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Generalized Theory of Diffusion

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The theory of diffusion in mixtures with more than two components has been developed as an extension of the theory of Enskog for binary mixtures. In particular, the various coefficients have been evaluated as functions of the binary coefficients of diffusion. Attention has also been given to the theory of osmotic diffusion in connection with the Loschmidt experiment. The analysis has been carried through in such a manner as to be applicable to Einstein-Bose and Fermi-Dirac gases as well as the Maxwell-Boltzmann Type. The paper has been divided into two parts which deal with first, pressure diffusion and second, with thermal diffusion.

INTRODUCTION

THE phenomena of diffusion are divisible roughly speaking into two classes which may be characterized as effects of the first and second orders, respectively. One generally considers in the first class the effects of pressure and potential gradients and in the second the effect of temperature gradients. In the treatment by means of perturbation theory the first class is a function chiefly of the first approximation to the first-order variation of the distribution function, while the second necessitates the consideration of the second approximation.

Rigorous analysis of the problem of diffusion in mixtures of two gases has been given by Enskog and Chapman. The work of Enskog,[1] who first discovered thermal diffusion, allows with some modification the generalization to mixtures with three or more components. It is evident with even first consideration that the problem of diffusion in this case is not simply a repetition of the theory of binary diffusion, since one immediately perceives that the possibility exists for diffusion induced by streaming of one gas through the mixture. This streaming roughly may be thought of as producing forces which act on each component gas with different magnitudes by virtue of the different interactions which exist between the individual molecules of each component. It is evident that, in special cases only, is the theory of binary diffusion applicable to mixtures.

One encounters experimentally the condition of streaming by one component quite frequently. This state occurs for example when a source or sink exists for a given element. That is, whenever the removal or creation of an element (by such processes as the condensation and vaporization or combination and decomposition) is not uniform throughout the gas enclosure, pressure gradients are set up which then induce these currents in the mixture. The phenomena of electron winds and ion drift produced by electric fields and of polarizable particles in inhomogeneous fields, are likewise familiar. Seemingly somewhat removed, but still in the same category, one may consider the case of high temperature radiation through gas mixtures.

In addition to the case of streaming of one component into the mixture we must consider the problem of diffusion of one component. This leads to an analysis closely related to the diffusion previously mentioned. Experiments which would fall into this category are those for which diffusion of air and some other gas is observed. Data on the coefficients for oxygen, nitrogen, hydrogen, and carbon dioxide into air have been given with considerable accuracy.

Last one must consider the thermal diffusion in mixtures of three or more components. This phenomenon is like the case of ordinary diffusion complicated by the existence of several components with different interactions. The expression becomes there the more involved and is not expressible in terms of binary thermal diffusion coefficients with any degree of simplicity.

The plan followed is to proceed from the Boltzmann equation with the left member transformed

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[1] D. Enskog, (a) "Kinetische Theorie der Vorgänge in Mässig Verdünnten Gasen," Dissertation, Upsala.

into derivatives of the pressures and potentials and temperature. In the work[2] cited below these equations were simplified at that point by the limitation to mixtures of two components only. All discussion up to this point is thus to be obtained in this work which will be referred to as H.U. for reference in the ensuing discussion.

FORMAL EXPRESSIONS FOR THE MASS CURRENT

One proceeds then from the equations for a mixture of N gases which are the equations obtained from the Boltzmann equations by considering a solution to first orders alone.

$$\frac{f_j^{\circ 2}\exp(\tau_j^2)}{A_j}\left[\frac{\xi_{j\alpha}}{n_jkTc_j^{\frac{1}{2}}}\left(\frac{\rho_j}{\rho}\right)\left\{\frac{\partial p^q}{\partial\chi_\alpha}-\rho_qX_{q\alpha}\right\}\right]=\sum_{s=1}^{N}I_{js}(\chi^j+\chi^s),\quad j\neq q \tag{1}$$

$$\frac{f_q^{\circ 2}\exp(\tau_q^2)}{A_q}\left[\frac{\xi_{q\alpha}}{n_qkTc_q^{\frac{1}{2}}}\left(\frac{\rho_q-\rho}{\rho}\right)\left\{\frac{\partial p^q}{\partial\chi_\alpha}-\rho_qX_{q\alpha}\right\}\right]=\sum_{s=1}^{N}I_{qs}(\chi^q+\chi^s),\quad j=q \tag{2}$$

where f_j^0 is the distribution function for the jth component. The remaining symbolism is that given in H.U. (see also Appendix A). In addition, it must be noticed that only a perturbation by forces acting on the qth component is considered. There is, however, no loss of generality since the equations are linear. If one now assumes that the perturbation of the distribution functions is given by

$$\chi^s=\frac{\pi^{\frac{3}{2}}}{kT}L_q^s\left(\frac{\partial p^q}{\partial\chi_\alpha}-\rho_qX_{q\alpha}\right)\equiv\pi^{\frac{3}{2}}L_q^sZ^q/kT, \tag{3}$$

and the collision integrals are transformed by using the relation

$$d\varphi_q=n_qd\omega_q/\pi^{\frac{3}{2}}F_{\frac{1}{2}}(A_q). \tag{4}$$

The equations which result are then expressible in the following form

$$\frac{f_j^{\circ 2}\exp(\tau_j^2)}{A_jF_{\frac{1}{2}}(A_j)}\,\frac{\xi_{j\alpha}}{(m_j)^{\frac{1}{2}}}\left(\frac{\rho_j}{\rho}\right)=\sum_{s=1}^{N}n_jn_s\left(\frac{m_j+m_s}{m_jm_s}\right)^{\frac{1}{2}}I_{js}'\{L_q^j+L_q^s\},\quad j\neq q \tag{5}$$

$$\frac{f_q^{\circ 2}\exp(\tau_q^2)}{A_qF_{\frac{1}{2}}(A_q)}\,\frac{\xi_{q\alpha}}{(m_q)^{\frac{1}{2}}}\left(\frac{\rho_q-\rho}{\rho}\right)=\sum_{s=1}^{N}n_qn_s\left(\frac{m_q+m_s}{m_qm_s}\right)^{\frac{1}{2}}I_{qs}'\{L_q^q+L_q^s\}.\quad j=q. \tag{6}$$

The I_{js}' are the collision integrals defined with integration on $d\omega$ and substitution of the variable γ for g, the relative velocity, where

$$\gamma_{r,s}=g_{r,s}\left(\frac{m_rm_s}{2kT(m_r+m_s)}\right)^{\frac{1}{2}}. \tag{7}$$

In the following we shall have occasion to use the definition of the mixed bracket given by Enskog[3]

$$[L,L]_{j,s}=\int L^jI_{js}'\{L^j+L^s\}d\omega_j+\int L^sI_{sj}'\{L^s+L^j\}d\omega_s. \tag{8}$$

It is necessary now to extend the definition of the curly bracket, H.U. (Enskog[4]). The new form

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[2] E. J. Hellund and E. A. Uehling, Phys. Rev. **56**, 818–835 (1939).

[3] Reference 1, p. 67.

[4] Reference 1, p. 68.

is to be taken as

$$\{L;N;L\}=\sum_{j\geq s} n_j n_s\left(\frac{m_j+m_s}{m_j m_s}\right)^{\frac{1}{2}}[L,L]_{j,s}. \tag{9}$$

In view of the properties of the mixed bracket $[F,G]_{j,s}$ there exist the same set for $\{F;N;G\}$,

$$\{F;N;G\}=\{G;N;F\}, \tag{10a}$$

$$\{F;N;G+H\}=\{F;N;G\}+\{F;N;H\}, \tag{10b}$$

$$\{F;N;cH\}=C\{F;N;H\}, \tag{10c}$$

$$\{F;N;F\}\geqslant 0. \tag{10d}$$

It may now be shown that the coefficient of mass diffusion is expressible in terms of this extended curly bracket, and that the solution of the perturbation problem resolves itself into a variational calculation.

It is desired to evaluate the difference of the velocity of streaming of the q component gas and the entire mixture. That is,

$$\begin{aligned} U_q-\sum_{s=1}^{N}\frac{U_s\rho_s}{\rho}&=U_q\left(\frac{\rho-\rho_q}{\rho}\right)-\sum_{s\neq q}^{N}\frac{U_s\rho_s}{\rho}\\ &=\int\frac{f_q{}^{\circ}(1+\theta_q f_q{}^{\circ})\chi^q U}{n_q}d\varphi_q\left(\frac{\rho-\rho_q}{\rho}\right)-\sum_{s\neq q}\int\frac{f_s{}^{\circ}(1+\theta_s f_s{}^{\circ})\chi^s U}{n_s}d\varphi_s\left(\frac{\rho_s}{\rho}\right). \end{aligned} \tag{11}$$

By transformation of variable this becomes

$$-\left(\frac{2}{kT}\right)^{\frac{1}{2}}\left[\int\frac{f_q{}^{\circ 2}\exp(\tau_q{}^2)}{A_q F_{\frac{1}{2}}(A_q)}\frac{\xi_q}{(m_q)^{\frac{1}{2}}}dw_q\left(\frac{\rho_q-\rho}{\rho}\right)L_q{}^q+\sum_{s\neq q}\int\frac{f_s{}^{\circ 2}\exp(\tau_s{}^2)}{A_s F_{\frac{1}{2}}(A_s)}\frac{\xi_s}{(m_s)^{\frac{1}{2}}}dw_s\frac{\rho_s}{\rho}L_q{}^s\right]Z^q. \tag{12}$$

The last expression is then by virtue of Eqs. (5) and (6), just $\{L_q;N;L_q\}$, so that,

$$U_q-\sum_{s=1}^{N}\frac{U_s\rho_s}{\rho}=-\left(\frac{2}{kT}\right)^{\frac{1}{2}}\{L_q;N;L_q\}. \tag{13}$$

The mass current of component q is given by

$$J_\rho{}^q=-\left(\frac{2}{kT}\right)^{\frac{1}{2}}\{L_q;N;L_q\}\rho_q Z^q. \tag{14}$$

To demonstrate that the function L may be arrived at by a variational calculation one proceeds just as in the case of two components. That is, if,

$$\{L^*;N;L^*\}=\{L^*;N;L\}, \tag{15}$$

where L^* is an approximation to the exact solution which is to be made as good a solution as possible, by adjustment of the parameters on which it depends, then

$$\begin{aligned} 0\leqslant\{L^*-L;N;L^*-L\}&=\{L^*;N;L^*\}+\{L;N;L\}-2\{L^*;N,L\}\\ &=\{L;N;L\}-\{L^*;N;L^*\}. \end{aligned} \tag{16}$$

Thus L^* must be chosen so as to maximize the bracket.

If temperature variations are considered one also finds the perturbation of the distribution function to be determined in like manner. However for the present, thermal diffusion will not be considered, but will be treated after the analysis of pressure diffusion.

EXPLICIT DETERMINATION OF THE MASS AND PARTICLE CURRENTS

When the method of solution has been determined there remains only the consideration of the auxiliary conditions relating to the macroscopic description of the state of the gas for the perturbed and unperturbed case, (H.U.). To satisfy the auxiliary conditions the solution may be formulated in terms of $MN+N-1$ parameters as follows,

$$L^*=\sum_{j=1}^{M}\sum_{s=1}^{N}\beta_s{}^j h_s{}^j+\sum_{1=s}^{N}\beta_0{}^s\left(\frac{\xi^q}{n_q(m_q)^{\frac{1}{2}}}-\frac{\xi^s}{n_s(m_s)^{\frac{1}{2}}}\right). \tag{17}$$

In the following we shall write

$$H_s{}^q=\frac{\xi^q}{n_q(m_q)^{\frac{1}{2}}}-\frac{\xi^s}{n_s(m_s)^{\frac{1}{2}}}. \tag{18}$$

One then obtains the system of equations which are the result of the maximal property for the best solution to be obtained from a given number of parameters.

$$\begin{gathered}
\{H_t{}^q; N; \sum_{s=1}^{N}\beta_0{}^s H_s{}^q+\sum_{1}^{M}\sum_{1}^{N}\beta_s{}^j h_s{}^j\}-\{H_t{}^q; N; L\}=0, \quad t=1\cdots N,\\
\{h_t{}^r; N; \sum_{1}^{N}\beta_0{}^s H_s{}^q+\sum_{1}^{M}\sum_{1}^{N}\beta_s{}^j h_s{}^j\}-\{h_t{}^r; N; L\}=0, \quad r=1\cdots M; t=1\cdots N,\\
\sum_{1}^{N}\beta_0{}^s H_s{}^q+\sum_{1}^{M}\sum_{1}^{N}\beta_s{}^j h_s{}^j-L^*=0.
\end{gathered} \tag{19}$$

This yields for L^*,

$$L^*=-\frac{\begin{vmatrix}\{H_t{}^q; N; H_s{}^q\}, & \{H_t{}^q; N; h_s{}^j\}, & \{H_t{}^q; N; L\}\\ \{h_t{}^r; N; H_s{}^q\}, & \{h_t{}^r; N; h_s{}^j\}, & \{h_t{}^r; N; L\}\\ H_s{}^q, & h_s{}^j, & 0\end{vmatrix}}{\begin{vmatrix}\{H_t{}^q; N; H_s{}^q\}, & \{H_t{}^q; N; h_s{}^j\}\\ \{h_t{}^r; N; H_s{}^q\}, & \{h_t{}^r; N; h_s{}^j\}\end{vmatrix}}. \tag{20}$$

Consequently we have for the mass current

$$J_\rho{}^q=-\left(\frac{2}{kT}\right)^{\frac{1}{2}}\rho_q Z^q\{L_q{}^*; N; L_q{}^*\}=-\left(\frac{2}{kT}\right)^{\frac{1}{2}}\rho_q\{L_q{}^*; N; L_q\}Z^q, \tag{21}$$

$$=+\left(\frac{2}{kT}\right)^{\frac{1}{2}}\rho_q\frac{\begin{vmatrix}\{H_t{}^q; N; H_s{}^q\}, & \{H_t{}^q; N; h_s{}^j\}, & \{H_t{}^q; N; L\}\\ \{h_t{}^r; N; H_s{}^q\}, & \{h_t{}^r; N; h_s{}^j\}, & \{h_t{}^r; N; L\}\\ \{H_s{}^q; N; L\}, & \{h_s{}^j; N; L\}, & 0\end{vmatrix}}{\begin{vmatrix}\{H_t{}^q; N; H_s{}^q\}, & \{H_t{}^q; N; h_s{}^j\}\\ \{h_t{}^r; N; H_s{}^q\}, & \{h_t{}^r; N; h_s{}^j\}\end{vmatrix}}Z^q. \tag{22}$$

Excluding the composition dependence of the diffusion coefficient the result for the mass current is given with sufficient accuracy by the zero-order functions $H_s{}^q$. Consequently we evaluate the brackets $\{H_r{}^q; N; H_s{}^q\}$. For the case $r \neq s$ we have,

$$\{H_r{}^q; N; H_s{}^q\} = n_r n_s \left(\frac{m_r+m_s}{m_r m_s}\right)^{\frac{1}{2}} [H_r{}^q, H_s{}^q]_{r,s} + n_q n_s \left(\frac{m_q+m_s}{m_q m_s}\right)^{\frac{1}{2}} [H_r{}^q, H_s{}^q]_{q,s}$$

$$+ n_q n_r \left(\frac{m_q+m_r}{m_q m_r}\right)^{\frac{1}{2}} [H_r{}^q, H_s{}^q]_{q,r} + \sum_{t \neq s,r} n_q n_t \left(\frac{m_q+m_t}{m_q m_t}\right)^{\frac{1}{2}} [H_r{}^q, H_s{}^q]_{q,t}. \tag{23}$$

And for the case $r = s$,

$$\{H_t{}^q; N; H_r{}^q\} = \sum_{s=1}^{N} n_s n_r \left(\frac{m_s+m_r}{m_s m_r}\right)^{\frac{1}{2}} [H_r{}^q, H_r{}^q]_{r,s} + \sum_{t \neq r} n_t n \left(\frac{m_t+m_r}{m_q m_r}\right)^{\frac{1}{2}} [H_r{}^q, H_r{}^q]_{t,q}. \tag{24}$$

There exist the following relations which serve to evaluate the mixed brackets

$$[\xi_r, \xi_r]_{r,s} = \frac{8}{3}\pi^{7/2} \frac{m_s}{m_r+m_s} \overset{1,5}{P}_{q,5}(1), \tag{25}$$

$$[\xi_r, \xi_s]_{r,s} = -\frac{8}{3}\pi^{7/2} \frac{(m_r m_s)^{\frac{1}{2}}}{m_r+m_s} \overset{1,5}{P}_{r,s}(1), \tag{26}$$

where the definition of the function $P_{1,2}{}^{1,5}(1)$ is that of Enskog[5] with the modifications due to statistics noted in H.U.

Also we have

$$\{H_r{}^q; N; L_q\} = -\pi^{\frac{3}{2}}/2\rho_q. \tag{27}$$

It is to be noted that the statistical density dependence is ignored as well as the interference effect (H.U.) in the expression for the brackets. Only the effect in the cross section is included in the form given. One obtains for the mixed brackets the expression

$$\underset{r \neq s}{\{H_r{}^q; N; H_s{}^q\}} = -\frac{8}{3}\pi^{7/2} \frac{\overset{1,5}{P}_{r,s}(1)}{(m_r m_s(m_r+m_s))^{\frac{1}{2}}} + \frac{8}{3}\pi^{7/2} \left(\frac{\rho_s+\rho_q}{\rho_q}\right) \frac{\overset{1,5}{P}_{s,q}(1)}{[m_s m_q(m_s+m_q)]^{\frac{1}{2}}}$$

$$+ \frac{8}{3}\pi^{7/2} \left(\frac{\rho_r+\rho_q}{\rho_q}\right) \frac{\overset{1,5}{P}_{r,s}(1)}{[m_r m_q(m_r+m_q)]^{\frac{1}{2}}} + \frac{8}{3}\pi^{7/2} \sum_{t \neq s,r} \frac{\rho_t}{\rho_q} \frac{\overset{1,5}{P}_{t,q}(1)}{[m_t m_q(m_t+m_q)]^{\frac{1}{2}}}, \tag{28}$$

$$\{H_r{}^q; N; H_r{}^q\} = \frac{(\rho_q+\rho_r)^2}{\rho_q \rho_r} \frac{\frac{8}{3}\pi^{7/2} \overset{1,5}{P}_{q,r}(1)}{[m_q m_r(m_q+m_r)]^{\frac{1}{2}}} + \sum_{s \neq q,r} \frac{\frac{\rho_s}{\rho_r} \cdot \frac{8}{3}\pi^{7/2} \overset{1,5}{P}_{r,s}(1)}{[m_r m_s(m_r+m_s)]^{\frac{1}{2}}} + \sum_{t \neq r} \frac{\rho_t}{\rho_q} \frac{8}{3}\pi^{7/2} \overset{1,5}{P}_{t,q}(1). \tag{29}$$

It is to be noted here that the coefficient of mass diffusion for two gases is given by

$$D_{12} = \frac{3}{16}\left(\frac{kT}{2\pi}\right)^{\frac{1}{2}} \frac{[m_1 m_2(m_1+m_2)]^{\frac{1}{2}}}{\rho_1+\rho_2} \cdot \frac{1}{\overset{1,5}{P}_{1,2}(1)}. \tag{30}$$

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[5] Reference 1, p. 91.

One may therefore express the brackets in term of the binary diffusion coefficients as follows,

$$\{H_r{}^q;\underset{r\neq s}{N};H_s{}^q\}=\frac{\pi^3}{2}\left(\frac{kT}{2}\right)^{\frac{1}{2}}\left[\frac{-1}{D_{r,s}(\rho_r+\rho_s)}+\frac{1}{\rho_qD_{q,s}}+\sum_{t\neq s,r}\frac{\rho_t}{\rho_q}\frac{1}{D_{t,q}(\rho_t+\rho_q)}+\frac{1}{\rho_qD_{q,r}}\right], \tag{31}$$

$$\{H_r{}^q;N;H_r{}^q\}=\frac{\pi^3}{2}\left(\frac{kT}{2}\right)^{\frac{1}{2}}\left[\frac{(\rho_q+\rho_r)}{\rho_q\rho_r}\cdot\frac{1}{D_{q,r}}+\sum_{s\neq q,r}\frac{\rho_s}{\rho_r}\cdot\frac{1}{D_{r,s}(\rho_r+\rho_s)}+\sum_{t\neq r}\frac{\rho_t}{\rho_q}\frac{1}{D_{t,q}(\rho_t+\rho_q)}\right]. \tag{32}$$

One therefore obtains for the mass current of the qth gas component into the mixture of which it is a member, the determinantal form,

$$J_\rho{}^q=(2kT)^{\frac{1}{2}}\rho_q\frac{\left|\begin{array}{cc}\frac{\pi^3}{2}\left(\frac{kT}{2}\right)^{\frac{1}{2}}\left[\begin{array}{c}-\frac{1}{D_{r,s}(\rho_r+\rho_s)}+\frac{1}{\rho_qD_{q,s}}+\frac{1}{\rho_qD_{q,r}}\\ +\sum\limits_{t\neq s,r}\frac{\rho_t}{\rho_q}\frac{1}{D_{t,q}}(\rho_t+\rho_q)^{-1}\end{array}\right] & \vdots\;\frac{-\pi^{\frac{3}{2}}}{2\rho_q}\\ \cdots\cdots\cdots & \ddots\;\vdots\\ -\frac{\pi^{\frac{3}{2}}}{2\rho_q}\cdots\cdots\cdots & 0\end{array}\right|}{\left|\frac{\pi^3}{2}\left(\frac{kT}{2}\right)^{\frac{1}{2}}\left[\begin{array}{c}-\frac{1}{D_{r,s}(\rho_r+\rho_s)}+\frac{1}{\rho_qD_{q,s}}+\frac{1}{\rho_qD_{q,r}}\\ +\sum\limits_{t\neq s,r}\frac{\rho_t}{\rho_q}\frac{1}{D_{t,q}(\rho_t+\rho_q)}\end{array}\right]\right|}\frac{\left(\frac{\partial p^q}{\partial \chi}-\rho_qX_{qx}\right)}{(kT)}. \tag{33}$$

In the above only the bracket form for $r\neq s$ has been used, but it must be remembered that the diagonal elements of the determinant require the expression (32). The diffusion coefficient itself is just the coefficient of $(\partial p^q/\partial x-\rho_qX_{qx})/kT$ in $J_\rho{}^q$. From the form it may be perceived that no explicit temperature dependence exists, since the determinant in the numerator has the last row and column free of temperature dependence. Likewise the factor π will cancel. Hence the coefficient of the gas q may be written,

$$\overset{*\rho,\,q}{D}_{1,2,\cdots N}=-\frac{\left|\begin{array}{cc}\left[-\frac{1}{D_{r,s}(\rho_r+\rho_s)}+\frac{1}{\rho_q}\left(\frac{1}{D_{q,s}}+\frac{1}{D_{q,r}}\right)+\sum\limits_{t\neq s,r}\frac{\rho_t}{\rho_q}\frac{1}{D_{t,q}(\rho_t+\rho_q)}\right] & \begin{array}{c}-1\\ \vdots\end{array}\\ -1\cdots\cdots\cdots\cdots & 0\end{array}\right|}{\left\|\left[-\frac{1}{D_{r,s}(\rho_r+\rho_s)}+\frac{1}{\rho_q}\left(\frac{1}{D_{q,s}}+\frac{1}{D_{q,r}}\right)+\sum\limits_{t\neq s,r}\frac{\rho_t}{\rho_q}\frac{1}{D_{t,q}(\rho_t+\rho_q)}\right]\right\|}. \tag{34}$$

For the case of three gases which is very nearly the case for experiments of diffusion of gases into air the result expanded is,

$$\overset{*\rho,\,3}{D}_{1,2}=\left(\frac{\rho_1+\rho_2}{\rho^2}\right)\left\{\frac{(\rho_1+\rho_2)(\rho_1+\rho_3)(\rho_2+\rho_3)D_{31}D_{32}+\rho_3\rho_2(\rho_3+\rho_2)D_{32}D_{12}+\rho_3\rho_1(\rho_3+\rho_1)D_{31}D_{12}}{\rho_3(\rho_1+\rho_2)D_{12}+\rho_2(\rho_1+\rho_3)D_{31}+\rho_1(\rho_3+\rho_2)D_{32}}\right\}. \tag{35}$$

The coefficient (35), just derived, as well as (34) is not the coefficient observed which corresponds to the binary diffusion coefficient, but must be changed by the factor,

$$\overset{*\rho,\,3}{D}_{1,2}\left(\frac{\rho}{\rho_1+\rho_2}\right)=\overset{3,\,\rho}{D}_{1,2}, \tag{36a}$$

and in general,

$$D_{1,2\cdots N}^{\rho,q}=\overset{*}{D}{}_{1,2\cdots N}^{\rho,q}\left(\frac{\rho}{\rho-\rho_q}\right). \tag{36b}$$

It is essential to recognize here that the coefficients given are taken as giving the mass current when multiplied into the gradient of pressure or particle density, and not the mass density. Likewise these coefficients are not with respect to the velocity of the mixture, but the mass velocity. If a steady state of pressure is to be maintained in an experiment of the Loschmidt type, the total particle current is zero and hence the diffusion measured with respect to a stationary partition must be compared with the coefficient calculated with respect to the particle velocity. Thus what must be calculated is,

$$n_q\left\{U_q-\sum_{s=1}^{N}\frac{n_sU_s}{\sum_{t=1}^{N}n_t}\right\}=J_n{}^q. \tag{37}$$

This expression is readily evaluated since the function $L_q\equiv L_q{}'$, $\cdots$ $L_q{}^N$ has already been obtained. One obtains

$$J_n{}^q=n_q\left[\int\frac{f_q{}^{\circ}(1+\theta_qf_q{}^{\circ})\chi^qU_qd\varphi_q}{n_q}-\sum_{s=1}^{N}\int\frac{f_s{}^{\circ}(1+\theta_sf_s{}^{\circ})}{n_s}\chi^sU_sd\varphi_s\frac{n_s}{n}\right] \tag{38}$$

or

$$J_n{}^q=n_q\left[\int\frac{f_q{}^{\circ}(1+\theta_qf_q{}^{\circ})}{F_{\frac{1}{2}}(A_q)}\frac{L^q\xi^q}{(m_q)^{\frac{1}{2}}}dw_q-\sum_{1}^{N}\frac{\int f_s{}^{\circ}(1+\theta_sf_s{}^{\circ})}{F_{\frac{1}{2}}(A_s)}\frac{L^s\xi^s}{(m_s)^{\frac{1}{2}}}dw_s\frac{n_s}{n}\right]\left(\frac{2}{kT}\right)^{\frac{1}{2}}Z^q, \tag{39}$$

where

$$L^q=\sum_{s\neq q}\beta_0{}^s\frac{\xi^q}{n_q(m_q)^{\frac{1}{2}}} \tag{40a}$$

$$L^r=-\beta_0{}^r\frac{\xi^r}{n_r(m_r)^{\frac{1}{2}}}. \tag{40b}$$

One obtains

$$J_n{}^q=n_q\left[\sum\frac{\pi^{\frac{3}{2}}}{2\rho_q}\beta_0{}^r\frac{[\rho_r(n-n_q)+n_r\rho_q]}{n\rho_r}\right]. \tag{41}$$

To obtain the diffusion coefficient which corresponds to (34), one replaces in the numerator determinant the last row by the elements,

$$-\left\{\frac{\rho_r(n-n_q)+n_r\rho_q}{n\rho_r}\right\};\ r\neq q. \tag{42}$$

In deriving the expression for the diffusion with pressure gradients on all components, with constant total pressure, one may use the same basic set of functions $H_s{}^q$ to evaluate the perturbations. The expression for $\{H_s{}^q; N; L_s\}$ are changed in the determinant, but the remaining elements remain unchanged in form and hence the successive contributions to the diffusion are easily summable. The new brackets are,

$$\{H_r{}^q; N; L_s\}=0;\quad r\neq s,\qquad \{H_s{}^q; N; L_s\}=\pi^{\frac{3}{2}}/2\rho_s. \tag{43}$$

Construction of the form $\{L_s; N; L_q\}$ then leads to the replacement of the last column in the numerator determinant of $-\pi^{\frac{3}{2}}Z^q/2\rho_q$ by,

$$-\frac{\pi^{\frac{3}{2}}}{2\rho_q}Z^q, \cdots \left(\frac{\pi^{\frac{3}{2}}}{2\rho_s}Z^s - \frac{\pi^{\frac{3}{2}}}{2\rho_q}Z^q\right), \frac{-\pi^{\frac{3}{2}}Z^q}{2\rho_q}, \cdots. \tag{44}$$

Summing for the last column and row, they appear as

$$\left|\begin{array}{cccc} & & & \frac{\pi^{\frac{3}{2}}}{2}\left[\frac{1}{\rho_1}Z^1 - \frac{1}{\rho_q}Z^q\right] \\ & & & \frac{\pi^{\frac{3}{2}}}{2}\left[\frac{1}{\rho_2}Z^2 - \frac{1}{\rho_q}Z^q\right] \\ & & & \vdots \\ & & & \frac{\pi^{\frac{3}{2}}}{2}\left[\frac{1}{\rho_{q-1}}Z^{q-1} - \frac{1}{\rho_q}Z^q\right] \\ & & & \frac{\pi^{\frac{3}{2}}}{2}\left[\frac{1}{\rho_{q+1}}Z^{q+1} - \frac{1}{\rho_q}Z^q\right] \\ & & & \vdots \\ & & & \frac{\pi^{\frac{3}{2}}}{2}\left[\frac{1}{\rho_N}Z^N - \frac{1}{\rho_q}Z^q\right] \\ -\frac{\pi^{\frac{3}{2}}}{2\rho_q}, & -\frac{\pi^{\frac{3}{2}}}{2\rho_q}, & \cdots\cdots\cdots\cdots & 0 \end{array}\right|. \tag{45}$$

For the case of 3 gases, if one assumes that $Z' = -Z^3\rho_1/(\rho_1 + {}_2)$ and that $Z^2 = -Z^3\rho_2/(\rho_1+\rho_2)$ one obtains the factor $\rho/(\rho-\rho_3)$ given in (36). The general factor follows from the same hypothesis for the various z_i. It would be necessary to justify the values given above in order to claim validity for the coefficients (36), for a given experiment. In general, however, the pressure variations are arbitrary, as well as the forces per unit mass for each component.

In (45) the elements of the last row replaced by (42) yield the expression desired to represent the number of particle which would diffuse through a stationary cross-sectional area in an enclosed vessel of the Loschmidt experiment, provided, with no external forces, we set

$$\sum_{s=1}^{N} Z^s = 0.$$

For the case of three gases one may write

$$-kTJ_\rho{}^3 = \left(\frac{1}{\rho_2}Z^2 - \frac{1}{\rho_3}Z^3\right)\left\{-\frac{1}{\rho_1 D_{1,2}} - \frac{1}{\rho_1 D_{3,1}} + \frac{1}{(\rho-\rho_1)D_{3,2}}\right\}\Big/\Delta$$

$$+\left(\frac{1}{\rho_1}Z^1 - \frac{1}{\rho_3}Z^3\right)\left\{\frac{-1}{\rho_2 D_{1,2}} + \frac{1}{(\rho-\rho_2)D_{3,1}} \frac{-1}{\rho_2 D_{3,2}}\right\}\Big/\Delta. \tag{46}$$

Also

$$-kTJ_n^3=\left(\frac{1}{\rho_2}Z^2-\frac{1}{\rho_3}Z^3\right)\left\{-\left(\frac{n_1+n_2}{n}\right)\frac{\rho}{\rho_1}\frac{1}{(\rho_1+\rho_2)}\cdot\frac{1}{D_{1,2}}+\frac{\rho}{n}\cdot\frac{n_1}{\rho_1}\cdot\frac{1}{(\rho_3+\rho_2)}\cdot\frac{1}{D_{3,2}}-\frac{1}{D_{3,1}}\cdot\frac{\rho n_2}{n\rho_2\rho_1}\right\}\Big/m_3\Delta$$

$$+\left(\frac{1}{\rho_1}Z'-\frac{1}{\rho_3}Z^3\right)\left\{-\left(\frac{n_1+n_2}{n}\right)\frac{\rho}{\rho_2}\cdot\frac{1}{(\rho_1+\rho_2)}\cdot\frac{1}{D_{1,2}}-\frac{\rho}{n}\cdot\frac{n_1}{\rho_1\rho_2}\cdot\frac{1}{D_{3,2}}+\frac{\rho}{n}\cdot\frac{n_2}{\rho_2}\cdot\frac{1}{(\rho_3+\rho_1)}\cdot\frac{1}{D_{3,1}}\right\}\Big/m_3\Delta, \quad (47)$$

where

$$\Delta=\frac{1}{D_{3,1}D_{3,2}D_{1,2}}\frac{\rho^2}{\rho_1\rho_2\rho_3(\rho_3+\rho_1)(\rho_3+\rho_2)(\rho_1+\rho_2)}[\rho_3(\rho_1+\rho_2)D_{1,2}+\rho_2(\rho_3+\rho_1)D_{3,1}+\rho_1(\rho_3+\rho_2)D_{3,2}]. \quad (48)$$

It is perhaps of some interest to show that in an experiment of the Loschmidt type, diffusion may occur even when the gradient of density of the gas in question is zero. The effect, like thermal diffusion, is due to differences in mass and cross sections of the remaining components. This diffusion is the analog of the osmotic diffusion of liquids. To show this point, let us set, $Z^3=0$ and $Z^1=-Z^2$. Then

$$J_\rho^3=\frac{-D_{1,2}\dfrac{\rho_3(\rho_1+\rho_2)}{\rho}[D_{3,2}(\rho_3+\rho_2)-D_{3,1}(\rho_3+\rho_1)]\left(\dfrac{Z^1}{kT}\right)}{[\rho_3(\rho_1+\rho_2)D_{1,2}+\rho_2(\rho_3+\rho_1)D_{3,1}+\rho_1(\rho_3+\rho_2)D_{3,2}]} \quad (49)$$

and

$$J_n^3=\frac{-D_{1,2}\dfrac{\rho_3(\rho_1+\rho_2)}{nm_3}\left[\dfrac{D_{3,2}(\rho_3+\rho_2)}{m_2}-\dfrac{D_{3,1}(\rho_3+\rho_1)}{m_1}\right]\left(\dfrac{Z^1}{kT}\right)}{[\rho_3(\rho_1+\rho_2)D_{1,2}+\rho_2(\rho_3+\rho_1)D_{3,1}+\rho_1(\rho_3+\rho_2)D_{3,2}]}. \quad (50)$$

For the special case when $S_{1,2}\rightarrow 0$,

$$J_n^3=-\frac{\dfrac{3}{8}\left(\dfrac{kT}{2\pi}\right)^{\frac{1}{2}}(kT)}{P}\left\{\left(\frac{m_3+m_2}{m_3m_2}\right)^{\frac{1}{2}}S_{3,2}^{-2}-\left(\frac{m_3+m_1}{m_3m_1}\right)^{\frac{1}{2}}S_{3,1}^{-2}\right\}\left(\frac{Z^1}{kT}\right), \quad (51)$$

where P is the total pressure.

In (51) the binary coefficients have been given the classical values for elastic spheres. The diffusion initially set up, produces an opposing pressure gradient which then sets up a diffusion current in the opposite direction restoring the initial constant density of the third component. This would necessarily imply that the currents, one and two, would alternately exceed one another. The effect initially, would be large and decrease as the distributions of the first two components tended toward spatial uniformity.

In conclusion it may be emphasized that all measurements on mixtures of three or more components are dependent on the density ratios as well as the total densities, although the former dependence is not particularly strong. This dependence is quite apart from the composition dependence taken into account by the consideration of further terms in the approximation to the distribution function.

APPENDIX

In view of the fact that some change in notation between this paper and H.U. exists, the following equations are given from H.U. as numbered in that paper, and the changes noted.

$$\frac{f_i^{\circ 2}}{A_i\exp(-\tau_i^2)}\left[\frac{1}{c_i^{\frac{1}{2}}}\frac{1}{T}\xi_{i\alpha}\frac{\partial T}{\partial x_\alpha}\left(\tau_i^2-\frac{5}{2}\frac{p^i}{n_ikT}\right)+\left(\xi_{i\alpha}\xi_{i\beta}-\frac{\tau_i^2}{3}\delta_{\alpha\beta}\right)\left(\frac{\partial U_\alpha}{\partial x_\beta}+\frac{\partial U_\beta}{\partial x_\alpha}\right)\right.$$

$$\left.+\frac{2c_i^{\frac{1}{2}}}{\rho_i}\xi_{i\alpha}\left\{\left(\frac{\partial p^i}{\partial x_\alpha}-\rho_iX_{i\alpha}\right)-\frac{\rho_i}{\rho}\sum_{j=1}^{N}\left(\frac{\rho p_j}{\partial x_\alpha}-\rho_jX_{j\alpha}\right)\right\}\right]=-\sum_{j=1}^{N}I_{ij}(\chi). \quad (28)$$

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

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

$$J_{ij}(\chi)=F_{\frac{1}{2}}^{-1}(A_i)F_{\frac{1}{2}}^{-1}(A_j)\int dw_j\int\gamma_{ij}\omega_{ij}(\theta,\alpha)d\Omega\cdot f_i^{\circ\prime}f_j^{\circ\prime}\cdot(1+\theta_if_i^{\circ})(1+\theta_jf_j^{\circ})(\chi_i+\chi_j-\chi_i'-\chi_j'). \tag{30}$$

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,

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

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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

THERMAL 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,[1] 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))*

$$\frac{f_j^{\circ 2}}{A_j}\exp(\tau_j^2)\frac{1}{c_j^{\frac{1}{2}}}\cdot\frac{1}{T}\xi_j\frac{\partial T}{\partial x}\left(\tau_j^2-\frac{5}{2}\frac{p^i}{n_jkT}\right)=\sum_{s=1}^{N}I_{js}\{\chi^j+\chi^s\}, \tag{1}$$

where the symbolism is that of (I).

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[1] Furry, Jones and Onsager, Phys. Rev. **55**, 1083 (1939).

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