g/sec.} \tag{435}$$

The mass of HCl^{37} which was transported into the last three stages may be found by a rough numerical integration of $\mu(c-0.24)$ along the ordinate of the authors' Fig. 8, and is found to be

$$\mu\int_0^{2000\text{ cm}}(c-0.24)dz=\mu(10.1\text{ meters}),\quad =0.58\text{ g}. \tag{436}$$

Here use was made of the value

$$\mu=0.57\times10^{-3}\text{ g/cm}, \tag{437}$$

computed from Eq. (396).

We now take the product of the initial transport (435) and the time (17 days) during which the apparatus was allowed to approach equilibrium, and equate it to 0.58 g. Solving for α, we find as a lower limit

$$\alpha\geqslant4.8\times10^{-3}, \tag{438}$$

or

$$R_T\geqslant0.194. \tag{439}$$

This lower limit to α is more than twice the value (433) obtained by assuming that the apparatus had reached equilibrium. We may therefore conclude that the apparatus had not reached equilibrium.

The explanation of the apparent variation of A with the concentration is now clear, since the concentration gradient near the positive end of a column will always reach its equilibrium value before it does in the remainder of the column, as is shown by the Debye effect (cf. Eqs. (156)–(176)).

5. G. Dickel and K. Clusius, Naturwiss. **28**, 461(L) (1940).

In this letter the authors again indicate the great effectiveness of the thermal separation column by obtaining 2.5 liters each of "pure" Ne^{20} and "pure" Ne^{22}. The lighter, more abundant isotope was obtained at the rate of 600 cm^3/week, and the heavier isotope was obtained at the rate of 300 cm^3/week.

The actual purity of the gases obtained cannot be estimated, because the relative abundances were determined by measuring the density of the gas, and because there were contaminations of He and N_2. It is unfortunate that these authors do not have available a mass spectrometer for the determination of isotopic abundances, since it would be pleasant to know more accurately how complete the purifications were. This difficulty affected also their work on HCl, in which the relative abundances were measured by atomic weight determinations. Determinations of isotopic abundances either by density or atomic weight measurements have the difficulty that the concentration of isotopes present in small quantities cannot be measured with adequate precision.

6. H. Korschning and K. Wirtz, Naturwiss. **27**, 110(L) and 367(L) (1939); Abhand. Preuss. Akad. Wiss. Berlin, No. 3 (1939).

The first of these references contains the first report on the separation of liquids by the method of Clusius and Dickel. Two apparatuses are described, each with a wall separation of only 0.025 cm, and each of the concentric tube variety. The authors report separation factors of about 1.2 in the separation of the zinc isotopes in solution.

7. W. Groth, Naturwiss. **27**, 260(L) (1939).

This author applied the method to xenon, using two different columns of the hot wire type. The first had a diameter of 1.2 cm, and the second a diameter of 0.5 cm. The diameter of the wire is not stated.

It was observed that with the larger column, the equilibrium separation factor *decreased* as the wire temperature was increased from 1000°C to 1650°C. This effect is almost certainly to be attributed to the onset of turbulence. With the column of smaller diameter the separation factor increased monotonically as the wire temperature was raised. Our theory predicts that a monotonic increase will always occur in the absence of turbulence.

Groth was able to displace the atomic weight of xenon 1.57 units with a column 2.5 meters long and with a diameter of 0.5 cm. He concludes that one meter of such a column is as effective as 12 Hertz pumps for xenon.

8. W. Groth and P. Harteck, Naturwiss. **27**, 584(L) (1939).

The authors describe a partial separation of the mercury isotopes with a hot wire column 2.2 meters long and 0.7 cm in diameter. The outer tube was maintained at a temperature of 350°C in order to prevent the condensation of the mercury vapor, and the wire was heated to 1800°C.

The lighter fraction was condensed at the top of the column. In order to reduce sufficiently the rate of condensation, a small amount of argon was introduced into the column. Because of the large difference in mass, the argon was immediately concentrated at the top, and formed a cushion through which the mercury vapor had to diffuse.

It was found possible to demonstrate the abnormal density of the light mercury so obtained by placing it in a barometric column designed to employ only a small volume of mercury. The increase in the barometric height was 0.04 cm.

9. A. Bramley and A. K. Brewer, J. Chem. Phys. **7**, 553(L) (1939); Brewer and Bramley, J. Chem. Phys. **7**, 972(L) (1939); Bramley and Brewer, Science **90**, 165 (1939).

Of these references, the last is the most extensive presentation (two pages).

The writers feel obliged to report that they are in substantial disagreement with the conclusions which are presented by these authors. The two conclusions which we regard as most misleading are (a) that the thermal separation column used by them does not depend on thermal diffusion for its operation, and (b) that the production of turbulence, or of "swirls," is an asset in the operation of the column.

The authors describe only one experiment in sufficient detail to make possible a comparison with theory: using a column containing a mixture in equal proportions of ammonia and methane with the specifications $r_1=1.2$ cm, $r_2=0.5$ cm, $\Delta T=350°$, they report that the separation was a maximum for a pressure of about one-fourth of an atmosphere. Now the wall separation of this column is almost exactly the same as that of Nier's column, and physical properties of the ammonia-methane mixture are very similar to those of methane. Further examination shows that the effect of the slightly larger ΔT is offset by the larger correction to be made because of the larger r_1/r_2, as far as the ratio K_c/K_d is concerned. Thus, just as with Nier's column, we have approximately

$$K_c/K_d \cong 6P^4 \tag{440}$$

(cf. Eqs. (359) and (360)), where P is in atmospheres.

We have seen that according to the experimental results of Onsager and Watson (O1), turbulence does not set in until this ratio reaches about 150. We therefore conclude that for pressures of the order of, or less than one atmosphere, there is no possibility of turbulence in the column in question. Furthermore, if we assume no parasitic currents, the pressure of maximum separation factor is given by $6P^4=1$, or $P=0.64$ atmosphere. This prediction is in rather poor agreement with the observed pressure of maximum separation factor: $P=0.26$ atmosphere. The maximum is broad, however, and the determination may have been rough. Furthermore, parasitic convection currents may have been important because of the poor conduction of the glass of which the columns were constructed, and these would reduce the pressure for maximum separation factor.

The authors describe a column with a wall separation of 2 cm containing the ammonia-methane mixture, and note that the separation factor is increased by the addition of washers placed at intervals of 2.2 cm along the inner tube. The authors conclude that the baffles increased the definition of the "swirls" and in this manner increased the separation factor. It seems to us more probable that this actually came about because the washer decreased the effective wall separation. A smaller wall separation would increase the value of A, and would suppress the turbulence which was probably present before the washers were introduced. It is not possible to be definite on these points because the authors state neither the temperatures nor the pressures used.

The writers feel it is worth stressing that in an apparatus whose essential properties depend upon the first, third, and seventh powers of the wall separation (or in the hot wire case, on the second, fourth, and eighth powers of the radius), it is not too easy to draw correct general conclusions from apparatus which is put together without a theoretical estimate of what the optimum value of these dimensions should be.

10. T. I. Taylor and G. Glockler, J. Chem. Phys. **7**, 851 (1939); J. Chem. Phys. **8**, 843 (1940).

Using a column 12.2 meters long, the authors obtain a separation factor of nine in the concentration of $C^{13}H_4$. The results have already been compared with our theory.

11. W. W. Watson, Phys. Rev. **56**, 703(L) (1939); Phys. Rev. **57**, 899 (1940).

In the second of these references there is described a two-stage apparatus for the concentration of $C^{13}H_4$. A separation factor of 2.77 was obtained. One of the stages was also used separately at a higher pressure for the concentration of Ne^{22}, and a separation factor of about eight was obtained.

The operation was found to be in good qualitative agreement with the theory presented in F1, but no detailed numerical comparison is made by the author.

12. A. O. Nier, Phys. Rev. **57**, 30 (1940).

We have already discussed the results presented here in the section on comparison with experiment. The approach to equilibrium is discussed by J. Bardeen (B2) in the article immediately following the one referred to, and is found to be in good agreement with theory.

13. G. T. Seaborg, A. C. Wahl, and J. W. Kennedy, J. Chem. Phys. **8**, 639 (1940).

These authors performed an experiment to determine whether the prediction that α is independent of the concentration was true for very small concentrations. With a hot wire column 7.5 meters in length, the concentration of deuterium in a deuterium-hydrogen mixture was raised from 0.18 to 0.87, as determined by measurement of the thermal conductivity of the mixture. This change of concentration corresponds to a separation factor of 30. The experiment was repeated under identical conditions using a mixture of deuterium and radioactive H^3, the latter having an initial concentration of 10^{-11}. The equilibrium separation factor was 5.0, as determined by measurement of the activity with a counter.

A precise interpretation of these results would require a more detailed account of the experimental conditions, and also improvements in our theoretical calculations, since the fractional differences of molecular weights were not small. It is clear, however, as the authors state, that there is no marked effect of the extreme difference in concentrations.

14.* Milton Farber and W. E. Libbey, J. Chem. Phys. **8**, 965–969 (1940).

The authors describe a series of experiments whose stated purpose is to determine the effects of varying the effective acceleration of gravity on the performance of a thermal separation column. In order to vary the effective value of g, the "column" was given the form of two parallel, coaxial circular plates, with a temperature difference maintained between them. The gas was placed in the space between the plates, and the entire system was rotated about the axis of the plates, at a speed calculated to provide the desired acceleration. The convective flow thus took place in a radial direction.

The published report contains detailed information about the dimensions of the apparatus and the temperatures of the two plates. Detailed results are given for a variety of operating conditions. No comparison with theory has been made, because the theory of the system is rather special, inasmuch as the values of both B and g vary along the radial direction—that is to say, along the length of the column.

It has been pointed out in the section on entropy efficiency, that there is no change in the performance of a given column which may be accomplished by a variation of g, which may not also be accomplished by a variation in the operating pressure of the column, and a change in the time-scale. Indeed, except for the expression for the characteristic time, all of the performance parameters depend on the pressure and the acceleration of gravity in the single combination P^2g. Accordingly it seems to us that any advantages to be obtained by using rotating systems would not be worth the considerable practical difficulties involved.

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REFERENCES

A1. L. W. Alvarez and R. Cornog, Phys. Rev. **56**, 613(L) (1939).
B1. Harrison Brown, Phys. Rev. **57**, 242(L) (1940).
B2. J. Bardeen, Phys. Rev. **57**, 35 (1940).
B3. J. Bardeen, Phys. Rev. **58**, 94(L) (1940).
C1. S. Chapman, Phil. Trans. **216A**, 279 (1916).
C2. S. Chapman, Phil. Trans. **217A**, 115 (1917).
C3. S. Chapman and W. Hainsworth, Phil. Mag. **48**, 593 (1924).
C4. S. Chapman, Phil. Mag. **7**, 1 (1929).
C5. S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (The Cambridge University Press, New York, 1939).
C6. S. Chapman and F. W. Dootson, Phil. Mag. **33**, 248 (1917).
C7. S. Chapman, Phil. Mag. **38**, 182 (1919).
C8. S. Chapman, Memoirs and Proc. of the Manchester Lit. and Phil. Soc. **66**, No. 1 (1922).
C9. K. Clusius and G. Dickel, Naturwiss. **26**, 546(L) (1938).
C10. K. Clusius and G. Dickel, Zeits. f. physik. Chemie **B44**, 397 (1939).
C11. K. Clusius and G. Dickel, Zeits. f. physik. Chemie **B44**, 451 (1939).
D1. P. Debye, Ann. d. Physik **36**, 284 (1939).
E1. D. Enskog, Physik. Zeits. **12**, 56 and 533 (1911).
E2. D. Enskog, Ann. d. Physik **38**, 731 (1912).
E3. D. Enskog, *Kinetische Theorie der Vorgänge in Mässig Verdünnten Gasen*, Doctoral Dissertation, Uppsala, 1917.
E4. D. Enskog, Arkiv f. Mat., Astron., och Fysik (Stockholm) **16**, No. 16 (1922).
F1. W. H. Furry, R. Clark Jones, and L. Onsager, Phys. Rev. **55**, 1083 (1939).
F2. S. P. Frankel, Phys. Rev. **57**, 661(L) (1940).
F3. R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (The Cambridge University Press, New York, 1939).
F4. W. H. Furry and R. Clark Jones, Phys. Rev. **69**, 459 (1946).
G1. W. van der Grinten, Naturwiss. **27**, 317(L) (1939).
H1. E. J. Hellund and E. A. Uehling, Phys. Rev. **56**, 818 (1939).
H2. E. J. Hellund, Phys. Rev. **57**, 319 and 328 (1940).
I1. T. L. Ibbs, Physica **4**, 1133 (1937).
J1. R. Clark Jones and W. H. Furry, Phys. Rev. **57**, 547(L) (1940).
J2. R. Clark Jones, Phys. Rev. **58**, 111 (1940).
K1. W. Krasny-Ergen, Phys. Rev. **58**, 1078 (1940).
L1. J. E. Lennard-Jones, Proc. Roy. Soc. **106**, 441 (1924).
L2. H. A. Lorentz, Proc. Amst. Acad. **7**, 438, 585 and 684 (1905).
M1. R. S. Mulliken, J. Am. Chem. Soc. **44**, 1033 (1922).
M2. H. M. Mott-Smith (private communication).
N1. A. O. Nier, Phys. Rev. **56**, 1009 (1939).
N2. A. O. Nier, Phys. Rev. **57**, 338(L) (1940).
N3. A. O. Nier, Phys. Rev. **57**, 30 (1940).

O1. L. Onsager and W. W. Watson, Phys. Rev. **56**, 474 (1939).
O2. L. Onsager, Phys. Rev. **55**, 1137(A) (1939).
R1. Lord Rayleigh, Proc. Roy. Soc. **66**, 68 (1900).
S1. W. Sutherland, Phil. Mag. **36**, 507 (1893).
S2. W. Sutherland, Phil. Mag. **17**, 320 (1909).
T1. M. Trautz and A. Narath, Ann. d. Physik **79**, 637 (1926).
V1. A. L. Vaughan, J. H. Williams, and J. T. Tate, Phys. Rev. **46**, 327(A) (1934).
W1. W. Walcher, *Ergeb. d. Exact. Naturwissenschaften* (Verlagsbuchhandlung Julius Springer, 1939) p. 155
W2. L. Waldmann, Zeits. f. Physik. **114**, 53 (1939).
W3. L. Waldmann, Naturwiss. **27**, 230(L) (1939).

BIBLIOGRAPHY, THERMAL DIFFUSION, 1940–45

(Added in February, 1946)

The following bibliography contains the references to articles, abstracts, and letters on the subject of thermal diffusion and its use in separating isotopes, which were published during the years 1940–45, inclusive, and which were abstracted either by Chemical Abstracts or the Industrial Arts Index during the years 1940–45, inclusive. The references contained in the abstract journals in the years 1940–43 were assembled by the Technical Library, Bell Telephone Laboratories, New York City. A few references not given in the abstract journals are also included.

1940

J. Bardeen, "Concentration of isotopes by thermal diffusion; rate of approach to equilibrium," Phys. Rev. **57**, 35–41 (1940); Phys. Rev. **58**, 94–95(L) (1940).

A. I. Brodskii, "Theory of the separation of mixtures and its applicability to the thermodiffusion method," Acta Physiochimica, U.S.S.R. **13**, 294–304 (1940) (In German); J. App. Chem. U.S.S.R. **13**, 663–668 (1940) (In French).

Harrison Brown, "Thermal separation ratios calculated from viscosity data," Phys. Rev. **57**, 242–243(L) (1940).

Harrison Brown, "On the temperature assignments of experimental thermal diffusion coefficients," Phys. Rev. **58**, 661–662(L) (1940).

S. Chapman, "The characteristics of thermal diffusion," Proc. Roy. Soc. **A177**, 38–62 (1940).

S. Chapman, "Dependence of thermal diffusion on the concentration ratio," Nature **146**, 431(L) (1940).

Klaus Clusius, Separating gaseous mixtures, German Patent No. 701,016. December 5, 1940.

K. Clusius and G. Dickel, "Separation of a mixture of Kr^{84} and Kr^{86} from normal krypton in a separation tube," Naturwiss. **28**, 711(L) (1940).

K. Clusius and H. Kowalski, "The further development of the separating tube method," Chemische Fabrik, 304–305 (1940).

Milton Farber and W. E. Libby, "Effect of gravitational field on the thermal diffusion separation method," J. Chem. Phys. **8**, 965–969 (1940).

S. Phillips Frankel, "Elementary derivation of thermal diffusion," Phys. Rev. **57**, 661(L) (1940).

W. H. Furry and R. Clark Jones, "Theory of isotope separation by thermal diffusion; the cylindrical case," Phys. Rev. **57**, 561(A) (1940).

J. W. Hiby and K. Wirth, "Application to liquids of the Clusius separation method," Physik. Zeits. **41**, 77–82 (1940).

R. Clark Jones, "On the theory of the thermal diffusion coefficient for isotopes. I.," Phys. Rev. **58**, 111–122 (1940).

R. Clark Jones and W. H. Furry, "On the calculation of the thermal diffusion constant from viscosity data," Phys. Rev. **57**, 547(L) (1940).

H. Korsching, L. Wirtz, and L. W. Masch, "The separation of liquid mixtures by thermal diffusion," Ber. d. chem. Ges. **B79**, 249–269 (1940).

William Krasny-Ergen, "The optimal dimensions of a Clusius-Dickel isotope separator," Phys. Rev. **58**, 1078–1085 (1940).

Alfred Nier, "The concentration of carbon 13 by thermal diffusion," Phys. Rev. **57**, 30–34 (1940).

Alfred Nier, "The coefficient of thermal diffusion of neon and its variation with temperature," Phys. Rev. **57**, 338(L) (1940).

Lars Onsager, "Separation of isotopes by thermal diffusion," Phys. Rev. **57**, 562(A) (1940).

N. G. Schmahl and J. Schewe, "The thermal separation of gas mixtures. II. Thermal diffusion," Zeits. f. Elektrochemie **46**, 203–212 (1940).

C. T. Seaborg, A. C. Wahl, and J. W. Kennedy, "Thermal diffusion separation of radioactive and ordinary hydrogen isotopes," J. Chem. Phys. **8**, 639–640 (1940).

Duncan Taylor and Mowbray Ritchie, "Demonstration of thermal diffusion in liquids," Nature **145**, 670(L) (1940).

T. I. Taylor and George Glockler, "A confirmation of the theory of thermal diffusion," J. Chem. Phys. **8**, 843–844 (1940).

F. T. Wall and C. E. Holley, "Thermal diffusion separation of different gases of the same molecular weight," J. Chem. Phys. **8**, 348(L) (1940).

F. T. Wall and C. E. Holley, "Separation by thermal diffusion of mixtures of gases having the same molecular weight," J. Chem. Phys. **8**, 949–953 (1940).

William W. Watson, "Thermal separation of isotopes," Phys. Rev. **57**, 899–902 (1940).

1941

K. Clusius and H. Kowalski, "The separation of molecules of equal masses in a diffusion tube," Zeits. f. Elektrochemie **47**, 819 (1941).

Klaus Clusius, Separation of gas mixtures by thermal diffusion. U. S. Patent No. 2,268,134. December 30, 1941.

L. J. Gillespie and Samuel Breck, "Thermal diffusion in ternary liquid mixtures, particularly aqueous solutions containing ferrous chloride," J. Chem. Phys. **9**, 370–374 (1941).

K. E. Grew, "Thermal diffusion in hydrogen-deuterium mixtures," Proc. Roy. Soc. **A178**, 390–399 (1941).

H. R. Heath, T. L. Ibbs, and N. E. Wild, "The diffusion and thermal diffusion of hydrogen-deuterium with a note on the thermal diffusion of hydrogen-helium," Proc. Roy. Soc. **A178**, 380–389 (1941).

Kozo Hirota, "Thermal diffusion of binary salt solutions. A note on the paper of Gillespie and Breck," Bull. Chem. Soc. Japan **16**, 232–234 (1941).

Kozo Hirota, "Researches on chemical reactions with the thermal-diffusion apparatus of Clusius and Dickel. 1. Thermal polymerization of methane," Bull. Chem. Soc. Japan **16**, 274–278 (1941).

Kozo Hirota, "Research on a chemical reaction by use of the thermal-diffusion column. Thermal polymerization of methane," J. Chem. Soc. Japan **62**, 392–395 (1941).

Kozo Hirota, "The thermal diffusion of solutions. I. Measurement of the thermal diffusion constant," J. Chem. Soc. Japan **62**, 480–484 (1941).

J. A. Hveding, "Thermodiffusion in separating tubes," Tidsskrift for Kjemi, Bergvesen, Metallurgi **1**, 110–112 (1941).

H. Jensen, "The Clusius separation tube and the physical-mathematical theory of its operation and efficiency," Angew. Chemie **54**, 405–412 (1941).

R. Clark Jones, "The effect of var der Waals forces on the thermal diffusion coefficient of gaseous isotopic mixtures," Phys. Rev. **59**, 688–689(A) (1941).

R. Clark Jones, "On the theory of the thermal diffusion coefficient for isotopes. II.," Phys. Rev. **59**, 1019–1033 (1941).

Hirosi Kitagawa, "Thermal diffusion. III. Measurement of thermal diffusion in a mixture of H_2 and HD," J. Chem. Soc. Japan **61**, 1243–1248 (1941).

Hirosi Kitagawa and Matube Wako, "Thermal diffusion. IV. Measurement of thermal diffusion in the mixture of carbon monoxide and carbon dioxide," J. Chem. Soc. Japan **62**, 100–106 (1941).

J. Meixner, "The thermodynamics of thermal diffusion," Ann. d. Physik **39**, 333–356 (1941).

A. N. Murin, "Thermodiffusion method for the separation of isotopes," Uspekhi Khim **10**, 671–679 (1941).

Alfred O. Nier and John Bardeen, "The production of concentrated carbon 13 by thermal diffusion," J. Chem. Phys. **9**, 690–692 (1941).

William W. Watson, "Heavy carbon production by thermal diffusion," Science **93**, 473–474 (1941).

S. Weber, "Thermal diffusion in gases," Physica **8**, 113–123 (1941).

S. B. Welles, "Partial separation of the oxygen isotopes by thermal diffusion," Phys. Rev. **59**, 920(A) (1941).

1942

H. E. Carr, "Thermal diffusion tube for liquids," Phys. Rev. **61**, 726(A) (1942).

S. R. deGroot, "Phenomenological theory of the Soret effect," Physica **9**, 699–707 (1942).

S. R. deGroot, "Phenomenological theory of the thermo-gravitational separation mechanism for liquids," Physica **9**, 801–816 (1942).

S. R. deGroot, W. Hoogenstraaten, and C. J. Gorter, "An effect neglected in the theory of the Clusius-Dickel method," Physica **9**, 923–924 (1942).

Andre Fournier, "Enrichment of CCl_4 in Cl^{37} by thermal diffusion," Comptes rendus **215**, 529–530 (1942).

W. H. Furry, "Elementary explanation of thermal diffusion," Phys. Rev. **61**, 388(A) (1942).

R. Fürth, "An elementary theory of thermal diffusion," Proc. Roy. Soc. **A179**, 461–469 (1942).

K. E. Grew, "Change of sign of thermal diffusion factor," Nature **150**, 320 (L) (1942).

G. E. Harrison, "The thermal diffusion of radon gas mixtures," Proc. Roy. Soc. **A181**, 93–100 (1942).

James Kendall, "Separation of isotopes and thermal diffusion," Nature **150**, 136–140 (1942).

Boris Leaf and F. T. Wall, "Separation of gas mixtures by thermal diffusion," J. Phys. Chem. **46**, 820–826 (1942).

K. C. Niyogi, "Separation of liquids from binary mixtures by the method of thermal diffusion," Science and Culture (Calcutta) **7**, 567–568(L) (1942).

H. Steinwedel, "Energy consumption in a Clusius separation column which is run continuously," Die Chemie **55**, 152–153 (1942).

Georg Stetter, "The separating tube effect," Oesterr. Chem.-Ztg. **45**, 130–134 (1942).

Louis Stier, "The coefficients of thermal diffusion of neon and argon and their variation with temperature," Phys. Rev. **62**, 548–551 (1942).

1943

D. G. Alkhazov, A. N. Murin, and A. P. Ratner, "The separation of liquid mixtures by thermodiffusion," Bull. Acad. Sci. U.R.S.S., Classe Sci. Chim. **1943**, 3–7 (1943).

B. N. Cacciapuote, "An elementary explanation of the phenomena of thermal diffusion," Nuovo Cimento [9] **1**, 126–136 (1943).

S. R. deGroot, D. J. Gorter, and W. Hoogenstraaten, "Thermo-gravitational separation method applied in the case of an aqueous solution," Physica **10**, 81–89 (1943).

Horst Korsching, "Separation of C_6H_6 and C_6D_6 by thermal diffusion in the liquid," Naturwiss. **31**, 348–349 (1943).

A. N. Murin, "Theory of concentration process caused by thermal diffusion in solutions," Comptes rendus U.S.S.R. **41**, 291–292 (1943).

R. N. Rai and D. S. Kothari, "A note on the elementary theory of thermal diffusion." Ind. J. Phys. **17**, 103–106 (1943).

L. Waldmann, "The diffusion thermal effect," Naturwiss. **31**, 204 (1943).

L. Waldmann, "Diffusion thermoeffect," Zeits. f. Physik **121**, 501–522 (1943).

W. W. Watson and D. Woernley, "Thermal diffusion with ammonia," Phys. Rev. **63**, 181–184 (1943).

K. Wirtz, "Kinetic theory of thermal diffusion in a crystal lattice," Physik. Zeits. **44**, 221–231 (1943).

K. Wirtz, "Direction of thermodiffusion in alcohol-water mixtures," Naturwiss. **31**, 416 (1943).

K. Wirtz, "Isotope separation by thermal diffusion in liquids according to kinetic theory," Naturwiss. **31**, 349 (1943).

K. Wirtz and J. W. Hiby, "Kinetic theory of thermodiffusion in liquids," Physik. Zeits. **44**, 369–382 (1943).

1944

Howard E. Carr, "Thermal diffusion in liquids," J. Chem. Phys. **12**, 349 (1944).

Andre Fournier, "Thermal diffusion of gases. Method of Clusius and Dickel," J. Phys. Rad. **5**, 11–16 (1944).

Andre Fournier, "Thermal diffusion in the liquid phase," J. Phys. Rad. **5**, 45–48 (1944).

K. E. Grew, "Thermal diffusion in mixtures of molecules of small mass difference," Phil. Mag. **35**, 30–36 (1944).

L. Gurevich, "Theory of thermal diffusion. I.," J. Exper. Theor. Phys. (U.S.S.R.) **14**, 60–62 (1944).

L. Gurevich, "Theory of thermal diffusion. II.," J. Exper. Theor. Phys. (U.S.S.R.) **14**, 121–124 (1944).

Thomas H. Osgood, "Physics in 1943," J. App. Phys. **15**, 89–107 (1944). Thermal diffusion, pp. 98–101.

1945

M. C. Fox, "Thermal diffusion as adjunct of electromagnetic processes," Chem. Metall. Eng. **52**, 102–103 (1945).

K. E. Grew, "Thermal diffusion and its application to the separation of gases," Gas Journal **245**, 221(A) (1945).

K. E. Grew, "Effect of pressure on thermal diffusion in gases," Nature **156**, 267–268 (1945).

S. R. deGroot, *L'Effet Soret*, Thesis, Amsterdam, 1945.

W. M. Spicer, "Demonstration of thermal diffusion," J. Chem. Ed. **22**, 593 (1945).