

In the present paper  $\chi$  is represented by  $\chi^i + \chi^j$ . Also

$$I_{ij}(\chi) = G_j \left( \frac{m_j}{n} \right)^3 \left( \frac{c_i + c_j}{c_i c_j} \right)^{\frac{1}{2}} c_j^{-3} F_i(A_i) F_j(A_j) J_{ij}(\chi), \quad (29)$$

$$J_{ij}(\chi) = F_i^{-1}(A_i) F_j^{-1}(A_j) \int dw_j \int \gamma_{ij} \omega_{ij}(\theta, \alpha) d\Omega \cdot f_i^{o'} f_j^{o'} \cdot (1 + \theta_i f_i^o)(1 + \theta_j f_j^o)(\chi_i + \chi_j - \chi_i' - \chi_j'). \quad (30)$$

The following identity holds,

$$I_{ij}'(\chi^i + \chi^j) = J_{ij}(\chi).$$

Also, definition of the square brackets in H.U. is related to the present one by,

$$[F, G]_{ij} + [F, G]_{ij} \text{H.U.} \equiv [F, G]_{ij}.$$

## Generalized Theory of Diffusion. II

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The theory of diffusion in ternary and higher order gas mixtures is completed with the discussion of thermal diffusion. The theory is carried to the point where assumptions about molecular interactions are necessary to obtain quantitative expression of the coefficients. In the special case of elastic spheres the formulae have been given in terms of the masses and cross sections, neglecting, however, the diffraction effects.

### INTRODUCTION

**T**HERMAL diffusion remains one of the few processes of diffusion which are difficult to analyze from elementary considerations, even for the case of binary mixtures. The coefficient is a function of differences in masses and force interactions and, in addition, respective particle concentrations and their ratios. No emphasis therefore need be given to the increased complication which the analysis of ternary and higher order mixtures introduces. It is nevertheless desirable to obtain formulae for the thermal coefficients in such cases in order to obtain additional insight into the processes involved as well as to check values obtained by direct experimentation.

In connection with the theory of isotope separation it is of interest to determine if the addition of new components has any optimum effect, and if so, to determine what the characteristics of these additional components must be in relation to the isotopes involved. It is also true that the isotopes occur frequently as groups of three or more so that from the point of view of application of theory to experiment, the binary analysis is inadequate for an actual description of results. These problems receive added interest and importance in light of the recent work of Furry, Jones and Onsager,<sup>1</sup> on isotope separation by thermal diffusion coupled with convective action.

The effect on the distribution function of the gas molecules by a temperature gradient is given by the equations which the first-order variations must satisfy (I APPENDIX (A))\*

$$\frac{f_j^{o2}}{A_j} \exp(\tau_j^2) \frac{1}{c_j^{\frac{1}{2}}} \frac{1}{T} \xi_j \frac{\partial T}{\partial x} \left( \tau_j^2 - \frac{5}{2} \frac{p^j}{n_j k T} \right) = \sum_{s=1}^N I_{js} \{ \chi^j + \chi^s \}, \quad (1)$$

where the symbolism is that of (I).

<sup>1</sup>Furry, Jones and Onsager, Phys. Rev. **55**, 1083 (1939).

\* Reference to the first part will throughout be indicated by I.

If we take  $\chi$  to be given by

$$\chi \equiv \frac{\pi^{\frac{1}{2}}}{kT} M \frac{\partial T}{\partial x},$$

one then obtains the following system of equations,

$$\frac{f_i^{02} \exp(\tau_i^2)}{A_i F_3(A_i)} \frac{\xi_{j\alpha}}{(m_i)^{\frac{1}{2}}} \left( \tau_i^2 - \frac{5}{2} \frac{p^{(i)}}{n_i kT} \right) n_i k = - \sum_{s=1}^N n_i n_s \left( \frac{m_i + m_s}{m_i m_s} \right)^{\frac{1}{2}} I' \{ M^i + M^s \}. \tag{2}$$

And one obtains as in (I),

$$M = \frac{\begin{vmatrix} \dots \dots \dots \{H_s^q; N; M\} \\ H_s^q \dots \dots \dots 0 \end{vmatrix}}{|\{H_s^q; N; H_t^q\}|} \tag{3}$$

As in I, attention has been focused on the  $q$ th component, and the basic set  $H_s^q$  of I employed in II. Eqs. (2), unlike the set in I, maintain symmetry with respect to all components. Since also the brackets  $\{\xi_r; N; M\}$  vanish, it is necessary to include functions quadratic in  $\tau$ . Thus, the simplest set sufficient to discuss thermal diffusion is,

$$H_s^q = \frac{\xi^q}{n_q(m_q)^{\frac{1}{2}}} - \frac{\xi^s}{n_s(m_s)^{\frac{1}{2}}}, \tag{4a}$$

$$h_s^1 = \xi^s \left[ \tau_s^2 - \frac{5}{2} \frac{F_{3/2}(A_s)}{F_{1/2}(A_s)} \right]. \tag{4b}$$

Since the experiment to which we wish to apply the theory is one wherein a gas-filled vessel is in equilibrium under a certain temperature gradient, it is convenient to add the perturbations of the distribution functions due to pressure and temperature variations.

$$\chi_{P,T} = \frac{\pi^{\frac{1}{2}}}{kT} \frac{\begin{vmatrix} \dots \dots \dots \left\{ H_r^q; N; M \frac{\partial T}{\partial x} + \sum L_s Z^s \right\} \\ \vdots \\ H_r^q \dots \dots \dots 0 \end{vmatrix}}{-\Delta}, \tag{5}$$

where  $\Delta$  is the denominator in (3), and the term  $\sum L_s Z^s$  is to be summed over all "s," (I). The conditions for equilibrium then demand that the particle current of any component calculated from (5) is zero, and that the total pressure be constant,

$$\left( \sum_{i=1}^N p^{(i)} = \text{const.} \right).$$

In analyzing the separations produced in a set of gases by thermal diffusion, one would then desire the values of all partial pressure gradients as well as the temperature gradient. From (5) it is possible to obtain  $N-1$  independent equations by making the particle currents vanish. One additional equation is obtained from the condition that the sum of all the partial pressure gradients must vanish.

The relations which may now be used to simplify (5) are

$$\{H_s^q; N; M\partial T/\partial x\} = 0, \tag{6}$$

$$\{h_s'; N; \sum L_s Z^s\} = 0, \tag{7}$$

$$\{h_j'; N; M\partial T/\partial x\} = -\frac{2}{3} \pi \frac{n_j k}{(m_j)^{\frac{1}{2}}} \frac{\Gamma(9/2)}{F_4(A_j)} \left[ F_{5/2}(A_j) - \frac{5}{7} \frac{F_{3/2}(A_j)^2}{F_{1/2}(A_j)} \right] \left( \frac{\partial T}{\partial x} \right), \tag{8}$$

$$\{H_j^q; N; \sum L_s Z^s\} = \frac{\pi^{\frac{1}{2}}}{2} \left( -\frac{1}{\rho_j} Z^j - \frac{1}{\rho_q} Z^q \right). \tag{9}$$

In computing the currents from (5), one finds that the contribution from the  $h$ 's vanishes. Moreover, one finds, apart from a common factor, that the functions  $H_1^q, H_2^q \dots$  contribute to the current of particles of type " $j$ ,"  $j \neq q$ , the amounts,

$$n_j \left( \frac{m_1 - m_q}{m_1} \right), n_j \left( \frac{m_2 - m_q}{m_2} \right), \dots \frac{\rho_j - m_q (n_j - n)}{m_j} \tag{10}$$

and to the current of particles of type " $q$ " the amounts,

$$\frac{m_1(n_q - n) - \rho_q}{m_1}, \frac{m_2(n_q - n) - \rho_q}{m_2}, \dots \tag{11}$$

If one replaces in (5) the values given (6), (7), (8), (9), (10), and (11), denoting the cofactors of the last column by  $A_{r,s}$  (where  $s$  denotes the particular current considered, and  $r$  the row), one finds the following set of equations to determine the various partial pressure gradients (where the classical values have been taken for the expressions (8)),

$$\sum A_j^s \left( \frac{1}{\rho_j} Z^j - \frac{1}{\rho_q} Z^q \right) - \sum_{v=N+1}^{2N} A_v^s k \frac{5}{2} \frac{n_{v-N}}{(m_{v-N})^{\frac{1}{2}}} \frac{\partial T}{\partial x} = 0, \tag{12a}$$

$$\sum_{v=1}^N Z^v = 0. \tag{12b}$$

It may be easily shown then, that

$$\frac{Z^j}{\rho_j} - \frac{Z^q}{\rho_q} = -\frac{5}{2} k \begin{vmatrix} b_{j1}, & b_{j2}, & \dots & \dots & 0 \\ \dots & \dots & \dots & \dots & n_1 \\ \dots & \dots & \dots & \dots & (m_1)^{\frac{1}{2}} \\ & & & & \vdots \\ & & & & n_N \\ & & & & (m_N)^{\frac{1}{2}} \end{vmatrix} \frac{\partial T}{\partial x}, \tag{13}$$

where

$$b_{js} = \{H_j^q; N; h_s'\}; \quad a_{r,s} = \{h_r'; N; h_s'\}.$$

To evaluate the determinants, it is necessary to calculate the  $a_{r,s}$  and  $b_{j,s}$ .

$$\{H_r^q; N; H_s^q\} = \frac{-(8/3)\pi^{7/2} P_{r,s}^{1,5}}{[m_r m_s (m_r + m_s)]^{\frac{1}{2}}} + \sum \frac{[\rho_j + \rho_q (\delta_r^j + \delta_s^j)]}{\rho_q} \cdot \frac{(8/3)\pi^{7/2} P_{q,i}^{1,5}}{[m_q m_j (m_q + m_j)]^{\frac{1}{2}}}. \tag{14a}$$

$$\{H_r^q; N; H_r^q\} = \frac{(\rho_q + \rho_r)^2}{\rho_q \rho_r} \cdot \frac{(8/3)\pi^{7/2} P_{q,r}^{1,5}(1)}{[m_q m_r (m_q + m_r)]^{3/2}} + \sum_{i \neq r} \frac{\rho_i}{\rho_q} \cdot \frac{(8/3)\pi^{7/2} P_{q,i}^{1,5}(1)}{[m_i m_r (m_i + m_r)]^{3/2}}, \quad (14b)$$

$$\{H_r^q; N; h_s'\} = n_s \cdot \frac{8}{3} \pi^{7/2} \left[ \frac{(m_r)^{3/2}}{(m_r + m_s)^{3/2}} \left\{ P_{r,s}^{1,7}(1) - \frac{5}{2} P_{r,s}^{1,5}(1) \right\} - \frac{(m_s)^{3/2}}{(m_q + m_s)^{3/2}} \left\{ P_{q,s}^{1,7}(1) - \frac{5}{2} P_{q,s}^{1,5}(1) \right\} \right], \quad (14c)$$

$$\begin{aligned} \{H_r^q; N; h_r'\} = & -\frac{8}{3} \pi^{7/2} \left[ n_r \frac{(m_q)^{3/2}}{(m_q + m_r)^{3/2}} \left\{ P_{q,r}^{1,7}(1) - \frac{5}{2} P_{q,r}^{1,5}(1) \right\} \right. \\ & \left. + \sum \frac{n_j}{m_r} \left( \frac{m_j}{m_j + m_r} \right)^{3/2} \left\{ P_{i,r}^{1,7}(1) - \frac{5}{2} P_{i,r}^{1,5}(1) \right\} \right], \quad (14d) \end{aligned}$$

$$\{h_r'; N; h_s'\} = \frac{-(8/3)\pi^{7/2} \rho_r \rho_s}{(m_r + m_s)^{5/2}} \left[ \frac{55}{4} P_{r,s}^{1,5}(1) - 5 P_{r,s}^{1,7}(1) - \frac{4}{3} P_{r,s}^{2,7}(1) + P_{r,s}^{1,9}(1) \right], \quad (14e)$$

$$\begin{aligned} \{h_r'; N; h_r'\} = & \frac{8}{3} \pi^{7/2} \sum_{s \neq r} n_r n_s \left( \frac{m_s}{m_r} \right)^{3/2} (m_r + m_s)^{-(5/2)} \cdot \left[ \frac{5}{4} (6m_r^2 + 5m_s^2) P_{r,s}^{1,5}(1) - 5m_s^2 P_{r,s}^{1,7}(1) \right. \\ & \left. + \frac{4}{3} m_r m_s P_{r,s}^{2,7}(1) + m_s^2 P_{r,s}^{1,9}(1) \right] + \frac{8}{9} \pi^{7/2} n_r^2 \left( \frac{2}{m_r} \right)^{3/2} P_{r,r}^{2,7}(1). \quad (14f) \end{aligned}$$

With the values of the various brackets given in the group (14) the problem of the determination of the separations which can be produced in gas mixtures is halted until definite assumptions about the force interactions have been made. The simplest force law which can be used, which may be regarded as a first approximation to the actual law, is the elastic sphere model. In this case the various  $P$  functions have the following values,

$$P_{r,s}^{1,5}(1) = S_{r,s}^2/2, \quad (15a) \quad P_{r,s}^{2,7}(1) = 3S_{r,s}^2/2, \quad (15c)$$

$$P_{r,s}^{1,7}(1) = 3S_{r,s}^2/2, \quad (15b) \quad P_{r,s}^{1,9}(1) = 6S_{r,s}^2, \quad (15d)$$

where the  $S_{r,s}$  are the elastic sphere diameters of interaction, equal to the average of the actual diameters of the two types of particles.

One has for then the case of three gases,

$$\frac{Z_2}{\rho_2} - \frac{Z_1}{\rho_1} = -k \frac{\begin{vmatrix} C_3^{12}, & -C_3^{21}, & f_3^2, & 0 \\ \dots & \dots & \dots & 1 \\ & B_{ij} & \cdot & 1 \end{vmatrix}}{|B_{ij}|} \frac{\partial T}{\partial x}, \quad (16)$$

$$\frac{Z_3}{\rho_3} - \frac{Z_1}{\rho_1} = -k \frac{\begin{vmatrix} C_2^{13}, & f_2^3, & -C_2^{31}, & 0 \\ \dots & \dots & \dots & 1 \\ & B_{ij} & \cdot & 1 \end{vmatrix}}{|B_{ij}|} \frac{\partial T}{\partial x}, \quad (17)$$

where

$$B_{ji} = \frac{1}{3} \left[ (2)^{5/2} S_{ij}^2 n_j + \binom{m_j}{m_k} S_{jk}^2 n_k + \binom{m_j}{m_t} S_{jt}^2 n_t \right], \quad j \neq k \neq t = 1, 2, 3, \quad (18)$$

$$\binom{m_j}{m_k} = \left( \frac{m_k}{m_j + m_k} \right)^{3/2} \left\{ \frac{30m_j^2 + 13m_k^2 + 16m_j m_k}{(m_j + m_k)^2} \right\}, \quad (19)$$

$$B_{ik} = -9 \left[ \frac{m_j^3 m_k^2}{(m_j + m_k)^5} \right]^{1/2} S_{jk}^2 n_k, \quad (20)$$

$$C_3^{12} = \frac{2}{3} \cdot \frac{1}{m_1} \left[ \frac{(\rho_1 + \rho_2)}{(m_1 + m_2)} \left( \frac{m_2}{m_1 + m_2} \right)^{3/2} S_{12}^2 + \frac{\rho_3 (m_3)^{3/2}}{(m_1 + m_3)^{3/2}} S_{13}^2 \right], \quad (21)$$

$$f_3^2 = \frac{2}{3} n_3 \left[ \frac{(m_2)^{3/2}}{(m_2 + m_3)^{3/2}} S_{23}^2 - \frac{(m_3)^{3/2}}{(m_1 + m_3)^{3/2}} S_{13}^2 \right]. \quad (22)$$

An application of the preceding theory has been made with respect to a mixture of hydrogen, deuterium, and helium. The ratio of hydrogen to deuterium was taken as 5000 to 1 and the concentration of helium was taken as 0, 1/5, 2/5, 3/5, 4/5 and 1 with respect to the hydrogen number density.

The collision diameter of deuterium was taken equal to that of hydrogen. This assumption appears to be sufficiently accurate in view of the experiments of Grew and Atkins<sup>2</sup> on thermal diffusion in deuterium mixtures.

The results on the deuterium, hydrogen, helium mixture are of particular interest in view of the equality of masses of deuterium and helium. Any effect between the latter in a binary mixture depends solely on differences in cross sections. It is found that helium is much "harder" relatively, than deuterium. In the case chosen for application it may be expected from the mass effect that the result of addition of helium is to increase the separation of hydrogen and deuterium, provided the separations are dependent mainly on the mass ratios. Similarly from the mass effect it may be expected that the addition of an element intermediate in mass will tend to increase the separation of any pair of elements. The character and extent of such separation will of course be influenced by the remaining variables, which describe the mixture (cross sections and concentrations). For particular mass ratios it is apparent that the latter variables may be most important.

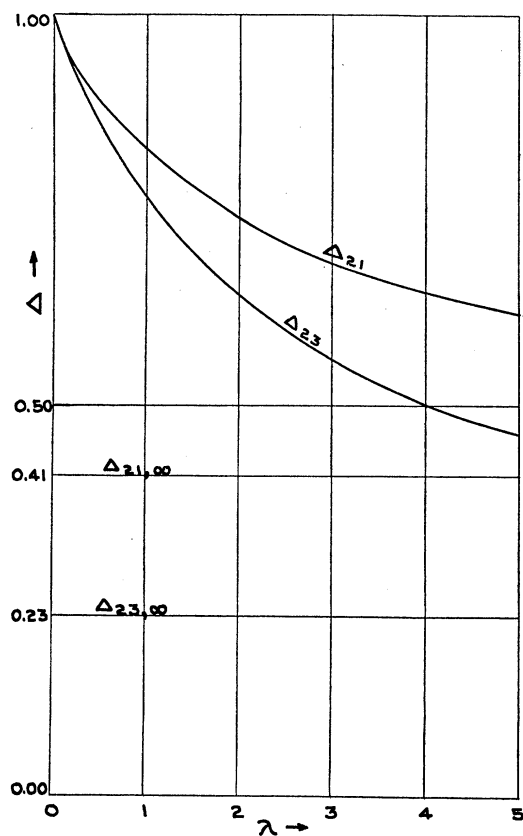


FIG. 1. Plot of the separation of deuterium and hydrogen, and of deuterium and helium against a variable helium concentration.

<sup>2</sup> K. E. Grew and B. E. Atkins, Proc. Phys. Soc. **48**, 415-420 (1936).

If hydrogen, deuterium, and helium are numbered successively 1, 2, and 3, then we find,

$$\frac{\partial p^{(1)}}{\partial x} = -\frac{5}{2} \frac{\rho_1}{\rho} \{ \rho_2 \delta_1 + \rho_3 \delta_2 \} \frac{\partial T}{\partial x}, \quad (23)$$

$$\frac{\partial p^{(2)}}{\partial x} = +\frac{5}{2} \frac{\rho_2}{\rho} \{ \rho_1 \delta_1 + \rho_3 (\delta_1 - \delta_2) \} \frac{\partial T}{\partial x}, \quad (24)$$

$$\frac{\partial p^{(1)}}{\partial x} + \frac{\partial p^{(2)}}{\partial x} + \frac{\partial p^{(3)}}{\partial x} = 0, \quad (25)$$

where

$$\delta_1 = \frac{89\lambda^3 + 2,065\lambda^2 + 14,057\lambda + 30,764}{344\lambda^3 + 7,090\lambda^2 + 50,637\lambda + 98,680}, \quad (26)$$

$$\delta_2 = \frac{73\lambda^3 + 1,664\lambda^2 + 11,070\lambda + 21,906}{344\lambda^3 + 7,090\lambda^2 + 50,637\lambda + 98,680}, \quad (27)$$

$$\frac{n_3}{n_2} = 1000\lambda, \quad \frac{n_1}{n_2} = 5000, \quad \frac{m_3}{m_1} = \frac{m_2}{m_1} = 2. \quad (28)$$

From (23) and (24) one readily obtains

$$\frac{\partial}{\partial x} \left( \log \frac{n_2}{n_1} \right) = -\frac{5}{2} \frac{\partial}{\partial x} (\log T) \left\{ \frac{[m_2(\rho_1 + \rho_3) + \rho_2 m_1] \delta_1}{\rho} + \frac{(m_1 - m_2)}{\rho} \rho_3 \delta_2 \right\}. \quad (29)$$

Let us define the coefficient  $\Delta$  as

$$\Delta_{21} = \frac{\partial(\log n_2/n_1)/\partial x}{[\partial(\log n_2/n_1)/\partial x]_{n_3=0}}. \quad (30)$$

It is this coefficient which will be used as a measure of the separations to be produced in a mixture, and in Fig. 1 has been plotted for deuterium-hydrogen and for deuterium-helium, against an increasing helium concentration.

It will be observed from Fig. 1 that in both cases the separation becomes less as the helium concentration increases. No experimental data appears to be available as a check on this behavior and thus no check on the effect of the elastic sphere approximation can be made. Both hydrogen and deuterium, admittedly are not symmetric molecules and deviations are likely to be found from the curves in Fig. 1, since the phenomenon of thermal diffusion is so dependent on the type of force interaction between molecules.