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FLUID MECHANICS AND THE TRANSPORT PHENOMENA

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FLUID MECHANICS AND THE TRANSPORT PHENOMENA †

Many of the current research problems in chemical engineering concern the simultaneous transfer of heat and mass in flow systems, sometimes further complicated by chemical reactions. Such flow problems are described by the "equations of change" of fluid mechanics. These basic differential equations form the starting point for the development of a number of topics of direct interest to chemical engineering science, such as: (i) the solution of laminar problems in fluid flow, diffusion, and heat flow; (ii) the study of turbulent flow and the eddy transport processes; (iii) the theory of boundary layers and films; (iv) the study of flow in particulate systems; (v) the applications and limitations of analogies between mass, momentum, and energy transport; and (vi) the dimensional analysis of complex flow problems with heat and mass transfer, which cannot be solved analytically. Because of the paramount importance of the equations of change in basic chemical engineering studies, we summarize these equations here in their most complete form. We further point out the major relationships between the equations of change, the flux vectors, the transport coefficients, and the forces between molecules.

The equations of change of fluid mechanics comprise the equations of continuity for each of the chemical species, the equation of motion, and the

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† Part of the material for this article is taken from "Molecular Theory of Gases and Liquids," by Hirschfelder, Curtiss, and Bird (18). In this recent book (hereinafter referred to as MTGL) the equations of change are discussed in detail, and their applications to the mathematical theory of flames, shock waves, sound propagation, and detonations are presented.

equation of energy balance. From the first of these equations come the basic equations for diffusion; from the second comes the basis for the study of fluid flow; and from the last equation comes the starting point for the study of heat flow. Most of the chemical engineering unit operations involve one or more of these processes. Hence advances in the fundamental understanding of the various irreversible processes occurring in the chemical engineering operations depend on the correct interpretation and use of the equations of change.

These equations of change are coupled, nonlinear differential equations, and one might well doubt the usefulness of such a complex set of equations beyond the pedagogical value of providing a compact formal representation of a number of related fields. Of principal interest to the chemical engineer are the solutions to these equations. These solutions can be divided into three categories; analytical, numerical, and experimental. Analytical solutions can be obtained for very simple problems only. It is nevertheless just these simple solutions which are the handy formulae for every-day calculations. -- Poiseuille's law, Stokes' law, Bernoulli's equation, and the formulae for mass transfer coefficients are a few examples. Other simple solutions, which are somewhat less familiar, describe flow near rotating or oscillating discs, flow of plastics through tubes, temperature profiles produced by viscous heat effects, temperature distributions in a hot fluid entering a cold pipe (the Graetz problem), and the thickness of falling films in wetted-wall towers. Numerical solutions can frequently be obtained when problems are too complex for analytical solutions. The current developments in high speed computing techniques open up tremendous new frontiers for the further development of

fluid mechanics and transport processes as applied to chemical engineering. Some examples of problems attacked by numerical methods are the study of flame propagation, the formation of shock waves, flow through nozzles, and flow around solid objects. Experimental solutions to extremely complex problems form the basis for many industrial design calculations in diffusional operations, heat transfer, and chemical kinetics. The experimental data can usually be correlated in terms of several dimensionless groups. The minimum number of correlating parameters needed can be deduced directly from the equations of change when they are written in dimensionless form. Such methods have proved quite useful in analyzing the flow around cylinders, the evaporation of droplets, and the flow patterns of convection. In fact, the dimensional analysis of the basic differential equations gives the justification for the friction factors, drag factors, and j-factors. Hence even for problems with turbulent flow in complex geometries the equations of change can be useful even though their analytical or numerical solution would be impossible.

In this paper we begin by giving the equations of change in their most general form in terms of the flux vectors. Most books on fluid mechanics do not give these equations for fluid mixtures or for systems with temperature gradients. Frequently these equations are quoted incorrectly and incompletely; it is hoped that the summary given here will be of use. We next proceed to give the expressions for the flux vectors in terms of the transport coefficients. It is at this stage where approximations are generally made concerning the mechanism of the transport processes. The general results of the thermodynamics of irreversible processes are set forth here. Finally we discuss

the transport coefficients and their relation to intermolecular forces. Since the chemical engineer has to deal with fluids of widely varying physical properties, this aspect of fluid mechanics is of considerable importance. Inasmuch as this subject has already been treated quite extensively in a recent review article (1), only the main points of the discussion are given here.

1. The Equations of Change in Terms of the Fluxes

The behavior of a flowing fluid in which heat and mass transfer is taking place is described by the equation of change, along with the thermal and caloric equations of state. The equations of change are differential equations which describe the changes in the macroscopic properties of the fluid (for example, the local density, stream velocity, and temperature) in terms of the flux of mass, the flux of momentum, the flux of energy, and the chemical kinetics. First we discuss these equations and give the meaning of the various terms contained therein; then we proceed to indicate the limits of their applicability.

a. Summary of the Equations of Change

The basic equations of continuity, motion, and energy balance correspond to the fundamental principles of conservation of mass, momentum, and energy respectively. They have been derived for very general conditions both in classical and quantum theory.† In terms of the fluxes, these equations of change for a fluid mixture containing n_c chemical species are:

Equation of continuity for component i:

$$D\rho_i / Dt = -\rho_i(\nabla\cdot\mathbf{v}) - (\nabla\cdot\mathbf{j}_i) + K_i \qquad i=1,2,\ldots n_c \qquad (1.1a)$$

Equation of continuity for the fluid as a whole:

$$D\rho / Dt = -\rho\,(\nabla\cdot\mathbf{v}) \qquad (1.1b)$$

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† The derivation of the equations of change from the Boltzmann equation for dilute monatomic gases is given in MTGL, §7.2-c, d, e. The analogous derivation for dense monatomic gases is given in MTGL, §9.4d.

Equation of motion:

$$D\underline{v}/Dt = -(1/\rho)(\nabla\cdot\underline{\underline{p}}) + (1/\rho)\sum_{i=1}^{n_c}\rho_i\hat{\underline{F}}_i \tag{1.2}$$

Equation of energy balance:

$$D\hat{U}/Dt = -(1/\rho)(\nabla\cdot\underline{q}) - (1/\rho)(\underline{\underline{p}}:\nabla\underline{v}) + (1/\rho)\sum_{i=1}^{n_c}(\underline{j}_i\cdot\hat{\underline{F}}_i) \tag{1.3}$$ ✠

In these equations the substantial derivative $D/Dt = \partial/\partial t + (\underline{v}\cdot\nabla)$ represents the time rate of change following a fluid element which is moving with a velocity $\underline{v}$. The symbols $\underline{j}_i$, $\underline{\underline{p}}$, and $\underline{q}$ represent the fluxes of mass, momentum, and energy with respect to the mass average velocity $\underline{v}$. These fluxes may be broken down into several parts:

$$\underline{j}_i = \underline{j}_i^{(\rho)} + \underline{j}_i^{(T)} + \underline{j}_i^{(p)} + \underline{j}_i^{(F)} \tag{1.4}$$

$$\underline{\underline{p}} = p\underline{\underline{I}} + \underline{\underline{p}}^{(v)} \tag{1.5}$$

$$\underline{q} = \underline{q}^{(T)} + \underline{q}^{(p)} + \underline{q}^{(d)} + \underline{q}^{(r)}$$

That is, the mass flux includes components due to gradients in the concentration, temperature, and pressure and an additional component due to external forces. The momentum flux (pressure tensor) includes a term associated with the static pressure p and another associated with viscous stresses.

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✠ It should be mentioned that the $\hat{U}$ in Eq. (1.3) is the thermodynamic internal energy (per unit mass), and does not include the kinetic energy associated with the stream velocity or the potential energy associated with the external forces.

† The symbol K_i stands for the net rate of production of chemical species i by chemical reaction, in units of gm/sec.

And the energy flux includes terms due to temperature and concentration gradients, a term which accounts for the energy flux accompanying diffusion, and the energy flux due to radiation. Explicit expressions for these various fluxes are given in §2.

According to Eq. (1.1a) the mass density of species i contained in a fluid element changes for three reasons: the first term on the right indicates the change due to the fluid expansion; the second term accounts for the change due to diffusion processes (this includes ordinary, thermal, pressure and forced diffusion); and the third term represents the change due to the production or loss of species i by chemical reactions. When the n_c equations given in Eq. (1.1a) are added together, one obtains the overall equation of continuity, Eq. (1.1b). The latter indicates that the density of the fluid as a whole changes only because of the expansion of the fluid as indicated by the single term on the right.

According to Eq. (1.2) the velocity of the fluid element undergoes a change because of the gradient in the pressure tensor and also because of the external forces acting on the various chemical species present. Since the pressure tensor may be written as the sum of two terms, the first term on the right hand side of Eq. (1.2) contains two terms: $-(1/\rho)\nabla p$ which represents the acceleration of a fluid element because of a gradient in the static pressure; and $-(1/\rho)(\nabla \cdot \underset{\sim}{p}^{(v)})$ which gives the deceleration of the fluid element because of internal friction (viscous stresses).

According to Eq. (1.3) the internal energy changes for the following reasons: the first term on the right represents the change due to energy

flux (this includes thermal conduction, energy flux due to a concentration gradient, energy transport by molecular diffusion, and energy transport by radiation); the second term includes both the energy change due to pV-work, $-(1/\rho)p(\nabla \cdot \underline{v})$, and that due to viscous dissipation‡, $-(1/\rho)(\underline{\tau}^{(v)} : \nabla \underline{v})$; and the third term describes the change due to the work done by the diffusing molecules in overcoming the external forces.

The equations of charge along with the appropriate boundary conditions form the starting point for any mathematical study of fluid flow, heat transfer, and diffusion. For the complete statement of the problem, one also needs to specify:

$$p = p(T, \rho_1, \rho_2, \cdots \rho_{n_c}) \qquad (1.7)$$
$$\hat{U} = \hat{U}(T, \rho_1, \rho_2, \cdots \rho_{n_c})$$

which are the thermal and c loric equations of state respectively. When explicit expressions are introduced for the flux vectors in terms of the transport coefficients, then there appear in the equations of change the coefficients of diffusion, viscosity, and thermal conductivity; the dependence of these quantities on the temperature and the mass-densities of the various species present also have to be specified in the solution of an actual problem.

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‡ The viscous dissipation terms have been included in the analytical solution of only several problems: flow in capillary tubes by Hausenblas (17) and by Brinkman (4); flow inconcentric cylinders by Weltmann and Kuhn (43) and by Blok (2); flow near a rotating plate by Millsaps and Pohlhausen (30).

b. The Equations of Change for Temperature and Entropy

The equation of energy balance as given in Eq. (1.3) is not in its most useful form for many problems. In heat transfer problems, for example, it is considerably more convenient to rewrite the energy equation in terms of the temperature. And in problems on sound waves, detonations, and flow through nozzles, it is more appropriate to work with an equation of change for entropy. Furthermore the entropy equation is important in the formulation of the thermodynamics of irreversible processes.

The equation of change for temperature may be obtained by using Eq. (1.8) to rewrite Eq. (1.3). When no assumptions are made, the final result is:

$$\rho \hat{C}_v (DT/Dt) = -(\nabla \cdot \underline{q}) - (\underline{p} : \nabla \underline{v}) + (p - T(\partial p/\partial T))(\nabla \cdot \underline{v}) + \sum_{i=1}^{n_c} [(\nabla \cdot \underline{j}_i) + K_i][(\bar{U}_i/m_i) + (p - T(\partial p/\partial T))(\bar{V}_i/m_i)] + \sum_{i=1}^{n_c} (\underline{j}_i \cdot \hat{\underline{F}}_i) \quad (1.9)$$

in which the derivative $(\partial p/\partial T)$ is taken at constant composition and constant volume. For an ideal gas the terms containing $(p - T(\partial p/\partial T))$ vanish, and for a fluid consisting of a single chemical species, the last two terms (those involving the summations over i) need not be considered.

Hence in most heat transfer problems with fluid flow, one has the equations of continuity (Eq. (1.1a)), the equation of motion (Eq. (1.2)), and the equation of energy balance in terms of the temperature (Eq. (1.9)), which have to be solved along with the appropriate initial and boundary conditions.

Furthermore one needs the thermal equation of state (Eq. (1.7)) and the equation for $\hat{C}_v(T, \rho_1, \rho_2, \ldots \rho_{n_c})$ which is obtainable from the caloric equation of state in Eq. (1.8).

The equation of change for entropy can be obtained from the equations of change as given in Eqs. (1.1, 1.2, and 1.3) and the differential relation $T d\hat{S} = d\hat{U} + p d(1/\rho) - \sum_{i=1}^{n_c} (\mu_i/m_i) d(\rho_i/\rho)$, in which μ_i is the chemical potential[§] (or partial molal Gibbs free energy $\bar{G}_i$). The equation of change for entropy can be written in the form

$$\rho (D\hat{S}/Dt) = -(\nabla \cdot \underline{\sigma}) + g \qquad (1.10)$$

in which $\underline{\sigma}$ is the flux of entropy and g is the rate of production of entropy. These quantities may, after considerable minipulation, be written in the form:

$$\underline{\sigma} = (1/T)\underline{q}^{(h)} + \sum_{i=1}^{n_c} (\bar{S}_i/m_i)\underline{j}_i \qquad (1.11)^{\ddagger}$$

$$g = -(1/T)\sum_{i=1}^{n_c} (\underline{j}_i \cdot \underline{\Delta}_i) - (1/T)(\underline{\underline{p}}^{(v)} : \nabla \underline{v})$$
$$- (1/T)(\underline{q}^{(h)} \cdot \nabla \ln T) + (1/T)\sum_{s=1}^{n_r} r_s Y_s$$

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§ All partial molal quantities used in this article are on a "per molecule" basis. This somewhat unusual convention is employed because of the fact that it is customary to define most kinetic theory quantities on this basis. The use of thermodynamic quantities per molecule then eliminates the appearance of Avogadro's number throughout the equations.

‡ Here the total energy flux has been arbitrarily separated into two parts, thus:

$$\underline{q} = \underline{q}^{(h)} + \underline{q}^{(d)} \qquad (1.11a)$$

in which

$$\underline{q}^{(h)} = \underline{q}^{(T)} + \underline{q}^{(p)} + \underline{q}^{(r)} \quad \text{and} \quad \underline{q}^{(d)} = \sum_{i=1}^{n_c} (\bar{H}_i/m_i)\underline{j}_i \qquad (1.11b)$$

in which r_s and Y_s are the net rate and the "chemical affinity" of the sth chemical reaction (these quantities are defined in a footnote below[†]), and $\underline{A}_i$ is:

$$\underline{A}_i = (1/m_i)\sum_{j=1}^{n_c}(\partial\mu_i/\partial\rho_j)_{T,\rho}\,\nabla\rho_j + (\bar{V}_i/m_i)\nabla p - \hat{\underline{F}}_i \qquad (1.13)$$

The quantity $\underline{A}_i$ may be regarded as a driving force which includes the concentration gradient, the pressure gradient, and the external forces.

Equation (1.11) indicates that the entropy flux is made up of two components: the first term is the reversible flux of entropy due to heat flow, and the second term is the flow incidental to the diffusion processes. Eq. (1.12) indicates that the rate of irreversible entropy production is a result of the various dissipative phenomena: the first term is the contribution due to mass transfer,

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[†] Suppose that the chemical kinetics of the reacting mixtures may be described in terms of a set of n_r chemical reactions, which may be written symbolically thus:

$$A_{1s}[1] + A_{2s}[2] + \cdots \rightleftharpoons B_{1s}[1] + B_{2s}[2] + \cdots \qquad (1.12a)$$

in which i indicates the chemical formula for the ith species and A_{is} and B_{is} are the integral stoichiometric factors in the sth reaction for the ith substance. Then if k_s and k_s' are the rate constants for the sth forward and backward reactions respectively, r_s and Y_s are defined by:

$$r_s = (k_s f_1^{A_{1s}} f_2^{A_{2s}} \cdots) - (k_s' f_1^{B_{1s}} f_2^{B_{2s}} \cdots) \qquad (1.12b)$$

$$Y_s = -\sum_{i=1}^{n_c}(B_{is} - A_{is})\mu_i \qquad (1.12c)$$

in which the f_i are fugacities.
The quantities r_s and Y_s are then "fluxes" and "driving forces" respectively.

the second due to viscous effects, the third due to heat transfer, and the last due to chemical reaction. It should be noticed that according to Eq. (1.12) the rate of entropy production g can be written as the sum of products of fluxes and driving forces (the latter are sometimes called "affinities"). This is an important result which can be used in conjunction with the thermodynamics of irreversible processes to obtain information concerning the relation between the fluxes and the transport coefficients. This is discussed further in §2.

c. Applicability of the Equations of Change

Although the equations of change as given above are general and apply to any fluid, they are clearly useful only under such conditions that it is physically meaningful to speak about point properties. The definitions of local density, velocity, and temperature are reasonable only if the fluid can be regarded as behaving as a continuum. When there are large differences in the macroscopic quantities over distances of the order of a mean free path, the distribution of the velocities of the molecules deviates considerably from a Maxwellian distribution. Under these conditions, the concepts of local composition, velocity, and temperature become meaningless. Two well-known examples of a fluid under such a condition are: (i) an extremely dilute gas (or "Knudsen gas") in which the dimensions of the containing vessel or an object immersed in the gas are of the same order of magnitude as the mean free path, and (ii) a shock wave in which the macroscopic properties as a function of the distance undergo an abrupt change within a distance of a few mean free paths. In both these cases it is meaningless to speak of point values of the macroscopic variables.

One might well question the applicability of the equations of change to the description of turbulent flow. As the flow conditions change from laminar to turbulent, small eddies appear, and there is superimposed on the overall flow a complex pattern of more or less random motions. The dimensions of these eddies are always large compared to the mean free path, so that the turbulent motion is macroscopic rather than molecular. Accordingly, the concept of the fluid as a continuum remains valid, and the ordinary equations of change may be used. In these equations the variables refer to instantaneous values at a point. For most practical purposes, however, we are interested in the values of these quantities averaged over a time long compared with the period of fluctuations. Hence, in turbulent flow, the equations of change given above are modified by time-averaging to obtain relations among the average macroscopic variables. When this is done one obtains a set of time-averaged equations of change which differ in two respects from the original equations: (i) the variables and fluxes appearing in the equations are now time-averaged quantities, and (ii) there are additional terms associated with the correlations of the fluctuations in the various physical properties (in the equation of motion, for example, one obtains the "Reynolds stresses"). The explaining of these added terms is one of the principal problems of turbulence. The simplest theories for this are the mixing length theories, which are analogous to the mean free path theories of elementary kinetic theories. Another even simpler approach is to presume that turbulent transport is analogous to laminar transport and thus to introduce the eddy coefficients of diffusion, viscosity, and thermal conductivity. These

quantities are not constants of the fluid, but depend on the position in the fluid, the Reynolds number for the flow, and also on the scale of the turbulence. Hence the use of eddy transport coefficients is not too satisfactory. A summary of the present state of experimental and theoretical knowledge of the Reynolds stresses and eddy viscosity has been prepared by Schlichting (35); and the subject of eddy diffusion is summarized by Sherwood and Pigford (39). Other recent work on mass and heat transfer in turbulent systems has been done at California Institute of Technology by Schlinger, Sage, and collaborators (8, 36, 37).

In flow systems consisting of more than one phase, such as one encounters in industrial contacting processes, the equations of change are valid in each of the phases concerned, but the solutions to the equations of change have to "match up" at the interfaces between the phases. At the present, there is only meager knowledge as to how the solutions to the equations of change should be joined at the phase boundary, inasmuch as very little is known about the mechanism of interphase mass, momentum, and energy transfer.

Recently two groups of investigators have studied the problem of the mechanism of interphase mass transfer. Scott, Tung, and Drickamer (38) solved the differential equations for equimolal diffusion across an interface, taking into account the fact that the interface itself would provide an additional resistance to the diffusional process. Subsequent radio-tracer experiments of Tung and Drickamer (40) indicated that the interfacial resistance can influence very markedly the concentration profiles during diffusion. Another approach to the problem was taken by Emmert and Pigford, (13) who studied

absorption in wetted wall towers in terms of accommodation coefficients. They also concluded that interfacial resistance is of considerable importance. Certainly this question of the mechanism of interphase mass-transfer needs further study. One aspect of the subject of interphase mass-transfer has been exhaustively studied by chemical engineers, namely that of correlating overall mass-transfer data with flow variables according to dimensional considerations. An excellent summary and evaluation of this material has been given by Sherwood and Pigford. (39)

§2. The Fluxes in Terms of the Transport Coefficients

The equations of change in terms of the flux vectors as given in §1 have been derived by means of non-equilibrium statistical mechanics. According to statistical mechanics the flux vectors in turn can be expressed in terms of integrals which involve distribution functions. Ultimately one would like to follow through this line of attack and obtain expressions for the distribution functions and thereby express the flux vectors in terms of the forces between the molecules in the fluid and the various derivatives of the macroscopic properties. The complete development of the connection between the flux vectors and the intermolecular forces has been worked out only for certain special types of molecules and for certain limited conditions: (i) For the dilute monatomic gas the Chapman-Enskog theory (6) gives the flux vectors explicitly in terms of the transport coefficients, which in turn are expressed in terms of intermolecular forces as described in §4. A considerable amount of computational work has been done for the dilute milticomponent monatomic gas mixtures with small gradients, and it is possible to predict quite accurately the flow properties under both classical and quantum conditions. (ii) For the dilute polyatomic gas a general theory has been developed by Wang Chang and Uhlenbeck (42) and also by de Boer (10) but no numerical results have yet been obtained whereby one can relate the transport coefficients to the intermolecular forces. (iii) For the dense monatomic gas formal results have been obtained by Kirkwood and coworkers (21) and by Born and Green (3) but much work needs to be done in order to make these results of practical value.

For a fluid made up of any kind of molecules and under any arbitrary conditions of temperature and pressure, it is not possible at the present time to use statistical mechanics to obtain the form of the flux vectors and to derive expressions for the transport properties in terms of intermolecular forces. For such a "general fluid", however, a certain amount of information may be obtained from the thermodynamics of irreversible processes. It is possible to derive the form of the flux vectors, and by means of the Onsager "reciprocal relations" to obtain certain relationships between the transport coefficients. It should be emphasized, however, that the thermodynamic approach cannot lead to any expressions for the transport coefficients in terms of the molecular properties. Hence we summarize in this section the most important useful results which are obtained about the flux vectors from the thermodynamics of irreversible processes and other sources.

a. The Thermodynamics of Irreversible Processes

In Eq. (1.11) it was found that the rate of entropy production could be written as a sum of products of fluxes and driving forces. That is:

$$g = (1/T) \sum_{n=1}^{3n_c+n_r+12} J_n X_n \qquad (2.1)$$

in which the J_n are the various fluxes and the X_n are the various driving forces or "affinities." These fluxes and forces are summarized in Table I.

In general, any driving force can give rise to any of the fluxes. For example, if there is in a system both a mass gradient and a temperature gradient, the following fluxes are observed (1) mass flux due to the concentration gradient

Table I

Fluxes and Forces in a Flowing Fluid

Flux, J_n	Force, X_n
$\underline{j}_i$	$-\underline{\Delta}_i$
$\underline{\underline{p}}^{(v)}$	$-\nabla \underline{v}$
$\underline{q}^{(h)}$	$-\nabla \ln T$
r_s	$+Y_s$

Notes: The quantity Δ_i is defined in Eq. (1.13), and r_s and Y_s are defined in Eqs. (1.12b). The subscript i goes from 1 to n_c (the total number of chemical species present), and s goes from 1 to n_r (the total number of chemical reactions taking place). The quantities r_s and Y_s are scalars; $\underline{j}_i$ and $\underline{q}^{(h)}$ and their associated forces are vector quantities with three components each; and $\underline{\underline{p}}^{(v)}$ and ∇v are second order tensors with nine components each. Hence, altogether we are concerned with $3n_c + n_r + 12$ fluxes and an equal number of forces.

(ordinary diffusion); (ii) energy flux due to the temperature gradient (thermal conductivity); (iii) mass flux due to the temperature gradient (thermal diffusion or the "Soret effect"); and (iv) energy flux due to the mass gradient (the diffusion-thermoeffect or the "Dufour effect"). We see thus that there are two types of effects---direct effects, such as (i) and (ii), and coupled effects, such as (iii) and (iv).

It is assumed as a postulate of the thermodynamics of irreversible processes that, for situations not too far removed from equilibrium, the fluxes may be written in the form:

$$J_n = \sum_m a_{nm} X_m \tag{2.2}$$

which states that the fluxes are linear functions of the driving forces. The a_{nm} are referred to as the phenomenological coefficients. The diagonal elements a_{nn} are the coefficients which represent the direct effects; the off-diagonal elemenets a_{nm} $(n \neq m)$ are the "phenomenological coefficients" for the coupled effects. The expressions for the fluxes obtained by statistical mechanical considerations are of this form. Also, such "linear" relations are found in connection with other types of physical and chemical phenomena--for example, in thermomagnetic effects, thermogalvanic effects, electrokinetic effects, etc.‖ Linear relations should always be adequate when the systems are sufficiently close to equilibrium. Hence the postulate of Eq. (2.2) defines the range of applicability of the thermodynamics of irreversible processes.

‖ Complete discussions of these applications may be found in the recent monograph of de Groot (12).

The fundamental theorem of the thermodynamics of irreversible processes is due to Onsager (31). This theorem states that for a "proper choice" of the fluxes and forces

$$a_{nm} = a_{mn} \tag{2.3}$$

These equations are commonly referred to as "Onsager's reciprocal relations," and are useful for relating coupled effects such as the Soret and Dufour effects.

Let us now consider the application of the linear law of Eq. (2.2) and the Onsager reciprocal relations to the study of transport phenomena in fluids, for which a proper choice of the fluxes and forces is indicated in Table I. When the linear law for the fluxes is applied to the flux vectors which are equivalent to the first approximation in the Chapman-Enskog kinetic theory. That is, one obtains expressions for the flux vectors which are linear in the first derivatives of the macroscopic variables and do not contain higher derivatives or powers of the first derivatives.

Hence, if the system under consideration is in a state not too far removed from equilibrium, the linear law of Eq. (2.2) indicates that each of the components of the fluxes in Table I may be written as a linear combination of all the components of all the forces in Table I. However, if the system is isotropic, it may be shown that those terms which correspond to a coupling of tensors whose orders differ by an odd number do not occur. Thus no coupling occurs between $\underline{j}_i$ or $\underline{q}^{(h)}$ (both vectors or first-order tensors) and $\underline{p}^{(v)}$ (a second order tensor) or r_s (a scalar or zero-order tensor). Coupling does occur between the heat flux $\underline{q}^{(h)}$ and the mass flux $\underline{j}_i$, resulting in the Soret effect and the Dufour effect.

Coupling also occurs between the momentum flux and the chemical reaction rates, since there is a difference of two in the order of the tensors. No experimental observations of such an effect have, however, been reported.

b. Momentum Flux and the Viscosity Coefficients

The application of the linear law (Eq. (2.2)) to the components of the viscous pressure tensor $\underline{\underline{p}}^{(v)}$ and the force $-\nabla \underline{v}$ gives:

$$p_{hk}^{(v)} = -\sum_{n=1}^{3}\sum_{m=1}^{3} a_{nm}^{hk} \left(\partial v_k/\partial x_h\right) \tag{2.4}$$

The set of phenomenological coefficients a_{nm}^{hk} is a matrix of eighty-one elements, but all of these are not independent. From Onsager's relations one sees that $a_{nm}^{hk} = a_{hk}^{nm}$; and since the pressure tensor is defined to be symmetric, it can be shown that $a_{nm}^{hk} = a_{nm}^{kh}$. Then Eq. (2.4) can be simplified to:

$$p_{hk}^{(v)} = -(1/2)\sum_{n=1}^{3}\sum_{m=1}^{3} a_{nm}^{hk} \left[\left(\partial v_k/\partial x_h\right) + \left(\partial v_h/\partial x_k\right)\right] \tag{2.5}$$

so that there are only thirty-six independent coefficients a_{nm}^{hk} .
If the further assumption is made that the fluid is isotropic, then it can be shown that the number of independent a_{nm}^{hk} is reduced to two. The pressure tensor then has the form:

$$\underline{\underline{p}}^{(v)} = -\mu\left[(\nabla \underline{v}) + (\nabla \underline{v})^{\dagger}\right] + \left(\tfrac{2}{3}\mu - \kappa\right)(\nabla\cdot\underline{v})\,\underline{\underline{I}} \tag{2.6}$$ †

in which μ and κ are the two independent phenomenological coefficients, which are called the coefficients of shear and bulk viscosity respectively.

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† Typical diagonal and non-diagonal elements of this tensor are:

$$p_{xx}^{(v)} = -2\mu\frac{\partial v_x}{\partial x} + \left(\tfrac{2}{3}\mu - \kappa\right)\left(\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z}\right); \qquad p_{xy}^{(v)} = -\mu\left(\frac{\partial v_x}{\partial y} + \frac{\partial v_y}{\partial x}\right) = p_{yx}^{(v)}$$

The coefficient of shear viscosity is important in flows in which successive plane layers of the fluid move with different velocities. The coefficient of bulk viscosity is important in the pure expansion of a fluid.

In a dilute gas made up of molecules without internal degrees of freedom, the coefficient of bulk viscosity is identically zero. It has been shown that the presence of internal degrees of freedom, even in a dilute gas, introduces a finite bulk viscosity; and the bulk viscosity has also been shown to be non-zero in a dense gas or liquid. Nevertheless the effect is generally small, and it is often sufficiently accurate to neglect the bulk viscosity. A survey of the topic of bulk viscosity has been given by Karim and Rosenhead (24). If the fluid under consideration is incompressible (then $(\nabla \cdot \underline{v}) = 0$), the last term of Eq. (2.6) vanishes, and the coefficient of bulk viscosity does not enter into the equation.

For the flow of a fluid in the x-direction with a velocity gradient in the y-direction only, Eq. (2.6) simplifies to:

$$p_{xy}^{(v)} = -\mu\,(\partial v_x/\partial y) \tag{2.7}$$

This is the well-known "Newton's law of viscosity" which states that the resistance to viscous forces is proportional to the velocity gradient, the constant of proportionality being the coefficient of shear viscosity. The coefficient of shear viscosity is determined experimentally by considering the flow of a fluid in a system of sufficiently simple geometry that the equation of motion can be solved after the expression for the viscous stress given in Eq. (2.7) has been substituted into it. In this way one analyzes the data for

capillary tube viscosimeters in terms of Poiseuille's law, and the data for concentric cylinder (Couette) viscosimeters in terms of the Margules equation. Eq. (2.7) then forms the basis for the entire subject of viscosimetry of newtonian fluids.

There are many fluids which do not behave according to the above ("newtonian") form of the pressure tensor, and such fluids are referred to as "non-newtonian". Examples of non-newtonian substances are glass, plastics melts, drilling muds, "bouncing putty," toothpaste, and concrete. For these substances the assumption of small gradients, made in connection with Eq. (2.2), is not tenable. Hence the pressure tensor depends upon higher derivatives of the velocity components and on higher powers of the velocity gradients. The inclusion of these additional terms would require the introduction of additional phenomenological coefficients; approaches of this sort have been quite limited.

In connection with the establishment of this relation between the shear stress and the shear rate for non-newtonian flow, considerable success has been obtained by Eyring and his collaborators (15) who have applied the methods of reaction rate theory to various postulated physical pictures of the elementary processes going on inside a fluid. It is this theory which predicts that the shear viscosity depends on the external force according the the hyperbolic sine law.

Actually most of the studies of the flow behavior of non-newtonian substances have been based on simple analytical assumptions concerning the relationship between the shear stress $(p_{xy}^{(v)})$ and the shear rate $(\partial v_x/\partial y)$. This is also

tantamount to saying that some assumption is made concerning the dependence of the coefficient of viscosity on the impressed shear force. By means of these assumed "models", one can solve the equation of motion for various simple geometries (such as capillary tubes, concentric cylinders, etc.) and obtain formulae which are useful for the viscosimetry of non-newtonian substances. (33). Formulae of this sort are available for various idealized non-newtonian models, such as the Bingham plastic, thixotropic substances, and power-law models (which just assume that the shear rate varies as some power of the shear stress, or vice versa). Unfortunately many investigators continue to analyze the flow data for non-newtonian substances in terms of Poiseuille's law and other newtonian formulae, thereby obtaining "effective viscosities" which are valuable only for analyzing flow in systems geometrically similar to the viscosity measurement apparatus. The study of the flow and deformation of these non-newtonian substances is now generally classified under the heading of "rheology." This subject includes the behavior of substances under stress, all the way from pure elastic deformation (Hooke's law to pure viscous flow (Newton's law).

c. Mass and Heat Flux and the Coefficients of Diffusion and Thermal Conductivity

The application of the linear law (Eq. (2.2)) to the components of the heat and mass flux vectors and the corresponding driving forces given in Table I gives (after some algebraic rearrangement):

$$\underline{q}^{(h)} = -a_{00} \nabla \ln T - p \sum_{j=1}^{n_c} (a_{0j}/\rho_j)\, \underline{d}_j \tag{2.8}$$

$$\underline{j}_i = -a_{i0} \nabla \ln T - p \sum_{j=1}^{n_c} (a_{ij}/\rho_j)\, \underline{d}_j \tag{2.9}$$

in which the driving forces d_j, closely related to the Λ_j, are defined thus:

$$\begin{aligned} \underline{d}_j &= (\rho_j/p)\,\underline{\Lambda}_j - (\rho_j/\rho)\,\nabla \ln p + (\rho_j/\rho p)\sum_{k=1}^{n_c} \rho_k \hat{\underline{F}}_k \\ &= (\rho_j/pm_j)\sum_{k=1}^{n_c} (\partial\mu_j/\partial\rho_k)_{T,p}\,\nabla\rho_k \\ &\quad + [(\rho_j\overline{V}_j/m_j) - (\rho_j/\rho)]\,\nabla \ln p \\ &\quad - (\rho_j/\rho p)(\rho\hat{\underline{F}}_j - \sum_{k=1}^{n_c} \rho_k \hat{\underline{F}}_k) \end{aligned} \tag{2.10}$$

In the above equations the index 0 refers to the temperature variable; the other the other subscripts (i, j, k) refer to the chemical species present in the mixture. The following restrictions have to be placed on the a_{ij}: (i) because of the Onsager relations the a_{ij} are symmetric; (ii) because of the fact that the $\underline{j}_i$ are not all independent (i.e., $\sum_i j_i = 0$), the a_{ij} must in addition satisfy the relations: $\sum_i a_{ij} = \sum_j a_{ji} = 0$.

The application of the Onsager relations to the phenomenological coefficients with one 0 subscript gives:

$$a_{i0} = a_{0i} = D_i^T \tag{2.11}$$

and we have equated these elements to the "multicomponent thermal diffusion coefficient," D_i^T. Thus the reciprocal relation in Eq. (2.11) gives the connection between the coupled effects known as thermal-diffusion and the diffusion-thermo effects.

The application of the Onsager relations to the remaining phenomenological coefficients gives:

$$a_{ij} = a_{ji} \qquad i,j \neq 0 \tag{2,12}$$

We now have to relate these quantities to the "multicomponent diffusion coefficients," D_{ij}, but this has to be done in such a way that Eq. (2.12) is obeyed.‖ Inasmuch as the D_{ij} are customarily defined so that the D_{ii} are identically zero (9), the relationships between the D_{ij} and the a_{ij} are rather involved:

$$a_{ij} = (n^2\rho_j/\rho^2 p)\left[-\rho m_i m_j D_{ij} + \sum_{k=1}^{n_c} \rho_k m_i m_k D_{ik}\right. \tag{2.13}$$

$$D_{ij} = -(\rho p/n^2 m_i m_j)\left[(1/\rho_j)a_{ij} + (1/\rho_i)\sum_{\substack{k=1\\k\neq i}}^{n_c} a_{ik}\right. \tag{2.14}$$

It should be noted that these D_{ij} are not symmetric with respect to an interchange of the subscripts i and j .

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‖ For a two-component mixture the "multicomponent diffusion coefficients" D_{ij} become the ordinary binary diffusion coefficients $\mathcal{D}_{ij}$, and then $\mathcal{D}_{ij} = \mathcal{D}_{ji}$. For two-component systems it is also customary to define a "thermal diffusion ratio," k_T, according to the relation:

$$k_T = (\rho/n^2 m_1 m_2)(D_1^T/\mathcal{D}_{12}) = -(\rho/n^2 m_1 m_2)(D_2^T/\mathcal{D}_{12}) \tag{2.14a}$$

For this definition of k_T, component "1" goes to the cold region if $k_T > 0$ and to the hot region if $k_T < 0$. The diffusion coefficients $\mathcal{D}_{ij}$ and the thermal diffusion ratio k_T defined thus are in agreement with the accepted definitions of the previous workers, and in particular with the textbooks of Chapman and Cowling[6] and Grew and Ibbs (16).

For a three-component mixture the multicomponent diffusion coefficients are not equal to the ordinary binary diffusion coefficients. For example, the kinetic theory of dilute multicomponent gas mixtures[9] shows that:

$$D_{12} = \mathcal{D}_{12}\left[1 + \frac{n_3\left[(m_3/m_2)\mathcal{D}_{13} - \mathcal{D}_{12}\right]}{n_1\mathcal{D}_{23} + n_2\mathcal{D}_{13} + n_3\mathcal{D}_{12}}\right] \tag{2.14b}$$

We now can substitute the results of the application of the Onsager relations (Eq. (2.11) and (2.13)) into the expressions for the heat and mass fluxes (Eq. (2.8) and (2.9)) to obtain:

$$\underline{q}^{(h)} = -a_{00}\,\nabla \ln T - p\sum_{j=1}^{n_c}(D_j^T/\rho_j)\,\underline{d}_j \qquad (2.15)$$

$$\underline{j}_i = -D_i^T\,\nabla \ln T + (n^2/\rho)\sum_{j=1}^{n_c} m_i m_j D_{ij}\,\underline{d}_j \qquad (2.16)$$

in which the phenomenological coefficient a_{00} still appears. The quantity a_{00}/T is not quite the coefficient of thermal conductivity as customarily defined, as can be seen in the following way: Imagine that Eq. (2.16) is solved for the $\underline{d}_i$ and that these quantities are in turn substituted into Eq. (2.15). This will then indicate that $\underline{q}^{(h)}$ has other terms proportional to ∇T besides the term containing a_{00}. When all of these terms are combined, the coefficient of the resulting term is defined to be the coefficient of thermal conductivity. This particular choice for the definition of is made for the sake of consistency with existing treatises on kinetic theory, such as that of Chapman and Cowling (6).

When the rearrangements just described have been performed, one finally obtains for the components of the energy flux vector (as given in Eq. (1.6)) the following:

$$\underline{q}^{(T)} = -\lambda\,\nabla T \qquad (2.17)$$

$$\underline{q}^{(d)} = +\sum_{i=1}^{n_c}(\bar{H}_i/m_i)\,\underline{j}_i \qquad (2.18)$$

$$\underline{q}^{(p)} = (kT/n)\sum_{i=1}^{n_c}\sum_{\substack{j=1\\ j\neq i}}^{n_c}(n_j/m_i)(D_i^T/\mathcal{D}_{ij})(\underline{V}_i^{(d)}-\underline{V}_j^{(d)}) \qquad (2.19)$$

The first term, $\underline{q}^{(T)}$, is the contribution to the energy flux due to thermal conduction and is the coefficient of thermal conductivity. The second term,

$\underline{q}^{(d)}$, is the energy flux associated with the diffusional processes occurring. These two terms are the most important contributions to the energy flux. The third term, $\underline{q}^{(\rho)}$, is related to (but not equal to) the energy flux resulting from the Dufour effect. Actually Eq. (2.19) is rigorously applicable only to a dilute gas mixture. The expression for $\underline{q}^{(\rho)}$ for a general fluid is extremely complex and the effect is small.

In the above set of equations we have given no expression for $\underline{q}^{(r)}$, the energy flux due to radiation. This set of equations applies only to systems near equilibrium. If radiative energy transport is taking place and if the radiation is in equilibrium with the matter, then the expression for $\underline{q}^{(r)}$ is of the same form as Eq. (2.17) for $\underline{q}^{(T)}$. This condition is usually not satisfied and the radiative energy flux depends in a detailed manner on the frequency and intensity of the radiation and the properties of the material.[§]

From Eqs. (2.16) and (2.10) one obtains the various contributions to the mass flux vector (as given in Eq. (1.4)), thus:

$$\underline{j}_i^{(\rho)} = +(n^2/\rho)\sum_{j=1}^{n_c} m_i m_j D_{ij}\left[(n_j/p)\sum_{k=1}^{n_c}(\partial\mu_j/\partial\rho_k)_{T,p}\,\nabla\rho_k\right] \tag{2.20}$$

$$\underline{j}_i^{(p)} = +(n^2/\rho)\sum_{j=1}^{n_c} m_i m_j D_{ij}\left[(\rho_j\bar{V}_j/m_j) - (\rho_j/\rho)\right]\nabla \ln p \tag{2.21}$$

$$\underline{j}_i^{(F)} = +(n^2/\rho)\sum_{j=1}^{n_c} m_i m_j D_{ij}\left[(\rho_j/p\rho)(\rho\hat{\underline{F}}_j - \sum_{k=1}^{n_c}\rho_k\hat{\underline{F}}_k)\right] \tag{2.22}$$

$$\underline{j}_i^{(T)} = -D_i^T\,\nabla \ln T \tag{2.23}$$

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§ The subject of radiative heat transfer is discussed further in MTGL, §11.3.

The first contribution, $\underline{j}_i^{(\rho)}$, is the most important one--the flux due to a concentration gradient. This expression indicates that the correct driving force for diffusion is a rather complicated function of the chemical potentials of all the components in the mixture. The mass flux due to a gradient in the static pressure, $\underline{j}_i^{(p)}$, has been studied only slightly because of its relatively negligible importance. The mass-flux due to forced diffusion, $\underline{j}_i^{(F)}$, is important when systems containing ions are under consideration. And the last term, $\underline{j}_i^{(T)}$, is the contribution to the mass flux due to thermal diffusion. This contribution can be neglected except under conditions of large terperature gradients such as are carefully maintained in devices such as the Clusius-Dickel column (16).

For <u>two-component systems</u> the mass-flux vectors become considerably simpler. The general expression for the flux of component "1" is:

$$\underline{j}_1 = \rho_1 \underline{V}_1^{(d)} = -(n^2/\rho)\, m_1 m_2 \mathcal{D}_{12} \left(\underline{d}_1 + k_T \nabla \ln T \right) \qquad (2.24)$$

in which we have also indicated the relation between the flux vector and the diffusion velocity, $\underline{V}_1^{(d)}$. The latter is the velocity with which component "1" moves with respect to the mass average velocity. Inasmuch as the binary diffusion constants are symmetric ($\mathcal{D}_{12} = \mathcal{D}_{21}$), and since $\underline{j}_1 = -\underline{j}_2$, it follows that:

$$\underline{V}_2^{(d)} - \underline{V}_1^{(d)} = (n^2/n_1 n_2)\,\mathcal{D}_{12}\,(\underline{d}_1 + k_T \nabla \ln T) \qquad (2.25)\dagger$$

This equation is the usual starting point for discussion of thermal diffusion.

For a two-component system in which thermal, pressure, and forced diffusion effects can be neglected, the expression for the mass flux given in Eq. (2.24) becomes:

$$\underline{j}_1 = -(n^2 n_2/p\rho)\, m_1 m_2 \mathcal{D}_{12}\, \nabla\mu_1 = -(n^2/\rho)(n_2 kT/p)\, m_1 m_2 \mathcal{D}_{12}\, \nabla \ln a_1 \qquad (2.26)$$

in which a_1 is the activity of component "1". From this it can be seen that it is the chemical potential or the activity which should correctly be considered to be the driving force for two-component diffusion. When the additional assumption is made that the components are dilute gases, then Eq. (2.26) becomes:

$$\underline{j}_1 = -(n^2/\rho)\, m_1 m_2\, \mathcal{D}_{12}\, \nabla x_1 \qquad (2.27)$$

This expression can be used in systems where there are temperature gradients, provided that they are not sufficiently large that the thermal diffusion contribution needs to be added.

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† For a dilute monatomic gas this result has been generalized for multicomponent mixtures:

$$\sum_{j=1}^{n_c} (n_i n_j / n^2 \mathcal{D}_{ij})(\underline{V}_j^{(d)} - \underline{V}_i^{(d)}) = \qquad (2.25a)$$

$$\underline{d}_i - (\nabla \ln T) \sum_{j=1}^{n_c} (n_i n_j / n^2 \mathcal{D}_{ij}) \left[(D_j^T / n_j m_j) - (D_i^T / n_i m_i) \right]$$

For systems at constant temperature and pressure and with no external forces, this simplifies to:

$$-\nabla p_i = \sum_{j=1}^{n_c} \alpha_{ij}\, c_i c_j\, (\underline{V}_i^{(d)} - \underline{V}_j^{(d)}) \qquad (2.25b)$$

in which the "resistance factors," α_{ij}, are defined as $(RT)^2/p\mathcal{D}_{ij}$, and c_i is the molar concentration of species i. This result, originally due to Maxwell and Stefan, is commonly used as the starting point for discussions of multicomponent diffusion (20).

It has been previously mentioned that the flux vectors defined above are fluxes with respect to a coordinate system moving with the mass average velocity of the gas. Sometimes it is convenient to define fluxes with respect to other coordinate frames. Two examples will illustrate the importance of specifying the reference frame for the fluxes: (i) The flux, J_1, in moles per unit area per unit time with respect to the molar average velocity (under the same restrictions of Eq. (2.27)) is:

$$\underline{J}_1 = -(p\mathcal{D}_{12}/RT)\nabla x_1 \tag{2.28}$$

(ii) The molar flux of component "1" with respect to a stationary coordinate system is:

$$\underline{N}_1 = -(p\mathcal{D}_{12}/RT)\nabla x_1 + (N_1 + \underline{N}_2)x_1 \tag{2.29}$$

The first term on the right hand side is the molar flux of component "1" by diffusion, and the second term is that due to the mass motion of the fluid. Eq. (2.29) is the basic starting point for the discussion of chemical engineering mass-transfer problems. A large number of the important applications involve either of two assumptions: (i) diffusion of "1" through stagnant "2", so that $\underline{N}_2 = 0$; and (ii) equimolal counterdiffusion for which $\underline{N}_1 = -\underline{N}_2$. The applications of Eq. (2.29) to various important industrial diffusional operations have been given by Sherwood and Pigford (39).

The expressions given in this section for the momentum flux (Eq. (2.6)), the components of the heat flux (Eqs. (2.17) to (2.19)), and the components of the mass flux (Eqs. (2.20) to (2.23)) are general results obtained from the thermodynamics of irreversible processes and which apply to both gases and

liquids. They are, of course, consistent with the expressions for the flux vectors for dilute monatomic gases, which have been previously obtained from the rigorous kinetic theory of gases.

When the expressions for the components of the mass flux (Eqs. (2.20) to (2.23)) are substituted into the equation of continuity for component i (Eq. (1.1a)), one obtains the diffusion equation in its most general form. When it is assumed that thermal, pressure, and forced diffusion is absent, and when it is further assumed that the diffusion is two-component equimolal counterdiffusion, then the diffusion equation simplifies to "Fick's second law" of diffusion. When the expression for the momentum flux (2.6) is substituted into the equation of motion (Eq. (1.2)), then, if the bulk viscosity is zero, one obtains the usual Navier-Stokes equations. When the expression for the energy flux (Eqs. (2.17) to (2.19)) is put into the energy balance equation in terms of the temperature (Eq. (1.9)) one obtains the heat flow equation in very general form. When the assumption is made that viscous dissipation effects and $p\nabla\cdot\mathbf{v}$-effects are negligible, then the temperature equation for a pure fluid assumes a form which is mathematically analogous to Fick's second law of diffusion. Hence we see that the equations of change and the expressions for the fluxes provide starting points for heat, momentum, and mass transfer studies which are more general than the usual starting equations. Since these equations and expressions have all been written in vector and tensor form, they may be used to get the correct starting point for calculations in cartesian, cylindrical, or spherical coordinates.

3. The Transport Coefficients in Terms of Intermolecular Forces

In order to use any results based on solutions of the equations of change, one must know the values of the transport coefficients involved, and in some problems the temperature, density, and concentration dependence of these quantities is also needed. Whenever possible, of course, experimental data should be used if they are available. Otherwise, one should use the best method of calculation which is consistent with the accuracy desired. In general, the most reliable methods are those based on statistical mechanical formulae, which relate the bulk properties in terms of the intermolecular forces. Hence this section begins with a summary of the various types of forces between molecules.

a. Intermolecular Forces and Potential Energy Functions ⌖

In principle it is possible to determine the force between a pair of molecules from *a priori* quantum mechanical calculations, inasmuch as the description of the mechanics of any collection of nuclei and electrons is given by the Schrödinger wave equation. In practice, however, it is possible to obtain solutions to the Schrödinger equation for only rather simple molecular systems, and then only after making numerous approximations the physical reality of which is difficult to assess. The quantum mechanical approach has nevertheless provided a considerable amount of information of a semi-quantitative character, which has been of great value in establishing the approximate functional form of the interaction energies.

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⌖ An elementary discussion of intermolecular forces and empirical potential energy functions may be found in MTGL §1.3, and a complete treatment is given in MTGL, Chs. 12, 13, and 14. See also the earlier review articles by London (26) and Margenau (27).

In the kinetic theory formulae for the transport coefficients it is the potential energy of interaction $\varphi(r)$ which appears rather than the force of interaction $F(r)$ between the molecules in the fluid. For two spherical non-polar molecules the force and potential energy are simply related according to the equation:

$$F(r) = -d\varphi/dr \quad ; \quad \varphi(r) = \int_r^\infty F(r)dr \tag{3.1}$$

For the interaction between more complex molecules, the potential energy is a function not only of the intermolecular separation, but also of the angles describing the mutual orientation of the molecules. From such an angle-dependent potential energy function one can derive both the force and torque of interaction as a function of the distance and orientation.

It is customary, although somewhat arbitrary, to divide intermolecular forces into two types--short-range forces and long-range forces. The <u>short-range forces</u> arise when the molecules come close enough together for their electron clouds to overlap appreciably. These forces are repulsive and often highly directional. There are some experimental indications of the nature of short-range intermolecular forces from crystal structure, properties of surfaces, and other properties, but most of our information comes from the specific quantum mechanical calculations which have been made for specific molecular interactions. These calculations usually are not highly accurate, inasmuch as many of the integrals encountered are so complicated that they are either approximated or simply neglected.

The long-range forces, on the other hand, may be treated in a fairly rigorous manner. Furthermore, it is easy to give formulae for various types of interaction which are applicable to a variety of types of molecules. The long-range forces may be subdivided into electrostatic, induction, and dispersion forces. The electrostatic forces are those between the various multipoles of the molecules and are described by electrostatics. The induction forces are those resulting from the fact that a multipole in one molecule can induce a multipole in the other molecule, which in turn reacts with the multipole of the first molecule. The dispersion forces result, in a sense, from the interaction of the instantaneous multipoles which exist even in neutral symmetrical molecules because of the electronic motion; these forces cannot be described correctly in terms of a simple physical picture and are derived by quantum mechanical second-order perturbation theory.

For nonpolar molecules the most important long-range contribution to the potential energy of interaction is the dispersion force proportional to the inverse sixth power of the intermolecular separation. The short-range force, which is known to be approximately exponential in form, ~~can be further approximately exponential in form~~, can be further approximated by an inverse power dependence, usually r^{-12}. It is these considerations which form the justification for the Lennard-Jones (6-12) potential:

$$\varphi(r) = 4\epsilon\left[(\sigma/r)^{12} - (\sigma/r)^{6}\right] \qquad (3.2)$$

in which σ is that value of the separation for which the potential energy is zero, and ϵ is the maximum attractive energy. This potential energy

function has been used with considerable success for the calculation of many equilibrium and non-equilibrium properties of dilute and moderately dense gases composed of molecules which are nonpolar and reasonable spherical.[‡]

Empirical potential energy functions, such as the Lennard-Jones potential, have played a very important role in connection with the determination of intermolecular forces. Many physical properties can be expressed by means of statistical mechanics in terms of integrals involving the intermolecular potential energy function. When an empirical potential function is used, these integrals can be evaluated and the results expressed in terms of the parameters (such as σ and ϵ in the Lennard-Jones potential). Experimental data for some bulk property can then be used in conjunction with these results to determine the potential parameters. Once the potential parameters are known, other physical properties can then be calculated. This interrelation of bulk properties and intermolecular forces is further discussed in connection with Eqs. (3.7), (3.8), and (3.9). Much more quantitative information about intermolecular forces has been obtained by means of this semi-empirical approach than by direct quantum mechanical calculation.

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‡ The following Lennard-Jones potential calculations are described in MTGL: second and third virial coefficients, §3.6; Joule-Thomson coefficient, §3.6; the Lennard-Jones–Devonshire equation of state for dense gases and liquids, §4.7; quantum calculations of the second virial coefficient, §§6.4c and 6.5c; transport properties of dilute gases, §8.4 Complete tables of all tabulated functions are given.

Extensive calculations have recently been made‡ for another empirical function for non-polar molecules, namely the modified Buckingham (6-exp) potential energy function. This potential contains the r^{-6} attractive term, but the repulsive component is represented by an exponential term thus:

$$\varphi(r) = \frac{\epsilon}{1 - \frac{6}{\alpha}} \left[\frac{6}{\alpha} \exp\left[\alpha\left(1 - \frac{r}{r_m}\right)\right] - \left(\frac{r}{r_m}\right)^{-6} \right] \qquad (3.3)$$

in which there are three adjustable parameters: the maximum energy of attraction ϵ, the separation corresponding to that energy r_m, and the parameter α which is a measure of the steepness of the energy of repulsion.‖ This intermolecular potential function represents an improvement over the Lennard-Jones potential and has been found to give somewhat better agreement between calculated and experimental transport coefficients and virial coefficients, particularly for H_2 and He.

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‡ Calculations of Mason (28) of the transport coefficients for the modified Buckingham potnetial are described in MTGL, §8.4. The corresponding calculations of Rice and Hirschfelder (34) are described in MTGL, §3.7. Further discussion of the modified Buckingham potential has been given by Mason and Rice (29).

‖ Actually for very small values of the intermolecular separation r, the function given in Eq. (3.3) has a maximum value and approaches minus infinity as r approaches zero. This would correspond to very strong attraction at very small separations. Hence, when Eq. (3.3) is used in statistical mechanical calculations, one can set $\varphi(r) = \infty$ for values of r less than the value of r at the spurious maximum.

b. The Transport Coefficients of Dilute Gases†

The earliest attempts to relate the transport coefficients to intermolecular forces were based on the assumption that molecules could be represented as rigid spheres with diameter σ_R. These early theories were based on the concept of the "mean free path"--the average distance traversed by the molecules between collisions. A simple calculation shows that this quantity is given by $L = (kT/\sqrt{2}\, p \pi \sigma_R^2)$. The quantity $\pi\sigma_R^2$ appearing in the denominator is called the "collision cross-section" for the rigid-spherical molecule. This cross-section appears in all the expressions for the transport coefficients and represents the cross-sectional area of the imaginary sphere surrounding a molecule, into which the center of an approaching molecule cannot penetrate.

According to the simple kinetic theory the transport coefficients can all be expressed in terms of the mean free path and the average molecular velocity $\bar{v} = \sqrt{8dT/\pi m}$. Thus the coefficients of self-diffusion,* viscosity, and thermal conductivity of a pure gas are given by:

$$\mathcal{D} = (1/3)\bar{v}L = C_{\mathcal{D}} \frac{\sqrt{\pi m k T}}{\pi\sigma_R^2} \frac{1}{\rho} \tag{3.4}$$

$$\mu = (1/3)\rho\bar{v}L = C_{\mu} \frac{\sqrt{\pi m k T}}{\pi\sigma_R^2} \tag{3.5}$$

$$\lambda = (1/3)\rho\hat{C}_v L = C_{\lambda} \frac{\sqrt{\pi m k T}}{\pi\sigma_R^2} \hat{C}_v \tag{3.6}$$

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† Transport properties of dilute gases and binary gas mixtures have been treated in a highly mathematical form in the book of Chapman and Cowling(6). An elementary discussion of kinetic theory is given in MTGL, §1.2, and the kinetic theory of multicomponent gas mixtures is given in MTGL, Chs. 7 and 8. Formulae in practical units are given, and complete tables for use in conjuction with these formulae may be found in the appendixes. A summary of the present status of calculating transport and other properties of gases and liquids has been given in a survey article written by the authors(1).

* This discussion is confined to the consideration of the properties of pure substances. Here the transport coefficient which characterizes mass-transfer is the coefficient of self-diffusion, which is the interdiffusion of particles of the same mass and size. Although this is a somewhat artificial quantity, it is not wholly without application. The interdiffusion of heavy isotopes and the diffusion of ortho and para forms are phenomena which can be described by self-diffusion formulae.

in which $C_{\mathfrak{D}}$, C_{μ}, and C_{λ} are constants; and $\hat{C}_{v}$ is the specific heat per unit mass, which is $(3k/2m)$ for monatomic substances. According to the simple kinetic theory treatment all these quantities are $(2/3)$. According to the detailed theory of Chapman and Cowling each of these quantities is different: $C_{\mathfrak{D}} = (3/8)$, $C_{\mu} = (5/16)$, and $C_{\lambda} = (25/32)$. This is an indication that the transport of mass, momentum, and energy cannot be treated exactly analogously to one another as is done in the simple treatments. Since for an ideal gas, $\rho = mp/kT$, Eq. (3.4) indicates that the coefficient of self-diffusion should vary inversely to the pressure and directly as the 3/2 power of the temperature. According to Eqs. (3.5) and (3.6) the coefficients of viscosity and thermal conductivity of a dilute gas should be independent of the pressure and directly proportional to the square root of the temperature. Thus the simple theory predicts the correct pressure dependence of the dilute gas transport coefficients and comes close to giving the correct temperature dependence. It also provided the early kinetic theory workers with a means for estimating molecular diameters from bulk properties.

The rigorous kinetic theory developed by Chapman and Enskog and described in the monograph of Chapman and Cowling (6) gives an indication as to how the results of the simple kinetic theory have to be modified in order to apply to real molecules rather than rigid spheres. The rigorous theory does not in the course of its development employ the concept of the mean free path. The rigorous theory has as its starting point the Boltzmann integro-differential equation for the velocity distribution function. Although

the details of the mathematical development are quite intricate the results for pure substances may be expressed in a simple form reminiscent of the results given above for the simple kinetic theory. Thus the rigorous expressions for the first approximations to the coefficients of self-diffusion, viscosity, and thermal conductivity for a dilute monatomic gas are:

$$[\mathcal{D}]_1 = \frac{3}{8}\frac{\sqrt{\pi m k T}}{\pi\sigma^2\Omega_{\mathcal{D}}}\frac{1}{\rho} \tag{3.7}$$

$$[\mu]_1 = \frac{5}{16}\frac{\sqrt{\pi m k T}}{\pi\sigma^2\Omega_{\mu}} \tag{3.8}$$

$$[\lambda]_1 = \frac{25}{32}\frac{\sqrt{\pi m k T}}{\pi\sigma^2\Omega_{\lambda}}\hat{C}_v = \frac{15}{4}\frac{k}{m}[\mu]_1 \tag{3.9}$$

in which the Ω -functions indicate the deviation of real gas behavior from rigid sphere behavior.†

The Ω -functions are complicated integrals which depend upon the force law between the molecules. When the Lennard-Jones potential is used, σ in Eqs. (3.7), (3.8), and (3.9) is the σ in the Lennard-Jones potential. The Ω -functions are, then, functions of a dimensionless temperature kT/ϵ , in which the ϵ is the maximum energy of attrac-

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† In terms of the notation used in MTGL:

$$\Omega_{\mathcal{D}} \equiv \Omega^{(1,1)*} \quad ; \quad \Omega_{\mu} = \Omega_{\lambda} \equiv \Omega^{(2,2)*}$$

Actually there is a whole set of $\Omega^{(l,s)*}$ in terms of which the transport properties can be expressed. The ones with indices (1, 1) and (2, 2) are the most important, but additional Ω -functions are required for mixtures and for higher approximations. All of the Ω -functions needed for calculations may be found in MTGL (18) for the following potential energy functions: rigid spheres, point centers of repulsion, the Sutherland model, the square well, the Lennard-Jones (6-12) potential, and a modified Buckingham (6-exp) potential.

tion appearing in the Lennard-Jones potential function. Hence the transport coefficients are expressed as universal functions of a reduced temperature and depend parametrically on the constants σ and ε which are characteristic of the substance under consideration. Hence if σ and ε are known for some substance, the self-diffusion, viscosity, or thermal conductivity can be calculated from the above equation by use of the tabulations available for the Ω-functions. Or, if the coefficient of viscosity, for example, is known for some substance at two different temperatures, then σ and ε for that substance can easily be found by the solution of two simultaneous equations. This illustrates the way in which intermolecular force information is obtained from the measurements of bulk properties.

Eqs. (3.7, 8, 9) are based on the rigorous kinetic theory for monatomic gases. The use of Eqs. (3.7, 8) for diffusion and viscosity of polyatomic gases turns out to be quite a good approximation, provided that the molecules are not polar and not too elongated. Eq. (3.9) for thermal conductivity, however, must be modified for polyatomic molecules by means of the approximate "Eucken correction" thus:

$$[\lambda]_1 = \frac{15}{4}\frac{k}{m}[\mu]_1 \left\{ \frac{4}{15}\frac{m}{k}\hat{C}_v + \frac{3}{5} \right\} \tag{3.10}$$

Until the further development of the existing theories for the transport phenomena of polyatomic molecules (42, 10), the Eucken correction can be used to a reasonably good approximation.†

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† A theoretical justification for the Eucken correction is given in MTGL, §7.6b.

Besides formulae and tables for computing the first approximation to the transport coefficients of pure substances as discussed above, there are also tabulated functions available for the Lennard-Jones potential for use with formulae for the transport coefficients of binary and multicomponent mixtures and for the higher corrections to the transport coefficients. The formulae are quite lengthy and are not given here since they are given in full elsewhere. Generally speaking these results are easy to use and give excellent agreement with the experimental data.(1,18) Quantum effects have been shown to be negligible at room temperature and above, even for helium and hydrogen (11,13).

The situation with respect to dilute gases is then quite satisfactory at the present time, particularly as far as nonpolar molecules are concerned. Much remains to be done on the development of the kinetic theory of polyatomic gases and particularly the applications to polar gases. Aside from the very general and highly mathematical developments of Wang Chang and Uhlenbeck (42) and de Boer (10), the only other work which has been done on the kinetic theory of non-spherical molecules has been that on several special models, such as perfectly rough spheres (5, 32), loaded spheres (23), and rigid ellipsoids (22).

c. Transport Coefficients of Dense Gases and Liquids

At the present time there are four main approaches used in the study of the transport properties of dense gases and liquids. None of these methods can be regarded as entirely satisfactory, and indeed none of them really provides usable results as far as interrelating bulk properties with intermolecular forces is concerned. We describe these methods in order of increasing mathematical complexity.

The principle of corresponding states, which has been of great value for estimating p-V-T and thermodynamic properties of fluids (20), can also be applied to the correlation of transport coefficient data. That is, the transport coeffients divided by their values at the critical point,✦ may be expressed as universal functions of the reduced pressure and reduced temperature:

$$\mathcal{D}_r = \mathcal{D}/\mathcal{D}_c = \mathcal{D}_r(p_r, T_r) \tag{3.11}$$

$$\mu_r = \mu/\mu_c = \mu_r(p_r, T_r) \tag{3.12}$$

$$\lambda_r = \lambda/\lambda_c = \lambda_r(p_r, T_r) \tag{3.13}$$

in which $T_r = T/T_c$ and $p_r = p/p_c$. Equation (3.12) provides the basis for Uyehara and Watson's (41, 20) generalized viscosity chart, and Eq. (3.13) for Gamson's (14) generalized thermal conductivity chart. The latter was prepared with relatively few experimental data. As soon as more data on high density transport coefficients are available, they should be correlated in the form of generalized charts based on the principle of corresponding states.

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† The material presented in this section is treated more extensively in MTGL, Ch. 9.

✦ Other methods of reducing the variables have been suggested. One can, for example, reduce the transport coefficients by dividing them by the appropriate combination of critical constants, thus:

$$\mu_R = \sqrt[6]{kT_c/m^3 p_c^4}\,\mu = \mu_R(p_r, T_r) \tag{3.12a}$$

In another method one divides the transport coefficient by its limiting zero-pressure value, thus:

$$\mu^* = \mu/\mu^0 = \mu^*(p_r, T_r) \tag{3.12b}$$

This method was used by Comings, Mayland, and Egly (7) in the preparation of a generalized chart.

¶ The theory of rate processes as developed by Eyring and his collaborators (15) has been moderately successful in explaining the transport phenomena in liquids on a simple pictorial basis. Such an approach does not lead to expressions for the transport coefficients in terms of intermolecular forces, but rather to relations between various macroscopic quantities:

$$\mu = nh \exp(0.408\, \Delta \tilde{H}_{vap}/RT) \tag{3.14}$$

$$\doteq nh \exp(3.8\, T_b/T) \tag{3.14a}$$

$$\mathcal{D} = n^{1/3} kT/\mu \tag{3.15}$$

$$\lambda = \sqrt{8/\pi}\, k\, n^{2/3} \gamma^{-1/2} c \qquad \begin{bmatrix}\text{monatomic}\\ \text{liquids}\end{bmatrix} \tag{3.16}$$

$$\lambda = 2.80\, k\, n^{2/3} \gamma^{-1/2} c \qquad \begin{bmatrix}\text{polyatomic}\\ \text{liquids}\end{bmatrix} \tag{3.17}$$

In these relations h is Planck's constant and c is the speed of sound in the liquid. Eq. (3.14a) is a simplified form of Eq. (3.14) made possible by the use of Trouton's rule. Equation (3.16a) is a generalization of Eq. (3.16) made possible by the use of a modified Eucken correction. The Eyring theory has been used to study the transport properties of liquids composed of nonspherical molecules such as long chain hydrocarbons and high polymers. It is the only theory of transport phenomena which predicts non-newtonian flow.

The kinetic theory for rigid spheres developed by Enskog (6, 18) is probably the best theory available at the present time for describing the transport coefficients of dense gases. The big difficulty in the development of a kinetic theory for condensed systems is that one must understand certain aspects of three-molecule and higher order collisions. For the rigid sphere model, however, it is theoretically impossible for three molecules to collide at exactly the same

moment. Hence a complete theory may be developed by considering two-body collisions only. The final results of the Enskog theory may be summarized in terms of the following relations, which interrelate the reduced transport coefficients (based on zero pressure values) and the compressibility factor for rigid spheres:

$$(\mu/\mu^\circ)(\tilde{V}/b_o) = (1/y) + 0.8 + 0.761\,y \tag{3.17}$$

$$(\kappa/\mu^\circ)(\tilde{V}/b_o) = 1.002\,y \tag{3.18}$$

$$(\lambda/\lambda^\circ)(\tilde{V}/b_o) = (1/y) + 1.2 + 0.755\,y \tag{3.19}$$

$$(\mathcal{D}/\mathcal{D}^\circ)(\tilde{V}/b_o) = (1/y) \tag{3.20}$$ †

In these relations $b_o = (2/3)\pi N\sigma_R^3$ and

$$y = (p\tilde{V}/RT) - 1 = (b_o/\tilde{V}) + 0.6250\,(b_o/\tilde{V})^2 + 0.2869\,(b_o/\tilde{V})^3 + 0.115\,(b_o/\tilde{V})^4 + \cdots \tag{3.21}$$

which is obtained from the virial equation of state for rigid spheres. Although these results were obtained for rigid spheres, Enskog showed that for the available experimental data the following procedure could be used for real gases: One replaces the pressure p in Eq. (3.21) by the "thermal pressure" $T(\partial p/\partial T)_V$ so that y may be determined from the experimental p-V-T data from the relation:

$$y = (\tilde{V}/R)(\partial p/\partial T)_V - 1 \tag{3.22}$$

(For rigid spheres Eqs. (3.21) and (3.21a) are the same, but such is not the case for real molecules.) Then one fits the minimum in the curve of the viscosity versus y in order to specify a value of b_o. It will be interesting to

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† $\mathcal{D}^\circ$ may be calculated as $\mathcal{D}^\circ = MD^1/\rho RT$ where $\mathcal{D}^1$ is the coefficient of self-diffusion calculated at 1 atm. pressure according to Eq. (4.7).

test this method further when more experimental data become available. The Enskog theory has been extended to binary mixtures by Thorne(6).

The methods of non-equilibrium statistical mechanics have been applied to the problem of transport phenomena in dense systems by Kirkwood (21) and by Born and Green (3). The final results are given in terms of a nonequilibrium radial distribution function. This function is the solution of an integral equation, which, however, involves the next higher order distribution function. A "superposition approximation" is introduced in order to get rid of the higher-order distribution function, but the validity of this assumption has not been fully assessed. At the present time only limited calculations have been made, and hence the method does not yet provide a means for practical computation. It is hoped that this approach will ultimately lead to the calculation of dense gas properties with accuracy comparable to that for dilute gases according to the Chapman-Enskog theory.

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Roman Letters

a_i = activity of species "i"

a_{nm} = phenomenological coefficients

b_0 = $(2/3)\pi N\sigma_R^3$

C_v = specific heat at constant volume

$\underline{d}_j$ = driving force defined in Eq. 2.10

D/Dt = substantial derivative operator

D_{ij} = multicomponent diffusion coefficients

$\mathcal{D}_{ij}$ = binary diffusion coefficients

D_i^T = multicomponent thermal diffusion coefficients

$\underline{F}_i$ = external force acting on species i

g = rate of irreversible production of entropy

G = Gibbs free energy

H = enthalpy

$\underline{\underline{I}}$ = unit tensor

$\underline{j}_i$ = mass flux of species i (gm/cm^2 sec) with respect to mass average velocity, $\underline{v}$

$\underline{J}_i$ = mass flux of species i (moles/cm^2 sec) with respect to molar average velocity

J_n = fluxes in the thermodynamics of irreversible thermodynamics

k = Boltzmann's constant

k_T = thermal diffusion ratio

K_i = rate of production of species i by chemical reaction (gm/sec)

L = mean free path in kinetic theory

m = molecular mass (gm)

m_i = molecular mass of species i

n = number density (number of molecules per unit volume)

n_i = number density of species i

n_c = number of chemical species in multicomponent system

n_r = number of reactions in multicomponent system

$\underline{N}_i$ = mass flux of i (moles/cm^2 sec) with respect to stationary axes

$\mathcal{N}$ = Avogadro's number

p = static pressure

p_i = partial pressure of species i

$\underline{\underline{p}}$ = pressure tensor

$\underline{\underline{p}}^{(v)}$ = viscous part of pressure tensor

$\underline{q}$ = energy flux vector

$\underline{q}^{(h)}$ = heat flux vector

r = distance between two colliding molecules

r_s = rate of the sth chemical reaction

R = gas constant

S = entropy

t = time

T = absolute temperature

T_b = normal boiling temperature

U = internal energy

$\underline{v}$ = mass average velocity (stream velocity)

$\bar{v}$ = average molecular speed

V = volume

$\underline{V}^{(d)}$ = diffusion velocity

x_i = mol fraction of species i

x_h = h^{th} coordinate--x, y, or z

X_h = generalized forces in the thermodynamics of irreversible thermodynamics

y = quantity defined in §3c

Y_s = chemical affinity for the sth reaction

Greek Letters

α_{ij} = "resistance factors"

ϵ = maximum energy of attraction in intermolecular potential energy function

κ = coefficient of bulk viscosity

λ = coefficient of thermal conductivity

Δ_i = driving force defined in Eq. 1.13

μ = coefficient of viscosity

μ_i = chemical potential of ith species (permolecule)

π = 3.14159...

ρ = mass density of fluid

ρ_i = mass density of ith component in fluid

σ = parameter in intermolecular potential energy function

σ_R = diameter of rigid sphere molecule

$\underline{\sigma}$ = entropy flux

$\varphi(r)$ = intermolecular potential energy function

$\left.\begin{matrix}\Omega_D \\ \Omega \\ \Omega_\lambda\end{matrix}\right\}$ = functions of the reduced temperature which are introduced in Eqs. 3.7, 8, 9

Subscripts

i, j, k = chemical species present in multicomponent mixture

s = quantities pertaining to sth chemical reaction

c = critical quantities

r = quantities reduced by division by the corresponding critical quantities

Superscripts

^{o} = ideal gas properties

† = transpose of a tensor or dyadic product

Above Symbols

$\hat{}$ = quantity per unit mass

$\tilde{}$ = quantity per mole

$\bar{}$ = partial molal quantity

Below Symbols

$\underline{\ }$ = vector quantity

$\underline{\underline{\ }}$ = tensor quantity

Vector and Tensor Operations

$\underline{i}, \underline{j}, \underline{k}$ = unit vectors in x, y, z, directions

$$\underline{v} = \underline{i}\, v_x + \underline{j}\, v_y + \underline{k}\, v_z$$

$$\nabla T = \underline{i}\,(\partial T/\partial x) + \underline{j}\,(\partial T/\partial y) + \underline{k}\,(\partial T/\partial z)$$

$$(\nabla \cdot \underline{v}) = (\partial v_x/\partial x) + (\partial v_y/\partial y) + (\partial v_z/\partial z)$$

$$(\nabla \cdot \underline{\underline{p}})_x = (\partial p_{xx}/\partial x) + (\partial p_{yx}/\partial y) + (\partial p_{zx}/\partial z)$$

$$(\underline{v} \cdot \nabla) T = v_x\,(\partial T/\partial x) + v_y\,(\partial T/\partial y) + v_z\,(\partial T/\partial z)$$

$$\begin{aligned}(\underline{\underline{p}} : \nabla \underline{v}) = {} & p_{xx}\,(\partial v_x/\partial x) + p_{xy}\,(\partial v_x/\partial y) + p_{xz}\,(\partial v_x/\partial z) \\ & + p_{yx}\,(\partial v_y/\partial x) + p_{yy}\,(\partial v_y/\partial y) + p_{yz}\,(\partial v_y/\partial z) \\ & + p_{zx}\,(\partial v_z/\partial x) + p_{zy}\,(\partial v_z/\partial y) + p_{zz}\,(\partial v_z/\partial z)\end{aligned}$$

$$DT/Dt = \partial T/\partial t + (\underline{v} \cdot \nabla) T$$

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