respectively, those numbering beyond n being unsigned. Considered in terms of various dimensions n, we may set up the following matrix correspondences.

(1)

$$\begin{array}{lcc} & \text{initial representative} \rightarrow & \text{resultant representative} \\ \boldsymbol{\psi}(x): & \left\{ \begin{matrix} \text{const.} \\ \langle x_1' | \rangle \\ \langle x_1' x_2' | \rangle \\ \cdot \\ \cdot \\ \cdot \end{matrix} \right\} & \left\{ \begin{matrix} \langle x | \rangle \\ \sqrt{2} \langle x x_1' | \rangle \\ \sqrt{3} \langle x x_1' x_2' | \rangle \\ \cdot \\ \cdot \\ \cdot \end{matrix} \right\} \end{array}$$

(2)

$$\begin{array}{lcc} \boldsymbol{\psi}(x)\boldsymbol{\psi}(x'): & \left\{ \begin{matrix} \text{const.} \\ \langle x_1' | \rangle \\ \langle x_1' x_2' | \rangle \\ \cdot \\ \cdot \\ \cdot \end{matrix} \right\} & \left\{ \begin{matrix} (2\cdot 1)^{\frac{1}{2}} \langle x x' | \rangle \\ (3\cdot 2)^{\frac{1}{2}} \langle x x' x_1' | \rangle \\ (4\cdot 3)^{\frac{1}{2}} \langle x x' x_1' x_2' | \rangle \\ \cdot \\ \cdot \\ \cdot \end{matrix} \right\} \end{array}$$

etc.

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Phenomenological Theory of Transport Processes in Fluids

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In this article a general theory of transport processes in fluids, developed from equations of hydrodynamics and thermodynamics which have been generalized for application to multicomponent systems, is presented. The equations for the flow of entropy and masses of components of the fluid, obtained from the local entropy dissipation, are used to treat the processes of viscosity, mobility, diffusion, electrical and thermal conductance, thermal transpiration, thermal diffusion, and the homogeneous thermoelectric effect. Reciprocal relations and other properties of the coefficients associated with each process are obtained and also inter-relationships between the coefficients of the various processes. The special conditions for the steady state, the state of pure thermal conduction, and the state of equilibrium are considered. Investigation of the steady state in thermal diffusion indicates that mass flow may persist, contrary to the usual assumption in treatment of experimental data.

VARIOUS attempts have been made to provide a phenomenological theory of specific, irreversible processes in fluids. One of the most recent appears in the thesis of S. R. de Groot.[1] The method there employed appeared susceptible to generalization into an inclusive theory of transport phenomena in fluids. Such a theory is presented here. In its development will be found results differing materially from those of de Groot.

DERIVATION OF THE EXPRESSION FOR ENTROPY DISSIPATION

Let us consider the hydrodynamic motion of a fluid composed of several constituents. The equation of continuity for the ith constituent is

$$\partial \rho_i / \partial t + \nabla \cdot \rho_i \mathbf{v}_i = 0, \tag{1}$$

or

$$d\rho_i / dt + \rho_i \nabla \cdot \mathbf{v}_i = 0, \tag{2}$$

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[1] S. R. de Groot, *L'Effet Soret. Diffusion Thermique dans Les Phases Condenseés* (N. V. Noord-Hollandsche Uitgevers Maatschappij, Amsterdam, Holland, 1945).

where

$$d/dt=\partial/\partial t+\mathbf{v}_i\cdot\boldsymbol{\nabla} \tag{3}$$

is the "mobile operator" or time derivative following the motion of the ith constituent, which has a density ρ_i and velocity $\mathbf{v}_i$ relative to the containing vessel.

In order to write the equation of motion we shall need the expression for the partial stress tensor for the ith constituent. This will be obtained by a generalization of the method for determining the stress tensor for a one-component fluid.[2] The total stress tensor $\boldsymbol{\Psi}$ is given by the sum of the partial stress tensors $\boldsymbol{\Psi}_i$ for the various constituents in the fluid. Also for each constituent we write down a rate-of-pure-strain tensor $\boldsymbol{\Phi}_i$.

$$\boldsymbol{\Psi}_i=\begin{pmatrix} P_i & W_i & V_i \\ W_i & Q_i & U_i \\ V_i & U_i & R_i \end{pmatrix}$$

and

$$\boldsymbol{\Phi}_i=\begin{pmatrix} a_i & \frac{1}{2}h_i & \frac{1}{2}g_i \\ \frac{1}{2}h_i & b_i & \frac{1}{2}f_i \\ \frac{1}{2}g_i & \frac{1}{2}f_i & c_i \end{pmatrix} \tag{4}$$

where

$$a_i=\partial v_{ix}/\partial x,\quad b_i=\partial v_{iy}/\partial y,\quad c_i=\partial v_{iz}/\partial z,$$
$$h_i=\partial v_{ix}/\partial y+\partial v_{iy}/\partial x,$$
$$g_i=\partial v_{ix}/\partial z+\partial v_{iz}/\partial x,$$
$$f_i=\partial v_{iy}/\partial z+\partial v_{iz}/\partial y.$$

For an isotropic fluid, by proper orientation of axes, all the symmetrical tensors $\boldsymbol{\Psi}_i$ and $\boldsymbol{\Phi}_i$ can be diagonalized simultaneously. We define the partial mean hydrostatic pressure for the ith constituent as

$$-3p_i=P_i+Q_i+R_i, \tag{5}$$

so that $\sum_i p_i=p$, the total hydrostatic pressure. The natural generalization for a system of several constituents of the relationships between the components of the stress tensor and the components of the rate-of-pure-strain tensor is

$$\begin{aligned} P_i&=-p_i+\textstyle\sum_j\lambda_{ij}(a_j+b_j+c_j)+\sum_j 2\eta_{ij}a_j,\\ Q_i&=-p_i+\textstyle\sum_j\lambda_{ij}(a_j+b_j+c_j)+\sum_j 2\eta_{ij}b_j,\\ R_i&=-p_i+\textstyle\sum_j\lambda_{ij}(a_j+b_j+c_j)+\sum_j 2\eta_{ij}c_j, \end{aligned} \tag{6}$$

since motion imparted to constituent i will be accompanied by motion of the other constituents in the same direction. Therefore

$$\lambda_{ij}=-\tfrac{2}{3}\eta_{ij}$$

so that

$$\boldsymbol{\Psi}_i=-p_i\mathbf{I}+\textstyle\sum_j 2\eta_{ij}(\boldsymbol{\Phi}_j-\frac{1}{3}\mathbf{I}\boldsymbol{\nabla}\cdot\mathbf{v}_j), \tag{7}$$

where $\mathbf{I}$ is the unit tensor. Let us write

$$\boldsymbol{\Psi}_i=-p_i\mathbf{I}+\mathbf{X}_i, \tag{8}$$

where the tensor $\mathbf{X}_i$ is given by

$$\mathbf{X}_i=\textstyle\sum_j 2\eta_{ij}(\boldsymbol{\Phi}_j-\frac{1}{3}\mathbf{I}\boldsymbol{\nabla}\cdot\mathbf{v}_j). \tag{9}$$

It can readily be shown that

$$\begin{aligned}(\mathbf{X}_i\cdot\boldsymbol{\nabla})\cdot\mathbf{v}_i=\textstyle\sum_j 2\eta_{ij}\{&(a_i-\tfrac{1}{3}\boldsymbol{\nabla}\cdot\mathbf{v}_i)(a_j-\tfrac{1}{3}\boldsymbol{\nabla}\cdot\mathbf{v}_j)+(b_i-\tfrac{1}{3}\boldsymbol{\nabla}\cdot\mathbf{v}_i)(b_j-\tfrac{1}{3}\boldsymbol{\nabla}\cdot\mathbf{v}_j)\\ &+(c_i-\tfrac{1}{3}\boldsymbol{\nabla}\cdot\mathbf{v}_i)(c_j-\tfrac{1}{3}\boldsymbol{\nabla}\cdot\mathbf{v}_j)+\tfrac{1}{2}(h_ih_j+g_ig_j+f_if_j)\}\end{aligned} \tag{10}$$

which reduces in the case of a one-component fluid to twice the Rayleigh dissipation function for viscosity.[3]

The equation of motion for the ith constituent can now be written:

$$\rho_i d\mathbf{v}_i/dt=\rho_i\mathbf{F}_i+\boldsymbol{\nabla}\cdot\boldsymbol{\Psi}_i, \tag{11}$$

from which we obtain the energy equation,

$$\rho_i\frac{dv_i^2/2}{dt}=\mathbf{F}_i\cdot\rho_i\mathbf{v}_i+\mathbf{v}_i\cdot(\boldsymbol{\nabla}\cdot\boldsymbol{\Psi}_i)=\mathbf{F}_i\cdot\rho_i\mathbf{v}_i+\boldsymbol{\nabla}\cdot(\boldsymbol{\Psi}_i\cdot\mathbf{v}_i)-(\boldsymbol{\Psi}_i\cdot\boldsymbol{\nabla})\cdot\mathbf{v}_i. \tag{12}$$

In these equations $\boldsymbol{\Psi}_i$ is the partial stress tensor of Eqs. (7) and (8) and $\mathbf{F}_i$ is the external force acting on unit mass of substance i in the fluid.

Consider now the three terms on the right of Eq. (12) contributing to the increase of the kinetic

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[2] See L. Page, *Introduction to Theoretical Physics* (D. Van Nostrand Company, Inc., New York, 1935), second edition, p. 254.

[3] Lord Rayleigh, *The Theory of Sound* (Dover Publications, New York, 1896), second revised edition, Vol. II, p. 315.

energy of the fluid element. The first, $\mathbf{F}_i\cdot\rho_i\mathbf{v}_i$, gives the rate at which external forces perform work on the element. If $\mathbf{F}_i$ is derivable from a potential function, then this term gives simply the rate of decrease of potential energy. For an element of volume τ, the second term can be written

$$\int_\tau \boldsymbol{\nabla}\cdot(\boldsymbol{\Psi}_i\cdot\mathbf{v}_i)d\tau=\int_\sigma \mathbf{v}_i\cdot\boldsymbol{\Psi}_i\cdot d\boldsymbol{\sigma}. \tag{13}$$

But $\boldsymbol{\Psi}_i\cdot d\boldsymbol{\sigma}$ is the force acting on surface $d\sigma$ as a result of the partial stress $\boldsymbol{\Psi}_i$, so that $\mathbf{v}_i\cdot\boldsymbol{\Psi}_i\cdot d\boldsymbol{\sigma}$ is the work done per unit time on $d\sigma$ moving with the fluid, without change in size or shape of the fluid element. On the other hand, the third term, $(\boldsymbol{\Psi}_i\cdot\boldsymbol{\nabla})\cdot\mathbf{v}_i$, represents work done on the element in a thermodynamic sense, tending to increase the internal energy E_i by changing size and shape. If we consider as a thermodynamic system a unit mass of constituent i in the fluid, we may therefore write

$$\rho_i dE_i/dt+\boldsymbol{\nabla}\cdot\mathbf{Q}_i=(\boldsymbol{\Psi}_i\cdot\boldsymbol{\nabla})\cdot\mathbf{v}_i, \tag{14}$$

where E_i is the internal energy per unit mass of substance i in the fluid and $\mathbf{Q}_i$ is the heat flow vector for this thermodynamic system. According to Eq. (8)

$$(\boldsymbol{\Psi}_i\cdot\boldsymbol{\nabla})\cdot\mathbf{v}_i=-p_i\boldsymbol{\nabla}\cdot\mathbf{v}_i+(\mathbf{X}_i\cdot\boldsymbol{\nabla})\cdot\mathbf{v}_i, \tag{15}$$

where the second term on the right is given by Eq. (10). Thus,

$$\rho_i dE_i/dt+\boldsymbol{\nabla}\cdot\mathbf{Q}_i=-p_i\boldsymbol{\nabla}\cdot\mathbf{v}_i+(\mathbf{X}_i\cdot\boldsymbol{\nabla})\cdot\mathbf{v}_i. \tag{16}$$

Using Eqs. (14), (12), and (8), we obtain

$$\rho_i dE_i/dt+\boldsymbol{\nabla}\cdot\mathbf{Q}_i=\mathbf{F}_i\cdot\rho_i\mathbf{v}_i-\boldsymbol{\nabla}\cdot(p_i\mathbf{v}_i)+\boldsymbol{\nabla}\cdot(\mathbf{X}_i\cdot\mathbf{v}_i)-\rho_i\frac{dv_i^2/2}{dt}. \tag{17}$$

At this point it is necessary to introduce partial pressures as thermodynamic functions and to develop the relations for the individual constituents of a multi-component system using these convenient functions. The energy E and entropy S per unit mass of system can be written as

$$\rho E=\textstyle\sum_i \rho_i E_i,\quad \rho S=\sum_i \rho_i S_i, \tag{18}$$

where E_i is the energy; S_i, the entropy, per unit mass of substance i; and $\rho=\sum_i\rho_i$ is the total density. But

$$dE=TdS-pd(1/\rho)+\textstyle\sum_i \mu_i d(\rho_i/\rho), \tag{19}$$

where μ_i is the chemical potential or free energy per unit mass of substance i. Therefore,

$$d(\textstyle\sum_i \rho_i E_i/\rho)=Td(\sum_i \rho_i S_i/\rho)-pd(1/\rho)+\sum_i \mu_i d(\rho_i/\rho). \tag{20}$$

Define partial pressure p_i so that

$$E_i=TS_i-p_i(1/\rho_i)+\mu_i. \tag{21}$$

Then

$$\textstyle\sum_i \rho_i E_i/\rho=T\sum_i \rho_i S_i/\rho-\sum_i p_i(1/\rho)+\sum_i \mu_i\rho_i/\rho, \tag{22}$$

$$d(\textstyle\sum_i \rho_i E_i/\rho)=Td(\sum_i \rho_i S_i/\rho)-\sum_i p_i d(1/\rho)+\sum_i \mu_i d(\rho_i/\rho) \\ +(\textstyle\sum_i \rho_i S_i/\rho)dT-1/\rho\sum_i dp_i+\sum_i(\rho_i/\rho)d\mu_i. \tag{23}$$

It is, therefore, consistent to let

$$\textstyle\sum_i p_i=p \tag{24}$$

so that from Eqs. (20), (23), and (18),

$$SdT-(1/\rho)dp+\textstyle\sum_i(\rho_i/\rho)d\mu_i=0, \tag{25}$$

which is the well-known Gibbs-Duhem equation. We shall identify the thermodynamic partial pressures defined by Eq. (21) with the hydrostatic partial pressures of Eq. (5). Differentiation of Eq. (21) gives

$$dE_i = TdS_i - p_i d(1/\rho_i) + S_i dT - (1/\rho_i)dp_i + d\mu_i. \tag{26}$$

But

$$dE_i = TdS_i - p_i d(1/\rho_i) \tag{27}$$

so that

$$S_i dT - (1/\rho_i)dp_i + d\mu_i = 0. \tag{28}$$

From Eqs. (2) and (27) we obtain

$$\rho_i dE_i/dt = \rho_i TdS_i/dt - p_i \nabla \cdot \mathbf{v}_i. \tag{29}$$

Let

$$\begin{aligned} H_i &= E_i + p_i/\rho_i = \mu_i + TS_i, \\ A_i &= E_i - TS_i = \mu_i - p_i/\rho_i, \\ F_i &= E_i - TS_i + p_i/\rho_i = \mu_i, \end{aligned} \tag{30}$$

where H_i, A_i, and F_i are the partial enthalpy, work function, and free energy, respectively, per unit mass of substance i in the system. According to Eq. (27)

$$\begin{aligned} dH_i &= TdS_i + (1/\rho_i)dp_i, \\ dA_i &= -S_i dT - p_i d(1/\rho_i), \\ dF_i &= -S_i dT + (1/\rho_i)dp_i. \end{aligned} \tag{31}$$

The conditions for exactness of the differentials in Eqs. (27) and (31) require that

$$\begin{aligned} (\partial S_i/\partial p_i)_{\rho i} &= 1/\rho_i^2(\partial \rho_i/\partial T)_{S_i}, \\ (\partial S_i/\partial \rho_i)_{p i} &= -1/\rho_i^2(\partial p_i/\partial T)_{S_i}, \\ (\partial S_i/\partial \rho_i)_T &= -1/\rho_i^2(\partial p_i/\partial T)_{\rho i}, \\ (\partial S_i/\partial p_i)_T &= 1/\rho_i^2(\partial \rho_i/\partial T)_{p i}, \end{aligned} \tag{32}$$

so that a set of Maxwell's relations holds for each substance i in the system.

Returning now to consideration of motion of a fluid we combine Eqs. (16) and (17) with Eq. (29).

$$\rho_i TdS_i/dt + \nabla \cdot \mathbf{Q}_i = (\mathbf{X}_i \cdot \nabla) \cdot \mathbf{v}_i = \mathbf{F}_i \cdot \rho_i \mathbf{v}_i - \mathbf{v}_i \cdot \nabla p_i + \nabla \cdot (\mathbf{X}_i \cdot \mathbf{v}_i) - \rho_i \frac{dv_i^2/2}{dt} \tag{33}$$

so that

$$\begin{aligned} T\{\rho_i dS_i/dt + \nabla \cdot (\mathbf{Q}_i/T)\} &= -(\mathbf{Q}_i/T) \cdot \nabla T + (\mathbf{X}_i \cdot \nabla) \cdot \mathbf{v}_i \\ &= -(\mathbf{Q}_i/T) \cdot \nabla T - \mathbf{v}_i \cdot (\nabla p_i - \rho_i \mathbf{F}_i) + \nabla \cdot (\mathbf{X}_i \cdot \mathbf{v}_i) - \rho_i \frac{dv_i^2/2}{dt}. \end{aligned} \tag{34}$$

But the entropy flow vector is defined by

$$\mathbf{S}_i = \mathbf{Q}_i/T. \tag{35}$$

Therefore, if $2\theta_i$ is the local entropy dissipation per unit mass,

$$2\rho_i T\theta_i \equiv T(\rho_i dS_i/dt + \nabla \cdot \mathbf{S}_i). \tag{36}$$

According to the second law of thermodynamics, θ_i cannot assume negative values. Hence,

$$2\rho_i T\theta_i = -\mathbf{S}_i \cdot \nabla T + (\mathbf{X}_i \cdot \nabla) \cdot \mathbf{v}_i \geq 0, \tag{37a}$$

$$2\rho_i T\theta_i = -\mathbf{S}_i \cdot \nabla T - \mathbf{v}_i \cdot (\nabla p_i - \rho_i \mathbf{F}_i) + \nabla \cdot (\mathbf{X}_i \cdot \mathbf{v}_i) - \rho_i \frac{dv_i^2/2}{dt} \geq 0. \tag{37b}$$

Subtraction of Eq. (37b) from Eq. (37a) gives

$$\mathbf{v}_i \cdot (\nabla p_i - \rho_i \mathbf{F}_i - \nabla \cdot \mathbf{X}_i + \rho_i d\mathbf{v}_i/dt) = 0, \tag{38}$$

a result which can also be obtained by combination of Eq. (8) with Eqs. (11) or (12). Summing over the index i we obtain the general relations for local entropy dissipation for hydrodynamic flow. The total dissipation per unit mass of solution at a given point in time and space is the sum of the dissipations for the individual flowing constituents whose motions are confluent at that point. Thus,

$$\rho\theta = \sum_i \rho_i\theta_i. \tag{39}$$

Therefore

$$2\rho T\theta = T(\sum_i \rho_i dS_i/dt + \nabla\cdot\mathbf{S}) \geq 0 \tag{40a}$$

$$= -\mathbf{S}\cdot\nabla T + \sum_i(\mathbf{X}_i\cdot\nabla)\cdot\mathbf{v}_i \geq 0 \tag{40b}$$

$$= -\mathbf{S}\cdot\nabla T - \sum_i \mathbf{v}_i\cdot(\nabla p_i - \rho_i\mathbf{F}_i) + \sum_i \nabla\cdot(\mathbf{X}_i\cdot\mathbf{v}_i) - \sum_i \rho_i\frac{dv_i^2/2}{dt} \geq 0, \tag{40c}$$

where we have written $\sum_i \mathbf{S}_i = \mathbf{S}$, the total entropy flow vector. According to Eq. (35), the total heat flow vector is given by $\mathbf{Q} = T\mathbf{S}$.

We shall use the term "energy dissipation" to indicate the function $T\theta$. The total energy dissipation for an element of fluid of volume τ is obtained from Eq. (40c):

$$-\int_\tau \{\mathbf{S}\cdot\nabla T + \sum_i \mathbf{v}_i\cdot(\nabla p_i - \rho_i\mathbf{F}_i)\}d\tau + \sum_i\int_\sigma \mathbf{v}_i\cdot\mathbf{X}_i\cdot d\boldsymbol{\sigma} - \sum_i\int_\tau \rho_i\frac{dv_i^2/2}{dt}d\tau \geq 0. \tag{41}$$

It can be considered as arising out of three processes. The first volume integral represents dissipation related to transport of heat and mass in the fluid. The other volume integral expresses dissipation associated with deceleration of the fluid element—distribution of its kinetic energy of macroscopic motion among the molecules of the fluid. Finally, the surface integral gives the work done by the viscous forces, acting on the fluid element as though it were a rigid body, i.e., without change in size or shape. (See the interpretation of the surface integral in Eq. (13).)

We now restrict our further discussion by the following assumptions:

(1)

$$\int_\sigma \mathbf{v}_i\cdot\mathbf{X}_i\cdot d\boldsymbol{\sigma} = \int_\tau \rho_i\frac{dv_i^2/2}{dt}d\tau \tag{42a}$$

or

$$\nabla\cdot(\mathbf{X}_i\cdot\mathbf{v}_i) = \rho_i\frac{dv_i^2/2}{dt}. \tag{42b}$$

We are assuming here essentially that the entire acceleration of any fluid element is produced by viscous forces alone, acting on the element as though it were rigid. Thus, we shall not consider the phenomena of "pressure flow" or bulk motion of the fluid, but rather those associated with diffusion of the fluid constituents, generally referred to as transport processes.

(2) The external force is derivable from a potential.

$$\mathbf{F}_i = -\nabla\phi_i. \tag{43}$$

Equation (38) now becomes

$$-\mathbf{v}_i\cdot(\nabla p_i + \rho_i\nabla\phi_i) = (\mathbf{X}_i\cdot\nabla)\cdot\mathbf{v}_i, \tag{44}$$

and the energy dissipation of Eq. (40c) becomes

$$2\rho T\theta = -\mathbf{S}\cdot\nabla T - \sum_i \mathbf{v}_i\cdot(\nabla p_i + \rho\nabla\phi_i) \geq 0. \tag{45}$$

Define

$$\mathbf{J}_i \equiv \rho_i\mathbf{v}_i \quad\text{and}\quad \Pi_i \equiv \mu_i + \phi_i. \tag{46}$$

Then, using Eq. (28) we obtain

$$2\rho T\theta = -(\mathbf{S} + \sum_i S_i\mathbf{J}_i)\cdot\nabla T - \sum_i \mathbf{J}_i\cdot\nabla\Pi_i \geq 0. \tag{47}$$

This expression appears in the form of Onsager's dissipation function for the case of interacting, simultaneous transport processes.[4] Let

$$\mathbf{J}_i = -\sum_j a_{ij}\nabla\Pi_j - b_i\nabla T, \tag{48}$$

$$\mathbf{S} + \sum_i S_i\mathbf{J}_i = -\sum_i b_i\nabla\Pi_i - c\nabla T, \tag{49}$$

where we employ the same coefficients b_i in both equations in conformity with Onsager's reciprocal relations. According to these relations, furthermore,

$$a_{ij} = a_{ji}. \tag{50}$$

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[4] L. Onsager, Phys. Rev. **37**, 405 (1931); **38**, 2265 (1931).

Substitution into Eq. (47) gives

$$\textstyle\sum_{ij} a_{ij}\nabla\Pi_i\cdot\nabla\Pi_j+2\sum_i b_i\nabla\Pi_i\cdot\nabla T+c(\nabla T)^2\geq 0, \quad (51)$$

so that, since the relation must hold for any choice of $\nabla\Pi_i$ and ∇T, the determinant

$$\begin{vmatrix} a_{11} & a_{12} & \cdots & a_{1n} & b_1 \\ a_{12} & a_{22} & \cdots & a_{2n} & b_2 \\ \cdots & & & & \\ a_{1n} & a_{2n} & \cdots & a_{nn} & b_n \\ b_1 & b_2 & \cdots & b_n & c \end{vmatrix} \geq 0 \quad (52)$$

and each of its principal minors must likewise be non-negative. Let

$$b_i=\textstyle\sum_j a_{ij}\sigma_j. \quad (53)$$

Then

$$\begin{aligned} \mathbf{J}_i&=-\textstyle\sum_j a_{ij}(\nabla\Pi_j+\sigma_j\nabla T), \\ \mathbf{S}&=\textstyle\sum_i(\sigma_i-S_i)\mathbf{J}_i-(c-\sum_{ij}a_{ij}\sigma_i\sigma_j)\nabla T, \quad (54) \\ \mathbf{Q}&=\textstyle\sum_i TS_i^*\mathbf{J}_i-\lambda\nabla T, \end{aligned}$$

where $S_i^*=\sigma_i-S_i$ is the entropy of transport per unit mass of substance i and $\lambda=T(c-\sum_{ij}a_{ij}\sigma_i\sigma_j)$ is the coefficient of thermal conductivity. We may easily show by Eq. (52) that $\lambda\geq 0$. Expansion of the determinant in terms of the elements of its last row and last column gives

$$-\textstyle\sum_i b_i(\sum_j b_j a_{ij}^*)+c|a_{mn}|\geq 0,$$

where the asterisk denotes the co-factor of the element a_{ij} in the determinant $|a_{mn}|$. But from Eq. (53),

$$\sigma_i=\textstyle\sum_j b_j a_{ij}^*/|a_{mn}|,$$

so that $c\geq\sum_i b_i\sigma_i=\sum_{ij}a_{ij}\sigma_i\sigma_j$ and therefore $\lambda\geq 0$. Elimination of the coefficients σ_i and c gives

$$\mathbf{J}_i=-\textstyle\sum_j a_{ij}\{\nabla\Pi_j+(S_j+S_j^*)\nabla T\}, \quad (55)$$

$$\mathbf{Q}=-T\textstyle\sum_{ij}a_{ij}S_i^*\nabla\Pi_j-\{T\sum_{ij}a_{ij}S_i^*(S_j+S_j^*)+\lambda\}\nabla T. \quad (56)$$

Alternatively, using Eq. (28) we may write

$$\mathbf{J}_i=-\textstyle\sum_j a_{ij}\{(\nabla p_j)/\rho_j+\nabla\phi_j+S_j^*\nabla T\}, \quad (57)$$

$$\mathbf{Q}=-T\textstyle\sum_{ij}a_{ij}S_i^*\{(\nabla p_j)/\rho_j+\nabla\phi_j\}-(T\sum_{ij}a_{ij}S_i^*S_j^*+\lambda)\nabla T. \quad (58)$$

The physical interpretation of the coefficients a_{ij} is apparent if we write

$$\mathbf{v}_i=-\textstyle\sum_j a_{ij}/\rho_i\{\nabla\Pi_j+(S_j+S_j^*)\nabla T\}. \quad (59)$$

We perceive that

$$a_{ij}=\rho_i U_{ij}, \quad (60)$$

where U_{ij} is the mobility of the ith constituent when the jth constituent is subject to unit force per unit mass. The force on a unit mass of constituent j arising from its presence in a temperature gradient is $-(S_j+S_j^*)\nabla T$ when Π_j is uniform. According to Eq. (52), the determinant $|U_{ij}|=|a_{ij}|/\rho_1\rho_2\cdots\rho_n\geq 0$ and any of its principal minors are likewise non-negative. From Eq. (50), $\rho_i U_{ij}=\rho_j U_{ji}$.

From Eqs. (47), (55), and (54) we find

$$2\rho T\theta=-\textstyle\sum_i \mathbf{J}_i\cdot\{\nabla\Pi_i+(S_i+S_i^*)\nabla T\}+\lambda/T(\nabla T)^2\geq 0,$$

$$2\rho T\theta=\textstyle\sum_{ij}\mathbf{J}_i\cdot\mathbf{J}_j a_{ij}^*/|a_{mn}|+\lambda/T(\nabla T)^2\geq 0,$$

where a_{ij}^* is the co-factor of a_{ij} in the determinant $|a_{mn}|$. The elements of the adjoint determinant

$$r_{ij}=a_{ij}^*/|a_{mn}| \quad (61)$$

are coefficients of flow resistance. The determinant $|r_{ij}|$ and each of its principal minors are non-negative. Also $r_{ij}=r_{ji}$.

$$2\rho T\theta=\textstyle\sum_{ij}r_{ij}\mathbf{J}_i\cdot\mathbf{J}_j+\lambda/T(\nabla T)^2\geq 0. \quad (62)$$

SPECIAL STATES OF THE SYSTEM

An important condition of a flowing fluid is the so-called steady state. From Eqs. (40a) and (47),

$$T(\textstyle\sum_i \rho_i dS_i/dt+\nabla\cdot\mathbf{S})=-(\mathbf{S}+\sum_i S_i\mathbf{J}_i)\cdot\nabla T-\sum_i\mathbf{J}_i\cdot\nabla\Pi_i \quad (63)$$

so that, acording to Eqs. (3) and (30),

$$T\textstyle\sum_i \rho_i\partial S_i/\partial t=-\nabla\cdot\mathbf{Q}-\sum_i\mathbf{J}_i\cdot\nabla(H_i+\phi_i). \quad (64)$$

Also from Eq. (1),

$$\partial\rho_i/\partial t=-\nabla\cdot\mathbf{J}_i. \quad (65)$$

In the steady state $\partial S_i/\partial t=0$ and $\partial\rho_i/\partial t=0$. These conditions defining the steady state are sufficient to require that every property at a given point in the system be independent of time. Therefore

$$\nabla\cdot\mathbf{J}_i=0 \quad\text{and}\quad \nabla\cdot\{\mathbf{Q}+\textstyle\sum_i\mathbf{J}_i(H_i+\phi_i)\}=0. \quad (66)$$

In the case of a closed system the components of $\mathbf{J}_i$ normal to the surface of the fluid must vanish at the surface, so that

$$\int_\tau \nabla\cdot\mathbf{Q}d\tau=0 \tag{67}$$

when integrated over the entire fluid. However, it is important to note that flow of mass in the interior of the fluid and tangential to the surface is not excluded and, moreover, there may even be sources and sinks of heat flow, whose total contribution must, however, vanish. If the system is also adiabatically insulated only tangential components of **Q** as well as of $\mathbf{J}_i$ are possible at the surface. The energy dissipation, of course, need not vanish in the steady state but continues to be given by Eqs. (40b), (47), or (62). Equation (40a) becomes

$$2\rho T\theta=T(\textstyle\sum_i \mathbf{J}_i\cdot\nabla S_i+\nabla\cdot\mathbf{S})\geq 0. \tag{68}$$

The condition $\mathbf{J}_i=0$ throughout the fluid will occur, according to Eqs. (55) and (57) only when

$$\nabla\Pi_j+(S_j+S_j^*)\nabla T =(\nabla p_j)/\rho_j+\nabla\phi_j+S_j^*\nabla T=0 \tag{69}$$

for every j such that $a_{ij}\neq 0$. When every $\mathbf{J}_i=0$, Eq. (69) must hold for all values of j. The system is then in a state of pure thermal conduction. According to Eq. (54),

$$\mathbf{Q}=-\lambda\nabla T \tag{70}$$

which is Fourier's law of heat conduction. From Eq. (63),

$$T(\textstyle\sum_i \rho_i\partial S_i/\partial t+\nabla\cdot\mathbf{S})=-\mathbf{S}\cdot\nabla T\geq 0, \tag{71}$$

so that

$$T\textstyle\sum_i \rho_i\partial S_i/\partial t=-\nabla\cdot\mathbf{Q}=\nabla\cdot(\lambda\nabla T). \tag{72}$$

But

$$\partial S_i/\partial t=(C_{pi}/T)\partial T/\partial t +1/\rho_i^2(\partial\rho_i/\partial T)_{pi}\partial p_i/\partial T \tag{73}$$

where C_{pi} is the partial specific heat at constant partial pressure.

$$\nabla\cdot(\lambda\nabla T)=\textstyle\sum_i \rho_i C_{pi}\partial T/\partial t +\sum_i 1/\rho_i^2(\partial\rho_i/\partial T)_{pi}\partial p_i/\partial T. \tag{74}$$

In the steady state $\nabla\cdot(\lambda\nabla T)=0$. If ∇T is small, λ can be considered constant so that in the steady state the temperature must satisfy Laplace's equation. The state of pure thermal conduction is analogous to the condition of a solid in a temperature gradient but must be relatively rare in a fluid.

It is instructive to consider the case of a pure gas in a temperature gradient in the absence of external forces. If $\mathbf{J}=0$, according to Eq. (69),

$$\nabla p=-\rho S^*\nabla T. \tag{75}$$

If we assume the relation $p=\rho RT$, we find

$$\nabla\ln p=-(S^*/R)\nabla\ln T. \tag{76}$$

Let us suppose the gas is contained in a straight cylindrical tube along whose length is the temperature gradient. Then, as is well known, the phenomenon of thermal transpiration occurs if pressure is sufficiently low so that the mean free path of the molecules is greater than the diameter of the tube. A pressure gradient is established so that

$$d(\ln p)/d(\ln T)=\tfrac{1}{2}. \tag{77}$$

Therefore at this low pressure $S^*=-R/2$. (R is the gas constant per unit mass.) Furthermore, S^* will be constant along the radius of the tube since the properties of the gas are determined throughout by collisions with the wall and not by the infrequent collisions between gas molecules. Now if we increase the pressure of gas in the tube, the wall will affect only a small surface layer of the gas and we can no longer expect S^* to be constant along the radius. With the increase in pressure the thermal transpiration effect disappears. In such a situation Eq. (75) cannot be satisfied and **J** does not vanish. Instead, a circulation of the gas occurs with the surface layer flowing toward the hot end of the tube and a return flow in the interior. All stages between the extremes of maximum pressure gradient with no flow and maximum flow with no pressure gradient are possible depending on the radial variation of S^*. Since we may write

$$\nabla\rho=(\partial\rho/\partial p)\nabla p+(\partial\rho/\partial T)\nabla T, \tag{78}$$

clearly the density gradient should depend only on the coefficient of thermal expansion in the case of $\nabla p=0$. For a liquid we would likewise expect a difference between S^* in the surface and in the interior and the consequent circulation. However, for a liquid we may not be justified in neglecting external forces, particularly in the surface.

The condition of a fluid in which no energy dissipation occurs at any point is the state of equilibrium. According to Eq. (51) this requires that everywhere, for each species i

$$\nabla \Pi_i = 0 \quad \text{and} \quad \nabla T = 0. \tag{79}$$

The temperature and each potential Π_i must be constant throughout the system. This of course implies that $\mathbf{Q}$ and $\mathbf{J}_i$ vanish everywhere. Equilibrium is a special case of the steady state. Equation (79) requires

$$\nabla \mu_i = -\nabla \phi_i \quad \text{or} \quad \nabla p_i = -\rho_i \nabla \phi_i. \tag{80}$$

If, for example, $\nabla \phi_i = g\mathbf{k}$ where $\mathbf{k}$ is the unit vector in the upward Z direction and g is the acceleration of gravity, there results the well-known formula

$$dp_i/dz = -\rho_i g \quad \text{or} \quad dp/dz = -\rho g. \tag{81}$$

Similarly if $\Delta \phi_i = e_i \Delta \psi$ where e_i is the electrical charge per unit mass of substance i and ψ, the electrostatic potential

$$\begin{aligned} \nabla \psi &= -(1/e_i)\nabla \mu_i = -(1/e_i\rho_i)\nabla p_i \\ &= -(1/e\rho)\nabla p, \end{aligned} \tag{82}$$

where $e = \sum_i e_i \rho_i / \rho$ is the total electrical charge per unit mass of fluid.

As is well known, a thermodynamically reversible process is one which occurs without energy dissipation, i.e., the system is in equilibrium throughout the process. Therefore, if we consider two points in the system, A and B, at each moment

$$\Pi_{ia} = \Pi_{ib} \quad \text{and} \quad T_a = T_b \tag{83}$$

or

$$d\Pi_{ia} = d\Pi_{ib} \quad \text{and} \quad dT_a = dT_b \tag{84}$$

so that

$$\begin{aligned} -S_{ia}dT &+ (1/\rho_{ia})dp_{ia} + d\phi_{ia} \\ &= -S_{ib}dT + (1/\rho_{ib})dp_{ib} + d\phi_{ib}. \end{aligned} \tag{85}$$

Thus, consider an isothermal system of two fluid phases A and B where A is the vapor in equilibrium with liquid B. In the absence of external forces

$$(1/\rho_{ia})dp_{ia} = (1/\rho_{ib})dp_{ib}. \tag{86}$$

The general equations of state relating partial pressures and densities are not known. For ideal gases we write

$$p_{ia} = \rho_{ia} RT / M_i \tag{87}$$

and for ideal liquids

$$p_{ia} = p^0_{ia} x_{ib} \text{ (Raoult's law)}, \tag{88}$$

where R is the gas constant per mole; M_i, the molecular weight of substance i; x_{ib}; its mole fraction in the liquid phase; and p^0_{ia}, its vapor pressure in the pure state. From Eqs. (86) and (88)

$$dp_{ib} = (\rho_{ib}/\rho_{ia}) p^0_{ia} dx_{ib} \tag{89}$$

which relates the partial pressure of a component of an ideal liquid solution to its mole fraction in the liquid.

Data obtained for non-ideal solutions are generally expressed in the form

$$d\Pi_i = (RT/M_i)d(\ln \rho_i \gamma_i), \tag{90}$$

where γ_i is an appropriate activity coefficient chosen so that under those conditions for which the solution approaches ideality, γ_i approaches unity. Lumped into the factor γ_i may be the effect of external forces, as in the treatment of electrolytes, for example. In this case

$$\phi_i = e_i \psi. \tag{91}$$

In the Debye-Hückel theory for dilute electrolytes the identification

$$e_i d\psi = (RT/M_i)d(\ln \gamma_i)$$

is made, so that

$$d\mu_i = (RT/M_i)d(\ln \rho_i),$$

i.e., apart from interionic attractions and repulsions the solution is considered as ideal. It would appear that the use of Eq. (90) for expressing experimental data with an arbitrarily defined "activity coefficient" does much toward obscuring the nature of the quantities measured. A more direct method would be to seek equations of state of the form

$$\Pi_i = \Pi_i(\rho_1, \rho_2, \cdots \rho_n, T), \tag{92}$$

which in the absence of external forces is equivalent to

$$\mu_i=\mu_i(\rho_1, \rho_2, \cdots \rho_n, T)$$

or

$$p_i=p_i(\rho_1, \rho_2, \cdots \rho_n, T), \tag{93}$$

and in the presence of external forces requires also knowledge of

$$\phi_i=\phi_i(\rho_1, \rho_2, \cdots \rho_n, T). \tag{94}$$

APPLICATION TO PARTICULAR TRANSPORT PROCESSES

Let us now turn to consideration of particular transport processes. We start with isothermal processes. For an isothermal fluid, according to Eqs. (40b) and (10) the energy dissipation is given by

$$\begin{aligned}\textstyle\sum_{ij} 2\eta_{ij}\{ &(a_i-\tfrac{1}{3}\boldsymbol{\nabla}\cdot\mathbf{v}_i)(a_j-\tfrac{1}{3}\boldsymbol{\nabla}\cdot\mathbf{v}_j)\\ &+(b_i-\tfrac{1}{3}\boldsymbol{\nabla}\cdot\mathbf{v}_i)(b_j-\tfrac{1}{3}\boldsymbol{\nabla}\cdot\mathbf{v}_j)\\ &+(c_i-\tfrac{1}{3}\boldsymbol{\nabla}\cdot\mathbf{v}_i)(c_j-\tfrac{1}{3}\boldsymbol{\nabla}\cdot\mathbf{v}_j)\\ &+\tfrac{1}{2}(h_ih_j+g_ig_j+f_if_j)\}\geq 0,\end{aligned} \tag{95}$$

or, if we write $\mathbf{B}_i=\boldsymbol{\Phi}_i-\frac{1}{3}\mathbf{I}\boldsymbol{\nabla}\cdot\mathbf{v}_i$, the dissipation becomes

$$\textstyle\sum_{ij} 2\eta_{ij}\mathbf{B}_i:\mathbf{B}_j\geq 0, \tag{96}$$

where $\mathbf{B}_i:\mathbf{B}_j$ is the double product of the two tensors, i.e., the sum of the principal diagonal elements of the tensor which is the product of $\mathbf{B}_i$ and $\mathbf{B}_j$. Therefore, if we use Eqs. (51) and (62),

$$\begin{aligned}\textstyle\sum_{ij} r_{ij}\mathbf{J}_j\cdot\mathbf{J}_j&=\textstyle\sum_{ij} a_{ij}\boldsymbol{\nabla}\Pi_i\cdot\boldsymbol{\nabla}\Pi_j\\ &=\textstyle\sum_{ij} 2\eta_j\mathbf{B}_i:\mathbf{B}_j=\sum_{ij} 2\eta_{ij}\mathbf{b}_i\cdot\mathbf{b}_j\geq 0,\end{aligned} \tag{97}$$

where $\mathbf{b}_i$ is the vector formed from the three principal diagonal components of $\mathbf{B}_i$ when the coordinate axes are oriented so as to diagonalize $\mathbf{B}_i$. Thus, $\mathbf{b}_i$ is the vector whose components are $a_i-\frac{1}{3}\boldsymbol{\nabla}\cdot\mathbf{v}_i$, $b_i-\frac{1}{3}\boldsymbol{\nabla}\cdot\mathbf{v}_i$, and $c_i-\frac{1}{3}\boldsymbol{\nabla}\cdot\mathbf{v}_i$ referred to a properly oriented set of coordinate axes. Let

$$\mathbf{b}_i=\textstyle\sum_l w_{il}\mathbf{J}_l=-\sum_{lm} w_{il}a_{lm}\boldsymbol{\nabla}\Pi_m, \tag{98}$$

where w_{il} is a quantity with dimensions of (length)^2/mass. Then

$$r_{lm}=\textstyle\sum_{ij} 2\eta_{ij}w_{il}w_{jm}. \tag{99}$$

Since $r_{ij}=r_{ji}$, it follows that $\eta_{ij}=\eta_{ji}$. Furthermore, we see from Eq. (97) that the determinant $|\eta_{ij}|$ and each of its principal minors are non-negative. In particular, for a one-component fluid the viscosity coefficient is non-negative.

Following Onsager[5] we write the generalized form of Fick's law of diffusion for a system of several components as

$$\mathbf{J}_i=-\textstyle\sum_j D_{ij}\boldsymbol{\nabla}\rho_j, \tag{100}$$

where D_{ij} are the coefficients of diffusion. According to Eq. (55) for an isothermal system

$$\mathbf{J}_i=-\textstyle\sum_j a_{ij}\boldsymbol{\nabla}\Pi_j, \tag{101}$$

so that, using a relation of the type of Eq. (92), we obtain

$$D_{ij}=\textstyle\sum_l a_{il}\partial\Pi_l/\partial\rho_j. \tag{102}$$

Therefore,

$$\partial\Pi_l/\partial\rho_j=\textstyle\sum_i r_{li}D_{ij}=\displaystyle\sum_{imn} 2\eta_{mn}w_{ml}w_{ni}D_{ij}. \tag{103}$$

It is interesting to consider this result for the case of self-diffusion of a single perfect gas in the absence of external forces. We find from Eq. (87)

$$\partial\Pi/\partial\rho=2\eta w^2D=RT/M\rho, \tag{104}$$

so that

$$D=RT/2M\rho w^2\eta. \tag{105}$$

The similarity in form of this equation to the equations of Stokes-Einstein[6] and Eyring[7] is at once apparent. From Eqs. (50) and (102) we obtain the reciprocal relations

$$\textstyle\sum_i(\partial\Pi_i/\partial\rho_m)D_{ij}=\sum_i(\partial\Pi_i/\partial\rho_j)D_{im}. \tag{106}$$

The dissipation function for isothermal flow may be written

$$\sum_{ijkl} r_{ij}D_{ik}D_{jl}\boldsymbol{\nabla}\rho_k\cdot\boldsymbol{\nabla}\rho_l\geq 0. \tag{107}$$

Closely related to fluid flow is electrolytic conduction. If species i carries an electrical charge e_i per unit mass, then the current density associated with flow of that species is

$$\begin{aligned}\mathbf{I}_i=e_i\mathbf{J}_i&=-\textstyle\sum_j e_ie_ja_{ij}\boldsymbol{\nabla}(\Pi_j/e_j)\\ &=-\textstyle\sum_j L_{ij}\boldsymbol{\nabla}(\Pi_j/e_j).\end{aligned} \tag{108}$$

The coefficients L_{ij} are the coefficients of con-

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[5] L. Onsager, Ann. N. Y. Acad. Sci. **46**, 241 (1945).

[6] A. Einstein, Ann. d. Physik **19**, 289 (1906).

[7] S. Glasstone, K. J. Laidler, and H. Eyring, *Theory of Rate Processes* (McGraw-Hill Book Company, Inc., 1941), first edition, p. 519.

ductance. The dissipation function becomes

$$\sum_{ij}(r_{ij}/e_ie_j)\mathbf{I}_i\cdot\mathbf{I}_j=\sum_{ij}(r_e)_{ij}\mathbf{I}_i\cdot\mathbf{I}_j\geq 0, \tag{109}$$

which is a generalization of the Joule heat. The coefficients $(r_e)_{ij}$ are the coefficients of electrical resistance. Now

$$\nabla\Pi_i/e_i=\sum_j(r_e)_{ij}\mathbf{I}_j, \tag{110}$$

so that if we let $\phi_i=e_i\psi$ where ψ is the electrostatic potential,

$$\nabla(\mu_i/e_i+\psi)=(\nabla p_i)/\rho_ie_i+\nabla\psi=\sum_j(r_e)_{ij}\mathbf{I}_j, \tag{111}$$

which is the generalized form of Ohm's law for fluid solutions. Obviously the determinants $|L_{ij}|$ and $|(r_e)_{ij}|$ as well as each of their principal minors must be non-negative. Also $L_{ij}=L_{ji}$ and $(r_e)_{ij}=(r_e)_{ji}$.

The above conductance equations were obtained under the assumption that every diffusing species carried an electrical charge. More generally, if electrically neutral species are also diffusing, for a charged species i,

$$\mathbf{I}_i=-\sum_j L_{ij}\nabla\Pi_j/e_j-\sum_k e_ia_{ik}\nabla\Pi_k, \tag{112}$$

where $\sum_j$ indicates summation over charged species and $\sum_k$, over neutral. The dissipation function becomes

$$\sum_{ij}(r_e)_{ij}\mathbf{I}_i\cdot\mathbf{I}_j+\sum_{ik}(r_{ik}/e_i)\mathbf{I}_i\cdot\mathbf{J}_k$$
$$+\sum_{kl} r_{kl}\mathbf{J}_k\cdot\mathbf{J}_l\geq 0. \tag{113}$$

The motion of uncharged constituents as well as that of charged constituents may influence the conduction of electricity in fluids. Thus, Eq. (111) becomes

$$\nabla(\mu_i/e_i+\psi)=(\nabla p_i)/\rho_ie_i+\nabla\psi$$
$$=\sum_j(r_e)_{ij}\mathbf{I}_j+\sum_k(r_{ik}/e_i)\mathbf{J}_k. \tag{114}$$

The condition for cessation of current was given in Eq. (82). If the fluid is electrically neutral, we see that although there may be gradients in the chemical potentials and partial pressures of individual species there can be no total pressure gradient. We may write

$$\nabla\psi=-1/e_i\sum_j(\partial\mu_i/\partial\rho_j)\nabla\rho_j, \tag{115}$$

where index j is summed over all components, charged or neutral. Thus in general, we must allow the possibility that existence of a gradient of electrostatic potential in a solution will be accompanied by concentration gradients in neutral as well as charged species.

Let us now consider transport phenomena in non-isothermal systems. Using Eq. (92) we write the mass flow vector of Eq. (55) as

$$\mathbf{J}_i=-\sum_{jl} a_{ij}(\partial\Pi_j/\partial\rho_l)\nabla\rho_l$$
$$-\sum_j a_{ij}(\partial\Pi_j/\partial T+S_j+S_j^*)\nabla T. \tag{116}$$

We may define the thermal diffusion coefficients D_i^T by the equation

$$\mathbf{J}_i=-\sum_j D_{ij}\nabla\rho_j-D_i^T\nabla T. \tag{117}$$

Therefore,

$$D_i^T=\sum_j a_{ij}(\partial\Pi_j/\partial T+S_j+S_j^*)$$
$$=\sum_j a_{ij}[(1/\rho_j)(\partial p_j/\partial T)+\partial\phi_j/\partial T+S_j^*] \tag{118}$$

and

$$D_{ij}=\sum_l a_{il}\partial\Pi_l/\partial\rho_j$$

as in the isothermal case (Eq. (102)), or

$$a_{ij}=\sum_l D_{il}\partial\rho_l/\partial\Pi_j \tag{119}$$

where

$$\rho_l=\rho_l(\Pi_1,\Pi_2,\cdots\Pi_n,T).$$

Substituting Eq. (119) into Eq. (118) we obtain

$$D_i^T=\sum_{jl} D_{il}(\partial\rho_l/\partial\Pi_j)(\partial\Pi_j/\partial T+S_j+S_j^*)$$
$$=\sum_l D_{il}\{-(\partial\rho_l/\partial T)_{\Pi_j}$$
$$+\sum_j(\partial\rho_l/\partial\Pi_j)(S_j+S_j^*)\}. \tag{120}$$

If we define the thermal diffusion ratios as

$$k_l^T=-(\partial\rho_l/\partial T)_{\Pi_j}+\sum_j(\partial\rho_l/\partial\Pi_j)(S_j+S_j^*) \tag{121}$$

we find

$$D_i^T=\sum_l k_l^TD_{il} \tag{122}$$

and

$$\mathbf{J}_i=-\sum_l D_{il}(\nabla\rho_l+k_l^T\nabla T). \tag{123}$$

Under conditions such that mass flow vanishes, i.e., $\mathbf{J}_i=0$ for all species i, in the presence of a temperature gradient (the state described as pure thermal conduction in Eq. (70)), we find the simple relation

$$k_i^T=-d\rho_i/dT \tag{124}$$

so that the thermal diffusion ratios can be determined directly from the observed density gradients, or knowing the ratios one may calculate the density gradients and thus the extent of separation of the components in a temperature gradient. It has been assumed by some authors[8] that in the steady state of gas mixtures subject to a temperature gradient the condition $\mathbf{J}_i=0$ will hold. But, as we have seen, the steady state need not be a state of pure thermal conduction, so that the $\mathbf{J}_i$ need not vanish. Hence, measurements made on the steady state and interpreted by the theory for the state of pure thermal conduction may well lead to erroneous conclusions. We considered earlier the behavior of a single gas in a temperature gradient in the absence of external forces and found that at normal pressures a circulation of the gas occurs in the steady state so that no pressure gradient is established as in the case of thermal transpiration. As an extreme possibility for a gas mixture we may suppose a similar circulation of each component occurs with the result that the gradients of the individual partial pressures vanish in the steady state. In such an event

$$\begin{aligned}\nabla\rho_i &= \textstyle\sum_j(\partial\rho_i/\partial p_j)\nabla p_j+(\partial\rho_i/\partial T)\nabla T \\ &= (\partial\rho_i/\partial T)\nabla T,\end{aligned}$$

and the density gradient of each component would depend only on its thermal expansion in the fluid. More likely, a steady-state condition intermediate between the extremes of no flow and of no partial pressure gradients occurs for the various components. The question requires experimental investigation. The general expression for the density gradients, from which the thermal diffusion separation can be calculated, is

$$\nabla\rho_i=-\textstyle\sum_j d_{ij}\mathbf{J}_j-k_i{}^T\nabla T, \qquad (125)$$

where $d_{ij}=D_{ji}{}^*/|D_{lm}|$, the asterisk denoting the adjoint of the element D_{ji} in the determinant $|D_{lm}|$.

Another transport process which may appear in non-isothermal fluids is the homogeneous thermoelectric effect. From Eq. (57) we find

$$\nabla\phi_i=-\textstyle\sum_j r_{ij}\mathbf{J}_j-(1/\rho_i)\nabla p_i-S_i{}^*\nabla T. \qquad (126)$$

For $\phi_i=e_i\psi$, where ψ is the electrostatic potential,

$$\begin{aligned}\nabla\psi = -\textstyle\sum_j(r_{ij}/e_i)\mathbf{J}_j \\ -(\nabla p_i)/\rho_i e_i-(S_i{}^*/e_i)\nabla T \qquad (127)\end{aligned}$$

so that

$$\rho e\nabla\psi=-\textstyle\sum_{ij}\rho_i r_{ij}\mathbf{J}_j-\nabla p-\rho S^*\nabla T, \qquad (128)$$

where e is the total electric charge and S^*, the total entropy of transport per unit mass of solution. If the solution is electrically neutral then

$$\nabla p=-\rho S^*\nabla T-\textstyle\sum_{ij}\rho_i r_{ij}\mathbf{J}_j. \qquad (129)$$

Under conditions for which $\mathbf{J}_j=0$ this result reduces to Eq. (75); we would expect a total pressure gradient to be evident. However, here again we point out that the steady-state condition is $\nabla\cdot\mathbf{J}_j=0$ and not necessarily $\mathbf{J}_j=0$.

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[8] S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, London, 1939), p. 252.