

Concentration of Isotopes by Thermal Diffusion: Rate of Approach to Equilibrium

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The time-dependent partial differential equation involved in the theory of the operation of a Clusius thermal diffusion column is discussed. Solutions presented give the concentration of a given isotope at any point in the column as a function of time. Some are compared with experimental results of Nier, and good agreement is obtained.

I. INTRODUCTION

THE thermal diffusion column, invented by Clusius and Dickel¹ promises to be of some importance for the concentration of isotopes. The theory of the method has been given independently by Waldmann² and by Furry, Jones, and Onsager.³ These authors consider only the equilibrium condition of the column. It is important to know how rapidly equilibrium is approached, and it is the purpose of the present paper to solve the time-dependent partial differential equation involved, with various boundary conditions at the ends of the column. Solutions obtained for several cases are compared with experimental results of Nier,⁴ who studied the operation of a column containing methane gas. The column was to be used for the separation of the carbon isotopes.

We use in large part the notation and many of the results obtained by Furry, Jones and Onsager. The discussion will be confined to the case where there are but two species of molecules present, whose concentrations we denote by c_1 and c_2 , so that $c_1 + c_2 = 1$. Let \mathbf{v}_1 be the convection velocity of species 1 and let \mathbf{v} be that of the gas as a whole. Then if both ordinary and thermal diffusion are present

$$c_1 \mathbf{v}_1 = c_1 \mathbf{v} - D \text{grad } c_1 + (D_T/T) \text{grad } T. \quad (1)$$

Here D is the coefficient of ordinary diffusion and

¹ K. Clusius and G. Dickel, *Naturwiss.* **26**, 546 (1938); **27**, 148 (1939); **27**, 487 (1939). For further references to the experimental data, see the paper by A. O. Nier in the present issue.

² L. Waldmann, *Naturwiss.* **27**, 230 (1939).

³ W. H. Furry, R. C. Jones and L. Onsager, *Phys. Rev.* **55**, 1083 (1939). *Added in proof.*—Two theoretical papers have appeared recently. P. Debye, *Ann. d. Physik* **56**, 284 (1939); L. Waldmann, *Zeits. f. Physik* **114**, 53 (1939). The first of these overlaps to some extent the results of the present investigation.

⁴ A. O. Nier, in the present issue.

D_T that of thermal diffusion. In the case of similar molecules (isotopes), these are related, according to the theoretical treatments of Enskog⁵ and Chapman⁶ by the equation:

$$D_T/D = k_T = \alpha c_1 c_2. \quad (2)$$

The parameter α is independent of the concentration, and, for the case of elastic spheres, also of the temperature.

The equation of continuity for species 1 is:⁷

$$\begin{aligned} \partial \rho c_1 / \partial t &= -\text{div} (\rho c_1 \mathbf{v}_1) \\ &= -\text{div} [\rho c_1 \mathbf{v} - \rho D \text{grad } c_1 \\ &\quad + (\rho D_T/T) \text{grad } T], \quad (3) \end{aligned}$$

in which ρ is the density of the gas. This equation is to be solved subject to the appropriate boundary conditions.

In the actual operation of the column, the gas is confined in the annular space between two vertical concentric cylinders, the inner one heated and the outer one cooled. Following Furry, Jones and Onsager, we may, for the purpose of analysis, suppose that the gas is enclosed in a thin flat slab of thickness d , equal to the difference in radii, of breadth B , equal to the mean circumference, and of length L , equal to the length of the column.⁸ Let T_1 and T_2 be the absolute temperatures of the outer and inner walls and let $\Delta T = T_2 - T_1$. Let the coordinate x ($0 < x < d$) run across the width of the slab, and z ($0 < z < L$) along its length. We suppose that the thermal convection of the gas as a whole takes place only in the vertical direction. (This will be true except near the ends of the

⁵ D. Enskog, *Physik. Zeits.* **12**, 56 and 533 (1911); Thesis, Upsala (1917).

⁶ S. Chapman, *Phil. Trans.* **A217**, 115 (1917).

⁷ Cf. H. Korsching and K. Wirtz, *Naturwiss.* **27**, 367 (1939).

⁸ Our d, L are related to w, l of Furry, Jones and Onsager by the equations: $d = 2w, L = 2l$.

column.) Then $v_x=v_y=0$ and $v_z=v(x)$ is independent of z . Furthermore, T , and consequently ρ and D , are independent of z . The differential Eq. (3) then becomes:

$$\frac{\partial \rho c_1}{\partial t} = -\rho v \frac{\partial c_1}{\partial z} + \rho D \frac{\partial^2 c_1}{\partial z^2} + \frac{\partial}{\partial x} \left[\rho D \frac{\partial c_1}{\partial x} + \frac{\rho D_T Q}{T \lambda} \right], \quad (4)$$

in which we have replaced $\partial T/\partial x$ by its value Q/λ , where Q is the heat flow per sq. cm and λ is coefficient of thermal conductivity. The boundary conditions at the walls of the slab require that

$$c_1 v_{1x} = -D(\partial c_1/\partial x) + D_T Q/T \lambda = 0 \quad \text{at } x=0 \text{ and } x=d. \quad (5)$$

The condition that there be no net flow of gas along the tube is:

$$\int_0^d \rho v(x) dx = 0. \quad (6)$$

A solution of (4) may be obtained by using conditions (5) and (6) and by making use of the fact that the actual variation of c_1 across the width is very small and that the width is small compared with the length. It will be simpler, however, to start with the expression derived by Furry, Jones and Onsager for the total net flow, τ_1 , in grams per second, of molecules of species 1 along the column:⁹

$$\tau_1 = H [c_1 c_2 - (2A)^{-1} (\partial c_1/\partial z)], \quad (7)$$

in which the constants H and $H/2A$ are, for the case of Maxwellian molecules, as follows:

$$H = (d^3 \rho^2 \alpha g B / 720 \eta) (\Delta T / T)^2 f(\Delta T / T), \quad (8)$$

and

$$H/2A = d^7 \rho^3 g^2 B (\Delta T / T)^2 / 362880 \eta^2 D + B d D (T_1^2 + T_1 T_2 + T_2^2) / 3 T^2. \quad (9)$$

The coefficient of viscosity, η , and the acceleration of gravity, g , have been introduced from the solution of the thermal convection problem. All the gas constants (ρ , D , η) are to be taken at the mean temperature $T = (T_1 + T_2)/2$. The function $f(\Delta T/T)$ arises from the variation of the gas constants with temperature, and is always very close to unity. The first term on the right-hand side of (9) arises from remixing by transverse diffusion which results from the combination of convection currents and a vertical concentration

gradient, and the second term represents simply the ordinary diffusion along the column.

The conservation of species (1) requires that

$$\begin{aligned} \rho \alpha \partial c_1 / \partial t &= -\partial \tau_1 / \partial z \\ &= -H [(\partial c_1 c_2 / \partial z) \\ &\quad - (2A)^{-1} (\partial^2 c_1 / \partial z^2)], \end{aligned} \quad (10)$$

in which $\alpha = Bd$ is the cross-sectional area of the column. In what follows we make the assumption that the concentration of species 1 is always small, so that we may replace $c_2 = 1 - c_1$ by unity without appreciable error. The resulting equation is then linear in c_1 and can be solved by standard methods. We further assume that Eq. (10) applies throughout the entire length of the column. The equation is, of course, incorrect near the ends where the convection currents are not vertical, but the length of these regions is but a small part of the total.

Four special cases are treated, in all of which it is assumed that the lower end of the column is closed. For the condition at the upper end we take: (1) The upper end is closed. (2) The upper end is directly connected to a reservoir of infinite capacity, so that the concentration, c_1 , is independent of time at this point. (3) The upper end is directly connected to a reservoir of finite capacity. (4) The reservoir is connected to the top of the column by a tube along which a concentration gradient can exist, so that the concentration in the reservoir is not the same as that in the top of the column.

Cases (1), (2) and (3) can be solved by the usual method of expansion in a series of characteristic functions of the partial differential equation which satisfy the proper boundary conditions at the ends. These functions form an orthogonal set, so that the expansion coefficients can be easily determined. In case (4) the characteristic functions are not orthogonal, but the solution can be obtained without difficulty by the operational method (Laplace transform). As (2) and (3) are really special cases of (4), we give the analysis only for case (1) which we treat by standard methods and case (4) for which we use the operational method.

II. BOTH ENDS OF COLUMN CLOSED

We suppose that a heavy isotope is being concentrated at the lower end of the column, and

⁹ Our A is equivalent to the A_d of FJO, (reference 3).

let $z=0$ represent the upper end and $z=L$ the lower end. The boundary conditions require that there be no flow ($\tau_1=0$) at these points. It will be simplest to first find τ_1 as a function of z and t , and then derive c_1 from τ_1 . The equation for τ_1 is the same as that for c_1

$$\rho\alpha\partial\tau_1/\partial t = -H[(\partial\tau_1/\partial z) - (2A)^{-1}(\partial^2\tau_1/\partial z^2)], \quad (11)$$

and the boundary conditions are:

$$\tau_1=0 \text{ at } z=0 \text{ and } z=L \text{ for all } t, \quad (12)$$

and

$$\tau_1 = Hc_1^0 \text{ at } t=0 \text{ for all } z. \quad (12')$$

In the last equation, c_1^0 is the (constant) initial concentration.

The particular solution of (11) which satisfies the boundary condition (12) is

$$\tau_1^{(n)} = \sin(n\pi z/L) \times \exp[Az - (AH/2\rho\alpha)(1+n^2\pi^2/A^2L^2)t], \quad (13)$$

where n is a positive integer. We take

$$\tau_1 = \sum a_n \tau_1^{(n)}. \quad (14)$$

Setting $t=0$, we find (using (12')):

$$Hc_1^0 e^{-Az} = \sum a_n \sin(n\pi z/L). \quad (15)$$

Thus, evaluating the Fourier coefficients,

$$a_n = (2Hc_1^0/L) \int_0^L e^{-Az} \sin(n\pi z/L) dz = (2n\pi Hc_1^0/A^2L^2)(1 - (-1)^n e^{-AL}) / (1 + n^2\pi^2/A^2L^2). \quad (16)$$

The expression for c_1 can be divided in two parts, a steady-state term giving the equilibrium concentration and a transient term. The equilibrium term is of the form

$$c_1^{(e)} = Ke^{2Az}, \quad (17)$$

where K is a constant which may be determined from the fact that the total mass is conserved. Thus

$$Lc_1^0 = K \int_0^L e^{2Az} dz$$

$$\text{or } K = 2ALc_1^0 / (e^{2AL} - 1). \quad (18)$$

The transient term may be found from the

expression (14) for τ_1 and the equation $\rho\alpha\partial c_1/\partial t = -\partial\tau_1/\partial z$. We must take the negative of the derivative of τ_1 with respect to z , integrate with respect to t , and divide by $\rho\alpha$. We thus finally obtain

$$c_1 = Ke^{2Az} + \sum b_n \{ \cos(n\pi z/L) + (AL/n\pi) \sin(n\pi z/L) \} \exp[Az - t/t_n], \quad (19)$$

in which K is given by (18),

$$b_n = 2a_n n\pi / LAH(1 + n^2\pi^2/A^2L^2) = 4c_1^0(n^2\pi^2/A^2L^2)(1 - (-1)^n e^{-AL}) / (1 + n^2\pi^2/A^2L^2)^2, \quad (20)$$

and

$$t_n = 2(\rho\alpha/AH)(1 + n^2\pi^2/A^2L^2)^{-1}. \quad (21)$$

The series in (19) converges extremely rapidly. For all except small values of t , only the first term is required.

Numerical calculations based on Eq. (19) have been made for the purpose of comparing the theory with the experimental results of Nier.⁴ Methane gas was used in Nier's work, and $C^{13}H_4$ was concentrated at the bottom of the column.¹⁰ For convenience, the dimensions of the column are listed below.

$$\begin{aligned} L &= 730 \text{ cm} & \alpha &= dB = 9.4 \text{ cm}^2 \\ d &= 0.712 \text{ cm} & \text{Volume} &= \alpha L = 6880 \text{ cm}^3 \\ B &= 12.5 \text{ cm} & T_1 &= 300^\circ\text{K}, \quad T_2 = 600^\circ\text{K}. \end{aligned} \quad (22)$$

The gas constants, extrapolated to the mean temperature, are, for one atmosphere of pressure,

$$\begin{aligned} \rho &= 0.433 \times 10^{-3} \text{ g/cm}^3, \\ \eta &= 1.60 \times 10^{-4} \text{ poise}, \\ D &= 1.4n/\rho = 0.52 \text{ cm}^2/\text{sec.}, \\ \alpha &= 0.0077. \end{aligned} \quad (23)$$

The value of α is that found in a direct measurement by Nier.¹¹ Using these values we find that at one atmosphere

$$H = 2.5 \times 10^{-5} \text{ gram/sec.}$$

Values for other pressures may easily be found from the fact that H is proportional to the square of the pressure.

Empirical values of AL , determined from the equilibrium separation, are used in the calcula-

¹⁰ Since the normal concentration of C^{13} is about one percent, the condition that c_1 be small is well satisfied.

¹¹ A. O. Nier, Phys. Rev. **56**, 1009 (1939).

tion. The extent of the agreement between the theoretical and experimental values of A is discussed in Nier's paper. Runs were made at three different pressures; 21.7, 40, and 65.6 cm of Hg. The ratio of the concentration at the bottom of the column to that at the top of the column is equal to $\exp [2AL]$ when equilibrium is attained. The values obtained by Nier are given in Table I.

Formulae for the ratio of the concentration of $C^{13}H_4$ at each end of the tube to the initial concentration, in which only the first term of the series in (19) is used, are listed below. In each case the time is in hours.

$$P = 21.7 \text{ cm}$$

$$2AL = 0.81.$$

$$2\rho\alpha/AH = 19 \times 10^5 \text{ sec.} = 530 \text{ hours.}$$

$$\text{Top: } c_1/c_1^0 = 0.65 + 0.26 \exp(-t/8.6).$$

$$\text{Bottom: } c_1/c_1^0 = 1.46 - 0.40 \exp(-t/8.6).$$

$$P = 40 \text{ cm}$$

$$2AL = 1.83.$$

$$2\rho\alpha/AH = 4.9 \times 10^5 \text{ sec.} = 136 \text{ hours.}$$

$$\text{Top: } c_1/c_1^0 = 0.35 + 0.44 \exp(-t/10.6).$$

$$\text{Bottom: } c_1/c_1^0 = 2.18 - 1.10 \exp(-t/10.6).$$

$$P = 65.6 \text{ cm}$$

$$2AL = 1.45.$$

$$2\rho\alpha/AH = 3.8 \times 10^5 \text{ sec.} = 105 \text{ hours.}$$

$$\text{Top: } c_1/c_1^0 = 0.45 + 0.40 \exp(-t/5.3).$$

$$\text{Bottom: } c_1/c_1^0 = 1.90 - 0.81 \exp(-t/5.3).$$

These formulae are valid for values of t greater than three or four hours.

Figure 1 gives a plot of the relative concentrations of $C^{13}H_4$ at the top and bottom of a column operating at a pressure of 40 cm as a function of time. Also shown are the experimental points. The agreement on the whole is good.

In Fig. 2 we show the ratio of the concentration at the bottom of the column to that at the top of the column as a function of time for the three different pressures. Again the agreement

TABLE I. Equilibrium separation factor, $\exp(2AL)$, for $C^{13}H_4$, according to measurements of Nier.

Pressure (cm)	21.7	40	65.6
$\exp(2AL)$	2.25	6.25	4.25
$2AL$	0.81	1.83	1.45

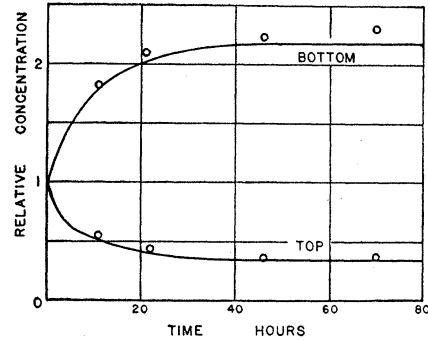


FIG. 1. Comparison of the theoretical and experimental values of the relative concentration of $C^{13}H_4$ at the top and bottom of a thermal diffusion column. Both ends of the column are closed. In plotting the experimental values of Nier, an allowance of one hour was made for the column to heat up. Methane pressure = 40 cm.

between experiment and theory is satisfactory. The measurements indicated by the solid triangles were taken at a pressure of 21.3 cm, while the curve (and the measurements indicated by the open triangles) refers to a pressure of 21.7 cm. This difference is sufficient to account for the discrepancy shown.

III. OPERATION WITH A RESERVOIR AT THE TOP

We now discuss case (4) referred to above. The top of the column is connected to a reservoir containing gas of mass M by means of a tube along which a concentration gradient can exist. It is supposed that the net flow of the molecules of species 1 through the tube is proportional to the concentration gradient. The bottom of the column is closed.

Again we let $z=0$ represent the top of the column and $z=L$ the bottom. The concentration c_1 at any point in the column as a function of time is given by the solution of the equation

$$\rho\alpha\partial c_1/\partial t = -H[(\partial c_1/\partial z) - (2A)^{-1}(\partial^2 c_1/\partial z^2)], \quad (24)$$

subject to the boundary conditions:

$$\tau_1 = H[c_1 - (2A)^{-1}(\partial c_1/\partial z)] = 0 \quad \text{at } z=L, \quad (25)$$

$$\text{and } c_1^{(\text{res})} - c_1 = R\tau_1/H \quad \text{at } z=0. \quad (26)$$

In Eq. (26) $c_1^{(\text{res})}$ represents the concentration in the reservoir and c_1 that in the top of the column. The constant R depends on the dimensions of the tube connecting the top of the column with the reservoir. If the tube has length l and area a ,

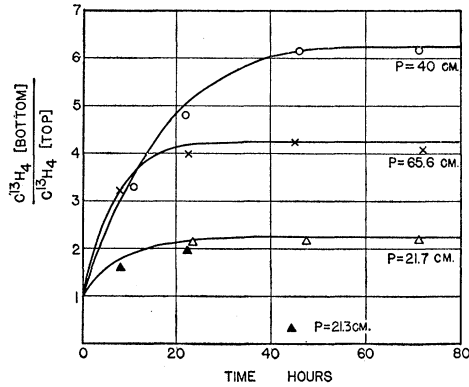


FIG. 2. Comparison of the theoretical and experimental values of the ratio of the concentration of $C^{13}H_4$ at the bottom of the column to that at the top of the column. Both ends of the column are closed. In plotting the experimental values of Nier, an allowance of one hour was made for the column to heat up.

and if the flow is by ordinary diffusion;

$$R = lH/a\rho D, \quad (27)$$

in which ρ is the density and D the coefficient of diffusion of the gas in the connecting tube.

The total mass of molecules of species 1 in the reservoir at any time is equal to the initial mass minus the mass which has flowed out. This gives

$$Mc_1^{(res)} = Mc_1^0 - \int_0^t \tau_1(0, t') dt'. \quad (28)$$

The constants K_1 and K_2 are to be determined from the boundary conditions (25) and (26'), which, by the same transformation become:

$$h = (2A)^{-1}(dh/dz) \quad \text{at } z=L, \quad (32)$$

and

$$p^{-1}c_1^0 - h = \{R + (H/Mp)\} \{h - (2A)^{-1}(dh/dz)\} \quad \text{at } z=0. \quad (33)$$

Substituting the expression for h given by Eq. (30) into Eq. (32) we find

$$p^{-1}c_1^0 + (e^{AL}/2)(K_2 - \gamma K_1) = 0 \quad \text{or} \quad K_2 = \gamma K_1 - (2c_1^0/p)e^{-AL}. \quad (34)$$

Similarly Eq. (33) becomes:

$$K_1 \sinh \gamma AL - K_2 \cosh \gamma AL = \{R + (H/Mp)\} \{p^{-1}c_1^0 - \frac{1}{2}(K_1 - \gamma K_2) \sinh \gamma AL + \frac{1}{2}(K_2 - \gamma K_1) \cosh \gamma AL\}. \quad (35)$$

Substituting the value for K_2 given by Eq. (34) into Eq. (35) and solving for K_1 , we find

$$\gamma K_1 = c_1^0 G(p) / p F(p), \quad (36)$$

in which $G(p) = \{R + (H/Mp)\} \{1 - e^{-AL}(\gamma \sinh \gamma AL + \cosh \gamma AL)\} - 2e^{-AL} \cosh \gamma AL$, (37)

and $F(p) = \gamma^{-1} \sinh \gamma AL - \cosh \gamma AL + (2\gamma)^{-1}(1 - \gamma^2)(R + (H/Mp)) \sinh \gamma AL$. (38)

Thus condition (26) may be written:

$$c_1^0 - c_1 - M^{-1} \int_0^t \tau_1(0, t') dt' = R\tau_1/H. \quad (26')$$

The operational method of solution will be used. The Laplace transform of $c_1(z, t)$ is

$$h(z, p) = \int_0^\infty e^{-pt} c_1(z, t) dt. \quad (27)$$

We will also need

$$\int_0^\infty e^{-pt} (\partial c_1 / \partial t) dt = -c_1^0 + ph, \quad (28)$$

which result follows by partial integration, and the fact that at $t=0$, $c_1 = c_1^0$, the initial concentration.

Multiplying (24) by $\exp[-pt]$ and integrating with respect to t between the limits zero and infinity, we find the following differential equation for h :

$$\rho \alpha (c_1^0 - ph) = H[(dh/dt) - (2A)^{-1}(d^2h/dt^2)]. \quad (29)$$

The general solution of this equation is:

$$h = p^{-1}c_1^0 + e^{Az} \{K_1 \sinh \gamma A(z-L) + K_2 \cosh \gamma A(z-L)\}, \quad (30)$$

where K_1 and K_2 are constants, and

$$\gamma = \{1 + (2\rho \alpha p / AH)\}^{1/2}. \quad (31)$$

Finally, substituting the values of K_1 and K_2 given by Eqs. (34) and (36) into Eq. (30), we find

$$ph/c_1^0 = 1 - 2e^{A(z-L)} \cosh \gamma(z-L) + e^{Az} \{G(p)/F(p)\} \{\gamma^{-1} \sinh \gamma A(z-L) + \cosh \gamma A(z-L)\}. \quad (39)$$

To transform back to find c_1 as a function of time, we make use of the following rules:¹² If $ph(p) = 1$, then

$$c_1(t) = 1. \quad (40)$$

If $ph(p) = p^n$ (n a positive integer) then

$$c_1(t) = 0. \quad (41)$$

If

$$ph(p) = f(p)/F(p)$$

then

$$c_1(t) = f(0)/F(0) + \sum_k \{f(p_k)/p_k F'(p_k)\} e^{p_k t}, \quad (42)$$

where $f(p)$ and $F(p)$ are series of positive powers of p , and p_k is a root of

$$F(p_k) = 0. \quad (43)$$

The roots are assumed to be distinct, and the sum in Eq. (42) runs over all roots. Eq. (42) expresses the Heaviside partial fraction rule. Thus we find

$$c_1(z, t)/c_1^0 = e^{2A(z-L)} \{e^{AL}G(0)/F(0) - 1\} + e^{Az} \sum_k \{G(p_k)/p_k F'(p_k)\} \\ \times \{\gamma_k^{-1} \sinh \gamma_k A(z-L) + \cosh \gamma_k A(z-L)\} \exp [p_k t], \quad (44)$$

in which γ_k is obtained by substituting p_k for p in the expression for γ (Eq. (31)). The first term on the right-hand side gives the equilibrium state,

$$c_1^{(e)}/c_1^0 = K e^{2Az}, \quad (45)$$

with

$$K = 2A(M + \rho \alpha L)/(2MA + \rho \alpha (e^{2AL} - 1)). \quad (46)$$

The series in Eq. (44) gives the transient terms. To evaluate them we must find the roots of $F(p) = 0$, which equation may be expressed in the form:

$$\tanh \gamma_k AL = \gamma_k / \{1 - (\rho \alpha / MA) - \frac{1}{2} R(\gamma_k^2 - 1)\}. \quad (47)$$

Depending on the value of R , there may or may not be a real value of γ_k which satisfies this equation. There are always an infinite number of pure imaginary roots. If γ_k is a root of this equation then, from Eq. (31) we find

$$p_k = -(AH/2\rho\alpha)(1 - \gamma_k^2).$$

The value of p_k is always real and negative.

Differentiating the expression for $F(p)$ given by Eq. (38) and making use of Eq. (47), we find

$$p_k F'(p_k) = (2\gamma_k)^{-1} (1 - \gamma_k^2) \{R \sinh \gamma_k AL + \gamma_k^{-1} \cosh \gamma_k AL - AL \operatorname{csch} \gamma_k AL\}. \quad (48)$$

With these substitutions, we finally obtain:

$$c_1/c_1^0 = K e^{2Az} + \sum_k \frac{2(R + (H/M p_k))(e^{AL} - \gamma_k \sinh \gamma_k AL - \cosh \gamma_k AL) - 4 \cosh \gamma_k AL}{(1 - \gamma_k^2)(\gamma_k^{-1} \sinh \gamma_k AL + \gamma_k^{-2} \cosh \gamma_k AL - AL \gamma_k^{-1} \operatorname{csch} \gamma_k AL)} \\ \times [\gamma_k^{-1} \sinh \gamma_k A(z-L) + \cosh \gamma_k A(z-L)] \exp [Az + p_k t]. \quad (49)$$

¹² See any book on operational calculus, e.g., J. R. Carson, *Electric Circuit Theory and Operational Calculus* (McGraw-Hill, 1926), p. 33.

This expression may appear rather formidable, but it is not difficult to use because the series converges so rapidly that at most only two or three terms are necessary.

Case (2) (infinite reservoir at the top, so that $c_1(=c_1^0)$ is constant in time at $z=0$) is obtained in the limit $M \rightarrow \infty$, $R \rightarrow 0$. Case (3) (no connecting tube, so that the concentration in the reservoir is the same as that in the top of the tube) is obtained in the limit $R \rightarrow 0$.

Nier⁴ made one run when a reservoir of 20 liters capacity was attached to the top of the column. The equivalent length/area of the connecting tube was rather large, 27.7 cm^{-1} . As we shall see, this materially lowered the rate of approach to equilibrium. The pressure (0.6 atmos.) was that which should give the largest possible separation factor ($\exp [2AL] = 6.62$). The total mass of gas in the reservoir (which was at room temperature) was about 7.8 grams as

compared with about 1.89 grams in the column. The expected equilibrium concentration in the bottom of the column is (from (45) and (46)) $4.84c_1^0$.

To evaluate the transient terms in Eq. (49) we need the following further data:

$$H = 0.6^2 \times 2.52 \times 10^{-5} \\ = 0.91 \times 10^{-5} \text{ gram/sec.}$$

$$AL = 0.945$$

$$2\rho\alpha/AH = 4.2 \times 10^5 \text{ sec.} = 117 \text{ hours.}$$

$$R = 27.7H / (1.4 \times 1.12 \times 10^{-4}) = 1.59.$$

Using the first three terms of the series, we find that at $z=L$ (bottom of the column)

$$c_1/c_1^0 = 4.84 - 2.9 \exp(-t/213) - 0.84 \\ \times \exp(-t/8.2) + 0.14 \exp(-t/2.7).$$

The time is measured in hours. This gives a rapid rise to a multiplication of about 2 and a slower rise thereafter. A plot of the curve is shown in Fig. 3. The experimental values of c_1/c_1^0 rise more rapidly than the theoretical with $R=1.59$. This may be due to the fact that there may be some convection in the vertical portion of the connecting tube, so that R is not as large as predicted from diffusion alone.

An excellent agreement between the experimental and theoretical values is obtained if we take arbitrarily $R=1.0$ instead of 1.59. The calculation then gives

$$c_1/c_1^0 = 4.84 - 3.0 \exp(-t/155) - 0.74 \\ \times \exp(-t/7.6) - 0.03 \exp(-t/2.4).$$

Also shown in the figure are the curves for $R=0$ (equilibrium is assumed at all times between the reservoir and the top of the column) and the curve for an infinite reservoir. In the latter case the equilibrium value of c_1/c_1^0 at the bottom of the column is 6.62 instead of 4.84.

In order to obtain the maximum possible speed, it is necessary to use a large connecting tube, so that R is made small in comparison with unity.

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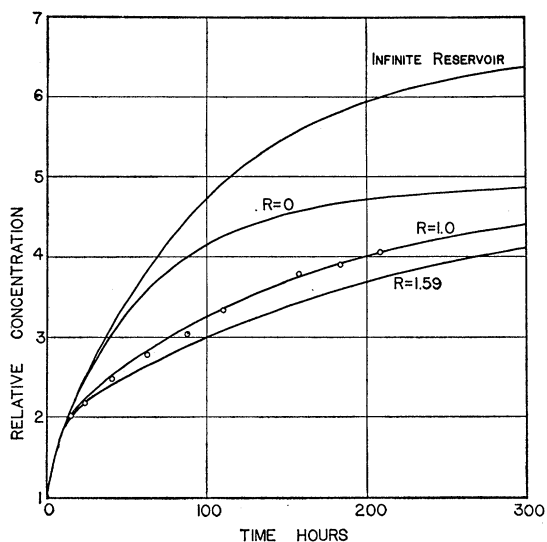


FIG. 3. Plot of the relative concentration of $C^{13}H_4$ at the bottom of a thermal diffusion column as a function of time. In all cases, the bottom of the column is closed. The upper curve represents the case of an infinite reservoir directly connected to the top of the column. The other three cases are for a reservoir of finite size connected to the top of the column by means of a tube along which a concentration gradient may exist. The parameter R is a measure of the resistance of this tube to flow by diffusion or convection. The experimental points are from a run made by Nier. The calculated value of R for the connecting tube used by Nier is 1.59 if it is assumed that flow is by diffusion alone; actually R may be smaller because of convection. Methane pressure = 46 cm (0.6 atmos.).