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Third Partial Report
on
Liquid Thermal Diffusion Research
Theory of Isotope Separation by Thermal
Diffusion, - I. Single Column

NAVAL RESEARCH LABORATORY
ANACOSTIA STATION
Washington, D. C.

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TABLE OF CONTENTS

Page

Abstract

ABSTRACT

The fundamental equations governing the process of isotope separation by thermal diffusion are derived. The equations are applied to the behavior of a single column in the cases of equilibrium, stationary flow and approach to equilibrium.

INTRODUCTION

1. The separation of isotopes by the method of thermal diffusion has assumed a practical significance in connection with the problem of obtaining concentrated uranium 235, an element which is capable of releasing large amounts of energy. While the work on this problem is primarily of an experimental nature, theoretical work can play an important role in guiding the work of the experimenter and in correlating his results.

2. The present paper deals with the theory of the thermal diffusion method. In the published literature there are a number of papers on the theoretical treatment of isotope separation by thermal diffusion, among which one might single out for mention those of Furry, Jones and Onsager[1] (to be referred to as F. J. O.), Waldmann[2], Bardeen[3], and Debye[4]. However, all of these but the last are concerned with gases rather than liquids. The paper of Debye is not satisfactory because of the rough approximations introduced, while the papers dealing with gases make some assumptions which are probably not valid for liquids. (Incidentally it is interesting to note that since 1940 no papers on isotope separation by thermal diffusion have appeared in German publications, although there had been numerous papers previously.)

3. Because there exists no satisfactory theoretical treatment of isotope separation by thermal diffusion in liquids, it seems desirable to attempt such a treatment. The purpose of the present paper is to discuss the case of a single liquid diffusion column, introducing assumptions and approximations which are appropriate to the type of column being used, and to obtain results which can be directly applied to it.

APPARATUS AND PROCESS

4. In order to be able to treat the problem theoretically, we must first have a clear picture before us of the system to be investigated. Some idealization will be necessary, to be sure, but it is important to try to retain the essential features.

5. We shall consider a column to consist of two vertical concentric tubes, spaced a distance a apart, each of length L, between which the diffusing liquid is contained, in the annular space of mean circumference b. The surfaces of the tubes in contact with the liquid will be referred to as the "walls". One wall is maintained at a low temperature T_1, the other at a high temperature T_2. The mass of the fluid contained between the walls will be denoted by M_c. At the top of the column there is a reservoir filled with liquid having a mass M_R. At the bottom of the column there is an outlet which may be connected to another reservoir, or else kept closed,

6. Because of the temperature difference between the walls, a convection current sets in, the liquid near the hot wall, having the

lower density, flowing upward, while that near the cold wall flows down. At the same time thermal diffusion takes place, the molecules of the lighter isotope diffusing from the cold toward the hot wall. The result is that there is an exchange of molecules between the upward convection stream and the downward one, by which the upward stream acquires an excess of the lighter isotope and carries it to the top of the column. The concentration of the lighter isotope at the top of the column, or in the reservoir, gradually increases, while that at the bottom decreases, unless the bottom is connected to a large reservoir or to another column, so that a constant concentration is maintained.

7. If this process is allowed to continue, a condition of equilibrium will be approached, at which there will be a definite relation between the concentrations at top and bottom. It is possible to stop the process at some stage, remove the enriched liquid from the reservoir and start the process over again. Such a procedure is referred to as intermittent operation. On the other hand, it is possible, beginning at a certain stage, to draw off a continuous stream of enriched liquid from the top of the column. This procedure is called continuous operation. Under working conditions, the rate at which the isotope is drawn off from the top of the column is equal to that at which it is carried to the top of the column by convection, so that one has a stationary condition within the column.

8. In the mathematical treatment of a column such as has been described, one can take into account the fact that the distance between the walls a is very small compared to the circumference b, by neglecting the curvature of the walls and treating them as plane surfaces. In discussing the convection and diffusion, one can simplify the calculations considerably by neglecting the small regions near the ends of the column where the temperatures vary from the values prevailing elsewhere and where the convection streams curve back to reverse their directions. These regions can be neglected because their dimensions are generally very small compared to the usual length of a column. (F.J.O.[1])

9. Finally, since a column in a practical case will produce a relatively small change in the isotope concentration, one can represent the concentration very often as a power series in the distance up from the bottom of the column. The series will usually converge so rapidly that only a small number of terms are required for reasonable accuracy. Such a power series expansion frequently reduces the work of mathematical calculation considerably.

CONVECTION

10. Since we are dealing with isotopes having a small percentage difference in atomic weight, the two kinds of molecules being separated are very similar in their properties, and the presence of thermal diffusion does not alter the behavior of the liquid to any marked extent. Hence one can first treat the convection of the liquid in the

absence of diffusion and afterwards treat the diffusion as influenced by the convection.

11. Let us suppose that we have the liquid between two parallel vertical walls a distance a apart, of breadth b and height L. Let us take a coordinate system with the X-axis at right angles to the plates and the Z-axis vertical, so that $0 \leq x \leq a$, $0 \leq z \leq L$. Since we shall consider the case in which none of t quantities to be discussed varies in the direction of the third coordinate axis, the latter will not be used. Let us take the "cold" wall, as the one at $x = 0$, and let its temperature be T_1, while the "hot" wall, at $x = a$, has a temperature T_2, so that $\Delta T = T_2 - T_1 > 0$. Let p be the pressure, g the acceleration of gravity, and Q the heat flow per unit area of plate. Furthermore let ρ, λ and μ denote the density, thermal conductivity, and viscosity of the liquid, as functions of the temperature T. Debye[4] assumed the last three quantities to be constant, corresponding to a small value of ΔT. However, these quantities may change rapidly with the temperature and therefore, for any appreciable value of ΔT, the dependence on temperature should be taken into consideration. On the other hand, because of the similarity of the two kinds of molecules, we shall assume that ρ, λ and μ do not depend on their concentrations. Finally, from the conditions of the problem, we can take these quantities independent of z.

12. To calculate the convection flow, we follow F. J. O. in determining the temperature distribution on the basis of the heat conduction alone. Except near the edges of the plate, one can write,

$$Q = \lambda \frac{dT}{dx}, \tag{1}$$

or, on integrating,

$$Q = \frac{\varkappa}{a}, \tag{2}$$

where

$$\varkappa = \int_{T_1}^{T_2} \lambda \, dT. \tag{3}$$

13. F.J.O.[1] showed that the convection flow can be treated as lamellar. To a sufficient accuracy, one can use the hydrodynamical equation for steady viscous flow in the form

$$(\nabla \cdot \mu \nabla) \vec{v} = \nabla p - \rho \vec{g}, \tag{4}$$

where $\vec{v}$, the velocity vector, is taken in the z-direction, but independent of z, while $\vec{g}$, the gravitational acceleration vector is taken in the (-z) direction and of magnitude g. Eq. (4) gives for the x-component:

$$\frac{\partial p}{\partial x} = 0, \tag{4}$$

and for the z component:

$$\frac{\partial}{\partial x}\left(\mu \frac{\partial v}{\partial x}\right) = \frac{\partial p}{\partial z} + \rho g. \tag{5}$$

Since, in (5), all terms other than $\frac{\partial p}{\partial z}$ depend only on x, we see that

$$\frac{\partial p}{\partial z} = B, \tag{6}$$

where B is a constant, and the equation can be written by means of (1) as

$$\frac{Q^2}{\lambda} \frac{d}{dT}\left(\frac{\mu}{\lambda} \frac{dV}{dT}\right) = B + \rho g. \tag{7}$$

This equation is to be solved subject to the boundary conditions

$$V(T_1) = V(T_2) = 0 \tag{8}$$

The solution of (7) can be obtained by quandratures and will depend linearly upon the constant B. The value of this constant will depend on the total flow of liquid. It will be seen from (7) that for given values of B, T_1 and T_2, v(T) for a fixed value of T will vary as $1/Q^2$, or by (1), as a^2.

DIFFUSION

14. Let the two types of molecules in the liquid be referred to by subscripts 1 and 2, so that, for example, c_1 and c_2 are the relative particle concentrations, ($c_1 + c_2 = 1$), and let 1 represent the species which it is desired to concentrate, i.e., the lighter one. The equation of diffusion can be written in the form

$$c_1(\vec{v}_1 - \vec{v}) = - D\nabla c_1 + C\nabla T, \tag{9}$$

where the first term on the right-hand side represents ordinary diffusion, while the second term represents thermal diffusion. In the case of ordinary diffusion, the diffusion coefficient D (often denoted by D_{12}) is known to be a function of the temperature. It will be assumed that it is independent of the concentrations c_1 and c_2, an assumption which is justified by the similarity of the two species of molecules.

15. The coefficient C of the thermal diffusion term must depend not only on the temperature, but also on the concentrations. Since there is no thermal diffusion if either species alone is present, one can assume C to contain a factor c_1c_2. Let us write

$$\frac{C}{D} = qc_1c_2 \qquad (10)$$

One can expect that q will depend on T and that it will be, in general, a slowly varying function of the concentrations. In particular, if the two species are very similar in their properties, it is reasonable to believe that q will be very nearly independent of c_1 and c_2. This is borne out by the fact that such is the case for thermal diffusion in gases[5]. We shall therefore assume, until there is evidence to the contrary, that q in (10) is a function only of the temperature. What this function is we do not know at present. In the case of gases, it has been found to be of the form α/T, where α is nearly a constant, and this is the function used by F.J.O.[1] For liquids, very rough theoretical arguments[6] have led to either α/T or α/T^2, depending on the model assumed. It seems best, in the present state of our knowledge, to leave open the question of what the dependence of q on T is.

16. From (9) and (10) the flux density of species 1 is given by

$$\vec{J}_1 = \rho c_1\vec{v}_1 = \rho\left[c_1\vec{v} + D(-\nabla c_1 + qc_1c_2\nabla T)\right] , \qquad (11)$$

so that we can write

$$\frac{\partial}{\partial t}(\rho c_1) = -\nabla\cdot\vec{J}_1, \qquad (12)$$

where t is the time. If we are dealing with a stationary condition, such as that of equilibrium, or of continuous operation, the left-hand member is zero, and we have

$$\nabla\cdot\vec{J}_1 = 0 \qquad (13)$$

As pointed out by F.J.O.[1], the condition will be essentially stationary even during the approach to equilibrium provided the end-reservoirs are sufficiently large.

STATIONARY CONDITION

17. Substituting (11) into (13), we get

$$\frac{\partial}{\partial x}\left[\rho D\left(-\frac{\partial c_1}{\partial x} + qc_1c_2\frac{\partial T}{\partial x}\right)\right] + \rho v\frac{\partial c_1}{\partial z} - \rho D\frac{\partial^2 c_1}{\partial z^2} = 0, \qquad (14)$$

or if we replace x by T, by means of (1),

$$\frac{\partial}{\partial T}\left[\frac{\rho D}{\lambda}\left(\frac{\partial c_1}{\partial T} - qc_1c_2\right)\right] = \frac{\lambda\rho}{Q^2}\left[v\frac{\partial c_1}{\partial z} - D\frac{\partial^2 c_1}{\partial z^2}\right] \qquad (15)$$

The boundary conditions at the walls are given by

$$J_{1x} = 0 \qquad (x = o, a), \qquad (16)$$

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or

$$\frac{\partial c_1}{\partial T} - g c_1 c_2 = 0. \qquad (17)$$

18. In solving these equations, we shall not look for an explicit solution giving the value of c_1 for each value of T and z; rather we shall follow F.J.O. in seeking information about the average value of c_1 across a section z=constant, for various values of z, since this is the quantity which is of the most direct concern to the experimenter, and since the concentration varies but little over the cross-section of the column.

19. Let us therefore integrate eq. (15) over T from T_1 to T_2. Making use of the boundary conditions (17) we obtain a result which can be written

$$\frac{\partial \tau_1}{\partial z} = 0, \qquad (18)$$

where τ_1 is the upward transport of species 1, given by

$$\begin{aligned} \tau_1 &= b \int_0^a \rho \left(v c_1 - D \frac{\partial c_1}{\partial z} \right) dx \\ &= \frac{b}{Q} \int_{T_1}^{T_2} \rho \lambda \left(v c_1 - D \frac{\partial c_1}{\partial z} \right) dT. \end{aligned} \qquad (19)$$

Eq. (18) states the obvious fact, that τ_1 is <u>constant</u> along the tube for a stationary state.

20. Let us now define a function

$$F(T) = Q^2 \int_{T_1}^{T_2} \lambda \rho v \, dT. \qquad (20)$$

We see that

$$F(T_1) = 0, \qquad F(T_2) = \frac{Q^3 \sigma}{b}, \qquad (21)$$

where σ is the total transport, given by

$$\sigma = b \int_0^a \rho v \, dx = \frac{b}{Q} \int_{T_1}^{T_2} \lambda \rho v \, dT. \qquad (22)$$

Eq. (19) can be written

$$\tau_1 = \frac{b}{Q^3} \int_{T_1}^{T_2} c_1 \frac{dF}{dT} dT - \frac{b}{Q} \int_{T_1}^{T_2} \lambda \rho D \frac{\partial c_1}{\partial z} dT. \qquad (23)$$

Integration by parts, with the aid of (21), gives

$$\tau_1 = \sigma c_1(T_2, z) - \frac{b}{Q^3}\int_{T_1}^{T_2} F \frac{\partial c_1}{\partial T}\, dT - \frac{b}{Q}\int_{T_1}^{T_2} \lambda\rho D \frac{\partial c_1}{\partial z}\, dT. \qquad (24)$$

21. If one now goes back to eq. (15) and integrates it with respect to T, one obtains an expression for $\partial c_1/\partial T$, which can then be substituted into (24). Taking into account the boundary conditions (17), one finds

$$\frac{\partial c_1}{\partial T} = q c_1 c_2 + \frac{\lambda}{\rho D Q^2}\int_{T_1}^{T}\left(v\frac{\partial c_1}{\partial z} - D\frac{\partial^2 c_1}{\partial z^2}\right)\lambda\rho\, dT, \qquad (25)$$

and, substituting this into (24), one obtains

$$\begin{aligned}\tau_1 = \sigma c_1(T_2, z) &- \frac{b}{Q^3}\int_{T_1}^{T_2} F q c_1 c_2\, dT - \frac{b}{Q^5}\int_{T_1}^{T_2}\frac{\lambda F}{\rho D}\, dT\int_{T_1}^{T}\lambda\rho v\frac{\partial c_1}{\partial z}\, dT \\ &+ \frac{b}{Q^5}\int_{T_1}^{T_2}\frac{\lambda F}{\rho D}\, dT\int_{T_1}^{T}\lambda\rho D\frac{\partial^2 c_1}{\partial z^2}\, dT - \frac{b}{Q}\int_{T_1}^{T_2}\lambda\rho D\frac{\partial c_1}{\partial z}\, dT. \end{aligned} \qquad (26)$$

22. If one neglects the small variation in concentration along a section z = const., one can write this equation as

$$\tau_1 = \sigma c_1 + H c_1 c_2 - K\frac{dc_1}{dz} - N\frac{d^2 c_1}{dz^2}, \qquad (27)$$

where H, K, and N are positive quantities defined by

$$\left.\begin{aligned} H &= -\frac{b}{Q}\int_{T_1}^{T_2} F q\, dT, \\ K &= K_c + K_d, \\ K_c &= \frac{b}{Q^5}\int_{T_1}^{T_2}\frac{\lambda F^2}{\rho D}\, dT, \\ K_d &= \frac{b}{Q}\int_{T_1}^{T_2}\lambda\rho D\, dT, \\ N &= \frac{b}{Q^5}\int_{T_1}^{T_2}\frac{\lambda F}{\rho D}\, dT\int_{T_1}^{T}\lambda\rho D\, dT, \end{aligned}\right\} \qquad (28)$$

and the concentrations are now regarded as depending only on z.

23. One can show that in practical cases the term in (27) involving d^2c_1/dz^2 will generally be small compared to the other quantities present. Hence we shall discard this term. For convenience we shall write c in place of c_1, 1-c in place of c_2, and τ in place of τ_1. The equation then becomes

$$\tau = \sigma c + Hc(1-c) - K\frac{dc}{dz}. \tag{29}$$

(a) Equilibrium

In the case of equilibrium both σ and τ are zero. Eq. (29) then becomes

$$K\frac{dc}{dz} - Hc(1-c) = 0. \tag{30}$$

If we let

$$\alpha = \frac{H}{K}, \tag{31}$$

this can be integrated to give

$$\ln\frac{c}{1-c} = \alpha z + \text{const} \tag{32}$$

24. Let the value of c at the top of the column be denoted by c_+, that at the bottom by c_o. It is customary to define the separation factor by

$$S = \frac{c_+(1-c_o)}{c_o(1-c_+)}. \tag{33}$$

If we let S_e denote the value of S at equilibrium, then it follows from (32) that

$$\ln S_e = \alpha L, \quad S_e = e^{\alpha L}. \tag{34}$$

Where L is the length of the column. An important feature of this result is that the value of the equilibrium separation factor is independent of the concentration at the bottom of the column.

25. It is desirable to investigate more closely the dependence of S_o on the variables of the system. In terms of the integrals listed in (28), it can be written

$$\ln S_e = \frac{HL}{K}, \tag{35}$$

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or, by the use of (2),

$$\ln S_e = \frac{-L a^2 \kappa^4 \int_{T_1}^{T_2} F q \, dT}{a^6 \int_{T_1}^{T_2} \frac{\lambda F^2}{\rho D} dT + \kappa^6 \int_{T_1}^{T_2} \lambda \rho D \, dT} \tag{36}$$

26. If one looks for the value of a, denoted by a_m, for which $\ln S_e$ has a maximum value, one finds that it satisfies the relation

$$2 a_m^6 \int_{T_1}^{T_2} \frac{\lambda F^2}{\rho D} dT = \kappa^6 \int_{T_1}^{T_2} \lambda \rho D \, dT. \tag{37}$$

The maximum value of $\ln S_e$ is then given by

$$\ln S_{em} = \frac{2^{-1/3} \int_{T_1}^{T_2} F q \, dT}{3 \left[\int_{T_1}^{T_2} \frac{\lambda F}{\rho D} dT \right]^{1/3} \left[\int_{T_1}^{T_2} \lambda \rho D \, dT \right]^{2/3}}. \tag{38}$$

This depends only on the wall temperatures T_1 and T_2. The dependence is rather complicated, however.

27. It might be pointed out that, on the basis of rough considerations of the behavior of the various quantities in (38), raising T_2 should generally increase S_{em}. However, this cannot be done indefinitely, since a high value of ΔT will lead to parasitic, or local convection, resulting in mixing of the liquid and lowering of the separation factor. It appears that the choice of optimum wall temperatures can best be made on the basis of experiment, rather than theory.

28. Returning to (36), we see, that, for fixed wall temperatures T_1 and T_2, the dependence of S_e on a can be expressed in the form

$$\ln S_e = \frac{k_1 a^2 L}{1 + k_2 a^6}, \tag{39}$$

where k_1 and k_2 are constants depending on the temperature. A similar relation was given by Waldmann[2] for gases.

29. In plate 1, the crosses indicate experimental values of lnS for a number of values of a, as determined by Dr. Philip H. Abelson for a particular set of conditions. The curve represents ln S_e as given by (39), k_1 and k_2 having been chosen to fit the experimental data. It will be seen that the agreement is good. However, the agreement may be fortuitous to some extent for, as Dr. Abelson pointed out, in the experiments what was kept constant was not the temperature of the wall in contact with the diffusing liquid, but rather the temperature of the heating or cooling substance in contact with the other side of

the wall. When the distance a is varied, the temperature of the diffusing liquid at the wall will vary somewhat in spite of the fact that the heating and cooling agents are kept at fixed temperatures.

30. If we wish to have a solution for the concentration c at equilibrium, we can obtain it in a convenient form by expanding it in a power series in z. Substituting into eq. (30) and equating to zero the coefficients of each power, we get

$$c(z) = c_0 + c_0(1-c_0)\left[\alpha z + (\tfrac{1}{2}-c_0)\alpha^2 z^2 + \cdots\right], \qquad (40)$$

provided we take $z = 0$ at the bottom of the column.

31. If the solution is desired in a closed form rather than as a power series, it can be obtained from (32). The result is

$$C(z) = \frac{C_0 e^{\alpha z}{}^{3}}{1 + C_0 (e^{\alpha z} - 1)} \qquad (40A)$$

(b) Stationary flow

32. We next consider the case in which there is a steady upward flow of liquid through the column at such a rate that the concentration at every point remains constant with time, a condition which might be referred to as "stationary". In this case eq. (29) applies, with σ and τ both constant, σ being the mass of liquid flowing upward per unit time through any cross-section of the column, while τ is the mass of the desired constituent crossing any section per unit time. These two quantities are related to each other by the equation

$$\tau = \sigma c_m \qquad (41)$$

where c_m is the value of c at the point where the enriched material is withdrawn. If one is operating a single column this will be the same as C_+, but if the column is part of a pyramid, c_m will be the concentration at the top of the pyramid. Let us for the present impose no restriction on c_m.

Eq. (29) can now be written

$$\sigma c_m = \sigma c + Hc(1-c) - K \frac{dc}{dz}. \qquad (42)$$

If we define α as in (31) and let

$$\nu = \frac{\sigma}{H}, \qquad (43)$$

the equation becomes

$$\frac{dc}{dz} - \alpha c(1-c) + \alpha \nu (c_m - c) = 0 \qquad (44)$$

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This can be solved most conveniently by means of a power series in z. In this way one obtains as the solution

$$c = c_0 + \left[c_0(1-c_0) - v\,(c_m - c_0)\right]\left[\alpha z + \tfrac{1}{2}\,(1-2c_0+v)\,\alpha^2 z^2\right] + \cdots \qquad (45)$$

Putting z = L gives us C_+, and from this we get the separation factor

$$S = 1 + \left[1 - \frac{v(c_m - c_0)}{c_0(1-c_0)}\right]\left\{\alpha L + \left[\frac{1}{2} + \frac{v(\frac{1}{2} + \frac{1}{2}c_0 - c_m)}{1-c_0}\right]\alpha^2 L^2\right\} + \cdots \qquad (46)$$

33. If we are dealing with the case in which $c_m = c_+$, we can put the result into a more convenient form. At the top of the column, (45) then becomes

$$c_+ = c_0 + \left[c_0(1-c_0) - v(c_+ - c_0)\right]\left[\alpha L + \tfrac{1}{2}(1-2c_0+v)\,\alpha^2 L^2\right] + \cdots \qquad (47)$$

we solve this equation for c_+ we obtain

$$c_+ = c_0 + c_0(1-c_0)\left[\alpha L + \tfrac{1}{2}\,(1-2c_0-v)\,\alpha^2 L^2\right] + \cdots \qquad (48)$$

and from this we find

$$S = 1 + \alpha L + \tfrac{1}{2}\,(1-v)\,\alpha^2 L^2 + \cdots \qquad (49)$$

34. It will be seen by a comparison of (49) with (34) that when liquid is withdrawn continuously from the top of the column the separation factor is less than that at equilibrium; the difference will be very small however if S_e is nearly equal to unity (αL small).

APPROACH TO EQUILIBRIUM

35. If one is interested in following the process by which the column goes from its initial state to the condition of equilibrium, one must replace eq. (29) by the more general equation involving the time. This equation can be obtained from eq. (12) in much the same way as (29) was obtained from (13). Such an equation was derived by Bardeen.[7] If we again omit terms which are small in practical cases, the equation can be written in the form

$$\rho a b \frac{\partial c}{\partial t} = -H \frac{\partial}{\partial z}\left[c(1-c)\right] + K \frac{\partial^2 c}{\partial z^2}. \qquad (50)$$

If we define α as in (31) and let

$$\eta = \frac{\rho a b}{K \alpha^2} = \frac{\rho a b}{H \alpha}, \qquad (51)$$

this becomes

$$\eta \alpha^2 \frac{\partial c}{\partial t} = -\alpha \frac{\partial}{\partial z}\left[c(1-c)\right] + \frac{\partial^2 c}{\partial z^2}. \qquad (52)$$

36. To solve this equation, we look for a solution which is a power series in z, with coefficients which are functions of t. Let us set

$$c = \gamma_0(t) + \gamma_1(t)\alpha z + \gamma_2(t)\alpha^2 z^2 + \dots \tag{53}$$

Substituting this into (52) and equating coefficients of corresponding powers of z on both sides of the equation, we obtain a series of relations

$$\left.\begin{aligned} \eta\gamma_0' &= -\gamma_1(1-2\gamma_0) + 2\gamma_2, \\ \eta\gamma_1' &= -2[\gamma_2(1-2\gamma_0) - \gamma_1^2] + 6\gamma_3, \\ \eta\gamma_2' &= -3[\gamma_3(1-2\gamma_0 - 2\gamma_1\gamma_2] + 12\gamma_4 \dots \end{aligned}\right\} \tag{54}$$

where a prime denotes differentiation with respect to time. It will be seen that two of the functions, γ_0 and γ_1 can be taken arbitrarily. The others will then be determined by the equations in terms of these two. One finds, for example,

$$\begin{aligned} \gamma_2 &= \gamma_1(1/2 - \gamma_0) + 1/2\,\eta\gamma_0' \\ \gamma_3 &= 1/6\,\gamma_1^2[(1-2\gamma_0)^2 - 2] + 1/6\,\eta[\gamma_1' + \gamma_0'(1-2\gamma_0)], \text{etc.} \end{aligned} \tag{55}$$

The upward transport τ, given by

$$\tau = Hc(1-c) - K\frac{\partial c}{\partial z}, \tag{56}$$

is found to be

$$\tau = H\left\{\gamma_0(1-\gamma_0) - \gamma_1 - \eta\gamma_0'\alpha z - 1/2\,\eta\gamma_1'\alpha^2 z^2 - 1/3\,\eta\gamma_2'\alpha^3 z^3 - \dots\right\} \tag{57}$$

37. The functions γ_0 and γ_1 will be chosen in any particular problem so as to satisfy the initial conditions and the boundary conditions at the top and bottom of the column.

38. This method of solution is much simpler than the usual method involving a Fourier series, and it should work satisfactorily for the cases encountered in practice. An example of its application will next be given.

(a) Fixed concentration at bottom of column.

39. We consider the case of a column of the type previously discussed which is operated by having its lower end connected to a large reservoir or to a stripper column so that the initial concentration is maintained there at all times. We have then, by taking z = 0,

$$\gamma_0(t) = \text{constant} = c_0 \tag{58}$$

whence it follows from (54) that

$$\left.\begin{aligned} \gamma_2 &= \gamma_1(1/2 - c_0) \\ \gamma_3 &= 1/3\left[\gamma_2(1-2c_0) - \gamma_1^2\right] + 1/6\,\eta\,\gamma_1' \\ \gamma_4 &= 1/4\left[\gamma_3(1-2c_0) - 2\gamma_1\gamma_2\right] + 1/12\,\eta\,\gamma_2' \ldots \end{aligned}\right\} \qquad (59)$$

40. In this case, eq. (57) gives for τ

$$\tau = H\left[c_0(1-c_0) - \gamma_1 - 1/2\,\eta\,\gamma_1'\alpha^2 z^2 - 1/3\,\eta\,\gamma_1'(1/2 - c_0)\alpha^3 z^3 \ldots\right] \qquad (60)$$

At the top of the column (z = L) we have

$$\tau_+ = H\left[c_0(1-c_0) - \gamma_1\right] - \rho a\, b\, L^2 \alpha\left[1/2\,\gamma_1' + 1/3\,\gamma_1'(1/2 - c_0)\alpha L\right] \qquad (61)$$

or, since

$$M_c = \rho a\, b\, L \qquad (62)$$

we can write

$$\tau_+ = H\left[c_0(1-c_0) - \gamma_1\right] - M_c\,\alpha L\gamma_1'\left[1/2 + 1/3(1/2 - c_0)\alpha L\right] + \ldots \qquad (63)$$

41. On the other hand, at the top of the column, we have the rate of change of concentration related to the transport,

$$\tau_+ = M_R\,\frac{dc_+}{dt} \qquad (64)$$

where M_R is the mass of the liquid in the reservoir, while c_+ is given by

$$c_+ = c_0 + \gamma_1\alpha L + \gamma_1(1/2 - c_0)\alpha^2 L^2 + \ldots \qquad (65)$$

Substituting (65) and (63) into (64) we get an equation for γ_1:

$$H\left[c_0(1-c_0) - \gamma_1\right] = \alpha L\gamma_1'\left\{M_R\left[1 + (1/2 - c_0)\alpha L\right] + M_c\left[1/2 + 1/3(1/2 - c_0)\alpha L\right]\right\} + \ldots \qquad (66)$$

Neglecting higher order terms, one integrates this to get

$$\gamma_1 = c_0(1-c_0)\left[1 - e^{-t/\theta}\right] \qquad (67)$$

where the relaxation time θ is given by

$$\theta = \frac{L}{K}\left\{M_R\left[1 + (1/2 - c_0)\alpha L\right] + M_c\left[1/2 + 1/3(1/2 - c_0)\alpha L\right]\right\} \qquad (68)$$

to the approximation considered.

42. The solution for the concentration can be written

$$c = c_0 + c_0(1-c_0)(1-e^{-t/\theta})\left[\alpha z + (1/2 - c_0)\alpha^2 z^2\right] + \ldots \qquad (69)$$

From this one finds for the separation factor

$$S = 1 + (1 - e^{-t/\theta})\left[\alpha L + (1/2 - c_0 e^{-t/\theta})\alpha^2 L^2\right] + \ldots \qquad (70)$$

Footnotes

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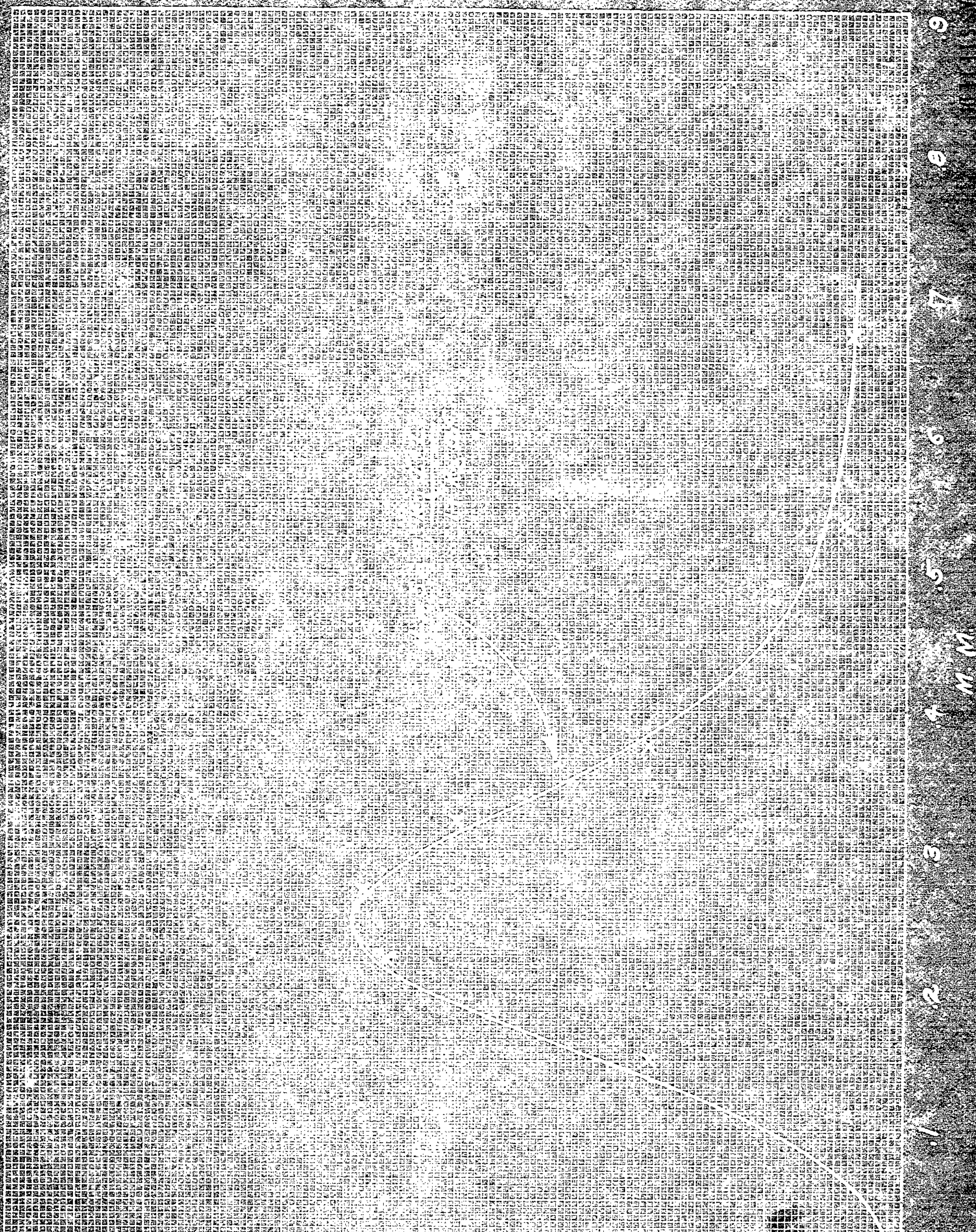

PLATE I