RATIONAL AND PRACTICAL NONEQUILIBRIUM THERMODYNAMICS

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ABSTRACT

RATIONAL AND PRACTICAL NONEQUILIBRIUM THERMODYNAMICS

By

Sara Erb Ingle

A fundamental theory of nonequilibrium thermodynamics based upon rational mechanics is presented, is compared with traditional nonequilibrium thermodynamics, and is applied to two practical problems: heat conduction of pure fluids and the Dufour effect in fluid mixtures.

The rational mechanical theory of nonequilibrium thermodynamics is developed logically and systematically from the conservation laws of mechanics and the Second Law of thermodynamics. Full account is taken of the kinetic energy of diffusion, and a variety of sets of independent variables is investigated. For the case of linear response functions, a full, illuminating comparison is made between the rational approach and the traditional approach. It is found that the two approaches give similar, but not identical, results.

Equations directly applicable to experimental determination of thermal conductivity are obtained from macroscopic transport equations by means of a well-defined, self-consistent perturbation scheme. The barycentric velocity and variability of all properties are included explicitly.

By introduction of a second perturbation scheme, the transport equations for the Dufour effect, which is the development of a temperature gradient due to diffusion, have been solved for geometrically well-defined cells which have either all adiabatic walls or adiabatic lateral walls and diathermic ends. The heat of mixing and variation of other physical properties are fully included. For typical nonelectrolytes, the temperature difference produced by the Dufour effect could be as large as 0.2 degrees for a diffusing mixture with initial mass fraction difference of 0.8. These results can be used (1) to design experiments to test the Onsager heat-matter reciprocal relation and (2) to avoid undesired temperature variations in diffusion experiments.

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By

SARA ERB INGLE

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LIST OF SYMBOLS FOR CHAPTER II

Roman miniscules

b_i^α -- external specific forces acting on component α (2.5)*

c_α -- number density of component α (2.19)

d_{ij}^α -- symmetric part of the gradient of the component velocity (3.3)

f_i -- total entropy flux (3.2)

j_i^α -- diffusion flux of component α relative to the barycentric velocity (5.2)

k_i -- entropy flux not due to heat flow (3.2)

m_i -- specific interaction force exerted on component 1 by component 2 (6.7)

m_i^α -- specific interaction forces acting on component α due to interaction with other components (2.5)

p -- a constitutive coefficient (6.47)

q_k -- a heat flux (Bartelt's) (2.8)

q_k^* -- heat flux for total energy balance equation (2.10)

r -- specific radiative heat supply (2.8)

t -- time (2.1)

u_i -- diffusion velocity of component 1 relative to component 2 (6.2)

u_i^α -- diffusion velocity of component α relative to the barycentric velocity (2.1)

v_k -- barycentric velocity (2.2)

v_i^α -- velocity of component α (2.2)

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*These numbers refer to the equations in Chapter II where the symbols first appear.

w_α -- mass fraction of component α (5.2)

x_k -- space coordinate (2.1)

Roman majiscules

A_I -- specific internal Helmholtz free energy (3.11)

$\bar{C}_p$ -- specific heat capacity at constant pressure (5.21)

$\bar{C}_v$ -- specific heat capacity at constant volume (5.20)

C'_{xy} -- constitutive coefficient (4.4), (4.6)

C'_{xy} -- constitutive coefficient (6.44), (6.45)

D_y -- combinations of constitutive coefficients (5.12)

E -- total energy (2.9)

E_B -- internal energy (total energy less bulk kinetic energy) (6.8)

E_I -- specific internal energy (total energy less kinetic energy) (2.8)

$\bar{E}_\alpha$ -- partial specific internal energy of component α (5.21)

$F_{i\alpha}^{(1)*}$ -- interaction forces of Bearman and Kirkwood (2.18)

$\bar{H}_\alpha$ -- partial specific enthalpy of component α (5.22)

K -- a constitutive coefficient (4.9)

M_α -- molecular weight of component (2.17)

P -- pressure (4.22)

P' -- ($= P$) a constitutive coefficient (6.46)

Q_i -- a generalized heat flux (7.2)

S -- specific internal entropy (3.9)

$\bar{S}_\alpha$ -- partial specific density of component (5.14)

T -- temperature

T_{ij} -- total stress tensor (2.10)

T'_{ij} -- sum of the partial stress tensors (6.7)

V -- specific volume (4.38)

V_α -- specific scalar potentials acting on component α (2.14)

$\overline{V}_\alpha$ -- partial specific volume of component α (5.5)

X_A -- a variable which must be zero at equilibrium (4.17)

X_i^α -- external forces of Bearman and Kirkwood (2.17)

Z_i -- any force in the entropy production which includes the gradient of the chemical potential difference (7.1)

Greek miniscules

α_x -- viscosity coefficients (6.47)

β -- thermal expansivity (5.5)

β' -- isothermal compressibility (5.5)

δ_{ij} -- Kronecker delta (3.15)

η -- shear viscosity coefficient (6.46)

$\eta_{\alpha\beta}$ -- viscosity coefficients (4.8)

μ -- viscosity coefficient (4.7)

μ' -- a viscosity coefficient (6.48)

μ_α -- specific chemical potential of component α (4.38)

μ'_α -- chemical potential of component α plus the external potentials (5.12)

μ_{11} -- derivative of the chemical potential with respect to w_1 (5.17)

ν -- number of components

ξ_{ij}^α -- symmetric part of the partial stress tensor (3.1)

π_α -- constitutive coefficients (4.8)

ρ_α -- density of component α (2.1)

ρ -- density

σ^α_{ji} -- partial stress tensor of component α (2.5)

${}^{BK}\sigma^\alpha_{ji}$ -- partial stress tensors of Bearman and Kirkwood (2.16)

τ_{ij} -- a difference of partial stress tensors (6.10)

τ^α_{ij} -- antisymmetric part of the partial stress tensor of component (2.6)

ϕ -- the coefficient of bulk viscosity (6.46)

$\phi_{\alpha\beta}$ -- viscosity coefficients (4.8)

χ_x -- viscosity coefficients (6.46)

ω_{ij} -- linear combination of the antisymmetric parts of the gradients of component velocity (3.3)

Greek majiscules

Ξ_i -- the force of rational mechanics and of Bearman and Kirkwood which corresponds to the diffusion flux (7.4)

Π_{ij} -- viscous pressure tensor (5.5)

Φ -- rate of specific entropy production (3.9)

Ω_{xy} -- phenomenological coefficients (7.1)

CHAPTER I

INTRODUCTION

Few chemists have an academic knowledge of the field of nonequilibrium thermodynamics, yet we encounter it in almost every chemical phenomenon we study. The treatment of processes as equilibrium phenomena is often reasonable, but the validity of such assumptions can be proven only by exploring the phenomena from nonequilibrium viewpoints. Moreover, the vast majority of physical phenomena are not at equilibrium. In order ultimately to understand such important phenomena as metabolism, at one extreme, and spectroscopy, at the other, we must treat them as dynamic nonequilibrium phenomena.

To these ends we use rational mechanics to examine the theory of nonequilibrium thermodynamics, and we compare this theory to the traditional macroscopic nonequilibrium theory which has been used in practical applications for many years. In the development either of an equilibrium or of a nonequilibrium theory, assumptions are made in order that the theory be viable; however, it is important that one knows the limitations of his theory as determined by these assumptions. Moreover, we make actual application of the full theory to two problems of considerable practical importance: namely, we develop complete phenomenological theories for thermal conduction experiments and for the Dufour effect.

The rational mechanics approach to nonequilibrium thermodynamics consists in the logical mathematical derivation of the consequences of the laws of physics and the Second Law of Thermodynamics when these laws are applied to some well-defined physical system. We restrict our work to fluids and, in general, define a rather simplistic (to the mathematical mind) system. Yet what we are concerned with as chemists is what we can measure; regrettably, the translation of a mathematical truth into an expression for an experimental observable is no easy process. If we had a handy entropy meter, nonequilibrium thermodynamics might not be so formidable, but even this quantity, fundamental to the definition of equilibrium and nonequilibrium, must be translated into observable quantities. We cannot deny that our mathematical statements are true; what we seek is to know what they can tell us about the world we observe.

Nonequilibrium thermodynamics in the form of a theory to fit empirical observations has been used since the Nineteenth Century, but its recent growth is due to the pioneer work of Onsager in 1931. A coherent, practical theory has been developed by Prigogine (1947, 1955), Kirkwood and Crawford (1952), de Groot (1945, 1955), Meixner and Reik (1959), Fitts (1962), and de Groot and Mazur (1962). This theory has been the foundation of modern applications in nonequilibrium thermodynamics. More recent still is the theory of thermodynamics and rational mechanics which has been developed by mathematicians of the first rank. Much work is still being done in the field of continuum mechanics, but among its greatest contributions we can name the works of Truesdell (1957), Truesdell and Toupin (1960), and Coleman and Noll (1963).

Our second chapter deals with rational mechanical theories of binary fluid mixtures. Though there exists a great body of works on such fluids, the significance of the theory to the experimentalist has not been explored and an explicit comparison of the rational mechanical theories to the practical theory has not been made. Such extensions and comparisons are the subject of Chapter II.

The third and fourth chapters rest heavily on the practical theory. Both chapters are experimentally oriented in that they concern the solution of nonequilibrium problems under particular initial and boundary conditions and, therefore, experiments could be designed using the results here. In Chapter III we present the theory of thermal conductivity for a pure fluid in a flat plate or thermal diffusion cell to which a temperature gradient is applied. A self-consistent, well-ordered perturbation scheme enables us to account for variations of thermodynamic quantities in space and time and to predict accurately temperature variations in the cell. Hopefully, these results will allow experimentalists to improve their accuracy.

Chapter IV is a theoretical investigation of the Dufour effect in liquids. This phenomenon is the production of a temperature gradient in response to a concentration gradient. The effect is quite small in liquids and is complicated by heat of mixing, and, thus, it has been ignored for many years. Our theory provides a quantitative prediction of the temperature variations caused by the Dufour effect and serves as a guide to the experimentalist in measuring the effect. Philosophically, the reason for measuring it is that such an experiment would test the previously untested heat-matter Onsager reciprocal relation. The most important practical usefulness of a full theory of the Dufour effect is that it gives guidelines to the diffusion experimentalist who wishes to avoid temperature effects.

CHAPTER II

RATIONAL NONEQUILIBRIUM THERMODYNAMICS

1. Introduction

In recent years many investigations of the thermodynamics of binary mixtures of nonequilibrium fluids have been made based on the works of Coleman and Noll (1963), Coleman and Mizell (1963, 1964), Truesdell (1957), and Truesdell and Toupin (1960). Typical of these are the works of Müller (1967, 1968), Bartelt (1968), Doria (1969), Bartelt and Horne (1970), and Truesdell (1969). The logical superiority of these methods, often referred to as rational mechanics, over the traditional heuristic approach called "thermodynamics of irreversible processes" (TIP) cannot be questioned, but it is also true that the TIP theory as exemplified by Fitts (1962), de Groot and Mazur (1962), Gyarmati (1970), and Haase (1969) has been most useful and has enjoyed wide, successful application. A full comparison of TIP results with those derived from rational mechanics is clearly desirable, although most of the expounders of rational mechanics disdain to make such a comparison. We show that the two approaches lead to very similar results and that the practitioners of TIP, with their practicality and intuition, have arrived at almost the same results as the rational mechanists, with their mathematical rigor and integrity. In the course of making the comparison, we also illuminate the meaning and significance of various parts of both theories.

The essential difference between the rational mechanics approach and the TIP approach is implied in the word "rational." The rational mechanics approach is based on known balance (or conservation) equations and the results of these laws are logically and systematically derived. There is no point at which the rational mechanist can interject his intuition as to how the physical system being described ought to behave; this is, in fact, why rational mechanists abhor the practical theory while, at the same time, the users of TIP have difficulty in grasping the physical significance of rational mechanics.

The assumption essential to rational mechanics is the Second Law of Thermodynamics. Further assumptions, called constitutive assumptions, are made after a set of variables has been chosen for the physical system. These constitutive assumptions are equations which mathematically describe how dependent quantities respond to the selected independent variables. Initially, all constitutive assumptions obey the principle of equipresence; *i.e.*, every constitutive equation depends on the same independent variables unless this dependence contradicts the symmetry of the material, the entropy inequality, or fundamental mathematics. Through such contradictions the response functions are limited to dependence only on certain independent variables or combinations thereof.

The theory of TIP likewise depends on balance equations and on the Second Law, but the phenomenological equations, which correspond to the constitutive equations, are not rigorously developed. The entropy production obtained is said to be a sum of products of "fluxes" and "forces." Just what is a flux and what is a force is decided by intuition. Moreover, the fluxes are always written only as linear functions of the forces in the phenomenological equations. All thermo*dynamic* functions are taken to be the same functions of a set of state variables as they are in thermo*statics*.

The work of Müller (1967, 1968) was the first successful formulation of a theory for binary fluids through a rational mechanical development. It was from this theory that both the theory of Doria (1969) and that of Bartelt (1968) and Bartelt and Horne (1970) were developed. The principles layed down by Coleman and Noll and extended to mixtures by Müller are used by both. The work of Bartelt and Horne is particularly valuable because through careful selection of variables it attained a bilinear form for the entropy production and because it gives more practical equations (*i.e.*, transport equations) than does the more general theory of Doria. Bartelt and Horne presented a linear theory, in that the constitutive equations are assumed to be linear functions of those independent variables which are not scalar state variables, whereas the theory of Doria is not restricted to the linear case. Bartelt did consider general non-linear constitutive equations, but the consequences of the Clausius-Duhem inequality were not fully taken into account in these general equations.

The choice of independent variables greatly affects the appearance of any rational mechanical theory; the choices even lead to some contradictory results in the limit of the linear theory. No matter how rigorously the linear approximation is made with respect to one set of variables, it is still an approximation, and an equally rigorous linearization with respect to another set of variables is not the same approximation. There is an obvious similarity between, on the one hand, the multitude of sets of conjugate fluxes and forces which TIP boasts and, on the other hand, the multitude of sets of independent variables with respect to which the rational mechanist can linearize his equations. The variables in each theory are selected by trial and error in order to attain the result in its best possible form for some context. The choices of TIP have traditionally been experimentally motivated; those of rational mechanics are mathematically motivated. The mere choice of variables even before linearization can cause varying results from the Clausius-Duhem inequality (Truesdell, 1969) if an insufficient number of variables is used.

The variables of Bartelt and Horne give a concise bilinear form for the entropy production, but, unfortunately, they do not lead to linear constitutive equations which are fully comparable to those found in TIP. The chief difficulty appears in attempting to relate the nine viscosity coefficients of the rational mechanics approach to the two more familiar coefficients of bulk and shear viscosity.

Doria's variables allow him to give rigorous mathematical interpretations of the Clausius-Duhem inequality together with proofs that some constitutive relations are independent of certain independent variables. When Doria's constitutive equations are linearized, however, one does not obtain a bilinear form for the entropy production. Many restrictions can, nevertheless, be obtained from the general entropy inequality.

We present here a new rational mechanical development of the thermodynamics of nonequilibrium binary fluid mixtures. It is based on a set of variables which is a mixture of those used by Bartelt and by Doria. Unlike the work of Bartelt, the independence of the internal Helmholtz free energy of the component density gradients is proven in general rather than only in the linear case.

Our development is superior to others in that more of our phenomenological coefficients can be given physical meaning, and the nature of their source can be better understood. Two of the nine viscosity coefficients are the recognized shear and bulk viscosity coefficients. The entropy production, though not bilinear in form, is readily comparable to the entropy production of TIP.

In addition, this work serves as clarification and extension of previous work by other authors. The implications of the transport theory of Bartelt and Horne are examined, the great similarity of Bearman and Kirkwood's (1958) microscopic theory to the theories of rational mechanics is demonstrated, the assumptions which must necessarily be made in a rational mechanical development in order to arrive at the results of TIP are illustrated, the limitations of the postulate of local state[1] are explored, and the similarities as well as the irreconcilable disparities among several approaches to nonequilibrium fluid mixture theory are discussed.

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[1] "For a system in which irreversible processes are taking place, all thermodynamic functions of state exist for each element of the system. These thermodynamic quantities for the nonequilibrium system are the same functions of the local state variables as the corresponding equilibrium thermodynamic quantities."--Fitts (1962). This is usually called the postulate of local equilibrium, which is a misnomer. Kestin (1966) introduced the more apt terminology, "postulate of local state."

Particular attention is given to the kinetic energy of diffusion[2] and its consequences. Rational mechanics has generally included the kinetic energy of diffusion, but has also failed to give transport equations which are as practical as those of TIP. The enigma of the contribution of kinetic energy of diffusion has been considered only by Gyarmati whose work is extremely lucid, but unviable. To avoid the problems created by inclusion or exclusion of the kinetic energy of diffusion he defines two total energies, one from which one subtracts the bulk kinetic energy, the other from which he subtracts the bulk and diffusion kinetic energies, thus arriving at the same internal energy in both cases. Both total energies are subject to the conservation of energy equation although they differ by the kinetic energy of diffusion. This implies that the kinetic energy of diffusion is conservative, which is clearly an incorrect assumption. We feel that the logical way to approach the subject is to define one total energy and two internal energies, one of which includes the kinetic energy of diffusion.

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[2] We take the kinetic energy of the volume element to be $\sum_{\alpha=1}^{\nu} (1/2)m_\alpha \underset{\sim}{v}_\alpha^2$, where m_α is the mass of component α, $\underset{\sim}{v}_\alpha$ is its velocity, and ν is the total number of components. Others, particularly practitioners of TIP, take the kinetic energy of the volume element to be $(1/2)m\underset{\sim}{v}^2$, where m is the mass of the volume element and $\underset{\sim}{v}$ is the velocity of the center of mass, $mv = \sum_{\alpha=1}^{\nu} m_\alpha \underset{\sim}{v}_\alpha$. The difference between the two energies, $\sum_{\alpha=1}^{\nu}(1/2)m_\alpha(\underset{\sim}{v}_\alpha^2 - \underset{\sim}{v}^2) = \sum_{\alpha=1}^{\nu}(1/2)m_\alpha(\underset{\sim}{v}_\alpha - \underset{\sim}{v})^2$, is the kinetic energy of diffusion.

It is the definition of two internal energies which presents a dilemma in the postulate of local state. To which internal energy does a Gibbsian equation apply? Certainly the energy internal to the macroscopic volume element under discussion includes the kinetic energy of diffusion. However, we know that the internal energy of the volume element changes due to work done on or by the volume element and to heat transferred to or from the body. This, too, would imply that internal energy includes the kinetic energy of diffusion. The internal energy is a function of three state variables (*e.g.*, temperature, pressure, and composition) in a binary fluid mixture; if kinetic energy is part of this energy, then it, too, is a function of three state variables, which seems unlikely. The postulate of local state obviously deserves the further investigation which we present here.

2. Thermodynamic Process and the Equations of Balance

In order to describe a thermodynamic process in any system, it is necessary to know how the several functions which are characteristic of the system change spatially and temporally and to know the balance equations which the system obeys. Bartelt (1968), whose notation is slightly different from ours, gave as the generalization for mixtures of the Coleman and Noll (1963) definition: A process is a thermodynamic process for a ν-component mixture if it can be described by the following set of $5\nu + 6$ functions[3]:

i. the component densities, ρ_α
ii. the component velocities, v_i^α
iii. the specific interaction forces, m_i^α, acting on component α due to interaction with other components
iv. the specific external forces, b_i^α, acting on component α
v. the partial stress tensors, σ_{ij}^α
vi. the specific internal energy, E_I
vii. the temperature, T
viii. the specific radiative heat supply, r
ix. the heat flux, q_i
x. the specific entropy, S
xi. the entropy flux, f_i.

These functions must satisfy the following $2\nu + 2$ balance equations for the system:

1. the balance of mass for each component[4],

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[3] Cartesian tensor notation is employed throughout this chapter. Vectors are denoted by a single subscript, v_i, while tensors are doubly subscripted, t_{ij}. The summation convention on indices is also used, i.e.,

$$v_i T_{ij} = \sum_{i=1}^{3} v_i T_{ij}.$$

[4] The local time derivative $(\partial/\partial t)$ is related to the substantial time derivative (d/dt) by:
$(d/dt) = (\partial/\partial t) + v_i(\partial/\partial x_i)$.

$$d\rho_\alpha/dt + \partial\rho_\alpha u_k^\alpha/\partial x_k + \rho_\alpha(\partial v_k/\partial x_k) = 0, \qquad (2.1)$$

where u_i^α is the diffusion velocity of component α defined by

$$u_i^\alpha = v_i^\alpha - v_i, \qquad (2.2)$$

where v_i is the barycentric velocity[5],

$$\rho v_i = \sum\rho_\alpha v_i^\alpha, \qquad (2.3)$$

and

$$\rho = \sum\rho_\alpha,\ \sum\rho_\alpha u_k^\alpha = 0. \qquad (2.4)$$

2. the balance of each vector component of linear momentum for each component,

$$\partial\rho_\alpha v_i^\alpha/\partial t + \partial(\rho_\alpha v_j^\alpha v_i^\alpha - \sigma_{ji}^\alpha)/\partial x_j = \rho m_i^\alpha + \rho_\alpha b_i^\alpha, \qquad (2.5)$$

3. the balance of angular momentum for the mixture,

$$\sum\tau_{ij}^\alpha = 0, \qquad (2.6)$$

where τ_{ij}^α is the antisymmetric part of the partial stress tensor, σ_{ij}^α:

$$\tau_{ij}^\alpha = (1/2)(\sigma_{ij}^\alpha - \sigma_{ji}^\alpha); \qquad (2.7)$$

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[5] $\sum = \sum_{\alpha=1}^{\nu}$, where ν is the total number of components in the system.

4. the balance of internal energy,

$$\rho(dE_I/dt) + \partial q_k/\partial x_k = \rho r - \rho\sum m_k^\alpha u_k^\alpha + \sum\sigma_{ij}^\alpha(\partial v_i^\alpha/\partial x_j). \qquad (2.8)$$

Equation (2.8) results from the equation of conservation of total energy after the balance equations for potential energy and kinetic energy have been subtracted. The "total energy" of Truesdell or Bartelt and that considered here includes only the internal and kinetic energies:

$$E = E_I + \sum\rho_\alpha v_i^\alpha v_i^\alpha/2\rho. \qquad (2.9)$$

The balance equation of this "total energy" is

$$\rho(dE/dt) + \partial(q_j^* - v_i T_{ij})/\partial x_j = \rho r + \sum\rho_\alpha v_i^\alpha b_i^\alpha, \qquad (2.10)$$

where q_i^* is a heat flux and T_{ij} is the total stress tensor defined by

$$T_{ij} = \sum(\sigma_{ij}^\alpha - \rho_\alpha u_i^\alpha u_j^\alpha). \qquad (2.11)$$

This total stress tensor is identical to the total stress tensor of the microscopic theory of Bearman and Kirkwood (1958). The balance of kinetic energy is derived from (2.4) with the help of (2.3), with the result

$$\rho d(\sum\rho_\alpha v_i^\alpha v_i^\alpha/2\rho)/dt = \partial[\sum(\sigma_{ji}^\alpha - \rho_\alpha u_j^\alpha u_i^\alpha)v_i^\alpha + (1/2)\sum\rho_\alpha u_j^\alpha u_i^\alpha u_i^\alpha]/\partial x_j - \sum\sigma_{ji}^\alpha(\partial v_i^\alpha/\partial x_j) + \rho\sum m_i^\alpha u_i^\alpha + \sum\rho_\alpha b_i^\alpha v_i^\alpha \qquad (2.12)$$

Subtraction of (2.11) from (2.10) gives (2.8), wherein the two heat fluxes are related by:

$$q_j = q_j^* + \sum(\sigma_{ji}^{\alpha} - \rho_\alpha u_j^\alpha u_i^\alpha)u_i^\alpha + (1/2)\sum\rho_\alpha u_j^\alpha u_i^\alpha u_i^\alpha. \quad (2.13)$$

Only conservative external forces are considered here; thus, in terms of a specific scalar potential, V_α:

$$b_i^\alpha = - \partial V_\alpha / \partial x_i. \quad (2.14)$$

The definition of internal energy is such that the internal energy does not include any external force terms. Inclusion of the conservative external forces is achieved through addition of terms to the chemical potential of each component. If terms for kinetic energy or external fields are included explicitly or implicitly in definitions of partial specific energies, it must be realized that the sum of these energies will not give the internal energy alone, but rather the internal energy plus all or some portion of the kinetic energy and of the potential energy.

The sum of the momentum balance equations (2.5) gives the total momentum balance equation which does not depend on the component interaction forces, m_i^α. This means that the interaction forces are not all independent:

$$\sum m_i^\alpha = 0. \quad (2.15)$$

The validity of these balance equations is generally accepted. One may work either with internal energy including or not including the kinetic energy of diffusion so long as he uses the balance equations appropriate to his choice. The greatest confusion arises in reviewing TIP, where the kinetic energy of diffusion is generally included in the internal energy and, therefore, is implicit in all partial quantities. Likewise, if one adopts the Gibbsian equations for enthalpy and the free energies, he must specify to which "internal" thermodynamic function he is applying them.

To specify a thermodynamic process only the $4\nu + 5$ functions, ρ_α, v_i^α, m_i^α, σ_{ij}^α, E_I, T, q_i, S, and f_i, must be specified while the $\nu + 1$ functions, b_i^α and r, can be obtained in terms of the other functions by use of the balance equations (2.5) and (2.8).

We now make several identifications between the present macroscopic theory and the microscopic theory of Bearman and Kirkwood. The partial stress tensors of Bearman and Kirkwood, ${}^{BK}\sigma_{ij}^\alpha$, are related to the macroscopic partial stress tensors by

$$ {}^{BK}\sigma_{ij}^\alpha = \sigma_{ij}^\alpha - \rho_\alpha u_i^\alpha u_j^\alpha . \tag{2.16} $$

The microscopic theory excludes radiative energy source terms which are included in the macroscopic theory. The conservative forces of Bearman and Kirkwood, X_i^α, are related to those of Bartelt by

$$ X_i^\alpha = -\rho(\partial V_\alpha/\partial x_i) = M_\alpha b_i^\alpha , \tag{2.17} $$

where M_α is the molecular weight. Likewise, for interaction forces, the relationship is

$$F^{(1)*}_{i\alpha} = (\rho/\rho_\alpha)M_\alpha m^\alpha_i. \tag{2.18}$$

Thus, the equation of Kirkwood and Bearman,

$$\partial\rho_\alpha v^\alpha_i/\partial t = \partial\{{}^{BK}\sigma^\alpha_{ji} - \rho_\alpha(v^\alpha_j v_i - v_j v^\alpha_i - v_j v_i)\}/\partial x_j$$
$$+ c_\alpha \overline{F}^{(1)*}_{i\alpha} + c_\alpha X^\alpha_i, \tag{2.19}$$

where c_α is the number density of component α, is identical to (2.5) when the identities, (2.16), (2.17), and (2.18) are used.

3. Constitutive Assumptions

A material is defined by a constitutive assumption which is a restriction on the processes admissible in a body of that material. A set of constitutive equations completely describes the response of the system to variations of the independent variables. A mixture of viscoelastic materials susceptible to diffusion and heat conduction is completely determined by the values of $3\nu + 4$ functions: A_I, S, q_i, k_i, ξ^α_{ij}, τ^α_{ij}, and m^α_i, where A_I is the specific internal Helmholtz free energy, and ξ^α_{ij} is the symmetric part of the stress tensor, σ^α_{ij},

$$\xi^\alpha_{ij} = 1/2(\sigma^\alpha_{ij} + \sigma^\alpha_{ji}). \tag{3.1}$$

The flux, k_i, is the difference between the total entropy flux and the entropy flux due to heat flow,

$$k_i = f_i - q_i/T. \tag{3.2}$$

The $3\nu + 4$ functions selected here could be replaced by any equivalent set of $3\nu + 4$ functions. The choice made in this section is motivated by those terms which appear in the balance equations of Section 2 and in the entropy balance equation.

According to Bartelt's definition, a <u>binary</u> mixture of fluids is one whose constitutive functionals are functions of the independent variables

$$\rho_1, \rho_2, T, (\partial\rho_1/\partial x_i), (\partial\rho_2/\partial x_i), u_i^1, d_{ij}^1, d_{ij}^2, \omega_{ij}, \tag{3.3}$$

where d_{ij}^α and ω_{ij} arise from the separation of $\partial v_j^\alpha/\partial x_i$ into its symmetric and antisymmetric components. The symmetric tensor is:

$$d_{ij}^\alpha = (1/2)(\partial v_j^\alpha/\partial x_i + \partial v_i^\alpha/\partial x_j) \tag{3.4}$$

and the antisymmetric tensor is given by

$$\begin{aligned} \omega_{ij}^\alpha = {} & [\rho/2(\rho - \rho_\alpha)]\{(\partial v_j^\alpha/\partial x_i - \partial v_i^\alpha/\partial x_j) \\ & - (\partial v_j/\partial x_i - \partial v_i \partial x_j) \\ & + (1/\rho)\sum_{\beta=1}^{\nu}[(\partial\rho_\beta/\partial x_i)u_j^\beta - (\partial\rho_\beta/\partial x_j)u_i^\beta]\} \end{aligned} \tag{3.5}$$

or by

$$\omega^1_{ij} = (1/2)[\partial(\rho u^1_j/\rho_2)/\partial x_i - \partial(\rho u^1_i/\rho_2)/\partial x_j]. \tag{3.6}$$

The terms added to the antisymmetric components of $\partial v^\alpha_j/\partial x_i$ change neither its symmetry nor its objectivity. This very complicated definition leads to a very simple relationship between ω^1_{ij} and ω^2_{ij}, which are not independent since

$$\omega_{ij} = \omega^1_{ij} = - \omega^2_{ij}, \tag{3.7}$$

and hence,

$$\omega^1_{ij} - \omega^2_{ij} = (1/2)(\partial v^1_j/\partial x_i - \partial v^1_i/\partial x_j) - (1/2)(\partial v^2_j/\partial x_i - \partial v^2_i/\partial x_j) = 2\omega_{ij}. \tag{3.8}$$

Thus, in the difference between the antisymmetric tensors (which appears frequently in subsequent sections) the terms which were added to the antisymmetric component of $\partial v^\alpha_j/\partial x_i$ have cancelled out. The variables of (3.3) satisfy the principle of objectivity, which means that they are independent of any reference frame. Extreme caution must be used in the manipulation of equations which contain these variables, for, while $\partial v^\alpha_i/\partial x_j$ is objective, v^α_i is not because an observed velocity depends on the observer's reference frame. We want to keep our equations in terms of objective expressions.

The entropy and entropy flux are related by the balance equation

$$\rho (dS/dt) = - \partial f_i/\partial x_i + \rho\Phi + \rho r/T, \tag{3.9}$$

where Φ is the rate of specific entropy production not due to external radiation sources. The function, Φ, can be obtained for any specified thermodynamic process from the constitutive equations for S and f_i and from the energy balance equation (2.8) used in conjunction with other constitutive relations.

The second law of thermodynamics here becomes the mathematical statement

$$\Phi \geq 0, \tag{3.10}$$

which is known as the Clausius-Duhem inequality or the entropy inequality. This inequality must hold for every admissible thermodynamic process.

The internal Helmholtz free energy, A_I, is defined by

$$A_I = E_I - TS. \tag{3.11}$$

Substitution of this expression into (3.9) and use of (3.2) and (2.8) gives

$$\begin{aligned} \rho T\Phi = &- \rho dA_I/dt - \rho S(dT/dt) + T(\partial k_j/\partial x_j) \\ &- (q_j/T)(\partial T/\partial x_j) - \rho\sum m_j^\alpha u_j^\alpha + \sum d_{ij}^\alpha \xi_{ij}^\alpha \\ &+ 2\omega_{ij}\tau_{ji}. \end{aligned} \tag{3.12}$$

Equations (2.7), (3.1), (3.4), and (3.7) have been used to obtain the last two terms.

Both of the derivatives, dA_I/dt and $\partial k_i/\partial x_i$, can be expanded in terms of the independent variables. After this procedure all terms which do not satisfy the second law postulate are dropped, i.e., we drop each term in which the independence of some particular variable allows the term to be either positive or negative when all other independent variables are set equal to zero. These restrictions reduce the constitutive equation for A_I to a function of five variables:

$$A_I = A_I\ (\rho_1,\rho_2,\partial\rho_1/\partial x_i,\partial\rho_2/\partial x_i,T). \qquad (3.13)$$

In particular, A_I is not a function of the diffusion velocity, u_i^1. Another requirement of the Clausius-Duhem inequality is

$$S = -\,\partial A_I/\partial T \qquad (3.14)$$

as is found in thermostatics. (Some equations of thermostatics are given in Appendix A.)

Chain-rule expansion of dA_I/dt and $\partial k_i/\partial x_i$, introduction of the conservation of mass (2.1) in the form

$$d\rho_\alpha/dt = -\,u_i^\alpha(\partial\rho_\alpha/\partial x_i) - \rho_\alpha d_{ij}^\alpha\delta_{ij}, \qquad (3.15)$$

expansion of $\partial u_j^\alpha/\partial x_i$ in the manner

$$\partial u_j^\alpha/\partial x_i = (\rho - \rho_\alpha)\omega_{ij}^\alpha/\rho + d_{ij}^\alpha - (1/\rho)\sum_{\beta=1}^{\nu}\rho_\beta d_{ij}^\beta$$

$$- (1/\rho)\sum_{\beta=1}^{\nu}(\partial\rho_\beta/\partial x_i)u_j^\beta, \qquad (3.16)$$

and use of equations (2.4) and (2.6), and of the restrictions for the Clausius-Duhem inequality permit (3.12) to be written as

$$\rho T\Phi = -\rho\left[\frac{1}{\rho_1}\left(\frac{\partial A_I}{\partial\rho_1}\right)\frac{\partial\rho_1}{\partial x_i} - \frac{1}{\rho_2}\left(\frac{\partial A_I}{\partial\rho_2}\right)\frac{\partial\rho_2}{\partial x_i}\right]\rho_1 u_i^1$$

$$- \sum\rho\left[\frac{A_I}{\partial\left(\frac{\partial\rho_\alpha}{\partial x_i}\right)}\right]\frac{\partial^2\rho_\alpha}{\partial t\partial x_i} + \sum T\left[\frac{\partial k_i}{\partial\left(\frac{\partial\rho_\alpha}{\partial x_j}\right)}\right]\frac{\partial^2\rho_\alpha}{\partial x_i\partial x_j}$$

$$+ \left(T\frac{\partial k_i}{\partial T} - \frac{q_i}{T}\right)\frac{\partial T}{\partial x_i} + \sum T\left(\frac{\partial k_i}{\partial\rho_\alpha}\right)\frac{\partial\rho_\alpha}{\partial x_i}$$

$$- \frac{\rho^2}{\rho_2}m_i^1 u_i^1 + T\frac{\rho_2}{\rho}\frac{\partial k_j}{\partial u_i}\omega_{ji} + T\frac{\partial k_j}{\partial u_i}d_{ij}^1$$

$$+ \sum\rho\frac{\partial A_I}{\partial\rho_\alpha}\rho_\alpha d_{ij}^\alpha\delta_{ij} - \sum T\frac{\rho_\alpha}{\rho}\frac{\partial k_j}{\partial u_i^1}d_{ij}^\alpha + \sum\xi_{ij}^\alpha d_{ij}^\alpha$$

$$- \frac{T}{\rho}\frac{\partial k_j}{\partial u_i^1}\left(\frac{1}{\rho_1}\frac{\partial\rho_1}{\partial x_j} - \frac{1}{\rho_2}\frac{\partial\rho_2}{\partial x_j}\right)\rho_1 u_i^1 + 2\tau_{ij}^1\omega_{ji}$$

$$+ T\left(\frac{\partial k_\ell}{\partial d_{ij}^\alpha}\right)\frac{\partial d_{ij}^\alpha}{\partial x_\ell} + T\left(\frac{\partial k_\ell}{\partial\omega_{ij}}\right)\frac{\partial\omega_{ij}}{\partial x_\ell}. \qquad (3.17)$$

4. Ordinary Binary Fluid Mixtures

An ordinary binary fluid mixture is defined as one whose constitutive assumptions are linear in the independent variables

$$(\partial \rho_1/\partial x_i), (\partial \rho_2/\partial x_i), u_i^1, d_{ij}^1, d_{ij}^2, \omega_{ij}, \partial T/\partial x_i. \qquad (4.1)$$

This definition includes all the variables given in (3.3) except those which are scalars. The constitutive functionals are restricted from being dependent on tensor or vector products of the independent variables. A tensor of one rank can only be a linear function of tensors of the same rank. Thus, vectors will be linear in the independent variables which are vectors and will have scalar coefficients which are functions of the independent scalar variables. Similarly, tensors of one symmetry will be functions of the variables which are tensors of the same symmetry and will have scalar coefficients. Scalars can only be functions of scalars.

Applying the principle of equipresence and eliminating immediately from each constitutive relation all variables which are not of the same tensorial rank or symmetry, we write the constitutive equations

$$A_I = A_I(\rho_1, \rho_2, T) \qquad (4.2)$$

$$S = S(\rho_1, \rho_2, T) \qquad (4.3)$$

$$q_i = - C_{qT}(\partial T/\partial x_i) - C_{q1}(\partial \rho_1/\partial x_i) - C_{q2}(\partial \rho_2/\partial x_i)$$

$$- C_{qu} u_i^1 \qquad (4.4)$$

$$m_i^1 = - C_{mT}(\partial T/\partial x_i) - C_{m1}(\partial \rho_1/\partial x_i) - C_{m2}(\partial \rho_2/\partial x_i)$$

$$- C_{mu}u_i^1 \tag{4.5}$$

$$k_i = C_{kT}(\partial T/\partial x_i) + C_{k1}(\partial \rho_1/\partial x_i) + C_{k2}(\partial \rho_\alpha/\partial x_i)$$

$$+ C_{ku}u_i^1 \tag{4.6}$$

$$\tau_{ij}^1 = - \mu\omega_{ij} \tag{4.7}$$

$$\xi_{ij}^\alpha = - \pi_\alpha\delta_{ij} + \sum_{\beta=1}^{2}\phi_{\alpha\beta}d_{kk}^\beta\delta_{ij} + \sum_{\beta=1}^{2}2\eta_{\alpha\beta}\{d_{ij}^\beta\}, \tag{4.8}$$

where d_{kk}^α is the trace of d_{ij}^α and $\{d_{ij}^\alpha\}$ is the traceless part of d_{ij}^α. Separation of d_{ij}^α into these two parts is significant physically in that the trace of d_{ij}^α is related to dilatation and the traceless part of d_{ij}^α is related to shear. Inclusion of the first term on the right hand side of (4.8) is required because δ_{ij} is the ever-present unit tensor and, since it is symmetric, the symmetric tensor ξ_{ij}^α depends on it; $- \pi_\alpha$ is a scalar coefficient.

The Clausius-Duhem inequality when applied to (3.17) with the linear constitutive equations for k_i and A_I requires that k_i not be a function of the density gradients or temperature gradient; therefore, (4.6) becomes

$$k_i = Ku_i^1, \; C_{ku} = K. \tag{4.9}$$

Insertion of the constitutive equations (4.4), (4.5), (4.7), (4.8), and (4.9) into (3.17) leads to the entropy production equation

$$\begin{aligned}\rho T\Phi &= D + Y + F\rho_1(\partial\rho_1/\partial x_i)u_i^1 + G\rho_1(\partial\rho_2/\partial x_i)u_i^1\\ &\quad + C_{q1}(\partial T/\partial x_i)(\partial\rho_1/\partial x_i) + C_{q2}(\partial T/\partial x_i)(\partial\rho_2/\partial x_i)\\ &\quad + Hd_{ii}^1 + Id_{ii}^2\end{aligned} \tag{4.10}$$

where

$$\begin{aligned}D &= (C_{qT}/T)(\partial T/\partial x_i)(\partial T/\partial x_i) + [(T/\rho_1)(\partial K/\partial T)\\ &\quad + C_{qu}/\rho_1 T + \rho^2 C_{mT}/\rho_1\rho_2]\rho_1 u_i^1(\partial T/\partial x_i)\\ &\quad + (\rho^2/\rho_2)C_{mu}u_i^1 u_i^1\end{aligned} \tag{4.11}$$

$$\begin{aligned}Y &= \sum_{\alpha=1}^{2}\sum_{\beta=1}^{2}\phi_{\alpha\beta}d_{\ell\ell}^{\alpha}d_{nn}^{\beta} + \sum_{\alpha=1}^{2}\sum_{\beta=1}^{2}2\eta_{\alpha\beta}\{d_{ij}^{\alpha}\}\{d_{ij}^{\beta}\}\\ &\quad + 2\mu\omega_{ij}\omega_{ji}\end{aligned} \tag{4.12}$$

$$\begin{aligned}F &= (\rho/\rho_1)(\partial A_I/\partial\rho_1) + (T/\rho_1)(\partial K/\partial\rho_1)\\ &\quad + \rho^2 C_{m1}/\rho_1\rho_2 - TK/\rho\rho_1\end{aligned} \tag{4.13}$$

$$\begin{aligned}G &= -(\rho/\rho_2)(\partial A_I/\partial\rho_2) + (T/\rho_1)(\partial K/\partial\rho_2)\\ &\quad + \rho^2 C_{m2}/\rho_1\rho_2 + TK/\rho\rho_2\end{aligned} \tag{4.14}$$

$$H = TK\rho_2/\rho + \rho\rho_1(\partial A_I/\partial\rho_1) - \pi_1 \tag{4.15}$$

$$I = - TK\rho_2/\rho + \rho\rho_2(\partial A_I/\partial \rho_2) - \pi_2 \qquad (4.16)$$

The entropy production (4.10) is a minimum at equilibrium. From equations (4.10), (4.11), and (4.12) we see that it can be written as a function of twenty-one variables, X_A,

$$X_A = (\partial T/\partial x_i, d^1_{ij}, d^2_{ij}, \omega^1_{ij}, u^1_i), \qquad (4.17)$$

and the condition for equilibrium is that every X_A be equal to zero. As Bartelt and Horne (1970) have noted, vanishing of density gradients and the barycentric velocity is not required for equilibrium.

The minimum entropy requirement can be expressed by the mathematical conditions

$$(\partial\Phi/\partial X_A)_o = 0 \qquad (4.18)$$

$$(\partial^2\Phi/\partial X_A \partial X_B)_o > 0, \qquad (4.19)$$

where the subscript o indicates that the derivative function is to be evaluated at equilibrium. Applications of (4.18) and (4.19) to (4.10) impose certain restraints on the coefficients of the bilinear form of the entropy production.

Two of these restrictions are

$$H = 0 \text{ or } \pi_1 = \rho\rho_1(\partial A_I/\partial \rho_1) - TK\rho_2/\rho \qquad (4.20)$$

and

$$I = 0 \text{ or } \pi_2 = \rho\rho_2(\partial A_I/\partial\rho_2) + TK\rho_2/\rho. \tag{4.21}$$

From (4.20) and (4.21) one can identify the sum of π_1 and π_2 as the pressure, P,

$$\pi_1 + \pi_2 = \rho\rho_1(\partial A_I/\partial\rho_1) + \rho\rho_2(\partial A_I/\partial\rho_2) = P, \tag{4.22}$$

where the thermostatic definition of pressure has been used. The coefficients π_1 and π_2 thus have characteristics of partial pressures.

Other results include

$$C_{q1} = C_{q2} = 0 \tag{4.23}$$

$$C_{qT} \geq 0 \tag{4.24}$$

$$\mu \geq 0 \tag{4.25}$$

$$\phi_{11} \geq 0 \tag{4.26}$$

$$\phi_{22} \geq 0 \tag{4.27}$$

$$\phi_{11}\phi_{22} - (1/4)(\phi_{12} + \phi_{21})^2 \geq 0 \tag{4.28}$$

$$\eta_{11} \geq 0 \tag{4.29}$$

$$\eta_{22} \geq 0 \tag{4.30}$$

$$\eta_{11}\eta_{22} - (1/4)(\eta_{12} + \eta_{21})^2 \geq 0 \tag{4.31}$$

$$C_{mu} \geq 0 \tag{4.32}$$

$$F = 0 \text{ or } \rho^2 C_{m1}/\rho_1\rho_2 = TK/\rho_1^2 - (T/\rho_1)(\partial K/\partial\rho_1) - \pi_1/\rho_1^2 \tag{4.33}$$

$$G = 0 \text{ or } \rho^2 C_{m2}/\rho_1\rho_2 = -(T/\rho_1)(\partial K/\partial \rho_2) + \pi_2/\rho_2^2 \quad (4.34)$$

$$\rho^2 C_{qT} C_{mu}/\rho_2 T - (1/4)[T(\partial K/\partial T) + C_{qu}/T$$
$$+ \rho^2 C_{mT}/\rho_2]^2 \geq 0. \quad (4.35)$$

These restrictions reduce the entropy production (4.1) to the form

$$\rho T\Phi = D + Y. \quad (4.36)$$

Moreover, (4.23) shortens the constitutive equation (4.4) to

$$q_i = - C_{qu}u_i^1 - C_{qT}(\partial T/\partial x_i). \quad (4.37)$$

Equations (4.33) and (4.34) make it possible to eliminate the coefficients C_{m1} and C_{m2} from (4.5). The complete set of constitutive relations is then (4.2), (4.3), (4.7), (4.8), (4.9), (4.37), and (4.5) with (4.33) and (4.34). The apparent lack of symmetry with respect to the two components in equations such as (4.13), (4.14), (4.33), and (4.34) is due to the non-independence of the variables u_i^1 and u_i^2 and can be eliminated by retaining both variables.

From the Gibbsian equation of thermostatics for two components

$$dA_I = PdV - SdT + (\mu_1 - \mu_2)dw_1, \quad (4.38)$$

where μ_α is the specific chemical potential of component α and V is the specific volume,

$$V = 1/\rho, \quad (4.39)$$

the Euler equation

$$\sum_{\alpha} w_{\alpha}\mu_{\alpha} = A_I + P/\rho \tag{4.40}$$

can be derived. Equations (4.38) and (4.40) yield a thermostatic identity,

$$\mu_{\alpha} = A_I + \rho(\partial A_I/\partial \rho_{\alpha})_{\rho_{\beta},T} \tag{4.41}$$

We assume that this is the <u>definition</u> of chemical potential in nonequilibrium processes. Using (4.20), (4.21), and (4.41), we find

$$\mu_1 - \mu_2 = \pi_1/\rho_1 - \pi_2/\rho_2 - TK/\rho_1, \tag{4.42}$$

which will be most useful later.

The constitutive equation for m_i^1 is particularly interesting. By (2.5) and (2.15)

$$\begin{aligned} \rho m_i^1 = {} & d\rho_1 u_i^1/dt - [(\rho_2/\rho)(\partial\sigma^1_{ji}/\partial x_j) - (\rho_1/\rho)(\partial\sigma^2_{ji}/\partial x_j)] \\ & + J_i - (\rho_1\rho_2/\rho)(b_i^1 - b_i^2), \end{aligned} \tag{4.43}$$

where J_i consists entirely of terms of the order of velocity squared,

$$\begin{aligned} J_i = {} & \rho_1 u_i^1(\partial v_j/\partial x_j) + \rho_1 u_j^1(\partial v_i/\partial x_j) \\ & - [(\rho_1 - \rho_2)/\rho_1\rho_2](\partial\rho_1^2 u_j^1 u_i^1/\partial x_j) \\ & - (\rho_1\rho_2 u_i^1 u_j^1/\rho)[(1/\rho_1)(\partial\rho_1/\partial x_j) \\ & - (\rho_1^2/\rho_2^3)(\partial\rho_2/\partial x_j)]. \end{aligned} \tag{4.44}$$

Equation (4.43) does not define m_i^1, as we have no constitutive equation for the external forces, but in the event that there were no external forces it would be a defining relationship. The difficulty in carrying out an explicit analysis under the restriction that there be no external forces lies in the fact that while the constitutive equations are required to be objective, the balance equations are not. The balance equations obey the principle of the invariance of work under changes of frame. The external forces which appear in the momentum equations are, in fact, only apparent external forces. True forces are defined in an inertial frame, and the momentum balance equations hold true in those inertial frames where real forces are exerted. A detailed discussion of inertial frames, forces, and apparent forces is given by Truesdell and Toupin (1960). Because we have written a general formulation which holds in all frames, it is impossible to require that the external forces be objective or, in fact, simultaneously zero in all reference frames.

The right hand side of (4.43) appears to be nonlinear according to the definitions of this section. Constitutive relations could be introduced for the stress tensors, and this would result in inclusion of second derivatives of the component velocities. The terms containing the barycentric velocity are even more unusual since they lead to terms containing three or more variables when the gradient of the barycentric velocity is expressed in terms of the objective independent variables chosen in Section 3. Comparing (4.43) with the constitutive equation for m_i^1, (4.5), we see that the linearity of m_i^1 there is in distinct contrast to the right hand side of (4.44). The first term in (4.43) is called an inertial term and all the terms in J_i are called viscous terms or non-linear terms. Clearly, no one-to-one correlation can be made between (4.43) and (4.5), but (4.43) places restrictions on m_i^1 which will be utilized later.

5. Transport Equations in the Independent Variables T, ρ, w_1

The transport equations given in this section follow algebraically from the equations of the previous sections. The independent thermodynamic variables considered in this section are the more commonly used ρ, w_1, and T rather than ρ_1, ρ_2, and T. These transport equations are equivalent to the $2\nu + 2$ balance equations of Section 2, where in the binary case we have ν equal to 2.

The balance of mass equations (2.1) are replaced by

$$d\rho/dt = - \rho(\partial v_i/\partial x_i) \tag{5.1}$$

and

$$\rho(dw_1/dt) = - \partial j_i^1/\partial x_i, \tag{5.2}$$

where j_i^1 is the diffusion flux,

$$j_i^1 = \rho_1 u_i^1. \tag{5.3}$$

The balance equation for linear momentum of the system as a whole is found by summing equations (2.5) over α to obtain

$$\rho(dv_i/dt) - \partial\sum(\sigma_{ji}^{\alpha} - \rho_{\alpha}u_j^{\alpha}u_i^{\alpha})/\partial x_j = \sum\rho_{\alpha}b_i^{\alpha}. \tag{5.4}$$

The form

$$\begin{aligned}\rho(dv_i/dt) = &- (\beta/\beta')(\partial T/\partial x_i) - (1/\rho\beta')(\partial\rho/\partial x_i)\\ &- [\rho(\overline{V}_1 - \overline{V}_2)/\beta'](\partial w_1/\partial x_i)\\ &+ \sum\rho_{\alpha}b_i^{\alpha} + \partial\Pi_{ji}/\partial x_j\end{aligned} \tag{5.5}$$

is obtained by simultaneous addition of $\partial P/\partial x_i$ and subtraction of its equivalent form,

$$\begin{aligned}\partial P/\partial x_i = &(\beta/\beta')(\partial T/\partial x_i) + (1/\rho\beta')(\partial\rho/\partial x_i)\\ &+ [\rho(\overline{V}_1 - \overline{V}_2)/\beta'](\partial w_1/\partial x_i).\end{aligned} \tag{5.6}$$

The viscous pressure tensor, Π_{ij}, is defined as

$$\Pi_{ij} = \sum_{\alpha}(\sigma_{ij}^{\alpha} - \rho_{\alpha}u_i^{\alpha}u_j^{\alpha} + \pi_{\alpha}\delta_{ij}) = T_{ij} + P\delta_{ij}. \tag{5.7}$$

Here β represents the thermal expansivity,

$$\beta = - (1/\rho)(\partial\rho/\partial T)_{P,W_1}, \tag{5.8}$$

β' is the isothermal compressibility,

$$\beta' = (1/\rho)(\partial\rho/\partial P)_{T,w_1}, \tag{5.9}$$

and $\bar{V}_\alpha$ is the partial specific volume of component α.

There exists another momentum balance equation corresponding to the second of the two balance equations introduced initially in (2.5). It can be termed the balance equation for diffusion momentum, dj_i^1/dt. One form of this equation is found by rearrangement of (4.43).

$$\frac{dj_i^1}{dt} = \frac{\rho_2}{\rho}\frac{\partial}{\partial x_j}\sigma_{ji}^1 - \frac{\rho_1}{\rho}\frac{\partial}{\partial x_j}\sigma_{ji}^2 - J_i + \rho m_i^1$$
$$+ \frac{\rho_1\rho_2}{\rho}(b_i^1 - b_i^2). \tag{5.10}$$

In terms of the variables of this section, J_i [see (4.44)] has the form

$$J_i = -\frac{(\rho_1 - \rho_2)}{\rho_1\rho_2}\frac{\partial j_j^1 j_i^1}{\partial x_j} + \frac{\partial v_j}{\partial x_j} j_i^1 + j_j^1\frac{\partial v_i}{\partial x_j}$$
$$+ j_i^1 j_j^1\left[\frac{(\rho_2 - \rho_1)}{\rho\rho_1\rho_2}\frac{\partial\rho}{\partial x_j}\right.$$
$$\left. + \frac{\rho}{\rho_1^2\rho_2^2}(\rho_2^2 - \rho_2\rho_1 + \rho_1^2)\frac{\partial w_1}{\partial x_j}\right]. \tag{5.11}$$

If the constitutive relation for m_i^1, (4.5), is introduced in (5.10) with the use of (4.33) and (4.34), the balance equation is

$$\frac{\rho}{\rho_1\rho_2}\,\frac{dj_i^1}{dt} = -\,D_u j_i^1 - D_T\,\frac{\partial T}{\partial x_i} - \partial_T(\mu_1' - \mu_2')/\partial x_i$$

$$+\,\frac{1}{\rho_1}\,\frac{\partial(\sigma_{ji}^1 + \pi_1\delta_{ij})}{\partial x_j}$$

$$-\,\frac{1}{\rho_2}\,\frac{\partial(\sigma_{ji}^2 + \pi_2\delta_{ij})}{\partial x_j} - \frac{\rho}{\rho_1\rho_2}\,J_i. \qquad (5.12)$$

The coefficients D_u and D_T in (5.12) are functions of T, ρ, and w_1 only:

$$D_u = (\rho^2/\rho_1^2\rho_2)\,C_{mu} \qquad (5.13)$$

$$D_T = (\rho^2/\rho_1\rho_2)\,C_{mT} + K/\rho_1 + (T/\rho_1)(\partial K/\partial T)$$

$$-\,(\overline{S}_1 - \overline{S}_2). \qquad (5.14)$$

The chemical potential, μ_α', includes external potentials, which have been introduced by means of (2.14),

$$\mu_\alpha' = \mu_\alpha + V_\alpha. \qquad (5.15)$$

The gradient of the chemical potential difference, which appeared in the form of (4.42), has been replaced by

$$\partial(\mu_1' - \mu_2')/\partial x_i = \partial_T(\mu_1' - \mu_2')/\partial x_i$$

$$-\,(\overline{S}_1 - \overline{S}_2)(\partial T/\partial x_i), \qquad (5.16)$$

where $\overline{S}_\alpha$ is the partial specific entropy of component α and where

$$\frac{\partial_T(\mu_1 - \mu_2)}{\partial x_i} = \frac{\beta(\bar{V}_1 - \bar{V}_2)}{\beta'} \frac{\partial T}{\partial x_i} + \left[\frac{\rho(\bar{V}_1 - \bar{V}_2)^2}{\beta'} + \frac{\rho\mu_{11}}{\rho_2}\right] \frac{\partial w_1}{\partial x_i} + \frac{(\bar{V}_1 - \bar{V}_2)}{\rho\beta'} \frac{\partial \rho}{\partial x_i} \tag{5.17}$$

with

$$\mu_{11} = (\partial\mu_1/\partial w_1)_{T,P}. \tag{5.18}$$

The conservation of moment of momentum or angular momentum is simply the requirement that the total stress tensor be symmetric,

$$\sum(\sigma^\alpha_{ij} + \rho_\alpha u^\alpha_i u^\alpha_j) = \sum(\sigma^\alpha_{ji} + \rho_\alpha u^\alpha_j u^\alpha_i). \tag{5.19}$$

The balance of energy can be replaced by a temperature equation by means of identities from thermostatics. Either of the following temperature equations containing heat capacities can be used:

$$\rho\bar{C}_v \frac{dT}{dt} = \rho T \frac{dS}{dt} + \frac{\beta T}{\rho\beta'} \frac{d\rho}{dt} - \rho T\left[(\bar{S}_1 - \bar{S}_2) - \frac{\beta(\bar{V}_1 - \bar{V}_2)}{\beta'}\right] \frac{dw_1}{dt}, \tag{5.20}$$

where $\bar{C}_v$ is the specific heat capacity at constant volume, or

$$\rho\frac{dE_I}{dt} = (\rho\bar{C}_P - P\beta)\,\frac{dT}{dt} - (T\beta - P\beta')\,\frac{dP}{dt}$$

$$- \rho(\bar{E}_1 - \bar{E}_2)\,\frac{dw_1}{dt}, \tag{5.21}$$

where $\bar{C}_p$ is the specific heat capacity at constant pressure and $\bar{E}_\alpha$ is the specific internal energy,

$$\bar{E}_\alpha = \bar{H}_\alpha - P\bar{V}_\alpha = \mu_\alpha + T\bar{S}_\alpha - P\bar{V}_\alpha \tag{5.22}$$

The balance of entropy, (3.9), can be used in (5.20) with any choice for the entropy production. The internal energy balance equation (2.8) can be used in (5.21). Comparison of the resulting two final equations is easily effected with the help of the thermostatic relationship

$$\bar{C}_P = \bar{C}_V + \beta^2 T/\rho\beta'. \tag{5.23}$$

The results of this comparison could be taken to be a measurement of the accuracy of representing the quantities which appear in the entropy production equation by constitutive equations, since (5.21) is exact while (5.20) contains the entropy production which is inevitably approximated to some extent by the linearity of the constitutive relations.

There is also the possibility, however, that the thermostatic equations (5.20) and (5.21) are not applicable in the nonequilibrium case. Equation (5.21) is indeed an equation for internal energy but in thermostatics this implies the internal equilibrium energy of some volume element. In the nonequilibrium case there are three ways in which we could interpret this. Firstly, the internal energy of (5.21) may be only the equilibrium part of the total internal energy which in the nonequilibrium case contains both equilibrium and nonequilibrium parts. Secondly, the internal energy of (5.21) might be the nonequilibrium internal energy plus the kinetic energy of diffusion, since the sum of these two energies is the total energy internal to the volume element being described. Finally, the energy of (5.21) could be the nonequilibrium internal energy, which would be consistent with our other usage of the symbol E_I in this chapter. If the first interpretation were true, an arbitrary separation of thermodynamic quantities into equilibrium and nonequilibrium parts would have to be made. In the second interpretation the partial specific thermodynamic quantities would be defined as previously with additional terms for the component kinetic energy of diffusion. Ramifications of these possibilities will be discussed in Section 8 after a survey of the possible forms of the entropy production which can be used in (5.20).

6. A New Rational Mechanical Derivation

The theory of mixtures presented in Sections 2 through 5 is a typical example of a rational mechanical development. It is only one of many theories which can be derived. The particular advantage of that theory is the very concise bilinear form of its entropy production. In this section we derive another theory in a similar manner, but in this instance we obtain more familiar viscosity coefficients while the entropy production equation becomes much more complicated.

The $5\nu + 6$ functions which define a thermodynamic process in mixtures need not be those of Section 2, but can be any set of equivalent functions; and, likewise, the balance equations may be written in many forms. In this section we choose to let our independent variables be

$$\rho_1, \rho_2, T, u_i, \frac{\partial \rho_1}{\partial x_i}, \frac{\partial \rho_2}{\partial x_i}, \frac{\partial T}{\partial x_i}, \frac{\partial v_i}{\partial x_j}, \left(\frac{\partial u_j}{\partial x_i}\right)^{\mathrm{sym}}, \omega_{ij}, \tag{6.1}$$

where

$$u_i = v_i^1 - v_i^2 = (\rho/\rho_2) u_i^1 = -(\rho/\rho_1)\, u_i^2. \tag{6.2}$$

One can readily verify that

$$(\partial u_j/\partial x_i)^{\mathrm{asym}} = \omega_{ij} \tag{6.3}$$

These variables are objective and more nearly symmetric with respect to the two components than the variables of Sections 2 through 4.

We have adopted here the diffusion velocity and tensors of Doria while retaining the component densities and density gradients of Bartelt (3.3) and Müller. Doria used ρ and w_1 and their derivatives in place of the component densities and their derivatives in (6.1). Müller's variables differ from Bartelt's in that he used the diffusion velocity, u_i, and an antisymmetric strain tensor, $2\omega_{ij}$.

The balance equations, written in terms of these variables when possible, are:

$$\frac{d\rho_1}{dt} = - \frac{\rho_2^2}{\rho^2} u_j \frac{\partial \rho_1}{\partial x_j} - \frac{\rho_1^2}{\rho^2} u_j \frac{\partial \rho_2}{\partial x_j} - \frac{\rho_1 \rho_2}{\rho} \frac{\partial u_j}{\partial x_j} - \rho_1 \frac{\partial v_j}{\partial x_j} \tag{6.4}$$

$$\frac{d\rho_2}{dt} = \frac{\rho_2^2}{\rho^2} u_j \frac{\partial \rho_1}{\partial x_j} + \frac{\rho_1^2}{\rho^2} u_j \frac{\partial \rho_2}{\partial x_j} + \frac{\rho_1 \rho_2}{\rho} \frac{\partial u_j}{\partial x_j} - \rho_2 \frac{\partial v_j}{\partial x_j} \tag{6.5}$$

$$\rho \frac{dv_i}{dt} = \frac{\partial}{\partial x_j} T_{ji} + \rho_1 b_i^1 + \rho_2 b_i^2 \tag{6.6}$$

$$\begin{aligned} &\frac{\rho_1 \rho_2}{\rho} \frac{du_i}{dt} + \frac{\rho_1 \rho_2}{\rho} u_j \frac{\partial v_i}{\partial x_j} + \frac{\rho_1 \rho_2}{\rho^2} (\rho_2 - \rho_1) u_j \frac{\partial u_i}{\partial x_j} \\ &\qquad - \frac{\rho_1 \rho_2^2}{\rho^3} u_i u_j \frac{\partial \rho_1}{\partial x_j} + \frac{\rho_1^2 \rho_2}{\rho^3} u_i u_j \frac{\partial \rho_2}{\partial x_j} \\ &\qquad = \frac{\partial \tau_{ji}}{\partial x_j} - \frac{\rho_1}{\rho^2} T'_{ij} \frac{\partial \rho_2}{\partial x_j} + \frac{\rho_2}{\rho^2} T'_{ij} \frac{\partial \rho_1}{\partial x_j} \\ &\qquad + \rho m_i + \frac{\rho_1 \rho_2}{\rho} (b_i^1 - b_i^2) \end{aligned} \tag{6.7}$$

$$\rho\frac{dE_B}{dt} = \frac{\partial v_i}{\partial x_j} T_{ij} - \frac{\partial q_j^*}{\partial x_j} + \rho r + \frac{\rho_1\rho_2}{\rho} u_i(b_i^1 - b_i^2). \quad (6.8)$$

The total stress tensor, T_{ij}, is that defined in Section 2, and T'_{ij} is defined by

$$T'_{ij} = T_{ij} + (\rho_1\rho_2/\rho)u_iu_j = T_{ij} + \sum\rho_\alpha u_i^\alpha u_j^\alpha = \sigma_{ij}^1 + \sigma_{ij}^2 \quad (6.9)$$

The second stress tensor, τ_{ij}, arises in the rearrangement of the momentum balance equations and has the definition

$$\tau_{ij} = (\rho_2/\rho)\sigma_{ij}^1 - (\rho_1/\rho)\sigma_{ij}^2. \quad (6.10)$$

This stress is a measure of the difference between the component stresses per unit mass. By writing

$$\tau_{ij} = \sigma_{ij}^1 - (\rho_1/\rho)(\sigma_{ij}^1 + \sigma_{ij}^2), \quad (6.11)$$

we see that τ_{ij} represents the difference between component 1's contribution to the stress and the ideal contribution of component 1 to the total stress if the stress of components 1 and 2 were the same per unit mass. The stress tensor is, of course, also just the negative of the difference between component 2's contribution and the ideal contribution to the stress. The specific interaction force m_i is the same as m_i^1 of Sections 2 through 5. The energy which appears in (6.8) is the total energy defined in (2.9), less the bulk kinetic energy, so

$$E_B = E_I + (\rho_1\rho_2/2\rho^2)u_iu_i. \tag{6.12}$$

In a manner completely analogous to that of Section 3, the entropy production can be obtained in terms of the set of variables (6.1). It has the form

$$\begin{aligned}\rho T\Phi = &- \rho(dA_I/dt) - \rho S(dT/dt) + T(\partial k_j/\partial x_j)\\ &- (q_j/T)(\partial T/\partial x_j) - \rho m_j u_j + T'_{ij}(\partial v_i/\partial x_j)\\ &+ \tau_{ij}(\partial u_i/\partial x_j)^{\mathrm{sym}} + \tau_{ij}\omega_{ji}\\ &- (\rho_2/\rho^2)\, T'_{ij}u_j(\partial\rho_1/\partial x_i)\\ &+ (\rho_1/\rho^2)T'_{ij}u_j(\partial\rho_2/\partial x_i).\end{aligned} \tag{6.13}$$

The heat flux, q_j, is still that of Bartelt, but it can now be written as

$$q_j = q_j^* + u_i\tau_{ij} + (\rho_1\rho_2/2\rho^2)(\rho_1 - \rho_2)u_ku_ku_j. \tag{6.14}$$

After examining the balance equations and the entropy production, we choose to write constitutive equations for A_I, S, T'_{ij}, τ_{ij}, q_j, k_j, and m_j. The derivatives dA_I/dt and $\partial k_j/\partial x_j$ in (6.13) must be expanded in terms of the independent variables, so that we then have

$$\begin{aligned}
-\rho\frac{dA_I}{dt} = -\rho\sum\frac{\partial A_I}{\partial\rho_\alpha}\frac{d\rho_\alpha}{dt} &- \sum\left(\frac{\partial A_I}{\partial\left(\frac{\partial\rho_\alpha}{\partial x_i}\right)}\right)\frac{d}{dt}\left(\frac{\partial\rho_\alpha}{\partial x_i}\right) \\
&- \rho\left(\frac{\partial A_I}{\partial T}\right)\frac{dT}{dt} - \rho\left(\frac{\partial A_I}{\partial\left(\frac{\partial T}{\partial x_i}\right)}\right)\frac{d}{dt}\left(\frac{\partial T}{\partial x_i}\right) - \rho\left(\frac{\partial A_I}{\partial u_i}\right)\frac{du_i}{dt} \\
&- \rho\left(\frac{\partial A_I}{\partial\omega_{ij}}\right)\frac{d\omega_{ji}}{dt} - \rho\left(\frac{\partial A_I}{\partial\left(\frac{\partial v_i}{\partial x_j}\right)}\right)\frac{d\left(\frac{\partial v_i}{\partial x_j}\right)}{dt} \\
&- \rho\left(\frac{\partial A_I}{\partial\left(\frac{\partial u_i}{\partial x_j}\right)}\right)\frac{d}{dt}\left(\frac{\partial u_i}{\partial x_j}\right)
\end{aligned} \tag{6.15}$$

and

$$\begin{aligned}
T\frac{\partial k_i}{\partial x_i} = \sum T\left(\frac{\partial k_i}{\partial\rho_\alpha}\right)\frac{\partial\rho_\alpha}{\partial x_i} &+ \sum T\left(\frac{\partial k_i}{\partial\left(\frac{\partial\rho_\alpha}{\partial x_j}\right)}\right)\frac{\partial^2\rho_\alpha}{\partial x_i\partial x_j} + T\left(\frac{\partial k_i}{\partial T}\right)\frac{\partial T}{\partial x_i} \\
&+ T\left(\frac{\partial k_i}{\partial\left(\frac{\partial T}{\partial x_j}\right)}\right)\frac{\partial^2 T}{\partial x_i\partial x_j} + T\left(\frac{\partial k_i}{\partial u_j}\right)\left(\frac{\partial u_j}{\partial x_i}\right)^{\text{sym}} + T\left(\frac{\partial k_i}{\partial u_j}\right)\omega_{ij} \\
&+ T\left(\frac{\partial k_\ell}{\partial\left(\frac{\partial u_i}{\partial x_j}\right)}\right)\frac{\partial^2 u_i}{\partial x_j\partial x_\ell} + T\left(\frac{\partial k_\ell}{\partial\left(\frac{\partial v_i}{\partial x_j}\right)}\right)\frac{\partial^2 v_i}{\partial x_\ell\partial x_j} + T\left(\frac{\partial k_\ell}{\partial\omega_{ij}}\right)\frac{\partial\omega_{ji}}{\partial x_\ell}\ .
\end{aligned} \tag{6.16}$$

The coefficient of any derivative of an independent variable in (6.13) must be zero since that derivative could be either positive or negative. However, several of the variable derivatives in (6.15) and (6.16) are not independent. The time derivatives of component densities and of component density gradients are given by the balance of mass equations. For $d\rho_1/dt$ and $d\rho_2/dt$ we use (6.4) and (6.5), while for the time derivatives of the density gradients, we use

$$d(\partial\rho_\alpha/\partial x_j)/dt = \partial(d\rho_\alpha/dt)/\partial x_j - (\partial v_i/\partial x_j)(\partial\rho_\alpha/\partial x_i) \tag{6.17}$$

as well as (6.4) and (6.5) to write

$$\begin{aligned}\frac{d}{dt}\left(\frac{\partial\rho_1}{\partial x_j}\right) = {} & -\left(\frac{\partial u_i}{\partial x_j}\right)\left(\frac{\rho_2^2}{\rho^2}\frac{\partial\rho_1}{\partial x_i} + \frac{\rho_1^2}{\rho^2}\frac{\partial\rho_2}{\partial x_i}\right) - \frac{2\rho_1\rho_2}{\rho^3}u_i\frac{\partial\rho_1}{\partial x_i}\frac{\partial\rho_2}{\partial x_j} \\ & - \frac{2\rho_1\rho_2}{\rho^3}u_i\frac{\partial\rho_2}{\partial x_i}\frac{\partial\rho_1}{\partial x_j} - \frac{\rho_2^2}{\rho^2}u_i\frac{\partial^2\rho_1}{\partial x_i\partial x_j} - \frac{\rho_1^2}{\rho^2}u_i\frac{\partial^2\rho_2}{\partial x_i\partial x_j} \\ & + 2\frac{\rho_2^2}{\rho^3}u_i\frac{\partial\rho_1}{\partial x_i}\frac{\partial\rho_1}{\partial x_j} + \frac{2\rho_1^2}{\rho^3}u_i\frac{\partial\rho_2}{\partial x_i}\frac{\partial\rho_2}{\partial x_j} - 2\frac{\partial\rho_1}{\partial x_j}\frac{\partial v_i}{\partial x_i} \\ & - \rho_1\frac{\partial^2 v_i}{\partial x_j\partial x_i} - \frac{\rho_1^2}{\rho^2}\frac{\partial\rho_2}{\partial x_j}\frac{\partial u_i}{\partial x_i} - \frac{\rho_2^2}{\rho^2}\frac{\partial\rho_1}{\partial x_j}\frac{\partial u_i}{\partial x_i} \\ & + \frac{\rho_1\rho_2}{\rho}\frac{\partial^2 u_i}{\partial x_i\partial x_j}\end{aligned} \tag{6.18}$$

$$\frac{d}{dt}\left(\frac{\partial\rho_2}{\partial x_j}\right) = \left(\frac{\partial u_i}{\partial x_j}\right)\left(\frac{\rho_2^2}{\rho^2}\frac{\partial\rho_1}{\partial x_i} + \frac{\rho_1^2}{\rho^2}\frac{\partial\rho_2}{\partial x_i}\right) + \frac{2\rho_1\rho_2}{\rho^3}u_i\frac{\partial\rho_2}{\partial x_i}\frac{\partial\rho_1}{\partial x_j}$$

$$+ \frac{2\rho_1\rho_2}{\rho^3} u_i \frac{\partial \rho_1}{\partial x_i} \frac{\partial \rho_2}{\partial x_j} + \frac{\rho_1^2}{\rho^2} u_i \frac{\partial^2 \rho_2}{\partial x_i \partial x_j}$$

$$+ \frac{\rho_2^2}{\rho^2} u_i \frac{\partial^2 \rho_1}{\partial x_i \partial x_j} - \frac{2\rho_1^2}{\rho^3} u_i \frac{\partial \rho_2}{\partial x_i} \frac{\partial \rho_1}{\partial x_j}$$

$$- \frac{2\rho_2^2}{\rho^3} u_i \frac{\partial \rho_1}{\partial x_i} \frac{\partial \rho_2}{\partial x_j} - \frac{2\partial \rho_2}{\partial x_j} \frac{\partial v_i}{\partial x_i} - \rho_2 \frac{\partial^2 v_i}{\partial x_j \partial x_i}$$

$$+ \frac{\rho_1^2}{\rho^2} \frac{\partial \rho_2}{\partial x_j} \frac{\partial u_i}{\partial x_i} + \frac{\rho_2^2}{\rho^2} \frac{\partial \rho_1}{\partial x_j} \frac{\partial u_i}{\partial x_i} - \frac{\rho_1 \rho_2}{\rho} \frac{\partial^2 u_i}{\partial x_i \partial x_j}. \tag{6.19}$$

The strain tensor derivatives are not all independent either since one can readily show that

$$\partial\omega_{ij}/\partial x_\ell = \partial(\partial u_i/\partial x_\ell)^{\mathrm{sym}}/\partial x_j - \partial(\partial u_\ell/\partial x_j)^{\mathrm{sym}}/\partial x_i. \tag{6.20}$$

Using this identity we write

$$\frac{\partial k_\ell}{\partial\left(\frac{\partial u_i}{\partial x_j}\right)^{\mathrm{sym}}} \frac{\partial}{\partial x_\ell}\left(\frac{\partial u_i}{\partial x_j}\right)^{\mathrm{sym}} + \left(\frac{\partial k_\ell}{\partial \omega_{ij}}\right)\frac{\partial \omega_{ji}}{\partial x_\ell}$$

$$= \frac{\partial k_\ell}{\partial\left(\frac{\partial u_i}{\partial x_j}\right)^{\mathrm{sym}}} + \left(\frac{\partial k_j}{\partial \omega_{\ell i}} + \frac{\partial k_i}{\partial \omega_{\ell j}}\right) \frac{\partial}{\partial x_\ell}\left(\frac{\partial u_i}{\partial x_j}\right)^{\mathrm{sym}}. \tag{6.21}$$

Recognizing that these substitutions must be made in (6.13), we invoke the Clausius-Duhem inequality in order to set equal to zero all those coefficients of derivatives of independent variables which can be positive or negative while all other variables can be set to zero. Thus, the coefficients of dT/dt, $d(\partial T/\partial x_i)/dt$, du_i/dt, $d(\partial v_i/\partial x_j)/dt$, $d(\partial u_i/\partial x_j)^{sym}/dt$, $d\omega_{ij}/dt$, $\partial^2 u_i/\partial x_\ell \partial x_j$, $\partial^2 T/\partial x_i \partial x_j$, and $\partial^2 v_i/\partial x_j \partial x_\ell$ must be set equal to zero.

An immediate consequence of this is that A_I, as before, cannot be a function of $\partial T/\partial x_i$, u_i, $\partial v_i/\partial x_j$, $(\partial u_i/\partial x_j)^{sym}$, or ω_{ij}. The normal thermostatic relationship between entropy and the Helmholtz free energy is found as before,

$$S = - \partial A_I/\partial T. \qquad (6.22)$$

These results reduce the entropy production to the form

$$\begin{aligned}
\rho T\Phi = &- \rho\sum\left(\frac{\partial A_I}{\partial \rho_\alpha}\right)\frac{d\rho_\alpha}{dt} - \rho{\sum}'\left(\frac{\partial A_I}{\partial\left(\frac{\partial \rho_\alpha}{\partial x_i}\right)}\right)\frac{d}{dt}\left(\frac{\partial \rho_\alpha}{\partial x_i}\right) + \sum T\left(\frac{\partial k_i}{\partial \rho_\alpha}\right)\frac{\partial \rho_\alpha}{\partial x_i} \\
&+ \sum T\left(\frac{\partial k_i}{\partial\left(\frac{\partial \rho_\alpha}{\partial x_j}\right)}\right)\frac{\partial^2 \rho_\alpha}{\partial x_i \partial x_j} + T\frac{\partial k_i}{\partial T}\,\frac{\partial T}{\partial x_i} + T\frac{\partial k_\ell}{\partial u_i}\left(\frac{\partial u_i}{\partial x_\ell}\right)^{sym} \\
&+ T\frac{\partial k_\ell}{\partial u_i}\omega_{\ell i} + T\left[\frac{\partial k_i}{\partial\left(\frac{\partial u_i}{\partial x_j}\right)} + \frac{\partial k_j}{\partial \omega_{\ell i}} + \frac{\partial k_i}{\partial \omega_{\ell j}}\right]\frac{\partial}{\partial x_\ell}\left(\frac{\partial u_i}{\partial x_j}\right)^{sym} \\
&- \frac{q_j}{T}\,\frac{\partial T}{\partial x_j} - \rho m_j u_j + \frac{\rho_1}{\rho^2}T'_{ij}u_i\frac{\partial \rho_2}{\partial x_j} - \frac{\rho_2}{\rho^2}T'_{ij}u_i\frac{\partial \rho_1}{\partial x_j} \\
&+ T_{ij}\frac{\partial v_i}{\partial x_j} + \tau_{ij}\left(\frac{\partial u_i}{\partial x_j}\right)^{sym} + \tau_{ij}\omega_{ji}. \qquad (6.23)
\end{aligned}$$

If we consider the coefficient of $\partial^2 v_i/\partial x_j \partial x_\ell$, we obtain the following restriction:

$$\frac{\partial k_\ell}{\partial\left(\frac{\partial v_i}{\partial x_j}\right)} + \frac{\partial k_j}{\partial\left(\frac{\partial v_i}{\partial x_\ell}\right)} + \rho_1 \rho \frac{\partial A_I}{\partial\left(\frac{\partial \rho_1}{\partial x_\ell}\right)} \delta_{ij} + \rho_2 \rho \frac{\partial A_I}{\partial\left(\frac{\partial \rho_2}{\partial x_\ell}\right)} \delta_{ij} = 0. \qquad (6.24)$$

This can be integrated at once to give

$$k_\ell = N_\ell - \rho\left[\rho_1 \frac{\partial A_I}{\partial\left(\frac{\partial \rho_1}{\partial x_\ell}\right)} + \rho_2 \frac{\partial A_I}{\partial\left(\frac{\partial \rho_2}{\partial x_\ell}\right)}\right] \frac{\partial v_i}{\partial x_i}, \qquad (6.25)$$

where N_ℓ is independent of $\partial v_i/\partial x_j$. Now, if this result is substituted into the coefficients of $\partial^2 \rho_1/\partial x_i \partial x_\ell$ and $\partial^2 \rho_2/\partial x_i \partial x_\ell$ which themselves must be equal to zero, two further restrictions ensue,

$$\frac{\rho_2^2}{\rho} \frac{\partial A_I}{\partial\left(\frac{\partial \rho_1}{\partial x_j}\right)} u_i + \frac{\rho_2^2}{\rho} \frac{\partial A_I}{\partial\left(\frac{\partial \rho_1}{\partial x_i}\right)} u_j - \frac{\rho_2^2}{\rho} \frac{\partial A_I}{\partial\left(\frac{\partial \rho_2}{\partial x_j}\right)} u_i - \frac{\rho_2^2}{\rho} \frac{\partial A_I}{\partial\left(\frac{\partial \rho_2}{\partial x_i}\right)} u_j$$

$$+ T \frac{\partial N_i}{\partial\left(\frac{\partial \rho_1}{\partial x_j}\right)} + T \frac{\partial N_j}{\partial\left(\frac{\partial \rho_1}{\partial x_i}\right)} + T\left[2\rho_1 \rho \frac{\partial^2 A_I}{\partial\left(\frac{\partial \rho_1}{\partial x_i}\right) \partial\left(\frac{\partial \rho_1}{\partial x_j}\right)}\right.$$

$$\left. + \rho_2 \rho \frac{\partial^2 A_I}{\partial\left(\frac{\partial \rho_1}{\partial x_i}\right) \partial\left(\frac{\partial \rho_2}{\partial x_j}\right)} + \rho \rho_2 \frac{\partial^2 A_I}{\partial\left(\frac{\partial \rho_1}{\partial x_j}\right) \partial\left(\frac{\partial \rho_2}{\partial x_i}\right)}\right] \frac{\partial v_k}{\partial x_k} = 0, \qquad (6.26)$$

and

$$\frac{\rho_1^2}{\rho}\frac{\partial A_I}{\partial\left(\frac{\partial\rho_1}{\partial x_j}\right)}u_i + \frac{\rho_1^2}{\rho}\frac{\partial A_I}{\partial\left(\frac{\partial\rho_1}{\partial x_i}\right)}u_j - \frac{\rho_1^2}{\rho}\frac{\partial A_I}{\partial\left(\frac{\partial\rho_2}{\partial x_j}\right)}u_i$$

$$- \frac{\rho_1^2}{\rho}\frac{\partial A_I}{\partial\left(\frac{\partial\rho_2}{\partial x_i}\right)}u_j + T\frac{\partial N_i}{\partial\left(\frac{\partial\rho_2}{\partial x_j}\right)} + T\frac{\partial N_j}{\partial\left(\frac{\partial\rho_2}{\partial x_i}\right)} + T\left[\rho\rho_1\frac{\partial^2 A_I}{\partial\left(\frac{\partial\rho_1}{\partial x_i}\right)\partial\left(\frac{\partial\rho_2}{\partial x_j}\right)}\right.$$

$$\left. + \rho\rho_1\frac{\partial^2 A_I}{\partial\left(\frac{\partial\rho_1}{\partial x_j}\right)\partial\left(\frac{\partial\rho_2}{\partial x_i}\right)} + 2\rho\rho_2\frac{\partial^2 A_I}{\partial\left(\frac{\partial\rho_2}{\partial x_i}\right)\partial\left(\frac{\partial\rho_2}{\partial x_j}\right)}\right]\frac{\partial v_k}{\partial x_k} = 0. \quad (6.27)$$

The coefficient of $\partial v_k/\partial x_k$ must be equal to zero in each equation so that from (6.26) we can write

$$\frac{\partial}{\partial\left(\frac{\partial\rho_1}{\partial x_j}\right)}\left[\rho\rho_1\frac{\partial A_I}{\partial\left(\frac{\partial\rho_1}{\partial x_i}\right)} + \rho\rho_2\frac{\partial A_I}{\partial\left(\frac{\partial\rho_2}{\partial x_i}\right)}\right] = - \frac{\partial}{\partial\left(\frac{\partial\rho_1}{\partial x_i}\right)}\left[\rho\rho_1\frac{\partial A_I}{\partial\left(\frac{\partial\rho_1}{\partial x_j}\right)}\right.$$

$$\left. + \rho\rho_2\frac{\partial A_I}{\partial\left(\frac{\partial\rho_2}{\partial x_j}\right)}\right]. \quad (6.28)$$

An equation of this form has the general solution

$$\rho\rho_1\frac{\partial A_I}{\partial\left(\frac{\partial\rho_1}{\partial x_i}\right)} + \rho\rho_2\frac{\partial A_I}{\partial\left(\frac{\partial\rho_2}{\partial x_i}\right)} = \Omega_{ij}\frac{\partial\rho_1}{\partial x_j} + f_i \quad (6.29)$$

The function Ω_{ij} is antisymmetric and neither Ω_{ij} nor f_i can be a function of $\partial\rho_1/\partial x_j$. They must, therefore, be functions of $\partial\rho_2/\partial x_j$ only. By the objectivity of the scalar, A_I, Ω_{ij} must be zero. From the coefficient of $\partial v_k/\partial x_k$ in (6.27) we obtain a similar expression in terms of $\partial\rho_2/\partial x_j$, and the two results imply that

$$\rho_2 \frac{\partial A_I}{\partial\left(\frac{\partial\rho_1}{\partial x_j}\right)} = -\rho_1 \frac{\partial A_I}{\partial\left(\frac{\partial\rho_2}{\partial x_j}\right)}. \tag{6.30}$$

Returning to (6.26), we see that all those terms but the last one, the one in $\partial v_k/\partial x_k$, must be zero independently. We rearrange this equation using (6.30) to a form similar to that of (6.28) and then using the general solution we find

$$TN_i - A_I\rho_1 u_i = \Omega_{ij}\frac{\partial\rho_2}{\partial x_j} + F_i \tag{6.31}$$

where Ω_{ij} and F_i are independent of $\partial\rho_2/\partial x_j$ and Ω_{ij} is antisymmetric. Considering the terms in (6.26) which are independent of $\partial v_k/\partial x_k$ and employing the results (6.30) and (6.31), we write

$$\frac{\partial}{\partial\left(\frac{\partial\rho_1}{\partial x_j}\right)}\left(A_I u_i + \Omega_{ik}\frac{\partial\rho_2}{\partial x_k} + F_i\right)$$

$$= -\frac{\partial}{\partial\left(\frac{\partial\rho_1}{\partial x_i}\right)}\left(A_I u_j + \Omega_{jk}\frac{\partial\rho_2}{\partial x_k} + F_j\right). \tag{6.32}$$

We multiply both sides of the equation by $(\partial\rho_2/\partial x_i)(\partial\rho_2/\partial x_j)$ and take advantage of the antisymmetry of Ω_{ij} to arrive at

$$\frac{\partial}{\partial\left(\frac{\partial\rho_1}{\partial x_j}\right)}\left[A_I u_i\left(\frac{\partial\rho_2}{\partial x_i}\right)\frac{\partial\rho_2}{\partial x_j} + F_i\left(\frac{\partial\rho_2}{\partial x_i}\right)\frac{\partial\rho_2}{\partial x_j}\right]$$

$$= -\frac{\partial}{\partial\left(\frac{\partial\rho_1}{\partial x_i}\right)}\left[A_I u_j\left(\frac{\partial\rho_2}{\partial x_j}\right)\frac{\partial\rho_2}{\partial x_i} + F_j\left(\frac{\partial\rho_2}{\partial x_j}\right)\frac{\partial\rho_2}{\partial x_i}\right] \quad (6.33)$$

Because both sides of (6.33) are scalars, this statement is equivalent to

$$\frac{\partial}{\partial\left(\frac{\partial\rho_1}{\partial x_i}\right)}\left[A_I u_j\frac{\partial\rho_2}{\partial x_j}\left(\frac{\partial\rho_2}{\partial x_i}\right) + F_j\left(\frac{\partial\rho_2}{\partial x_j}\right)\frac{\partial\rho_2}{\partial x_i}\right] = 0. \quad (6.34)$$

Therefore,

$$\frac{\partial A_I}{\partial\left(\frac{\partial\rho_1}{\partial x_i}\right)}u_j = -\frac{\partial F_j}{\partial\left(\frac{\partial\rho_1}{\partial x_i}\right)}, \quad (6.35)$$

and A_I cannot be a function of $(\partial\rho_1/\partial x_j)(\partial\rho_2/\partial x_j)$. Thus, A_I can be an objective function only of $(\partial\rho_1/\partial x_i)^2$ and $(\partial\rho_2/\partial x_i)^2$. But we know that

$$\frac{\rho_2}{\rho_1}\frac{\partial A_I}{\partial\left(\frac{\partial\rho_2}{\partial x_j}\right)} = -\frac{\partial F_j}{\partial\left(\frac{\partial\rho_1}{\partial x_j}\right)} \neq f\left(\frac{\partial\rho_2}{\partial x_j}\right), \quad (6.36)$$

so A_I can be at most only first order in $\partial\rho_2/\partial x_j$ and this is impossible. The only remaining possibility is that A_I is independent of both $\partial\rho_1/\partial x_i$ and $\partial\rho_2/\partial x_i$, so we have shown that

$$A_I = A_I(\rho_1, \rho_2, T). \qquad (6.37)$$

This result is very desirable in that we would hope that our thermodynamic variables are functions only of the state variables, ρ_1, ρ_2, T, in the nonequilibrium case as they are in the equilibrium situation. This we have shown to be true of the Helmholtz free energy.

The result of equation (6.37) greatly simplifies the entropy production equation so that we now have the form

$$\begin{aligned}
\rho T \Phi = {} & T\frac{\partial k_i}{\partial \rho_1}\frac{\partial \rho_1}{\partial x_i} + T\frac{\partial k_i}{\partial \rho_2}\frac{\partial \rho_2}{\partial x_i} + T\frac{\partial k_i}{\partial T}\frac{\partial T}{\partial x_i} - \frac{q_j}{T}\frac{\partial T}{\partial x_j} \\
& - \rho m_i u_i + \left(T\frac{\partial k_j}{\partial u_i} + \tau_{ij}\right)\omega_{ji} \\
& + \rho_1\rho_2\left(\frac{\partial A_I}{\partial \rho_1} - \frac{\partial A_I}{\partial \rho_2}\right)\delta_{ij} + \left(T\frac{\partial k_j}{\partial u_i} + \tau_{ij}\right)\left(\frac{\partial u_i}{\partial x_j}\right)^{sym} \\
& + \rho\left(\rho_1\frac{\partial A_I}{\partial \rho_1} + \rho_2\frac{\partial A_I}{\partial \rho_2}\right)\delta_{ij} + T'_{ij}\frac{\partial v_i}{\partial x_j} \\
& + \left[\frac{\rho_2^2}{\rho}\left(\frac{\partial A_I}{\partial \rho_1} - \frac{\partial A_I}{\partial \rho_2}\right)\delta_{ij} - \frac{\rho_2}{\rho^2}T'_{ij}\right]u_i\frac{\partial \rho_1}{\partial x_j} \\
& + \left[\frac{\rho_1^2}{\rho}\left(\frac{\partial A_I}{\partial \rho_1} - \frac{\partial A_I}{\partial \rho_2}\right)\delta_{ij} + \frac{\rho_1}{\rho^2}T'_{ij}\right]u_i\frac{\partial \rho_2}{\partial x_j} \geq 0. \qquad (6.38)
\end{aligned}$$

Among the restrictions which are obtained in arriving at this form are:

$$\partial k_i/\partial(\partial\rho_\alpha/\partial x_j) + \partial k_j/\partial(\partial\rho_\alpha/\partial x_i) = 0 \qquad (6.39)$$

$$\partial k_\ell/\partial(\partial v_i/\partial x_j) = 0 \qquad (6.40)$$

$$T[\partial k_\ell/\partial(\partial u_j/\partial x_i) + \partial k_j/\partial\omega_{\ell i} + \partial k_i/\partial\omega_{\ell j}] = 0. \qquad (6.41)$$

Although further restrictions on the general forms of the response functions could be derived, their physical significance becomes less and less clear. For this reason we now restrict ourselves to a linear theory. The omission of terms which are of second or higher order in the independent variables will naturally introduce approximation into a theory which until this point has had none. (Recall that this section is not merely a continuation of the previous one.) The error due to these omissions is minimized by retaining explicit second order dependence of the total stress tensor and of the energy, E, and by using linear functions to represent only those parts of E and T_{ij} which do not have explicit second order dependence.

As in Section 4, we can immediately limit the constitutive equations to functions of tensors of the same rank. We also have the restriction (6.39) and the independence of A_I from density gradients which say that k_i cannot be a function of $\partial\rho_1/\partial x_j$, $\partial\rho_2/\partial x_j$, or u_i, so the constitutive equations take the forms

$$A_I = A_I(\rho_1,\rho_2,T) \qquad (6.42)$$

$$k_j = K'u_j \tag{6.43}$$

$$q_j = - C'_{qu}u_j - C'_{qT}\frac{\partial T}{\partial x_j} - C'_{q1}\frac{\partial \rho_1}{\partial x_j} - C'_{q2}\frac{\partial \rho_2}{\partial x_j} \tag{6.44}$$

$$m_j = - C'_{mu}u_j - C'_{mT}\frac{\partial T}{\partial x_j} - C'_{m1}\frac{\partial \rho_1}{\partial x_j} - C'_{m2}\frac{\partial \rho_2}{\partial x_j} \tag{6.45}$$

$$T'_{ij} = - P'\delta_{ij} + \phi\frac{\partial v_n}{\partial x_n}\delta_{ij} + 2\eta\frac{\partial v_i}{\partial x_j} + \chi_1\frac{\partial u_n}{\partial x_n}\delta_{ij} + \chi_2\frac{\partial u_i}{\partial x_j} \tag{6.46}$$

$$\tau_{ij}{}^{sym} = - p\delta_{ij} + \alpha_1\frac{\partial v_n}{\partial x_n}\delta_{ij} + \alpha_2\frac{\partial v_i}{\partial x_j} + \alpha_3\frac{\partial u_n}{\partial x_n}\delta_{ij} + \alpha_4\frac{\partial u_i}{\partial x_j} \tag{6.47}$$

$$\tau_{ij}{}^{asym} = \mu'\omega_{ij} \tag{6.48}$$

The primes are to indicate that the coefficients may not necessarily have the same dependence on ρ_1, ρ_2, and T as similar coefficients of Section 4. These explicit functions can be placed in the entropy production equation which again becomes a function of twenty-one variables, all of which must be zero at equilibrium. The equations (4.18) and (4.19) still apply for the variables

$$u_j, \partial T/\partial x_j, \partial v_i/\partial x_j, (\partial u_i/\partial x_j)^{sym}, \omega_{ji}.$$

The final form of the entropy production is then

$$\rho T\Phi = C'_{mu}u_iu_i + \left(T\frac{\partial K'}{\partial T} + \frac{C'_{qu}}{T} + C'_mT\right)u_j\frac{\partial T}{\partial x_j} + C'_{qT}\frac{\partial T}{\partial x_j}\frac{\partial T}{\partial x_j} + \phi\frac{\partial v_k}{\partial x_k}\frac{\partial v_\ell}{\partial x_\ell} + 2\eta\frac{\partial v_i}{\partial x_j}\frac{\partial v_j}{\partial x_i} + L, \tag{6.49}$$

where

$$
\begin{aligned}
L = {} & (\chi_1 + \alpha_1)\frac{\partial \mu_k}{\partial x_k}\frac{\partial v_\ell}{\partial x_\ell} + (\chi_2 + \alpha_2)\frac{\partial u_i}{\partial x_j}\frac{\partial v_j}{\partial x_i} + \alpha_3 \frac{\partial u_k}{\partial x_k}\frac{\partial u_\ell}{\partial x_\ell} \\
& + \alpha_4\left(\frac{\partial u_i}{\partial x_k}\right)^S\left(\frac{\partial u_k}{\partial x_i}\right)^S + \mu'\omega_{ij}\omega_{ji} - \frac{\rho_2}{\rho^2}\phi\frac{\partial v_k}{\partial x_k}u_i\frac{\partial \rho_1}{\partial x_i} \\
& + \frac{\rho_1}{\rho^2}\phi\frac{\partial v_k}{\partial x_k}u_i\frac{\partial \rho_2}{\partial x_i} - \frac{\rho_2}{\rho^2}2\eta\frac{\partial v_i}{\partial x_j}u_i\frac{\partial \rho_1}{\partial x_j} + \frac{\rho_1}{\rho^2}2\eta\frac{\partial v_i}{\partial x_j}u_i\frac{\partial \rho_2}{\partial x_j} \\
& - \frac{\rho_2}{\rho^2}\chi_1\frac{\partial u_k}{\partial x_k}u_\ell\frac{\partial \rho_1}{\partial x_\ell} + \frac{\rho_1}{\rho^2}\chi_1\frac{\partial u_k}{\partial x_k}u_\ell\frac{\partial \rho_2}{\partial x_\ell} - \frac{\rho_2}{\rho^2}\chi_2\left(\frac{\partial u_i}{\partial x_j}\right)^S u_i\frac{\partial \rho_1}{\partial x_j} \\
& + \frac{\rho_1}{\rho^2}\chi_2\left(\frac{\partial u_i}{\partial x_j}\right)^S u_i\frac{\partial \rho_2}{\partial x_j}.
\end{aligned}
\tag{6.50}
$$

The positive-definiteness of entropy production, (4.18) and (4.19), has also generated the requirements

$$C'_{q1} = C'_{q2} = 0 \tag{6.51}$$

$$\frac{\rho_2^2}{\rho}\left(\frac{\partial A_I}{\partial \rho_1} - \frac{\partial A_I}{\partial \rho_2}\right) + \frac{\rho_2}{\rho^2}P' + T\frac{\partial K'}{\partial \rho_1} + \rho C'_{m1} = 0 \tag{6.52}$$

$$\frac{\rho_1^2}{\rho}\left(\frac{\partial A_I}{\partial \rho_1} - \frac{\partial A_I}{\partial \rho_2}\right) - \frac{\rho_1}{\rho^2}P' + T\frac{\partial K'}{\partial \rho_2} + \rho C'_{m2} = 0 \tag{6.53}$$

$$P' = \rho\left(\rho_1\frac{\partial A_I}{\partial \rho_1} + \rho_2\frac{\partial A_I}{\partial \rho_2}\right) \tag{6.54}$$

$$p = TK' + \rho_1\rho_2\left(\frac{\partial A_I}{\partial \rho_1} - \frac{\partial A_I}{\partial \rho_2}\right) = TK' + \frac{\rho_1\rho_2}{\rho}(\mu_1 - \mu_2). \tag{6.55}$$

Again we have identified the thermostatic pressure, P', in (6.46) and we can use (4.41) for the difference in chemical potential. Equation (6.55) gives us some physical feeling for the coefficient K'. It is dependent on the difference between the specific partial pressures (equilibrium parts of the specific stress tensors) and on the chemical potential difference. Using (6.55), (6.52), and (6.53) we can solve for the coefficients C'_{m1} and C'_{m2},

$$\rho C'_{m1} = -(\rho_2/\rho^2)P - \partial p/\partial \rho_1 + (\rho_1\rho_2/\rho)\partial(\mu_1 - \mu_2)/\partial\rho_1 \tag{6.56}$$

$$\rho C'_{m2} = (\rho_1/\rho^2)P - \partial p/\partial \rho_2 + (\rho_1\rho_2/\rho)\partial(\mu_1 - \mu_2)/\partial\rho_2. \tag{6.57}$$

Many other restrictions similar to those imposed on the coefficients of Section 4 can also be found.

At this point we have only fourteen unidentified coefficients in the constitutive equations. Nine of these are viscosity coefficients of which we readily recognize ϕ and η as the coefficients of bulk and shear viscosity, respectively. We have some feeling for p, but C'_{mu}, C'_{mT}, C'_{qu}, and C'_{qT} remain unidentified.

By using (6.56) and (6.57) in the constitutive equation for internal force and by making transformations analogous to those in Section 3, we can write

$$\rho m_i = -\frac{\rho_1\rho_2}{\rho}\frac{\partial_T(\mu_1 - \mu_2)}{\partial x_i} + \left[-\rho C'_{mT} + \frac{\rho_1\rho_2}{\rho}(\bar{S}_1 - \bar{S}_2)\right.$$

$$\left. + \frac{\rho_1\rho_2}{} \frac{\partial(\mu_1 - \mu_2)}{\partial T}\right]\frac{\partial T}{\partial x_i} + \left(\frac{\rho_2}{\rho^2} P + \frac{\partial p}{\partial \rho_1}\right)\frac{\partial \rho_1}{\partial x_i}$$

$$+ \left(-\frac{\rho_1}{\rho^2} P + \frac{\partial p}{\partial \rho_2}\right)\frac{\partial \rho_2}{\partial x_i} - \rho C'_{mu} u_i. \qquad (6.58)$$

When this equation is put in the balance of diffusion momentum equation, the result is again identical to that of Bearman and Kirkwood except that the coefficients are more clearly identifiable. One form of this equation is

$$\rho C'_{mu} j_i^1 = \left[-\rho C'_{m1} + \frac{\rho_1\rho_2}{\rho}(\bar{S}_1 - \bar{S}_2) + \frac{\rho_1\rho_2}{\rho}\frac{\partial(\mu_1 - \mu_2)}{\partial T}\right.$$

$$\left. + \frac{\partial p}{\partial T}\right]\frac{\partial T}{\partial x_i} + \frac{\rho_2}{\rho}\frac{\partial}{\partial x_j}(\sigma_{ji}^1 + \pi_1\delta_{ij})$$

$$- \frac{\rho_1}{\rho}\frac{\partial}{\partial x_j}(\sigma_{ji}^2 + \pi_2\delta_{ji}) - \left[\frac{\rho_1\rho_2}{\rho}\frac{\partial(\mu'_1 - \mu'_2)}{\partial x_i}\right.$$

$$+ \frac{dj_i^1}{dt} + \frac{\rho_2 - \rho_2}{\rho_1\rho_2}\frac{\partial}{\partial x_j}(j_j^1 j_i^1)$$

$$- j_i^1 j_j^1\left(\frac{\rho_2}{\rho\rho_1^2}\frac{\partial \rho_1}{\partial x_j} - \frac{\rho_1}{\rho\rho_2^2}\frac{\partial \rho_2}{\partial x_j}\right) + j_i^1\frac{\partial v_j}{\partial x_j}$$

$$\left. + j_j^1\frac{\partial v_i}{\partial x_j}\right]. \qquad (6.59)$$

This theory does not vary radically from that of Sections 2 through 5, but it is decidedly different from it. The entropy production (6.49) contains five terms which are predicted by TIP and also those terms in L, (6.50), which would typically be called viscous terms. The constitutive equations are very similar to those of Section 4 but not interchangeable with them.

7. Comparison of Several Theories for Binary Mixtures of Fluids

There have been many approaches to the thermodynamics of irreversible processes in binary fluid mixtures. Both of the rational mechanical theories presented here compare readily with the microscopically grounded theory of Bearman and Kirkwood and with the theories of Fitts, de Groot and Mazur, etc., for nonequilibrium thermodynamics. All of these are so-called "linear theories" with functions being represented in a linear manner such as that presented in Section 4. However, some also contain "linearization" of other forms including dropping of terms in any equation in which such terms appear to be non-linear.

The theory of Bearman and Kirkwood is based upon the same balance equations as those of Section 2, including partial stress tensors which are defined in a slightly different manner as discussed in Section 2. The TIP theories do not treat partial stress tensors and only rarely include any terms arising from kinetic energy of diffusion. The exact limitations of the balance equations used in TIP and their differences from those used in rational mechanics can best be seen by studying the balance equations of Section 6 which are equivalent to those of Section 2. The theories of TIP neglect entirely balance of diffusion momentum (6.7) and all terms which are introduced in this equation and not in any other balance equations, i.e., interaction forces and partial stress tensors. The energy, E_B, of the balance equation (6.8) is then taken as the thermodynamic internal energy since there is no longer a substitution to be made for the external forces of (6.8) which would introduce kinetic energy of diffusion. It is, thus, obvious that TIP and rational mechanics will not yield the same entropy production equation. It is interesting to note that the results of a rational mechanical approach to the problem as defined by the TIP balance equations leads precisely to the usual TIP result. This development is given in Appendix B.

It is also possible to show that rational mechanics and TIP are the same except for kinetic energy of diffusion terms. We do this by rearranging the equations of the rational mechanical theory of Sections 2 through 5. In both microscopic and macroscopic TIP theory the diffusion flux, j_i^1, as well as the heat flux, Q_i, is written as a linear function of two forces:

$$- j_i^1 = \Omega_{10} \partial \ell n T / \partial x_i + \Omega_{11} Z_i \qquad (7.1)$$

$$- Q_i = \Omega_{00} \partial \ell n T / \partial x_i + \Omega_{01} Z_i \qquad (7.2)$$

where the $\Omega_{\alpha\beta}$ are Onsager or phenomenological coefficients. In microscopic theory the force, Z_i, generally takes the form

$$Z_i = \partial_T(\mu_1 - \mu_2)/\partial x_i. \tag{7.3}$$

(De Groot and Mazur, by inclusion of kinetic energy of diffusion in their energy, E, admit the possibility of an inertial term, but not of viscous terms, in Z_i but do not generally include it in their work.)

Equation (5.12) can be solved for j_i^1 to yield

$$-j_i^1 = (D_T/D_u)T(\partial \ell nT/\partial x_i) + \Xi_i/D_u \tag{7.4}$$

where

$$\Xi_i = \partial_T(\mu_1' - \mu_2')/\partial x_i - (1/\rho_1)\partial(\sigma_{ji}' + \pi_1\delta_{ji})/\partial x_j$$
$$+ (1/\rho_2)\partial(\sigma_{ji}^2 + \pi_2\delta_{ji}) + (\rho/\rho_1\rho_2)d_{ji}^1/dt$$
$$+ (\rho/\rho_1\rho_2)J_i.$$

In the microscopic theory the force, Z_i, is identical to the Ξ_i given in (7.5). The work here is the first successful reproduction of that force with a macroscopic theory.

At this point we note from (7.1) and (7.4) the coefficient identities

$$\Omega_{10} = TD_T/D_u \tag{7.6}$$

$$\Omega_{11} = 1/D_u. \tag{7.7}$$

In order to determine the heat flux, Q_i, which corresponds for rational mechanics to the heat flux in the entropy production of TIP, we turn to the entropy production in (4.36) and specifically to the term D given by (4.11). Each time u_i^1 appears, it can be replaced by j_i^1/ρ_1. In both the TIP and the microscopic theories, the entropy production is a bilinear form of independent fluxes and their conjugate forces, where the vectorial fluxes and forces are those of equations (7.1) and (7.2), so that

$$\rho T\Phi = - j_i^1 Z_i - Q_i(\partial \ell nT/\partial x_i). \qquad (7.8)$$

However, in order to obtain this relationship in the microscopic theory, all of the equations of Bearman and Kirkwood are linearized to the extent that Ξ_i of (7.5) now contains only the one term in (7.3). All viscous and inertial terms are dropped. The assumptions by Fitts that Ξ_i can replace $\partial_T(\mu_1 - \mu_2)/\partial x_i$ directly in the entropy production with no change in the non-vectorial terms is incorrect.

In order to determine what Q_i represents in the rational mechanical theory in terms of the work described here, we rearrange our entropy production. Since D of (4.36) contains all of the bi-vectorial terms of the entropy production, we can equate it with the first two terms of (7.8). In this manner we find for the general Q_i denoted in this theory as q_i',

$$- q_i' = C_{qT}(\partial T/\partial x_i) + [C_{qu}/\rho_1 - KT/\rho_1 + T(\bar{S}_1 - \bar{S}_2)]j_i^1 \qquad (7.9)$$

Introducing (7.4) into (7.9) and equating coefficients with (7.2), we find

$$\Omega_{00} = TC_{qT} + T(D_T/D_u)[C_{qu}/\rho_1 - KT/\rho_1 + T(\bar{S}_1 - \bar{S}_2)] \tag{7.10}$$

$$\Omega_{01} = [C_{qu}/\rho_1 - KT/\rho_1 + T(\bar{S}_1 - \bar{S}_2)]/D_u. \tag{7.11}$$

By application of equations (3.2), (4.9), and (4.37) to (7.9), the new heat flux is seen to be the difference between the entropy flux and the entropy of the components carried by the diffusion flux:

$$q_i' = Tf_i - T(\bar{S}_1 - \bar{S}_2)j_i^1 = q_i + Tk_i - T(\bar{S}_1 - \bar{S}_2)j_i^1. \tag{7.12}$$

This agrees with the identity of q_i' in TIP from the work of Kirkwood and Crawford.

The non-vectorial terms of $\rho T\Phi$ in TIP are the form

$$(T_{ij} - P\delta_{ij})(\partial v_i/\partial x_j), \tag{7.13}$$

where this term can be split into symmetric second order tensor and scalar parts. The phenomenological relations of TIP include (7.1) and (7.2) with (7.3) as well as

$$\{T_{ij}\} = - 2\eta\{\partial v_j/\partial x_i\} \tag{7.14}$$

$$T_{ij}\delta_{ij} - 3P = - \phi(\partial v_i/\partial x_i). \tag{7.15}$$

The general heat flux, Q_i, in terms of TIP is

$$Q_i = q_i^* - j_i^1(\bar{H}_1 - \bar{H}_2), \tag{7.16}$$

so that

$$\rho T\Phi = -\{q_i^* - j_i^1(\overline{H}_1 - \overline{H}_2)\}\partial \ln T/\partial x_i - j_i^1\partial_T(\mu_1' - \mu_2')/\partial x_i$$
$$- (T_{ij} - P\delta_{ij})(\partial v_i/\partial x_j) \qquad (7.17)$$

is the entropy production of TIP.

8. Expressions for the Entropy Production and the Entropy Balance Equation

In this section we first discuss five possible forms that the entropy production and entropy balance equations can assume and then discuss the similarities and discrepancies of these forms.

a) The final expression which we obtained for the entropy production in Section 4 by using all of the constitutive equations including that for m_i^1 gives us

$$\rho T\Phi = D + Y, \qquad (8.1)$$

where

$$Y = \sum_{\alpha=1}^{2}\sum_{\beta=1}^{2}\phi_{\alpha\beta}d_{\ell\ell}^{\alpha}d_{nn}^{\beta} + \sum_{\alpha=1}^{2}\sum_{\beta=1}^{2}\eta_{\alpha\beta}\{d_{ij}^{\alpha}\}\{d_{ij}^{\beta}\} + 2\mu\omega_{ij}\omega_{ji} \qquad (8.2)$$

$$D = (C_{qT}/T)(\partial T/\partial x_\ell)(\partial T/\partial x_\ell) + [(T\rho_1)(\partial K/\partial T)$$
$$+ (\rho^2/\rho_1\rho_2)C_{mT}]\rho_1 u_\ell^1(\partial T/\partial x_\ell) + (\rho^2/\rho_1\rho_2)C_{m1}\rho_1 u_\ell^1 u_\ell^1. \qquad (8.3)$$

The expression for D can be modified by replacing the constitutive equation for q_i by q_i itself to yield

$$\begin{aligned} D = &- (q_i/T)\,\partial T/\partial x_i + [(T/\rho_1)\,\partial\kappa/\partial T \\ &+ (\rho^2/\rho_1\rho_2)C_{mT}]\,\rho_1 u^1_\ell(\partial T/\partial x_\ell) \\ &+ (\rho^2/\rho_1\rho_2)C_{m1}\rho_1 u^1_\ell u^1_\ell, \end{aligned} \tag{8.4}$$

where

$$q_j = q^*_j + \sum(\sigma^\alpha_{ji} - \rho_\alpha u^\alpha_j u^\alpha_i)\,u^\alpha_i + (1/2)\sum\rho_\alpha u^\alpha_j u^\alpha_i u^\alpha_i. \tag{8.5}$$

The entropy balance equation

$$\rho T(dS/dt) = - T(\partial f_k/\partial x_k) + \rho T\Phi + \rho r \tag{8.6}$$

then has the form

$$\begin{aligned} T(dS/dt) = &- T(\partial f_k/\partial x_k) - q_i(\partial \ell n T/\partial x_i) + \rho r \\ &+ [(T/\rho_1)\,\partial\kappa/\partial T + (\rho^2/\rho_1\rho_2)C_{mT}]\,\rho_1 u^1_\ell(\partial T/\partial x_\ell) \\ &+ (\rho^2/\rho_1\rho_2)C_{mu}\rho_1 u^1_\ell \mu^1_\ell + Y. \end{aligned}$$

b) A second form of the entropy production is obtained as in Section 7 by introduction of a new heat flux into the linear equations. Again we have used the constitutive equation for m^1_i. Thus,

$$\rho T\Phi = F + Y, \tag{8.8}$$

where

$$F = - q'_i(\partial \ell n T/\partial x_i) - j^1_i \Xi_i \tag{8.9}$$

and

$$\begin{aligned} q_i' &= Tf_i - T(\bar{S}_1 - \bar{S}_2)j_i^1 \\ &= q_i^* + \sum(\sigma_{ij}^\alpha - \rho_\alpha u_i^\alpha u_j^\alpha)u_j^\alpha + (1/2)\sum\rho_\alpha u_i^\alpha u_j^\alpha u_j^\alpha \\ &\quad + Tk_i - T(\bar{S}_1 - \bar{S}_2)j_i^1. \end{aligned} \tag{8.10}$$

The entropy production is then

$$\begin{aligned} \rho T(dS/dt) &= - T(\partial f_k/\partial x_k) - j_i^1 \Xi_i \\ &\quad - q_i'(\partial \ell nT/\partial x_i) + Y + \rho r. \end{aligned} \tag{8.11}$$

c) A third form of the entropy production is obtained by returning to the expression for entropy production before the introduction of the constitutive equations. Equation (3.17) for $\rho T\Phi$ is rewritten using the restrictions from the constitutive equations and (4.41), (4.15), and (4.16):

$$\begin{aligned} \rho T\Phi &= f_j(\partial T/\partial x_j) - [\partial(\mu_1 - \mu_2)/\partial x_j]j_j^1 \\ &\quad - \sum(\rho m_i^\alpha - \partial\pi_\alpha/\partial x_i)u_i^\alpha \\ &\quad + \sum(\sigma_{ij}^\alpha + \pi_\alpha\delta_{ij})(\partial v_i^\alpha/\partial x_j). \end{aligned} \tag{8.12}$$

For $\sum m_i^\alpha u_i^\alpha$ we multiply (4.43) by $\rho u_i^1/\rho_2$ and rearrange this expression to find

$$\begin{aligned} \rho\sum m_i^\alpha u_i^\alpha &= \rho d(\sum\rho_\alpha u_i^\alpha u_i^\alpha/2\rho)dt - \partial\{\sum u_i^\alpha(\sigma_{ij}^\alpha - \rho_\alpha u_i^\alpha u_j^\alpha)\}/\partial x_j \\ &\quad - \partial(\sum\rho_\alpha u_i^\alpha u_i^\alpha u_j^\alpha/2)\partial x_j - \sum(\sigma_{ij}^\alpha - \rho_\alpha u_i^\alpha u_j^\alpha)(\partial v_i/\partial x_j) \\ &\quad + \sum\sigma_{ij}^\alpha(\partial v_i^\alpha/\partial x_j) - \sum\rho_\alpha u_i^\alpha b_i^\alpha. \end{aligned} \tag{8.13}$$

This uses the second of the two expressions for m_i^1 which were discussed in Section 4. Substituting (8.13) and (8.12) into (8.6) and rearranging, we arrive at an entropy balance equation

$$\begin{aligned} T(dS/dt) + \rho d(\textstyle\sum \rho_\alpha u_i^\alpha u_i^\alpha/2\rho)/dt = &- j_j^1 \, \partial_T(\mu_1' - \mu_2')/\partial x_j \\ &- \{q_j^* - j_j^1(H_1 - H_2)\}\partial \ln T/\partial x_j + \Pi_{ij}(\partial v_i/\partial x_j) \\ &+ \rho r - T\partial\{\tfrac{1}{T}[q_j^* - j_j^1(\mu_1 - \mu_2)]\}/\partial x_j. \quad (8.14) \end{aligned}$$

In (8.14) we no longer have the balance equation for entropy alone, but for entropy plus kinetic energy of diffusion. The flux in this balance equation is q_j^* - - $j_j^1(\bar{H}_1 - \bar{H}_2)$, which is related to the heat flux, q_j^* $j_j^1(\mu_1 - \mu_2)$, of this equation by

$$q_j^* - j_j^1(\bar{H}_1 - \bar{H}_2) = q_j^* - j_j^1(\mu_1 - \mu_2) - T(\bar{S}_1 - \bar{S}_2)j_j^1, \quad (8.15)$$

which is the same difference between the two entropy fluxes as that given in (8.10). By inclusion of all constitutive equations except that for m_i^1, we have succeeded in changing the form of the entropy balance equation radically. In particular, the tensorial term, Y, has been replaced by the single term, $\Pi_{ij}(\partial v_i/\partial x_j)$.

d) The expression for entropy production given in Section 6, (6.42), and the concommittant entropy balance equation are not readily comparable to others discussed because the entropy production is not a bilinear form. It can be written

$$\rho T\Phi = q_j(\partial T/\partial x_j) + \{C'_{mu}u_j + [T(\partial K'/\partial T)](\partial T/\partial x_j)\}u_j + \phi(\partial v_k/\partial x_k)(\partial v_\ell/\partial x_\ell) + 2\eta(\partial v_i/\partial x_j)(\partial v_j/\partial x_i) + L. \tag{8.16}$$

All non-linear terms are in L.

Because the expression for the balance of momentum of diffusion is the same as that of Bearman and Kirkwood, the entropy production equation will reduce in the same way as that of the Bartelt-Horne theory to the equation of section c with slightly modified coefficients. One could also note at this point that it would also be entirely possible to obtain a bilinear entropy production for this theory if, instead of writing a linear constitutive equation for m_i, one represented the expression $m_i + T_{ij}u_j(\rho_1 - \rho_2)/\rho$ by a linear constitutive equation. This may seem to be an arbitrary choice, and indeed it is--representing the product of an independent variable and a dependent tensor by a linear constitutive equation. However, this choice is no more arbitrary than the definition for heat flux, (2.14), used in both theories. This choice for a constitutive relation to represent a term which is poorly understood in the first place would hardly make the theory more obscure.

e) The traditional form of entropy balance equation in TIP is

$$\begin{aligned}\rho T(dS/dt) = &- T\partial\{\tfrac{1}{T}[q_j^* - j_j^1(\mu_1 - \mu_2)]\} \\ &- [q_j^* - j_j^1(\overline{H}_1 - \overline{H}_2)](\partial \ell nT/\partial x_j) \\ &- j_j^1[\partial_T(\mu_1' - \mu_2')/\partial x_j] - \Pi_{ij}(\partial v_i/\partial x_j).\end{aligned} \tag{8.17}$$

All of the quantities appearing in (8.17) have the same definitions as those in this paper, assuming that as discussed in Section 5 the thermodynamic quantities are based on the same thermodynamic energy.

By comparing the five forms of the entropy production we see first that all forms except that of d are bilinear. Success in attaining bilinear forms is due to proper choices of the functions to be represented by linear constitutive equations. The second and third forms, (8.8) and (8.12), are very different. The third form, which does not use the constitutive equation for m_i^1 is identical to the classical form of TIP, (8.17), except for the term for the kinetic energy of diffusion which appears in the entropy balance equation. From this comparison one can readily see that the only contribution of kinetic energy of diffusion to the entropy production is in a single term, so that if one wants to exclude kinetic energy of diffusion systematically, then only this term need be dropped and the form will be reduced to that found from TIP. The fourth form is also very similar to the TIP theory in that the tensorial terms are the same and there is no inertial term. The entropy flux, heat flux, and conjugate force of u_j are present in both but are different, and the non-linear terms do not appear in TIP.

Having reviewed our entropy production equations, we can measure the success of the Bartelt-Horne theory in approximating reality by re-examining the two temperature equations of Section 5. By putting (8.14) into (5.20), with some rearrangements, we have

$$\begin{aligned}\rho\bar{C}_v(dT/dt) + \rho d(\textstyle\sum\rho_\alpha u_i^\alpha u_i^\alpha/2p)/dt = \\ - \partial\{q_j^* - j_j^1(\bar{H}_1 - \bar{H}_2)\}/\partial x_j + \rho r \\ - j_j^1[\partial_T(\bar{H}_1' - \bar{H}_2')/\partial x_j] + (\beta T/\rho\beta')(d\rho/dt) \\ + \Pi_{ij}(\partial v_i/\partial x_j) + (\rho\beta T/\beta')(\bar{V}_1 - \bar{V}_2)(dw_1/dt).\end{aligned} \tag{8.18}$$

To obtain the temperature and pressure equation we use (5.21). There is considerable controversy over the inclusion or exclusion of kinetic energy of diffusion in such an equation. If this kinetic energy were included, as Truesdell has suggested it should be, the equation would have the form

$$\begin{aligned}\rho(dE_I/dt) + \rho d(\textstyle\sum\rho_\alpha u_i^\alpha u_i^\alpha/2\rho)/dt = (\rho\bar{C}_p - P\beta)(dT/dt) \\ - (T\beta - \rho\beta')(dP/dt) \\ + \rho[\bar{E}_1 - \bar{E}_2 + (1/2)u_i^1u_i^1 - (1/2)u_i^2u_i^2](dw_1/dt).\end{aligned} \tag{8.19}$$

In either case the disputed terms are sometimes small and are usually neglected justifiably or not. The assumption of the validity of the Gibbs equation for nonequilibrium processes is part of the principle of local state. The principle applies to a small volume element as a whole, the internal energy of which includes kinetic energy of diffusion. With the adoption of this principle, however, the state of the volume element is described by three state functions (w_1, ρ, and T) and cannot be a function of u_i^1, so that we have the relationship

$$\rho d(\sum \rho_\alpha u_i^\alpha u_i^\alpha / 2\rho) dt = - \sum (1/2) u_i^\alpha u_i^\alpha (\partial j_j^\alpha / \partial x_j) \qquad (8.20)$$

under the postulate of local state, and equation (8.19) reduces to (5.21). Thus, if (8.20) holds true, (5.21) and (8.19) are precisely the same equation. However, what (8.20) implies is that

$$du_i^\alpha / dt = 0, \qquad (8.21)$$

which seems unlikely for it implies the cancellation of the contributions of partial stress tensors and interaction forces in the diffusion momentum balance equation. TIP never refers to the diffusion momentum balance equation; only the barycentric momentum is considered.

However, if the energy balance equation (2.8) is used in (5.21) with the time derivative of P analogous to (5.6), we have

$$\begin{aligned}\rho\bar{C}_v(dT/dt) + \rho d(\textstyle\sum\rho_\alpha u_i^\alpha u_i^\alpha/2\rho)/dt = \\ - \partial q_j^*/\partial x_j + j_j^1\partial(\bar{H}_1' - \bar{H}_2')/\partial x_j \\ + \Pi_{ij}(\partial v_i/\partial x_j) + (\beta T/\rho\beta')(d\rho/dt) \\ + \rho T(\bar{V}_1 - \bar{V}_2)(\beta/\beta')(dw_1/dt), \qquad (8.22)\end{aligned}$$

where we have used (5.23). Comparison of (8.22) with (8.18) shows that they are identical. To the extent that the principle of local state holds, our theory is valid, but if the principle of local state were really true, then there would be no need for improvement of the equations of TIP.

The only modification which we have introduced in the temperature equation is the time derivative of the kinetic energy of diffusion. It is this term which is responsible for introducing internal forces and which necessitates partial stress tensors, both of which (interaction forces and partial stress tensors) are routinely included in the development by rational mechanics. These quantities are also the most difficult to express by constitutive relations because we have little experimental feeling for them.

Although we have managed to make several rational mechanical forms of the entropy balance equation resemble the TIP form of the balance equation, we have lost sight of the Clausius-Duhem inequality. Because we defined our entropy flux at the outset of our theories, we can only apply the Clausius-Duhem inequality to those terms of the entropy balance equation which are not the gradient of the entropy flux. We cannot redefine entropy flux in midstream, as is done in TIP, for the purpose of application of the Clausius-Duhem inequality. Thus, the inequality applies to (8.1), (8.8), and (8.16) but not to the terms outside of the flux gradient in (8.14). This is a difficulty in the TIP theory. According to Appendix B, all terms in the right hand side of (8.18) except $- \partial(q_j^*/T)/\partial x_j$ are in the entropy production, and therefore greater than or equal to zero. In normal TIP theory the entropy production is considered to be given by those terms which are not the gradient of a flux. When terms which are not included in the entropy flux as defined initially are put in the entropy production, it no longer will be a bilinear form composed of the products of fluxes and forces.

9. Conclusions and Discussion

In the preceding sections we have investigated the progress of rational mechanics in describing transport in fluid mixtures. Hopefully, we have dispelled some myths about the irreconcilability of TIP and rational mechanics. At the same time we have laid no claim to verification or denunciation of Onsager's microscopic theory. The necessary assumptions in defining a linear theory have been given. The real danger in any theory is inconsistency in the linearization scheme. It is the theories which have tried, more or less randomly, to take into account some degree of non-linearity that have remained farthest from internal consistency and applicability.

Now that we have defined a linear theory formulation and have given several examples of such, we must ask to what extent are such theories valid. The simple relations of TIP have been known for years due to the fact that they are empirically motivated and are adequate for the description of any experimental system now available (excepting those in which chemical reactions occur). That the linear relations represent ultimate truth is not only doubtful, but impossible. So long as a sufficient number of variables are introduced the rational mechanical theories are correct until they are linearized, but from this point on they can only approximate the truth and frequently they contradict one another. One knows that any properly chosen set of independent variables must be equivalent to any other such set in generating a general theory; but, when one writes a linear theory in terms of one set of variables and then tries to change his set of variables, he finds he no longer has a linear theory and in fact is lucky if his transformed theory still contains only objective terms. Perhaps one linear theory presents a description very near to reality, but no one knows which theory it might be.

Another problem arises in Section 6, which treats the only theory which was presented with a non-bilinear form for the entropy production. There is no apparent reason for the entropy production necessarily to be bilinear in the rational mechanical case. However, in examining the restrictions placed by (4.18) and (4.19) on the coefficients of terms in the entropy production, we find relationships such as

$$\rho C'_{mu} - (\phi/4)[(\rho_1/\rho)(\partial\rho_1/\partial x_i) - (\rho_2/\rho)(\partial\rho_2/\partial x_i)]^2 > 0. \tag{9.1}$$

If the coefficients ϕ and C'_{mu} depend only on ρ_1, ρ_2, and T, it would seem that this expression places a restriction on among the variables ρ_1, ρ_2, T, $\partial\rho_1/\partial x_i$, and $\partial\rho_2/\partial x_i$. At what point did our variables lose their independence?

We have assumed that thermodynamic quantities are the same functions of state variables in nonequilibrium thermodynamics as they are in thermostatics. If this postulate is not true, we have a whole new problem. Truesdell actually gives a chemical potential tensor for each component. Of course, we can define any combination of terms by any name we desire.

An interesting point to investigate will be the nine viscosity coefficients that appear in rational mechanical theories. Only two coefficients have ever been measured. The problem of actually measuring stress in a fluid due to a diffusion velocity gradient seems insurmountable and much work remains to be done in this area.

Certainly there are many implications of rational mechanical theory which remain to be investigated. However, the theory needs also to be extended, particularly to include second order terms in the constitutive equations. This is an immense problem which would more than quadruple the number of terms in each constitutive equation. It would produce a more realistic theory, but attainment of relationships between constitutive coefficients would be much more difficult since (4.18) and (4.19) tell us nothing of terms with more than two of the 21 nonequilibrium variables. One would also be tempted to try to formulate a theory by adding only those second order terms which he feels are likely to be important. This would be highly subjective, however, for who among us knows how interaction forces depend on a velocity gradient dotted into a temperature gradient and so forth? Nevertheless, it will not be possible, except by experiment, to assess the accuracy of the linear theory until a second-order theory is formulated and the contributions of terms added are evaluated.

We have seen that terms which are second order in u_i^α have caused the greatest problems in comparing the rational mechanics theories to the theories of TIP. Ideally, one would minimize these contributions in an experimental situation. This, however, implies that the diffusion flux itself will be minimized and that we are approaching the study of a binary mixture behaving as a pure fluid in nonequilibrium. We would be more certain that our experiments were correct as evaluated by the theory of rational mechanics or TIP, but problems of diffusion would be unanswered.

If a complete non-linear treatment of rational mechanics is done, many, many more terms which are second order in u_i^α will no doubt arise. It may well be that these terms in combination with the terms which come out of the linear theory will vanish, or will at least form clearly nonlinear combinations. The foundations of TIP are the same as those of rational mechanics except that TIP does not treat the balance of diffusion momentum, and we have established that the theories are identical except for the second order terms in diffusion velocity.

In thermostatic derivations, a change of state variables gives formal results different from the original equations, but each set of results equally well describes reality and gives the same calculable results. One's choice of state variables is usually directed toward giving the simplest formulation for the problem at hand. In TIP one can change his reference frame (reference velocity to which component velocities are compared) and derive several formally different theories. A comparison of the entropy productions of these theories allows one to obtain readily relationships among the various phenomenological coefficients because the entropy production is invariant. We would suggest then that, since all the rational mechanics theories have been developed from proper sets of objective independent variables applied to the same balance equations and since all the theories have been linearized in exactly the same rigorous manner, the entropy productions of the theories should be equivalent and any formal difference occurring between them can be equated to zero. This procedure would hopefully give us new insights into the meaning of the constitutive coefficients or at least give us relationships among the coefficients of various theories.

CHAPTER III

THERMAL CONDUCTIVITY

1. Introduction

A great deal of research on thermal conductivity in fluids has been done over many years, particularly because of the diverse technological applications of heat conducting liquids. A review of theories of conductivity, all of which are microscopic, is given by McLaughlin (1964). However, a fully rigorous mathematical treatment of thermal conductivity as a macroscopic process has not been presented in the literature. Solutions of the macroscopic heat transport equations for liquids have, in general, been found by assuming that physical properties such as heat capacity, density, and thermal conductivity are constants. These solutions then resemble solutions for heat conduction in solids as discussed by Carslaw and Jaeger (1959).

Many experimental techniques have been developed for measuring thermal conductivity in liquids, but most of these depend on calorimetry measurements and measurements of heat flow and, therefore, either require calibration or are subject to large experimental error.

These problems are emphasized in a recent review (Tree and Leidenfrost, 1969) of the methods that have been used to measure the thermal conductivities of carbon tetrachloride and toluene. The values measured by these methods show a variation of more than ten percent for each of the fluids. Such findings suggest that one needs a better theoretical treatment for liquids and more reliable experiments.

We have completed a theoretical investigation of heat conduction in a flat plate cell (thermal diffusion cell). The theory does not treat coefficients in the thermal conductivity equation as constants, and thus an analysis of the error introduced by such an assumption is possible through comparison with this rigorous theory. The attainment of general macroscopic solutions for temperature as a function of thermal conductivity makes possible the design of new time dependent experiments based on temperature measurements rather than on measured heat flow. The time needed for a liquid to adjust to new temperature boundary conditions is a relaxation time dependent directly on the liquid's thermal conductivity. Experiments which measure these relaxation times can be done with greater accuracy than those which depend on calorimetry and heat flow.

In order to determine the thermal conductivity of a pure fluid, one needs a completely general description of temperature variation as a function of space, time, and thermal conductivity in a cell. Then, after determining the temperature or its gradient at specific positions and times, one can fit the general temperature solution to the measured temperatures by varying the value of the thermal conductivity. If one's solution is correct and his experiments accurate, the value which gives the best fit will be the best experimental estimate of the true thermal conductivity.

Horne and Anderson (1970) have recently developed such a temperature solution for binary mixtures of fluids in a pure thermal diffusion cell. Using a perturbation scheme, they solved the transport equations for both the heat conduction and the mass fraction as functions of position and time under the initial and boundary conditions of the pure thermal diffusion cell. Their solutions are superior to those of others in that Horne and Anderson account for convective heat and mass transfer, the dependence of density and other properties upon composition and temperature, and warming-up effects. Their perturbation scheme is readily applicable to many problems, and we use it here to solve the transport equation for heat conduction in a pure fluid. The transport equations for a pure fluid are actually simpler than those for mixtures, but the solutions of interest in such a case must be known at very short times, during which the temperature gradient is being established in the cell, whereas the equations of Horne and Anderson are primarily intended to describe diffusion effects after this warming-up period is over.

The classical thermal diffusion cell is a rectangular parallelepiped bounded above and below by metal plates in contact with heat reservoirs which can be maintained at any temperatures. The area of the plates is made much greater than the distance between them in order to minimize edge effects. The cell often has glass walls so that refractive index changes resulting from temperature changes in the fluid can be measured. After the plates, reservoirs, and fluid in the cell have equilibrated at some temperature, a positive temperature gradient is applied to the cell by simultaneous heating of the upper plate and cooling of the lower plate through their respective reservoirs. This temperature gradient produces a negative density gradient without convection (for the normal fluid, whose thermal expansivity is positive). The establishment of the density gradient occurs within the time necessary to reach the temperature steady state in the cell. This is a much shorter time than that within which a density steady-state is established in a pure thermal diffusion experiment.

As in the work of Horne and Anderson, we use empirical parameters to characterize the times needed for the plate temperatures to reach their steady values.

Horne and Anderson assumed in their solutions that the upper and lower plate parameters are equal, while our solutions include a different parameter for each plate.

In Section 2 we present the complete set of practical macroscopic transport equations for a pure fluid and the conditions which the solutions of these equations must satisfy in a typical cell. In Section 3 we introduce the approximations which must necessarily be made in order to solve the equations of Section 2. The solutions of the temperature equations are presented and analyzed in Section 4.

2. Transport Equations

Our fundamental transport equations correspond to equations (II.5.1), (II.5.5), and (II.8.22) with (II.5.23). These equations are greatly simplified when the fluid in question is assumed to be a one component liquid subject to only a gravitational external force. The above equations under these conditions are also those of TIP (Horne and Bearman, 1967). We assume that the temperature gradient is applied only in the vertical direction with no horizontal effects and that the cell walls are adiabatic so that there is no horizontal heat flux through the walls. Heat and matter flow only in the vertical direction and there is no steady state convection.

The hydrodynamic equation of continuity of mass is

$$(d\rho/dt) + \rho(\partial v/\partial z) = 0, \tag{2.1}$$

where ρ is the density, v is the barycentric velocity, t the time, and z, the vertical position coordinate, and where the substantial time derivative, d/dt, is related to the local time derivative by

$$(d/dt) = (\partial/\partial t) + v(\partial/\partial z) = 0. \tag{2.2}$$

For the equation of energy transport we have

$$\rho\bar{C}_p(dT/dt) - T\beta(dP/dt) = \phi_1 - (\partial q/\partial z), \tag{2.3}$$

where $\bar{C}_p$ is the specific heat capacity at constant pressure, T is the temperature, β is the thermal expansivity, ϕ_1 is the entropy source term for bulk flow, and q is the heat flux.

The linear phenomenological equation for the heat flux is

$$-q = \kappa(\partial T/\partial z), \tag{2.4}$$

where κ is the thermal conductivity of the fluid.

The initial conditions in the cell are

$$v(z,0) = 0, \quad T(z,0) = T_M, \tag{2.5}$$

and the boundary conditions at all times are

$$v(a/2,t) = 0 = v(-a/2,t)$$

$$T(a/2,t) = \Phi_U(t) \qquad T(-a/2,t) = \Phi_L(t), \tag{2.6}$$

where a is the cell height.

Warming-up effects are taken into account by the time dependent functions for plate temperatures, Φ_U and Φ_L. One can empirically determine the time required for a plate to achieve its steady state. It will generally depend on the plate material and thickness, on the reservoir heat capacity, and on the means of supplying heat to and removing it from the reservoirs. A typical functional form for the plate temperatures is

$$\Phi_U(t) = T_M + (T_U - T_M)[1 - \exp(-t/\gamma_U)]$$

$$\Phi_L(t) = T_M + (T_L - T_M)[1 - \exp(-t/\gamma_L)], \tag{2.7}$$

where T_U and T_L are the temperatures applied to the upper and lower plates, respectively, and γ_U and γ_L are the characteristic relaxation times of the upper and lower plates. These times are best obtained experimentally. Typically (Anderson, 1968), γ_U and γ_L are of the order of 40 to 60 seconds.

3. Approximation Methods

In order to solve the transport equations given above we must make approximations on three levels: (i) the equations are simplified by suppressing demonstrably negligible terms; (ii) a self-consistent, well-ordered perturbation scheme is introduced to take into account variable coefficients; and (iii) a Fourier sine or cosine solution is obtained for each perturbation equation. It is essential to recognize that at no point do we assume that coefficients are constant or that the barycentric velocity is zero.

Simplification of Equations.--We can neglect terms in the transport equations (2.1), (2.3), and (2.4) if they are very small compared with other terms. Obviously equations (2.1) and (2.4) cannot be simplified; but in equation (2.3) we examine the pressure and entropy source terms. The magnitude of these terms in a pure fluid is comparable to their magnitude in a mixture, and the magnitude of the heat flux in a pure fluid is comparable to its magnitude in a mixture, when both the pure fluid and mixture are subjected to the same experimental conditions. For this reason, the arguments of Horne and Anderson for the suppression of these two terms are valid for pure fluids as well as for mixtures. The time dependence of pressure is neglected because we assume that the steady-state pressure distribution in the cell is attained instantaneously. Horne and Anderson found that ϕ_1 is at most $10^{-15} J\ m^{-3} s^{-1}$, whereas $\partial q/\partial z$ is on the order of $25 J\ m^{-3} s^{-1}$, so ϕ_1 in (2.3) is certainly negligible in comparison to the heat flux gradient.

These approximations simplify our energy transport equation (2.3) so that with (2.4) we have

$$\rho\bar{C}_p(\partial T/\partial t) = -\rho\bar{C}_p v(\partial T/\partial z) + \partial[\kappa(\partial T/\partial z)]/\partial z. \qquad (3.1)$$

By equation (2.2) we have for (2.1)

$$(\partial v/\partial z) = -(\partial \ell n\rho/\partial t) - v(\partial \ell n\rho/\partial z), \qquad (3.2)$$

where density derivatives are simply related to temperature derivatives by the chain rule,

$$d\ell n\rho = -\beta dT, \qquad (3.3)$$

when pressure derivatives are neglected as assumed above.

Perturbation Scheme.--The perturbation scheme of Horne and Anderson is used to take the non-constancy of coefficients in the transport equations into account. It is certain that the coefficients vary with temperature (and pressure) in the cell, but it is also true that fairly reasonable solutions to the transport equations have been obtained using constant coefficients. Following this reasoning, we treat every coefficient as a constant plus perturbation terms which depend on temperature fluctuations. This scheme modifies the usual solutions of the energy equation and also allows the density of the system to vary, thus permitting the barycentric velocity to change.

The most general expression for the representation of a coefficient which varies with temperature (or other state variables) about some value for a fixed set of state variables is the Taylor series; therefore, we write each coefficient, L, as a Taylor series with successive higher order derivatives being preceded by higher orders of the ordering parameter, ε:

$$\hat{L} = L_o + \varepsilon(T - T_M)L_T + \varepsilon^2(1/2)(T - T_M)^2 L_{TT} + O(\varepsilon^3), \tag{3.4}$$

where

$$L_o = L(T_M) \quad L_T = (\partial L/\partial T)_{T_M} \quad L_{TT} = (\partial^2 L/\partial T^2)_{T_M}. \tag{3.5}$$

When $\varepsilon = 1$, $\hat{L} = L$ and we have the exact Taylor series expression for L (neglecting pressure dependence in accordance with our previous assumption). The increasing orders of ε indicate the decreasing contribution of those terms to $\hat{L}$. Accordingly we write our solutions as perturbations in ε also so that

$$\hat{T} = T_M + T_0 + \varepsilon T_1 + \varepsilon^2 T_2 + O(\varepsilon^3),$$

$$\hat{v} = v_0 + \varepsilon v_1 + \varepsilon^2 v_2 + O(\varepsilon^3), \tag{3.6}$$

where $\hat{T} = T$ and $\hat{v} = v$ if $\varepsilon = 1$. All of the solutions T_n and v_n are functions of space and time. The total solutions are actually Taylor series in ε about $\varepsilon = 0$.

The parameter ε is a dummy device used to order subsequent manipulation of equations in accordance with the temperature derivatives of the coefficients. Thus, the zeroth-order problem and solution involve no temperature derivatives, the first-order problem involves first derivatives, the second-order problem and solution involve second derivatives and products of first derivatives, and so forth. As in any perturbation method, one cannot be certain a priori whether the solutions (3.6) converge when $\varepsilon = 1$. A reasonable procedure is to find the solutions through the second-order in ε and to compare the zeroth-, first-, and second-order solutions. If the importance of the results diminishes relatively rapidly with increasing order, then one may stop. If, on the other hand, some higher-order result appears to be more important than a corresponding zeroth-order result, one must adjust his perturbation scheme so that the offender is included at zeroth order. The scheme proposed in equations (3.4)-(3.6) works well for thermal conduction in a pure fluid.

The first application of equation (3.6) is to equation (3.4), which becomes

$$\hat{L} = L_o + \varepsilon T_0 L_T + \varepsilon^2[(1/2)T_o^2 L_{TT} + T_1 L_T] + O(\varepsilon^3), \quad (3.7)$$

wherein all of the subscripted L's are constants as defined in (3.5) and all of the T's vary spatially and temporally.

The second application of the perturbation scheme is to the velocity equation (3.2). The initial and boundary conditions at each order of ε are, by equations (2.5) and (2.6),

$$v_n(z,0) = 0 \quad v_n(\pm a/2,t) = 0, \quad n = 0,1,.... \tag{3.8}$$

Putting $L = \ell n \rho$ in (3.3) and (3.7) we have for the zeroth-order velocity

$$\frac{\partial v_0}{\partial t} = 0, \tag{3.9}$$

which by (3.9) implies

$$v_0(z,t) = 0. \tag{3.10}$$

By equations (3.2), (3.3), (3.7), and (3.10), the velocity equations for higher powers of ε are all of the type

$$(\partial v_n/\partial z) = \beta_o(\partial T_{n-1}/\partial t) + V_n(z,t), \quad n = 1,2,... \tag{3.11}$$

where for the first and second powers of ε

$$V_1(z,t) = 0,$$

$$V_2(z,t) = T_0\beta_T(\partial T_0/\partial t) + v_1\beta_o(\partial T_0/\partial z). \tag{3.12}$$

The result of our perturbation scheme is thus a differential equation for each order whose inhomogeneous part contains only terms of lower order.

Substitution of equations (3.6), (3.7), and (3.10) into equation (3.1) and separation of the results according to the power n of ε yields the following temperature equations:

$$(\partial T_n/\partial t) - \kappa_o(\rho\bar{C}_p)_o^{-1}(\partial^2 T_n/\partial z^2) = U_n(z,t) \quad n = 0,1,\ldots \tag{3.13}$$

with

$$\begin{aligned} U_0(z,t) &= 0 \\ U_1(z,t) &= (\rho\bar{C}_p)_o^{-1}\{\partial[T_0\kappa_T(\partial T_0/\partial z)]/\partial z\} \\ &\quad - (\rho\bar{C}_p)_T(\rho\bar{C}_p)_o^{-1}T_0(\partial T_0/\partial t) - v_1(\partial T_0/\partial z). \end{aligned} \tag{3.14}$$

The similar but very long expression for $U_2(z,t)$ is omitted for brevity. The initial and boundary conditions for each power n of ε are, by equations (2.5), (2.6), and (3.6),

$$\begin{aligned} &T_n(z,0) = 0 \quad n = 0,1,\ldots, \; T_n(\pm a/2,t) = 0 \quad n = 1,2,\ldots, \\ &T_0(a/2,t) = \Phi_U(t) - T_M, \; T_0(-a/2,t) = \Phi_L(t) - T_M. \end{aligned} \tag{3.15}$$

Fourier Transforms.--Inspection of equations (3.11) --(3.15) reveals that the equations must be solved in the progression T_0, v_1, T_1, v_2, T_2, etc., and that the temperature equations are all of one type. For this reason the method of solution will be the same, and we use the method of Fourier transforms for the temperature solutions as did Horne and Anderson. Whether we choose a sine or cosine transform solution is dictated by our boundary conditions, i.e., whether we know the solution or its spatial derivative as a function of time at the boundary. In the first instance, we use a sine transform; in the latter, a cosine. Now, for our temperature equations, we know the behaviour with time of the temperature at the walls rather than the behaviour of its derivative, so we can write for every order, T_n,

$$T_n = \sum_{m=1}^{\infty} g_{nm}(t)\sin(m\pi x/a)\,, \qquad n = 0,1,\ldots, \tag{3.16}$$

where

$$x = z + a/2 \tag{3.17}$$

and where

$$g_{nm}(t) = (2/a)\int_0^a T_n(x,t)\sin(m\pi x/a)\,dx, \quad \begin{array}{l} m = 1,2,\ldots \\ n = 0,1,2,\ldots\ . \end{array} \tag{3.18}$$

We multiply each term of equation (3.13) by $(2/a)\sin(m\pi x/a)$ and integrate each of them over x from 0 to a. This procedure gives us

$$dg_{nm}(t)/dt - \kappa_o(\rho\bar{C}_p)_o^{-1}(2/a)\int_0^a \{\partial^2[T_n(t)]/\partial x^2\}\sin(m\pi x/a)\,dx$$
$$= (2/a)(\rho\bar{C}_p)_o^{-1}\int_0^a U_n(x,t)\sin(m\pi x/a)\,dx, \quad \begin{array}{l} n = 0,1,\ldots, \\ m = 1,2,\ldots\ . \end{array} \tag{3.19}$$

The second term is readily integrated by parts using the boundary conditions (3.15) to yield

$$dg_{nm}(t)/dt + (m^2/\tau)g_{nm}(t) = \Phi_{0m}(t)\delta_{0n}$$

$$+ (2/a)\int_0^a U_n(x,t)\sin(m\pi x/a)\,dx, \quad n = 0,1,\ldots,$$

$$m = 1,2,\ldots, \qquad (3.20)$$

where δ_{0n} is a Kronecker delta, where

$$\Phi_{0m}(t) = -(2m/\pi\tau)\{(-1)^m[\Phi_U(t)-T_M] - [\Phi_L(t) - T_M]\}, \qquad (3.21)$$

and where τ is a thermal relaxation time,

$$\tau = a^2(\rho\bar{C}_p)_o/\pi^2\kappa_o. \qquad (3.22)$$

The differential equation for each $g_{nm}(t)$ is easily solved, in principle, by means of the integrating factor, $\exp(m^2t/\tau)$. The initial conditions are readily found by inserting the intial conditions (3.15) in equation (3.18). Thus we have

$$g_{nm}(0) = 0, \quad n = 0,1,\ldots, \quad m = 1,2,\ldots\,. \qquad (3.23)$$

4. Practical Results

We can now find our temperature solutions to any desired degree of accuracy by solving equation (3.2) repeatedly for successively higher values of n. We solve the first two orders rigorously and estimate the contribution of the solution which is second-order in ε from its steady state solution.

By equations (3.16)--(3.23) we find the solution for zero-order temperature.

$$
\begin{aligned}
T_0 = {} & (z/a + 1/2)(T_U - T_M)[1 - \exp(-t/\gamma_U)] \\
& + (z/a + 1/2)(T_M - T_L)[1 - \exp(-t/\gamma_L)] \\
& + \sum_{n=1}^{\infty} (-1)^n(\pi n)^{-1}\{[4n^2(\gamma_U/\tau)-1]^{-1}(T_U - T_M) \\
& \times [\exp(-t/\gamma_U) - \exp(-4n^2 t/\tau)] \\
& + [4n^2(\gamma_L/\tau)-1]^{-1}(T_M - T_L)[\exp(-t/\gamma_L) - \exp(-4n^2 t/\tau)]\} \\
& \times \sin(2n\pi z/a) \\
& + \sum_{\ell=0}^{\infty} (2/\pi)(-1)^{\ell}(2\ell+1)^{-1}\Bigl([(2\ell+1)^2(\gamma_U/\tau)-1]^{-1}(T_U - T_M) \\
& \times \{\exp[-(2\ell+1)^2 t/\tau] - \exp(-t/\gamma_U)\} \\
& - [(2\ell+1)^2(\gamma_L/\tau)-1]^{-1}(T_M - T_L) \\
& \times \{\exp[-(2\ell+1)^2 t/\tau] - \exp(-t/\gamma_L)\}\Bigr)\cos[2\ell+1)\pi 2z/a]. \qquad (4.1)
\end{aligned}
$$

If the initial temperature, T_M, is the average of the applied temperatures, T_U and T_L, the form of this equation is reduced to

$$
\begin{aligned}
T_0 = {} & \Delta T(z/a)[2 - \exp(-t/\gamma_U) - \exp(-t/\gamma_L)] \\
& + (\Delta T/4)[\exp(-t/\gamma_L) - \exp(-t/\gamma_U)] \\
& + (\Delta T/2\pi) \sum_{n=1}^{\infty} (-1)^n n^{-1}\{[4n^2(\gamma_U/\tau)-1]^{-1}
\end{aligned}
$$

$$
\begin{aligned}
&\times\ [\exp(-t/\gamma_U) - \exp(-4n^2 t/\tau)] \\
&+ [4n^2(\gamma_L/\tau)-1]^{-1}[\exp(-t/\gamma_L) - \exp(-4n^2 t/\tau)]\} \\
&\times\ \sin(2n\pi z/a) \\
&+ (\Delta T/\pi) \sum_{\ell=0}^{\infty} (-1)^{\ell}(2\ell+1)^{-1}\Big([(2\ell+1)^2(\gamma_U/\tau)-1]^{-1} \\
&\times\ \{\exp[-(2\ell+1)^2 t/\tau]-\exp(-t/\gamma_U)\} \\
&-\ [(2\ell+1)^2(\gamma_L/\tau)-1]\{\exp[-(2\ell+1)^2 t/\tau]-\exp(-t/\gamma_L)\}\Big) \\
&\times\ \cos[(2\ell+1)\pi z/a] \qquad (4.2)
\end{aligned}
$$

where

$$\Delta T = T_U - T_L. \qquad (4.3)$$

If the plate relaxation times are the same, but the initial temperature is not the same as the average of the applied temperatures, we have the reduced form

$$
\begin{aligned}
T_0 = {} & (z/a)(T_U - T_L)[1 - \exp\,(-t/\gamma)] \\
&+ 1/2(T_U + T_L - 2T_M)[1 - \exp(-t/\gamma)] \\
&+ \sum_{n=1}^{\infty} (-1)^n(\pi n)^{-1}(T_U - T_L)[4n^2(\gamma/\tau)-1]^{-1} \\
&\times\ [\exp(-t/\gamma) - \exp(-4n^2 t/\tau)]\sin(2n\pi z/a) \\
&+ \sum_{\ell=0}^{\infty} (2/\pi)(-1)^{\ell}(2\ell+1)(T_U + T_L - 2T_M)[(2\ell+1)^2(\gamma/\tau)-1]^{-1} \\
&\times\ \{\exp[-(2\ell+1)^2 t/\tau] - \exp(-t/\gamma)\}\cos[(2\ell+1)\pi z/a], \qquad (4.4)
\end{aligned}
$$

where

$$\gamma = \gamma_U = \gamma_L. \tag{4.5}$$

Finally, if both plates have the same relaxation time and the initial temperature is the average of the applied temperatures, we have the greatly simplified form

$$T_0 = \Delta T\{(z/a)[1 - \exp(-t/\gamma)] + \sum_{n=1}^{\infty}(-1)^n(\pi/n)[4n^2(\gamma/\tau)-1]^{-1}$$
$$\times [\exp(-t/\gamma) - \exp(-4n^2t/\tau)]\sin(2n\pi z/a) . \tag{4.6}$$

The complex forms of equations (4.1), (4.2), (4.4), and (4.6) might discourage one from attempting numerical evaluation for specific experiments. The series converge rapidly for times of ten seconds or more after the application of the temperature gradient and could be evaluated on a calculator, but evaluation by a digital computer is faster and can be carried further with a greater degree of accuracy. At short times the series term of (4.6) is nearly cancelled by the leading term, thus it needs to be known to a very high degree of accuracy. All evaluation of such equations has been done on an CDC 6500 computer. The series have been calculated until changing their length by ten percent fails to change their value by approximately 0.1% or more (e.g., 100 terms of a series are calculated and summed and then the next ten terms are calculated and summed; if these ten terms do not change the initial sum of 100 terms by more than 0.1% of its original value, the series is truncated after these 110 terms and all further terms are assumed negligible). In higher order solutions where multiple series appear, this criterion is applied to each of them.

A plot of T_0 versus cell position at various times as calculated from equation (4.6) is shown in Figure 1. The approximate parameters for carbon tetrachloride shown in Table 1 have been used. The solution is antisymmetric about $z = 0$.

Table 1--Approximate physical properties of CCl_4

$\beta = 1.2 \times 10^{-3} K^{-1}$

$\kappa = 1.1 \times 10^{-1} J\ m^{-1} s^{-1} K^{-1}$

$\kappa^{-1}(\partial\kappa/\partial T) = -\ 1.2 \times 10^{-3} K^{-1}$

$\rho\bar{C}_p = 1.4 \times 10^{6} J\ m^{-3} K^{-1}$

$(\rho\bar{C}_p)^{-1}[\partial(\rho\bar{C}_p)/\partial T] = 7.1 \times 10^{-4} K^{-1}$

In every case, our temperature equation depends only on time, position, length of the cell, temperatures of the plates, relaxation times of the plates, heat capacity of the fluid at its initial temperature, and the thermal conductivity of the fluid at its initial temperature. The experimentalist can determine all of these factors prior to and during his experiment, with the

Figure 1--Plot of T_0 versus (z/a) for CCl_4; a = 30s, b = 60s, c = 90s, d = 120s, e = 150s.

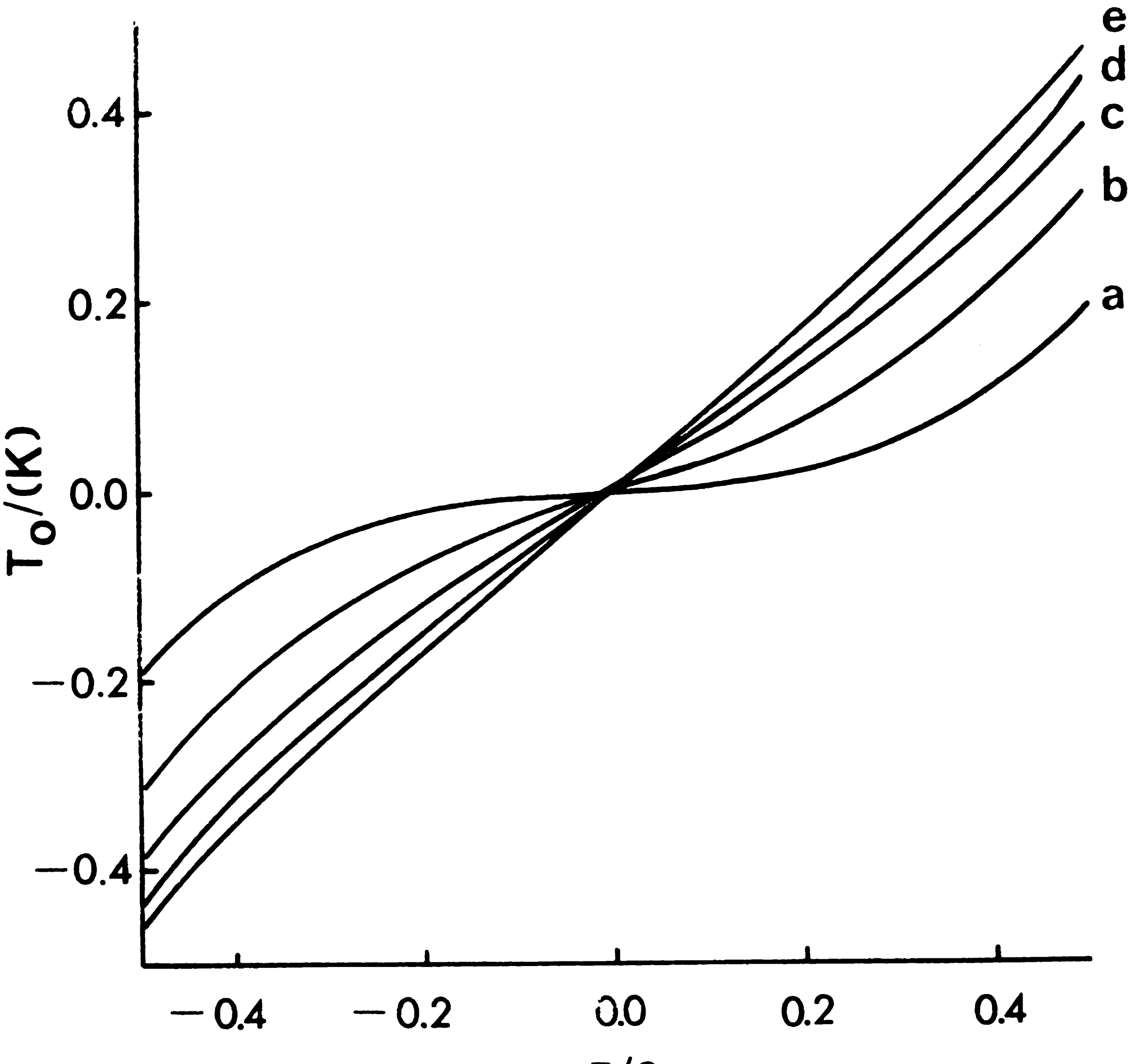

Figure 1

exceptions of the heat capacity and of the thermal conductivity. If, however, the heat capacity of the fluid is known from other experiments, the thermal conductivity can be determined by monitoring the temperature of the fluid (or some parameter which is simply related to temperature) and fitting it to whichever of equations (4.1), (4.2), (4.6), or (4.4) is applicable by variation of the thermal conductivity. Such an application of these equations has been made by Olson (1972).

In order to make such measurements, however, we have assumed that only T_0 in the perturbation solution $T - T_M = T_0 + T_1 + T_2 + \ldots$ is important. To test this hypothesis the solution for T_1 is found and evaluated for typical parameters in order to determine its magnitude. We have a complete solution T_1 for $\gamma = \gamma_U = \gamma_L$ and $T_U + T_L = 2T_M$. Minor variations from these conditions do not affect the magnitude of T_1. The Fourier solution of (3.20) with $n = 1$ and subject to the above conditions is very complex, involving triple sums of infinite series. It is given in full detail in Appendix C. This solution has been evaluated for typical values for carbon tetrachloride. The results are shown in Figure 2. It is symmetric about $z = 0$; therefore, its derivative is zero at $z = 0$ for all t and will add nothing to the temperature derivative monitored at $z = 0$. T_1 is zero initially, rises to a maximum of 5×10^{-5}K at a time of approximately one-half τ, and

Figure 2--Plot of T_1 versus (z/a) for CCl_4; a = 30s, b = 60s, c = 90s, d = 120s, e = 150s.

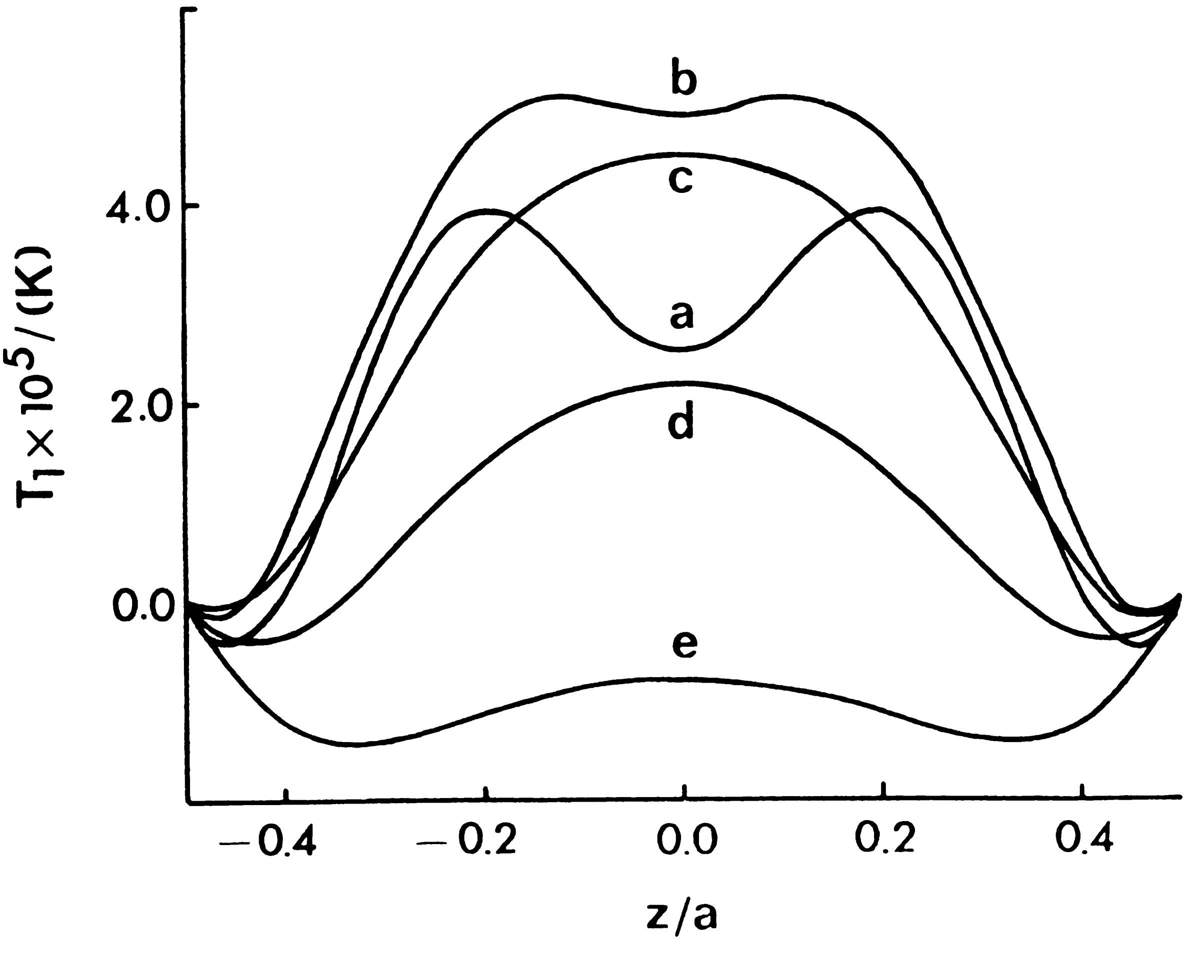

Figure 2

then falls steadily, going negative until the steady-state solution,

$$T_1(\infty) = (1/2)(\Delta T)^2(\kappa_T/\kappa_o)[(1/4)-(z/a)^2], \qquad (4.7)$$

is achieved. The steady-state value in carbon tetrachloride at $z = 0$ is approximately $- 1.6 \times 10^{-4}$K. The behaviour of T_1 at $t < 2\tau$ is shown in Figure 2 and may be compared to the values of T_0 shown in Figure 1.

We can also investigate the behaviour of T_2. It too will have a maximum absolute value in the steady state where

$$T_2(\infty) = (1/2)(\Delta T)^3[(\kappa_T/\kappa_o)^2 - (\kappa_{TT}/3\kappa_o)] \times [(z/a)^3 - (z/4a)]. \qquad (4.8)$$

This value has been shown to be small everywhere by Horne and Anderson, and it is zero at $z = 0$ while its gradient is on the order of 10^{-6}K.

Comparison of the values of T_0, T_1, and T_2 shows that, indeed, the solution T_0 gives a very good approximation to the total temperature solution particularly at short times, and thus, that the thermal conductivity as fitted by equation (4.1), (4.2), (4.4), or (4.6) should be a very good approximant to the true thermal conductivity. The estimates above indicate that the theoretical error caused by truncation of the temperature solution after T_0 is probably less than experimental error.

CHAPTER IV

THE DUFOUR EFFECT

1. Introduction

When a concentration gradient is imposed on an originally isothermal fluid mixture, the phenomenological equation for the heat flux predicts that a temperature gradient will develop as diffusion occurs. This phenomenon is called the Dufour effect, after its discoverer (1873), or the diffusion thermoeffect, to indicate that it is the reverse of thermal diffusion. The effect is of interest in liquids for three important reasons: (1) because it can be used to verify the heat-matter Onsager reciprocal relations, (2) because the temperature variations could cause complications in diffusion experiments, and (3) because it has never been unambiguously observed. The purpose of this work is to predict theoretically the magnitude of the Dufour effect when liquid mixtures are allowed to diffuse into one another and to determine where the Dufour effect can be best measured in a geometrically well-defined cell.

Interest in the Dufour effect rose early in World War II when Clusius and Waldmann (1942) and Waldmann

(1939, 1943, 1946, 1947a, 1947b, 1949), who were interested in determining thermal diffusion factors for gases, developed kinetic and phenomenological theories and experiments to measure the Dufour effect in gases. The equations of the phenomenological theory were solved for adiabatic diffusion and diffusion between cylindrical chambers with diathermic walls. Waldmann's final results depend heavily on the ideal gas law, and they therefore cannot be extended to liquids. The work also requires constancy of thermal conductivity and the heat of transport within each chamber of the experimental apparatus, and the solutions are based on the assumption that the temperature at the boundary of the two chambers does not change during the course of the experiment. Miller (1949), noting the great fluctuations of the temperature at this boundary, suggested that they might be due to heat of mixing as well as to variations in density and specific heat. He did not, however, develop any theory to take these into account. Further kinetic theory has been developed by Grew and Ibbs (1952), and the phenomenological theory is presented by Meixner (1943) who assumed that the reciprocal relations hold.

Waldmann (1947a) used his phenomenological theory to estimate, for the liquid mixture hexane-octane, that the variation of temperature in one chamber would be a maximum of 0.04 K. He neglected heat of mixing. The only investigations of the Dufour effect in liquids have been done by Rastogi and Madan (1965) and Rastogi and Yadava (1969, 1970). Their work is primarily experimental and their results are based on ill-founded mathematical assumptions about the behaviour of their system. We shall discuss their work in more detail at the end of this chapter.

Thus, for many years the Dufour effect in liquids was ignored because it was felt to be too small to measure. Its presence in liquids is masked by the heat of mixing which is not present (at least to any great extent) in gases. Any measurement of the Dufour effect is complicated by the fact that no steady-state other than the equilibrium state is reached by a system which initially has a concentration gradient, and thus the measurement of the temperature gradient arising from the Dufour effect must be time dependent (Fitts, 1962).

The work reported here is a theoretical examination of the temperature effects which result when two binary fluids of different composition are allowed to mix. These are the effects predicted by the macroscopic transport equations, which include in the temperature equation terms for the transported enthalpy. These are the terms that take into account the heat capacities of the two fluids and their heat of mixing. Terms which are demonstrably small are omitted from the transport equations, and transport coefficients are allowed to vary with the thermodynamic variables of the system by expressing them in Taylor series in composition and temperature.

Two ideal experiments which could be approximated in the laboratory are defined. The results of any real experiment should extrapolate to the results given here. We determine optimal conditions for (1) measurement of and (2) neglect of the Dufour effect.

We define our first system to be an adiabatic cylinder or rectangular tube of length a. The value of a will be chosen to get maximum temperature variations as predicted by the solutions of the transport equations with consideration of experimental practicality. The length would probably never exceed ten centimeters. The cell is divided into an upper and a lower chamber, each of which contains a mixture of the same two liquids but in different proportions. In the extreme case each half could contain a pure liquid. The more dense liquid is placed in the lower chamber and the boundary between the two mixtures is assumed to be infinitely sharp initially. The two mixtures, originally at the same temperature, are allowed to diffuse into one another. Diffusion occurs only in the vertical direction and causes vertical temperature variations in the cell. At infinite time the composition in the cell will be uniform (except for sedimentation effects) and the temperature will again be uniform throughout the cell, though not necessarily at the initial temperature.

The second system is identical to the first except that the ends of the cylinder are assumed to be diathermic. The lateral walls of the cylinder are still adiabatic, or the cylinder is of sufficient diameter that variations in edge temperature will be negligible, and diffusion will hence occur only in the vertical direction.

2. Transport Equations

The equation of energy transport in a binary liquid is [*cf.* (II.8.22) with (II.5.6)]

$$\rho \bar{C}_p (dT/dt) - T\beta (dp/dt) = \phi_1 - (\partial q/\partial z) - j_1[\partial(\bar{H}_1 - \bar{H}_2)/\partial z], \tag{2.1}$$

where $\bar{C}_p$ is the specific heat capacity, ρ the density, T the temperature, β the thermal expansivity, p the pressure, ϕ_1 the entropy source term for bulk flow, q the heat flux, j_1 the diffusion flux of component 1 relative to the barycentric velocity, and $\bar{H}_i$ the partial specific enthalpy of component i. The time variable is t, and z is the vertical position coordinate (the initial boundary is at $z = 0$, the ends of the cell at $\pm a/2$).

The conservation of mass equations for the fluid are [*cf.* (II.5.1) and (II.5.2)]

$$(d\rho/dt) = -\rho(\partial v/\partial z) \tag{2.2}$$

and

$$\rho(\partial w_1/\partial t) + (\partial j_1/\partial z) + \rho v(\partial w_1/\partial z) = 0, \tag{2.3}$$

where v is the barycentric velocity and w_1 is the mass fraction of component 1.

The linear phenomenological equations for the fluxes of heat and mass are (Horne and Bearman, 1967)

$$-q = \kappa(\partial T/\partial z) + \rho DQ_1^*(\partial w_1/\partial z) + \rho DQ_1^* S_1 w_1 w_2(\partial p/\partial z) \tag{2.4}$$

and

$$-j_1 = \rho D(\partial w_1/\partial z) - \rho D\alpha_1 w_1 w_2\, T^{-1}(\partial T/\partial z) + \rho DS_1 w_1 w_2(\partial p/\partial z), \tag{2.5}$$

where κ is the thermal conductivity of the mixture when there is no concentration gradient (at infinte time), D is the mutual diffusion coefficient, Q_1^* is the heat of transport of component 1, α_1 is the thermal diffusion factor of component 1, and S_1 is the sedimentation coefficient of component 1.

The solutions to the transport equations for concentration and temperature must fit the initial and boundary conditions of the systems described. Initially we have

$$\begin{aligned} & & w_1(z<0,0) &= w_{1A} + \tfrac{1}{2}\omega_1^o, & & \\ v(z,0) &= 0, & w_1(z>0,0) &= w_{1A} - \tfrac{1}{2}\omega_1^o, & T(z,0) &= T_M, \\ & & w_1(0,0) &= w_{1A}, & & \end{aligned} \tag{2.6}$$

where w_{1A} is the mean of the mass fractions in the two chambers of the cell and $\pm (1/2)\omega_1^o$ are the initial displacements of w_1 from w_{1A} in each half of the cell. At the ends of the cell we have no matter flux and either no heat flux in the adiabatic case or constant temperature in the diathermic case, so

$$v(\pm a/2,t) = 0, \quad j_1(\pm a/2,t) = 0, \quad \begin{array}{c} q(\pm a/2,t) = 0, \\ \text{(adiabatic)} \\ T(\pm a/2,t) = T_M. \\ \text{(diathermic)} \end{array} \tag{2.7}$$

In order to solve the problems which have been posed, we assume that the equations above are correct and can be applied to the idealized experiments described above. We must make further assumptions about terms which can be shown to be essentially constant in order to solve these equations. By using the same arguments as Horne and Anderson (1970) as our first approximation, we neglect pressure terms where now we consider $|\partial T/\partial z| \lesssim 1$ deg cm^{-1} and $|\partial w_1/\partial z| \lesssim 10$ cm^{-1}. The size of the two derivatives will diminish simultaneously. Secondly, we neglect the thermal diffusion term in equation (2.5) because $|\alpha_1 w_1 w_2/T|$ is on the order of 10^{-3} deg^{-1}, and magnitude of the thermal diffusion term is therefore at most 0.01% of the diffusion term. Finally, we neglect the entropy source term of equation (2.1) since (Horne and Anderson, 1970) it is proportional to the square of the velocity gradient,

$(\partial v/\partial z)^2$, which we assume to be unmeasurable in a diffusion experiment. Subsequent results verify this assumption.

The equations remaining are then:

$$-q = \kappa(\partial T/\partial z) + \rho D Q_1^*(\partial w_1/\partial z), \tag{2.8}$$

$$\rho\bar{C}_p(\partial T/\partial t) = \rho D[\partial(\bar{H}_1-\bar{H}_2)/\partial z](\partial w_1/\partial z)+\partial[\rho D Q_1^*(\partial w_1/\partial z)]/\partial z$$
$$- \rho\bar{C}_p v(\partial T/\partial z) + \partial[\kappa(\partial T/\partial z)]/\partial z, \tag{2.9}$$

$$\rho(\partial w_1/\partial t) = \partial[\rho D(\partial w_1/\partial z)]/\partial z - \rho v(\partial w_1/\partial z), \tag{2.10}$$

$$(\partial v/\partial z) = -(\partial \ell n\rho/\partial t) - v(\partial \ell n\rho/\partial z). \tag{2.11}$$

3. Perturbation Scheme

The coefficients in equations (2.9)--(2.11) are functions of w_1, T, and p. In order to solve these equations we must devise a perturbation scheme which allows us to take into account the nonconstancy of the coefficients in space and time. For this purpose we use the perturbation scheme of Horne and Anderson, introduced in Chapter III of this thesis. Here, we expand the coefficients in w_1 and T about w_{1A} and T_M. Variations with pressure are neglected in accordance with our previous assumption, and successive derivatives with respect to w_1 and T are multiplied by higher powers of the ordering parameter, ε. Thus, we have for any coefficient, L,

$$\hat{L} = L_o + \varepsilon[(T-T_M)L_T + (w_1-w_{1A})L_w]$$
$$+ \varepsilon^2[(1/2)(T-T_M)^2L_{TT}+(T-T_M)(w_1-w_{1A})L_{wT}+(1/2)(w_1-w_{1A})^2L_{ww}]$$
$$+ O(\varepsilon^3), \qquad (3.1)$$

where

$$L_o = L(T_M,w_{1A}) \quad L_w = (\partial L/\partial w_1)_{T_M,w_{1A}} \quad L_T = (\partial L/\partial T)_{T_M,w_{1A}}$$
$$L_{ww} = (\partial^2L/\partial w_1^2)_{T_M,w_{1A}} \quad L_{wT} = (\partial^2L/\partial w_1\partial T)_{T_M,w_{1A}} \quad L_{TT} = (\partial^2L/\partial T^2)_{T_M,w_{1A}}$$
$$(3.2)$$

The first and third terms on the right hand side of equation (2.9) arise because we are studying mixtures. Without these terms equation (2.9) would simply be the thermal conductivity equation for a pure fluid. Because we do not expect thermal conductivity in a mixture to differ very much from that in a pure fluid, we can treat the two terms which arise in the thermal conductivity of mixtures as perturbations on the pure thermal conductivity equation. We recognize these perturbations by multiplying each of the two terms by a second perturbation parameter, δ. Thus, we have

$$\rho\overline{C}_p(\partial T/\partial t) = \delta\rho D[\partial(\overline{H}_1-\overline{H}_2)/\partial z]\ (\partial w_1/\partial z) - \rho\overline{C}_p v(\partial T/\partial z)$$
$$+ \partial[\kappa(\partial T/\partial z)]/\partial z + \delta\partial[\rho DQ_1^*(\partial w_1/\partial z)]/\partial z. \qquad (3.3)$$

Our solutions for T, w_1, and v are the perturbation solutions

$$\hat{T} = T_M + T_o + \delta T_\delta + \delta^2 T_{\delta\delta} + \varepsilon T_\varepsilon + \varepsilon\delta T_{\varepsilon\delta} + \varepsilon\delta^2 T_{\varepsilon\delta\delta}$$
$$+ O(\delta^3) + O(\varepsilon^2)$$

$$\hat{w}_1 = w_{1A} = \omega_o + \delta\omega_\delta + \delta^2\omega_{\delta\delta} + \varepsilon\omega_\varepsilon + \varepsilon\delta\omega_{\varepsilon\delta} + \varepsilon\delta^2\omega_{\varepsilon\delta\delta}$$
$$+ O(\delta^3) + O(\varepsilon^2)$$

$$\hat{v} = v_o + \delta v_\delta + \delta^2 v_{\delta\delta} + \varepsilon v_\varepsilon + \varepsilon\delta v_{\varepsilon\delta} + \varepsilon\delta^2 v_{\varepsilon\delta\delta}$$
$$+ O(\delta^3) + O(\varepsilon^2), \qquad (3.4)$$

Each term in equations (3.4) (except w_{1A} and T_M) is a function of space and time. When $\varepsilon = 1$ and $\delta = 1$, $\hat{T} = T$, $\hat{w}_1 = w_1$, and $\hat{v} = v$.

The second perturbation parameter δ has the effect of making all mass fraction derivatives appear in lower order equations than their counterpart temperature derivatives. We select this scheme because coefficient variations with temperature are in general considerably smaller than variations with mass fraction and because we are dealing with small temperature variations and large mass fraction variations. In Chapter III we investigated the behaviour of zeroth-, first-, and second-order solutions in ε and found for the case of thermal conductivity that the magnitude of these solutions decreased rapidly with increasing order. We assume that the behaviour here will be similar and terms of order ε^2 should be very small indeed. Terms of order ε should be smaller than terms of zeroth-order in ε, although inversion of these contributions will occur in a system with very large heat of mixing and small heat of transport. We have not previously investigated the behaviour of terms which are zeroth-, first-, and second-order in δ so we investigate our temperature solutions to order δ^2.

We first apply (3.4) to (3.2) to obtain

$$\hat{L} = L_o + \varepsilon(T_o L_T + \omega_o L_w) + \varepsilon\delta(D_w \omega_\delta + D_T T_\delta) + \varepsilon\delta^2(D_w \omega_{\delta\delta} + D_T T_{\delta\delta}) + O(\delta^3) + O(\varepsilon^2). \tag{3.5}$$

By inserting equations (3.4) into equations (2.9), (2.11), and (3.3) and by using equation (3.5), we obtain a set of differential equations which can readily be solved for each order of ε and δ. Very good approximations to T, w_1, and v can be found by solving for the first few terms of equations (3.4), provided that the series is convergent. We are, of course, primarily interested in the equation for T, but it is necessary to have lower order terms in w_1 and v in order to evaluate terms in T.

4. Zeroth-Order Solutions for an Adiabatic System

Before stating general equations for all orders of ε and δ, we solve our zeroth-order equations for v_o, T_o, and ω_o. These results can then be used to simplify the general equations.

The initial and boundary conditions for the barycentric velocity are

$$v_n(z,0) = 0, \quad v_n(\pm a/2,t) = 0, \quad n = o,\delta,\varepsilon,\ldots \ . \tag{4.1}$$

The zeroth-order equation for velocity is

$$(\partial v_o/\partial z) = 0, \tag{4.2}$$

so from equations (4.1) and (4.2) we find

$$v_o(z,t) = 0. \tag{4.3}$$

The zeroth-order mass fraction equation has the form

$$(\partial \omega_o/\partial t) - D_o(\partial^2 \omega_o/\partial z^2) = 0. \tag{4.4}$$

The solution of this equation can be obtained through Fourier transform methods as discussed in Chapter III. We first change our space variable to x such that

$$x = z + (a/2), \tag{4.5}$$

Our boundary conditions dictate that a cosine transform be used because we know the gradient of the mass fraction at the boundaries from equations (2.7) and (2.8) (after neglecting the last two terms):

$$(\partial w_1/\partial x)_{0,t} = (\partial w_1/\partial x)_{a,t} = 0, \tag{4.6}$$

so that

$$(\partial \omega_n/\partial x)_{0,t} = (\partial \omega_n/\partial x)_{a,t} = 0, \quad n = o,\delta,\varepsilon,\ldots \ . \tag{4.7}$$

We assume ω_o has the form

$$\omega_o(x,t) = (1/2)f_{oo}(t) + \sum_{m=1}^{\infty} f_{om}(t)\cos(m\pi x/a), \quad (4.8)$$

where

$$f_{om}(t) = (2/a)\int_0^a \omega_o(x,t)\cos(m\pi x/a)\,dx, \; m = 0,1,2,\ldots . \quad (4.9)$$

The Fourier transform of equation (4.4) using (4.8) and (4.9) is

$$[\partial f_{om}(t)/\partial t] + (m^2/\Theta)f_{om}(t) = 0, \quad (4.10)$$

where

$$\Theta = a^2/(\pi^2 D_o). \quad (4.11)$$

This equation (or any similar inhomogeneous equation) can readily be solved using an integrating factor, $\exp(m^2t/\Theta)$, and we find

$$f_{om}(t) = A\exp(-m^2t/\Theta) \quad (4.12)$$

where A is a constant not yet determined. Our initial conditions on f_{om} are found by requiring that

$$\omega_o(x,0) = w_1(x,0) - w_{1A}, \quad (4.13)$$

and leaving

$$\omega_n(x,0) = 0, \qquad n = \delta,\varepsilon,\ldots . \quad (4.14)$$

Applying the initial conditions on mass fraction, we find

$$f_{om}(0) = \begin{cases} 0 & m \text{ is even} \\ 2\omega_1^o(\pi m)^{-1}(-1)^{(m-1)/2} & m \text{ is odd.} \end{cases} \qquad (4.15)$$

Thus, we have

$$\omega_o(x,t) = 2\omega_1^o\pi^{-1}\sum_{\ell=0}^{\infty}(-1)^{\ell}(2\ell+1)^{-1}\exp[-(2\ell+1)^2 t/\Theta]\cos[(2\ell+1)\pi x/a]. \qquad (4.16)$$

as our zeroth-order solution for composition.

Our zeroth-order equation for temperature has the same form,

$$(\partial T_o/\partial t) - \kappa_o(\rho\bar{C}_p)_o^{-1}(\partial^2 T_o/\partial z^2) = 0. \qquad (4.17)$$

A solution is again found using a finite Fourier cosine transform:

$$T_o = (1/2)g_{oo}(t) + \sum_{m=1}^{\infty} g_{om}(t)\cos(m\pi x/a) \qquad (4.18)$$

because equations (2.7) and (2.4) (consistently considering the heat flux in a mixture as a perturbation of the heat flux in a pure fluid) we have

$$[\kappa(\partial T/\partial z) = -\delta\rho D Q_1^*(\partial w_1/\partial z)]_{z=\pm a/2}, \qquad (4.19)$$

so that in the zeroth-order case we have from (4.7)

$$(\partial T_o/\partial x)_{0,t} = (\partial T_o/\partial x)_{a,t} = 0. \qquad (4.20)$$

The time contribution to the solution is

$$g_{om}(t) = B \exp(-m^2 t/\tau), \tag{4.21}$$

where

$$\tau = (\rho\bar{C}_p)_o a^2/(\kappa_o \pi^2). \tag{4.22}$$

However, we have $B = 0$ because

$$T(x,0) = T_M \tag{4.23}$$

from (2.6), so

$$T_n(x,0) = 0, \qquad n = o,\delta,\varepsilon,\ldots\ . \tag{4.24}$$

Thus,

$$T_o(x,t) = 0. \tag{4.25}$$

5. Higher Order Solutions for an Adiabatic System

We use equations (4.3) and (4.25) to simplify the differential equations for higher order terms. The velocity equations have the form

$$(\partial v_n/\partial z) = V_n(z,t), \qquad n = \delta,\varepsilon \tag{5.1}$$

where the $V_n(z,t)$ are explicit functions determined from previous solutions:

$$V_\delta(z,t) = 0, \qquad V_{\delta\delta} = 0,$$

$$V_\varepsilon(z,t) = -\ (\ell n\rho)_w(\partial\omega_o/\partial t),$$

$$V_{\varepsilon\delta}(z,t) = -(\ell n\rho)_w(\partial\omega_\delta/\partial t) - (\ell n\rho)_T(\partial T_\delta/\partial t) - v_\delta(\ell n\rho)_w(\partial\omega_o/\partial z),$$

$$V_{\varepsilon\delta\delta}(z,t) = -(\ell n\rho)_w(\partial\omega_{\delta\delta}/\partial t) - (\ell n\rho)_T(\partial T_{\delta\delta}/\partial t)$$
$$- v_\delta(\ell n\rho)_w(\partial\omega_\delta/\partial z) - v_\delta(\ell n\rho)_T(\partial T_\delta/\partial z). \qquad (5.2)$$

We immediately see from (5.2) and (4.1) that

$$v_\delta = 0, \qquad v_{\delta\delta} = 0. \qquad (5.3)$$

The equations for mass fraction have the form

$$(\partial\omega_n/\partial t) - D_o(\partial^2\omega_n/\partial z^2) = W_n(z,t) \quad n = \delta,\varepsilon,\ldots,(5.4)$$

where

$$W_\delta(z,t) = -v_\delta(\partial\omega_o/\partial z),$$

$$W_{\delta\delta}(z,t) = -v_{\delta\delta}(\partial\omega_o/\partial z) - v_\delta(\partial\omega_\delta/\partial z)$$

$$W_\varepsilon(z,t) = [D_o(\ell n\rho)_w + D_w](\partial\omega_o/\partial z)^2 + D_w\omega_o(\partial^2\omega_o/\partial z^2)$$
$$- v_\varepsilon(\partial\omega_o/\partial z),$$

$$W_{\varepsilon\delta}(z,t) = [2D_o(\ell n\rho)_w + 2D_w](\partial\omega_o/\partial z)(\partial\omega_\delta/\partial z)$$
$$+ [D_o(\ell n\rho)_T + D_T](\partial T_\delta/\partial z)(\partial\omega_o/\partial z)$$
$$+ D_w\omega_o(\partial^2\omega_\delta/\partial z^2) + D_w\omega_\delta(\partial^2\omega_o/\partial z^2)$$
$$+ D_T T_\delta(\partial^2\omega_o/\partial z^2)$$
$$- v_{\varepsilon\delta}(\partial\omega_o/\partial z) - v_\delta(\partial\omega_\varepsilon/\partial z) - v_\varepsilon(\partial\omega_\delta/\partial z),$$

$$W_{\varepsilon\delta\delta} = [(\ell n\rho)_T D_o + D_T](\partial T_{\delta\delta}/\partial z)(\partial\omega_o/\partial z)$$
$$+ 2[(\ell n\rho)_w D_o + D_w](\partial\omega_{\delta\delta}/\partial z)(\partial\omega_o/\partial z)$$
$$+ [(\ell n\rho)_T D_o + D_T](\partial T_\delta/\partial z)(\partial\omega_\delta/\partial z)$$

$$+ \ [(\ell n\rho)_w D_o + D_w](\partial\omega_\delta/\partial z)^2$$

$$- v_\varepsilon(\partial\omega_{\delta\delta}/\partial z) - v_{\varepsilon\delta}(\partial\omega_\delta/\partial z) - v_{\varepsilon\delta\delta}(\partial\omega_o/\partial z). \qquad (5.5)$$

The temperature equations are very similar with

$$(\rho\bar{C}_p)_o(\partial T_n/\partial t) - \kappa_o(\partial^2 T_n/\partial z^2) = U_n(z,t), \ n = \delta,\varepsilon,\ldots, \qquad (5.6)$$

where

$$U_\delta(z,t) = (\rho D Q_1^*)_o(\partial^2\omega_o/\partial z^2),$$

$$U_{\delta\delta}(z,t) = -(\rho\bar{C}_p)_o v_\delta(\partial T_\delta/\partial z) + (\rho D Q_1^*)_o(\partial\omega_\delta/\partial z),$$

$$U_\varepsilon(z,t) = 0$$

$$U_{\varepsilon\delta}(z,t) = -(\rho\bar{C}_p)_w\omega_o(\partial T_\delta/\partial t) + [(\rho D)_o(\bar{H}_1-\bar{H}_2)_w + (\rho D Q_1^*)_w](\partial\omega_o/\partial z)^2$$

$$- (\rho\bar{C}_p)_o v_\varepsilon(\partial T_\delta/\partial z) - (\rho\bar{C}_p)_o v_\delta(\partial T_\varepsilon/\partial z) + \kappa_w(\partial\omega_o/\partial z)(\partial T_\delta/\partial z)$$

$$+ \kappa_w\omega_o(\partial^2 T_\delta/\partial z^2) + (\rho D Q_1^*)_w\omega_o(\partial^2\omega_o/\partial z^2) + (\rho D Q_1^*)_o(\partial^2\omega_\varepsilon/\partial z^2).$$

The similar but very long expression for $U_{\varepsilon\delta\delta}$ is given in Appendix E.

The initial conditions for equations (5.4) and (5.6) are given by equations (4.13) and (4.23), respectively. It is obvious that the equations must be solved in a certain order, although there is some flexibility. We choose to solve them in the order T_δ, v_δ, ω_δ, $T_{\delta\delta}$, $v_{\delta\delta}$, $\omega_{\delta\delta}$, T_ε, v_ε, ω_ε, $T_{\varepsilon\delta}$, $v_{\varepsilon\delta}$, $\omega_{\varepsilon\delta}$, $T_{\varepsilon\delta\delta}$, $v_{\varepsilon\delta\delta}$, $\omega_{\varepsilon\delta\delta}$. The order in which the solutions are found is immaterial unless an unknown function is required in the inhomogeneous part of some equation, in which case solution is impossible.

Obvious solutions of the above equations include

$$v_\delta = \omega_\delta = T_{\delta\delta} = v_{\delta\delta} = \omega_{\delta\delta} = T_\varepsilon = v_{\varepsilon\delta\delta} = \omega_{\varepsilon\delta\delta} = 0. \tag{5.8}$$

These results greatly simplify the expressions (5.1), (5.3), and (5.5). In order to have a complete set of equations through second order we would actually have to solve the velocity expressions (5.1) for v_ε and $v_{\varepsilon\delta}$ with

$$\begin{aligned} V_\varepsilon &= -\ (\ell n\rho)_w\ (\partial\omega_o/\partial t) \\ V_{\delta\varepsilon} &= -\ (\ell n\rho)_T\ (\partial T_\delta/\partial t), \end{aligned} \tag{5.9}$$

the mass fraction equations (5.4) for ω_ε and $\omega_{\varepsilon\delta}$ where

$$\begin{aligned} W_\varepsilon &= [D_o(\ell n\rho)_w + D_w](\partial\omega_o/\partial z)^2 + D_w\omega_o(\partial^2\omega_o/\partial z^2) - v_\varepsilon(\partial\omega_o/\partial z), \\ W_{\varepsilon\delta} &= [D_o(\ell n\rho)_T + D_T](\partial T_\delta/\partial z)(\partial\omega_o/\partial z) + D_T T_\delta(\partial^2\omega_o/\partial z^2), \end{aligned} \tag{5.10}$$

and the temperature equations (5.6) for T_δ and $T_{\varepsilon\delta}$ where

$$\begin{aligned} U_\delta &= (\rho DQ_1^*)_o\ (\partial^2\omega_o/\partial z^2), \\ U_{\varepsilon\delta} &= -\ (\rho\overline{C}_p)_w\omega_o(\partial T_\delta/\partial t) \\ &\quad + [(\rho D)_o(\overline{H}_1-\overline{H}_2)_w + (\rho DQ_1^*)_w](\partial\omega_o/\partial z)^2 \\ &\quad - (\rho\overline{C}_p)_o v_\varepsilon(\partial T_\delta/\partial z) + \kappa_w(\partial\omega_o/\partial z)(\partial T_\delta/\partial z) \\ &\quad + (\rho DQ_1^*)_w\omega_o(\partial^2\omega_o/\partial z^2) \\ &\quad + \kappa_w\omega_o(\partial^2 T_\delta/\partial z^2) + (\rho DQ_1^*)_o(\partial^2\omega_o/\partial z^2). \end{aligned} \tag{5.11}$$

The solutions of equations (5.1) have been obtained using the boundary conditions (4.1). They are

$$\begin{aligned}
v_{\varepsilon} &= D_o(\ell n\rho)_w 2\omega_1^o a^{-1} \sum_{\ell=0}^{\infty} (-1)^{\ell}\{\exp[-(2\ell+1)^2 t/\Theta]\} \\
&\qquad \times \sin[(2\ell+1)\pi x/a], \\
v_{\delta\varepsilon} &= (\rho D Q_1^*)_o (\ell n\rho)_T (\rho\overline{C}_p)_o^{-1}[1-(\tau/\Theta)]^{-1} 2\omega_1^o a^{-1} \\
&\qquad \times \sum_{\ell=0}^{\infty} (-1)^{\ell+1}\{\exp[-(2\ell+1)^2 t/\Theta]\}\sin[(2\ell+1)\pi x/a].
\end{aligned} \tag{5.12}$$

The equations (5.4) are solved by Fourier cosine transforms as described previously. The result for ω_{ε} is

$$\begin{aligned}
\omega_{\varepsilon} = (2\omega_1^{o2}/\pi^2) \biggl\{ &(\ell n\rho)_w \sum_{\ell=0}^{\infty} (2\ell+1)^{-2}\{1-\exp[-2(2\ell+1)^2(t/\Theta)]\} \\
&+ \sum_{n=1}^{\infty} \sum_{\ell=0}^{\infty} (2\ell+1)^{-1}(-1)^{n+1} \biggl[\{(\ell n\rho)_w - n(D_w/D_o)(2\ell+1-2n)^{-1}\} \\
&\times [2\ell+1-2n]^{-1} \\
&\times \Bigl(\exp\{-[(2\ell+1)^2+(2\ell+1-2n)^2](t/\Theta)\}-\exp[-4n^2(t/\Theta)]\Bigr) \\
&+ \{(\ell n\rho)_w + n(D_w/D_o)(2\ell+1+2n)^{-1}\}[2\ell+1+2n]^{-1} \\
&\times \Bigl(\exp\{-[(2\ell+1)^2+(2\ell+1+2n)^2](t/\Theta)\}-\exp[-4n2(t/\Theta)]\Bigr)\biggr] \\
&\times \cos(2n\pi x/a)\biggr\}.
\end{aligned} \tag{5.13}$$

The result for $\omega_{\varepsilon\delta}$ is similar to that for ω_{ε} but smaller in magnitude though much greater in length. Like ω_{ε} it is an even function. This result is not given here as it is not necessary for determining the temperature solution through first order in ε and second-order in δ.

The temperature equations which do not have trivial solutions as shown in (5.8) are better expressed in the form

$$(\rho\bar{C}_p)_o(\partial T_{j\delta}/\partial t)-\kappa_o(\partial^2 T_{j\delta}/\partial z^2)$$

$$= (\rho DQ_1^*)_o(\partial^2\omega_j/\partial z^2) + Y_j(z,t)$$

$$j = o,\varepsilon \qquad (5.14)$$

where

$$Y_o(z,t) = 0,$$

$$\begin{aligned} Y_\varepsilon(z,t) = &- (\rho\bar{C}_p)_w\omega_o(\partial T_\delta/\partial t) \\ &+ [(\rho D)_o(\bar{H}_1-\bar{H}_2)_w+(\rho DQ_1^*)_w](\partial\omega_o/\partial z)^2 \\ &- (\rho\bar{C}_p)_o v_\varepsilon(\partial T_\delta/\partial z) + \kappa_w(\partial\omega_o/\partial z)(\partial T_\delta/\partial z) \\ &+ \kappa_w\omega_o(\partial^2 T_\delta/\partial z^2) + (\rho DQ_1^*)_w\omega_o(\partial^2\omega_o/\partial z^2). \end{aligned}$$

$$(5.15)$$

The equation for $T_{\varepsilon\delta\delta}$ is given in Appendix E along with its solution. The boundary conditions for each order are found from (4.18):

$$[\kappa_o(\partial T_{j\delta}/\partial z) + (\rho DQ_1^*)_o(\partial\omega_j/\partial z)]_{\pm a/2,t} = C_j(\pm a/2,t), \; j = o,\varepsilon \qquad (5.16)$$

with

$$C_o(\pm a/2,t) = 0$$

$$C_\varepsilon(\pm a/2,t) = [(\rho DQ_1^*)_w\omega_o(\partial\omega_o/\partial z)]_{\pm a/2,t}. \qquad (5.17)$$

The Fourier cosine transform of equation (5.14) is

$$\partial[g_{j\delta m}(t)]/\partial t + (m^2/\tau)g_{j\delta m}(t) = C_{jm}(t)(\rho\bar{C}_p)_o^{-1}$$
$$+ (2\pi^2/a^3)(\rho DQ_1^*)_o(\rho\bar{C}_p)_o^{-1}m^2 \int_0^a \omega_j \cos(m\pi x/a)\,dx$$
$$+ (2/a)(\rho\bar{C}_p)_o^{-1} \int_0^a Y_j(x,t)\cos(m\pi x/a)\,dx, \qquad (5.18)$$

where

$$C_{jm}(t) = (2/a)[(-1)^m C_j(a/2,t) - C_j(-a/2,t)]. \qquad (5.19)$$

The temperature solution T_δ is then given by

$$T_\delta = (2\omega_1^o/\pi)(\rho DQ_1^*)_o\,\kappa_o^{-1}[1-(\tau/\Theta)]^{-1}$$
$$\times \sum_{\ell=0}^{\infty} (-1)^{\ell+1}(2\ell+1)^{-1}\{\exp[-(2\ell+1)^2 t/\Theta]-\exp[-(2\ell+1)^2 t/\tau]\}$$
$$\times \cos[(2\ell+1)\pi x/a]. \qquad (5.20)$$

and the expression for $T_{\varepsilon\delta}$ is given in Appendix C.

6. Solutions for a Cell with Diathermic Ends

The temperature solutions for the cell whose ends are diathermic differ radically from the adiabatic solutions of Sections 4 and 5. However, the equations to be solved and the initial conditions are the same; the only difference is in the boundary conditions. This, fortunately, causes all those solutions which were zero in the adiabatic case to again be zero in the diathermic case; namely, equation (5.8) is true in the diathermic case also.

Our solutions are found in a manner similar to that described in Sections 4 and 5. The boundary conditions for temperature now are

$$T_n(\pm a/2,t) = 0, \qquad n = \delta, \varepsilon\delta, \ldots, \qquad (6.1)$$

and all of the temperature solutions have the form

$$T_n(x,t) = \sum_{m=1}^{\infty} g_{nm}(t)\sin(m\pi x/a), \quad n = \delta, \varepsilon\delta, \ldots\,. \qquad (6.2)$$

For order δ we have

$$\begin{aligned} T_\delta = {} & (8\omega_1^o/\pi^2)(\rho D Q_1^*)_o \kappa_o^{-1} \sum_{m=1}^{\infty} \sum_{\ell=0}^{\infty} (-1)^{\ell+1}(2\ell+1)\,2m[4m^2-(2\ell+1)^2]^{-1} \\ & \times [4m^2-(\tau/\Theta)(2\ell+1)^2]^{-1}\{\exp[-(2\ell+1)^2 t/\Theta]-\exp[-(2\ell+1)^2 t/\tau]\} \\ & \times \sin(2m\pi x/a) \qquad (6.3) \end{aligned}$$

and $T_{\varepsilon\delta}$ is given in Appendix D. We expect $T_{\varepsilon\delta\delta}$ to be very small as it is in the adiabatic case.

7. Calculated Temperature Variations

In order to examine the behaviour of the temperature solutions, we assign typical values for organic liquids to all of the coefficients and calculate the values of the solutions at various times during the experiment and at various positions in the cell. The thermal conductivity, heat of mixing, heat of transport, and initial concentrations are varied in order to demonstrate their respective contributions to the temperature distribution Table 2 gives the values which have been assigned to those coefficients which we have not varied in our calculations. These coefficients would not be correct for all systems, but they represent typical behaviour in any system at relatively short times ($t < 2\Theta$).

Table 2--Typical values of physical properties for a binary mixture of organic liquids

$\rho = 0.8 \times 10^3$ kg m^{-3}	$D_w/D_o = 0.1$
$(\ell n\rho)_w = 0.1$	$(\rho DQ_1^*)_w/(\rho DQ_1^*)_o = 0.1$
$(\ell n\rho)_T = - 1.0 \times 10^{-3}$	$(\rho DQ_1^*)_T/(\rho DQ_1^*)_o = 2.0 \times 10^{-3}$
$\rho\bar{C}_p = 1.4 \times 10^6$ J K^{-1}m^{-3}	$\kappa_o/\kappa_w = - 0.1$
$(\rho\bar{C}_p)_w/(\rho\bar{C}_p)_o = 0.1$	$\kappa_o/\kappa_T = - 2.0 \times 10^{-3}$
$(\rho\bar{C}_p)_T/(\rho\bar{C}_p)_o = - 1.0 \times 10^{-3}$	$(\bar{H}_1 - \bar{H}_2)_T = 2.0 \times 10^2$ J kg^{-1}K^{-1}
$D = 1.4 \times 10^{-9}$ m^{2}s^{-1}	

The coefficients $(\bar{H}_1 - \bar{H}_2)_w$ have been calculated from typical heats of mixing (Rock, 1969; Lewis, Randall, Pitzer, and Brewer, 1961) as is shown in Appendix F. Heats of transport have never been measured in liquids, but by assuming that the heat matter Onsager reciprocal relation is valid so that (Horne and Bearman, 1967)

$$Q_1^* = - \alpha_1 w_1 (\partial \mu_1 / \partial w_1)_{T,P}, \tag{7.1}$$

we have calculated values from thermal diffusion factors. Thermal conductivity does not vary radically among systems which could be studied, but, because it has a marked effect on the speed with which temperature variations in the cell relax, we consider two thermal conductivities.

In all cases the results are presented in reduced time (t/Θ) and reduced cell coordinate (z/a). Because the length of the cell enters into the solutions only through these two factors, the results are the same for any length cell. The factor τ depends on $\underline{a}$ also, but it can be replaced in all solutions by $(\tau/\Theta)\Theta$. The factor (τ/Θ) is independent of $\underline{a}$. From the definition of Θ(4.11) we see that it is proportional to a^2 and, thus, for longer cells much larger absolute times will be needed to reach the temperature distributions which are rapidly attained in shorter cells. This fact will cause problems for the experimentalist in that, since his cell cannot be truly adiabatic, deviations from predicted behaviour due to non-adiabaticity will be larger at longer times. For this reason short cells should be used. In a 3 cm cell with D of Table 2, Θ is 108 minutes; for a 10 cm cell, Θ is 1200 minutes.

All computations have been done on a CDC 6500 computer with series truncation criteria similar to those discussed in Chapter III. More terms are needed at shorter times, and with double and triple sums the computational cost becomes quite high at these very short times ($t/\Theta \leq 0.01$). Computation at forty-nine points in the cell was done simultaneously for each t/Θ because the time dependent parts for every point z/a are identical.

The results presented here have been determined from

$$T = T_\delta + T_{\varepsilon\delta}. \tag{7.2}$$

Since $T_{\varepsilon\delta\delta}$ is very small in the adiabatic cell, with $\rho DQ_1^* = 3 \times 10^{-2}$J m^{-1}s^{-1}, $(\bar{H}_1 - \bar{H}_2)_w = 5 \times 10^4$J kg^{-1}, $\kappa = 2 \times 10^{-1}$J m^{-1}s^{-1}K^{-1}, and $\omega_1^o = 0.8$, equation (E.4) of Appendix E yields a maximum value of 4.32×10^{-4}K at $t/\Theta = 0.09$. The value becomes more negative as t/Θ increases and asymptotically approaches its equilibrium value. The $T_{\varepsilon\delta\delta}$ term contributes less than 1.0% to the total temperature perturbation and is symmetric about $z = 0$, so that it does not affect the temperature difference between any two symmetrical points in the cell. Because $T_{\varepsilon\delta\delta}$ is so small, we have omitted it from further work without thereby introducing any measurable error.

The symmetries of the solutions T_δ and $T_{\varepsilon\delta}$ make it possible to observe the Dufour effect. T_δ, which is due solely to heat of transport, is antisymmetric about $z = 0$. The $T_{\varepsilon\delta}$ solution is symmetric about $z = 0$. The value of this solution depends on the variations of physical properties and on the heat of mixing. It is generally small except for the contribution of a large absolute heat of mixing. However, if one is interested in measuring the Dufour effect, he must measure the temperature difference in the cell. The solution, $T_{\epsilon\delta}$, because of its symmetry adds nothing to the temperature difference which is measured at two points symmetric about $z = 0$. These symmetries can be seen in the next twelve figures. Note that the ordinate scale of these figures changes from one to another.

Figure 3 shows calculated temperature distributions in an adiabatic cell with no heat of mixing, $\rho DQ_1^* = 3 \times 10^{-2} \mathrm{J\ m^{-1} s^{-1}}$ ($\alpha_1 = -\ 0.9$), and thermal conductivity of $2 \times 10^{-1} \mathrm{J\ m^{-1} s^{-1} K^{-1}}$ at various times. The most important feature of this plot is that a temperature difference of approximately 0.12K exists between the right and left hand sides of the cell. This difference is due almost entirely to the Dufour effect, and we thus predict that the Dufour effect in liquid mixtures is measurable. The slight deviation of the curves from true antisymmetry about $z = 0$ is due to our inclusion of spatial variations of coefficients in the cell. We observe that the temperature fluctuations arise in the center of the cell where there is a concentration gradient and that the temperature throughout the cell changes as heat is conducted and convected. We also see that the temperature

Figure 3--Temperature variations in an adiabatic cell for $\Delta\overline{H}_m = 0.0$, $\rho DQ_1^* = 3 \times 10^{-2} \text{J m}^{-1}\text{s}^{-1}$, $\kappa = 2 \times 10^{-1} \text{J m}^{-1}\text{s}^{-1}\text{K}^{-1}$, and $\omega_1^o = 0.8$ at (t/Θ) = 0.01 (● ● ● ● ●), (t/Θ) = 0.05 (————), (t/Θ) = 0.09 (—— ——), (t/Θ) = 0.13 (– – – – –), and (t/Θ) = 0.17 (—— - —— -).

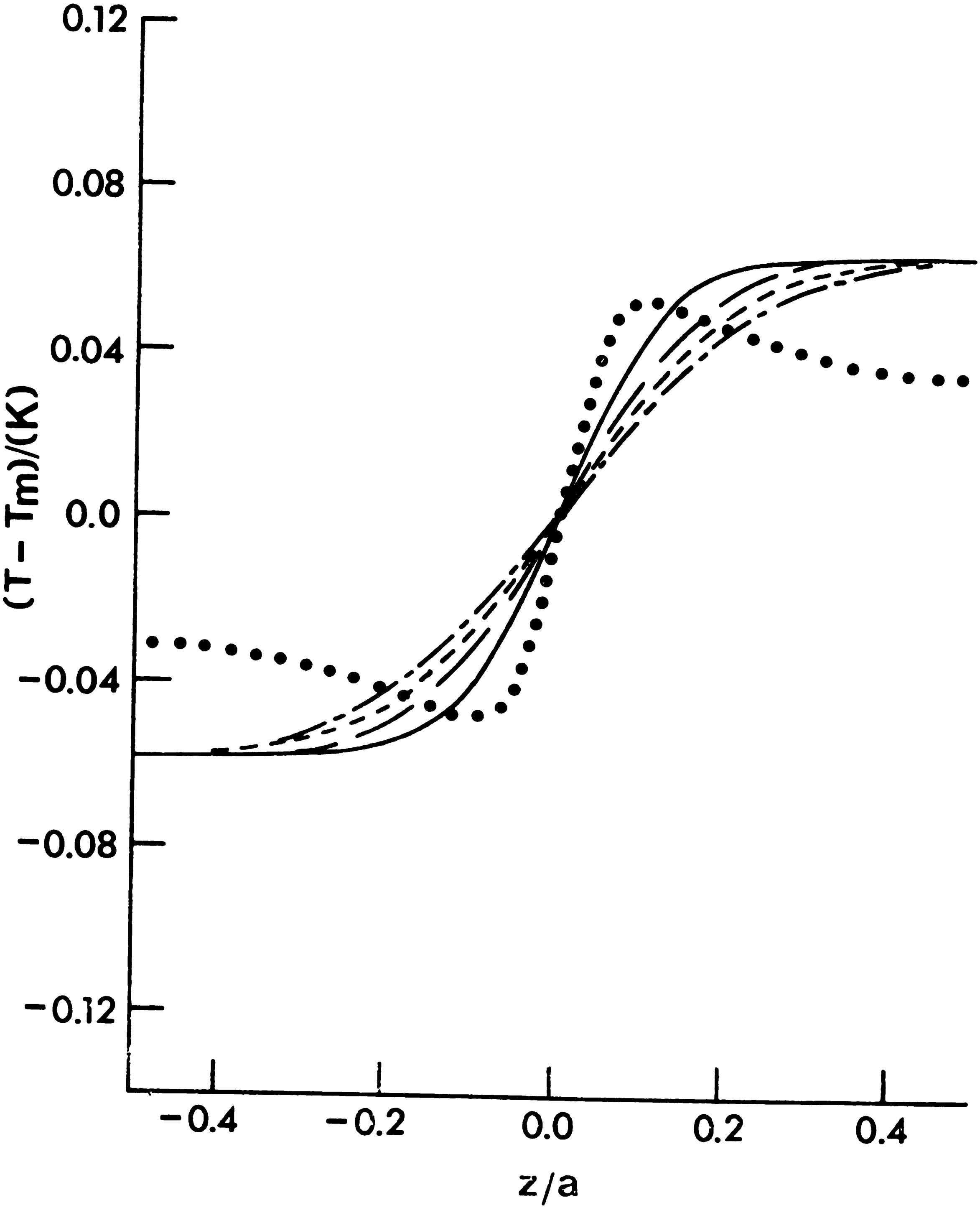

Figure 3

difference initially rises and then falls again, with the maximum difference being observed at 0.05-0.09 t/Θ. The fact that the temperature is quite stable for $z > .35$ and $z < -.35$ for these times should enable the experimentalist to make accurate temperature measurements well inside the cell; i.e., end effects will not matter. We note that, since $\partial \ell n \rho / \partial w_1$ is positive, the end of the cell which originally has the greater density is that which has the greater concentration of substance 1, i.e., the end for which $z < 0$. The temperature gradient arises to oppose this density gradient so that the end for which $z > 0$ is the warmer end. This is what would be ordinarily expected although a negative heat of transport would reverse the effect.

The fourth figure shows temperature distributions in a system identical to that considered in the first figure except for the thermal conductivity. The lower thermal conductivity produces much larger temperature effects because heat is not conducted so rapidly. Measurements will be easier for systems with low thermal conductivities.

We have again studied the first system in Figure 5 where in this instance $(\bar{H}_1 - \bar{H}_2)_w = 5.0 \times 10^4$ J kg^{-1}. which corresponds to a heat of mixing $(\Delta \bar{H}_m)$ of $- 6.5 \times 10^3$ J kg^{-1}. We see that this causes a general rise in the temperature of the entire cell. The temperature difference

Figure 4--Temperature variations in an adiabatic cell for $\Delta\overline{H}_m = 0.0$, $\rho DQ_1^* = 3 \times 10^{-2}$ J m^{-1}s^{-1}, $\kappa = 1 \times 10^{-1}$ J m^{-1}s^{-1} K^{-1}, and $\omega_1^o = 0.8$ at $(t/\Theta) = 0.01$ (● ● ● ● ●), $(t/\Theta) = 0.05$ (————), $(t/\Theta) = 0.09$ (—— ——), $(t/\Theta) = 0.13$ (– – – – – –), and $(t/\Theta) = 0.17$ (—— - ——-).

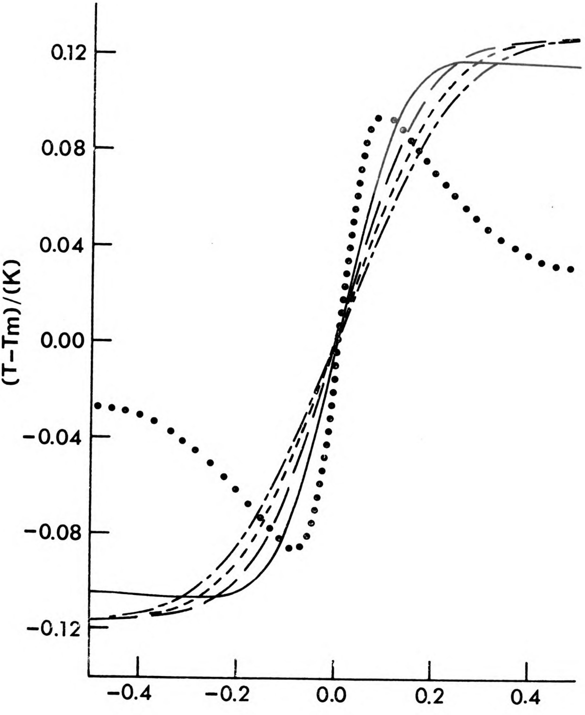

Figure 4

Figure 5--Temperature variations in an adiabatic cell for $\Delta\overline{H}_m = -6.5 \times 10^3$ J kg^{-1}, $\rho DQ_1^* = 3 \times 10^{-2}$ J m^{-1}s^{-1}, $\kappa = 2 \times 10^{-1}$ J m^{-1}s^{-1}K^{-1}, and $\omega_1^o =$ 0.8 at (t/Θ) = 0.01 (● ● ● ● ●), (t/Θ) = 0.05 (————), (t/Θ) = 0.09 (——— ———), (t/Θ) = 0.13 (— — — — —), and (t/Θ) = 0.17 (——— - ———).

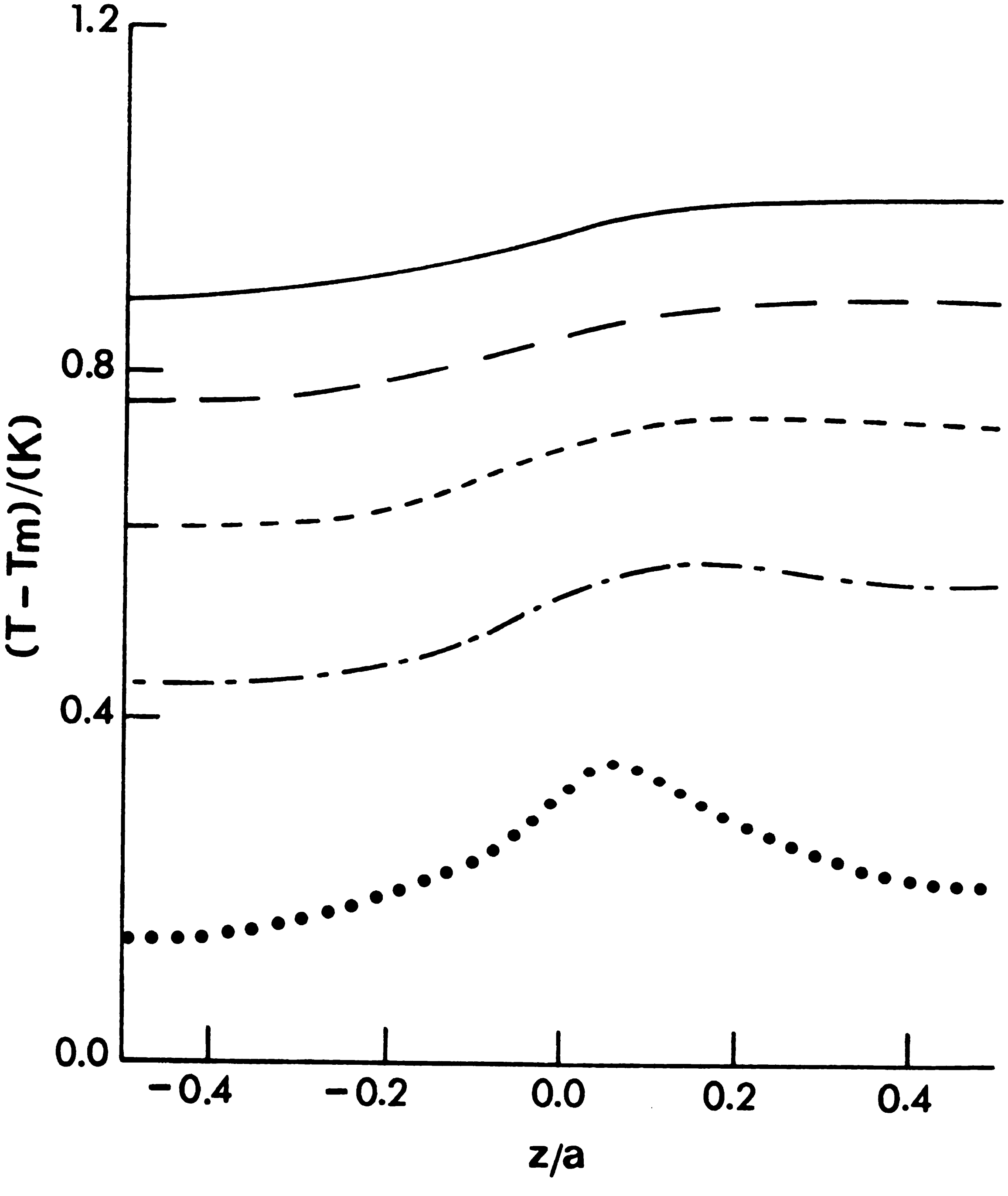

Figure 5

due to the Dufour effect is remarkably constant, however, at about 0.12K for $t/\Theta = 0.05$-0.13. Because the overall heating of the cell will cause slight errors in constants used even though the constants can be calculated correctly at any temperature, it would be best to measure the temperature difference as soon as it is well established ($t/\Theta = 0.09$) and before it begins to decay.

Our next three figures are also for the adiabatic cell, but the effects of varying various constants are illustrated at a fixed time ($t/\Theta = 0.1$). Figure 6 illustrates the variations of the temperature distribution with $(\bar{H}_1 - \bar{H}_2)_w$ or heat of mixing. Values used for $(\bar{H}_1 - \bar{H}_2)_w$ are 1.5×10^5, 5.0×10^4, 0, and $- 5.0 \times 10^4$ J kg^{-1} which represent heats of mixing ranging from -19.5×10^3 J kg^{-1} to 6.5×10^3 J kg^{-1}. We see that large heats of mixing cause much greater effects on the temperature than do heats of transport.

Illustrated in Figure 7 is the variation of the temperature difference with heat of transport. Values for $\rho D Q_1^*$ are 6×10^{-2}, 3×10^{-2}, 3×10^{-3}, and $- 3 \times 10^{-2}$ J m^{-1}s^{-1}. The small heat of transport is swamped by the heat of mixing and has a temperature difference of 0.012K. In every case we have seen that the temperature difference at its maximum is directly proportional to the heat of transport.

Figure 6--Temperature variations in an adiabatic cell for $(t/\Theta) = 0.1$, $\rho D Q_1^* = 3 \times 10^{-2}\,J\ m^{-1} s^{-1}$, $\kappa = 2 \times 10^{-1}\,J\ m^{-1} s^{-1} K^{-1}$, and $\omega_1^o = 0.8$ with $\Delta \bar{H}_m = -\ 19.5 \times 10^3$ (—— - ——-), - 6.5 10^3 (- - - - - - -), 0.0 (—— ——), and $6.5 \times 10^3\ J\ kg^{-1}$ (——————).

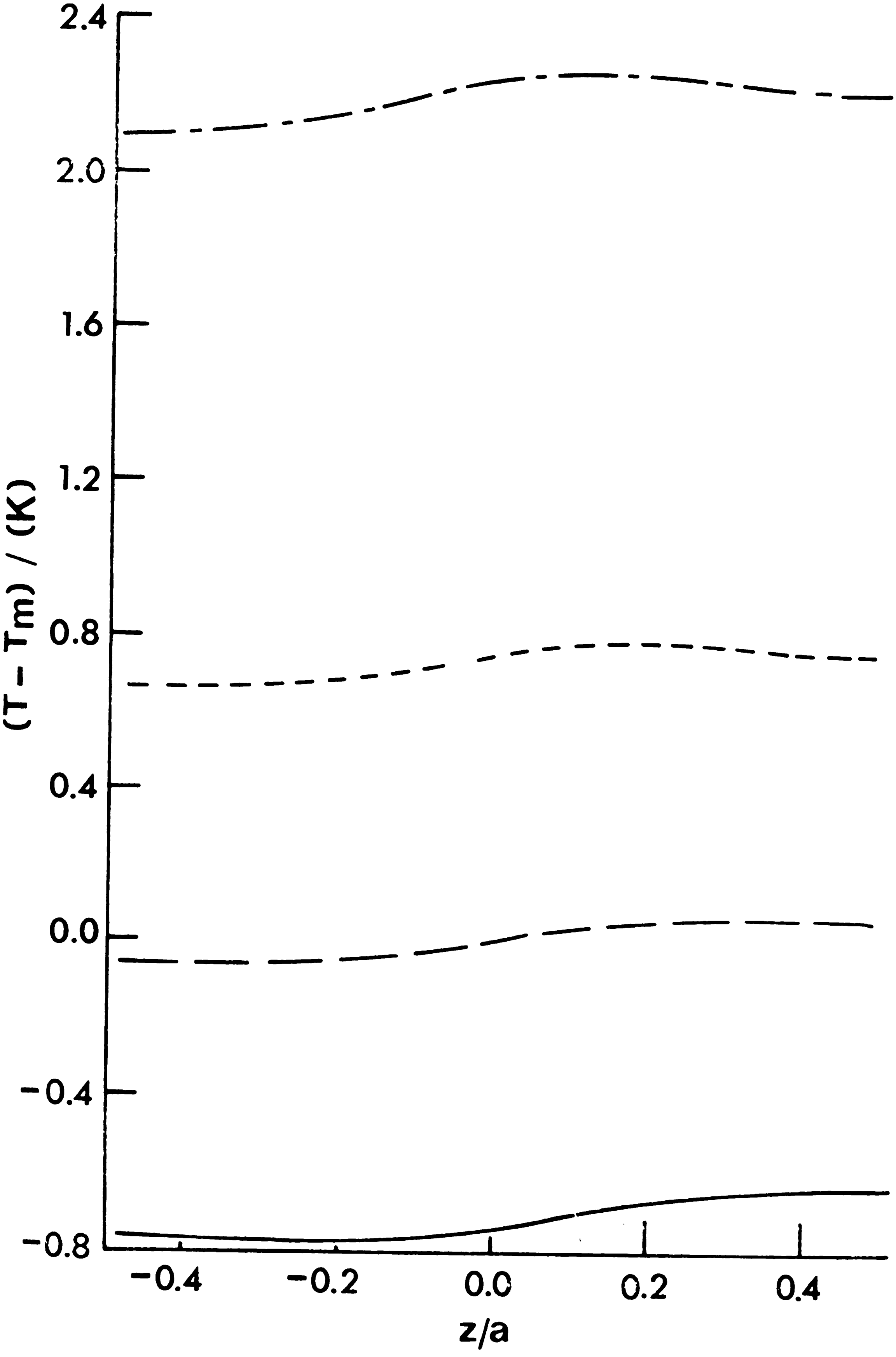

Figure 6

Figure 7--Temperature variations in an adiabatic cell for $(t/\Theta) = 0.1$, $\Delta\bar{H}_m = -6.5 \times 10^3 J\ kg^{-1}$, $\kappa = 2 \times 10^{-1} J\ m^{-1} s^{-1} K^{-1}$, and $\omega_1^o = 0.8$ with $\rho D Q_1^* = 6 \times 10^{-2}$ (——— ———), 3×10^{-2} (—— - ——-), 3×10^{-3} (————————), and $- 3 \times 10^{-2} J\ m^{-1} s^{-1}$ (— — — — —).

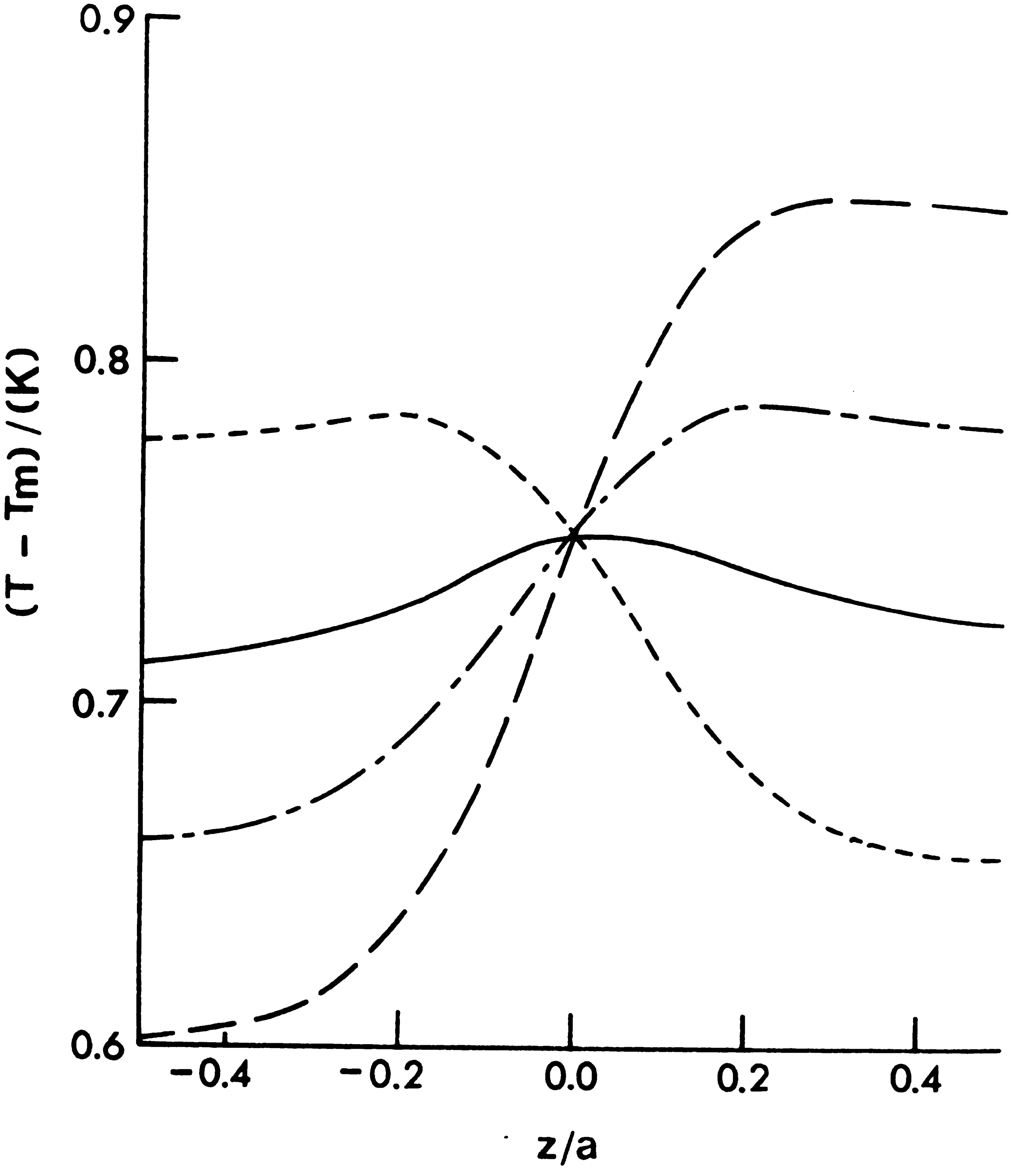

Figure 7

The last graph for an adiabatic system, Figure 8, shows how greatly temperature variations in the cell are reduced as the two initial mixtures become more similar. An 0.075K difference can still be seen with an initial difference of 0.5 in the weight fractions. The heat of mixing effect has been greatly reduced, however, as it is proportional to ω_1^{o2}. Some sacrifice of temperature difference for suppression of the heat of mixing might be advisable in experimental systems with large heats of mixing. Interesting to note are the very small variations of temperature (0.005K) in the region of $\omega_1^o = 0.05-0.01$. Such variations would not affect diffusion measurements at these relative concentrations.

Our final six figures deal with a cell whose ends are diathermic. These figures present a much greater challenge to the experimentalist because the temperature fluctuations are much smaller and there is no temporal region in which the temperature distribution remains relatively constant. These six figures correspond to the Figures 3-8 except that Figure 14 has a heat of mixing. In Figure 9 we see that our temperature difference falls rapidly with increasing time. At $t/\Theta = 0.05$ the difference is 0.07K and at $t/\Theta = 0.17$ it has fallen to 0.04K. The maxima occur between 0.15 and 0.25 z/a and the minima between - 0.15 and - 0.25 z/a. The curves are again not symmetric, but they are more so than in the adiabatic

Figure 8--Temperature variations in an adiabatic cell for $(t/\Theta) = 0.1$, $\Delta\bar{H}_m = 0.0$ J kg^{-1}, $\kappa = 2 \times 10^{-1}$ J $m^{-1}s^{-1}K^{-1}$, and $\rho DQ_1^* = 3 \times 10^{-2}$ J $m^{-1}s^{-1}$ with $\omega_1^o = 0.8$ (● ● ● ● ● ●), 0.5 (—— - ——-), 0.2 (- - - - - - -), 0.05 (—— ——), and 0.01 (————).

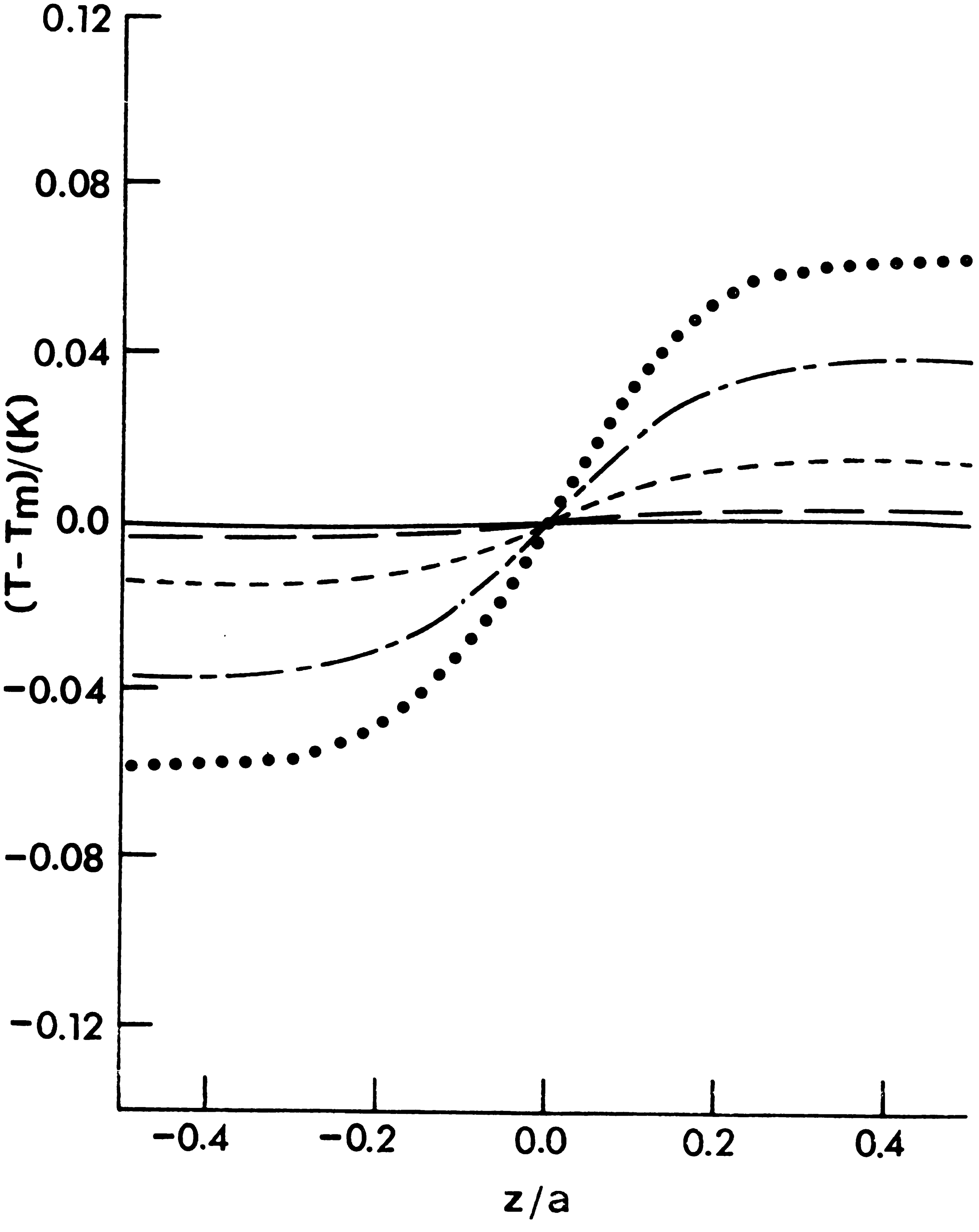

Figure 8

Figure 9--Temperature variations in a cell with diathermic ends for $\Delta\bar{H}_m = 0.0$, $\rho D Q_1^* = 3 \times 10^{-2}$ J $m^{-1}s^{-1}$, $\kappa = 2 \times 10^{-1}$ J $m^{-1}s^{-1}K^{-1}$, and $\omega_1^o = 0.8$ at $(t/\Theta) = 0.05$ (——— - ———-), $(t/\Theta) = 0.09$ (- - - - - - -), $(t/\Theta) = 0.13$ (——— ———), and $(t/\Theta) = 0.17$ (——————).

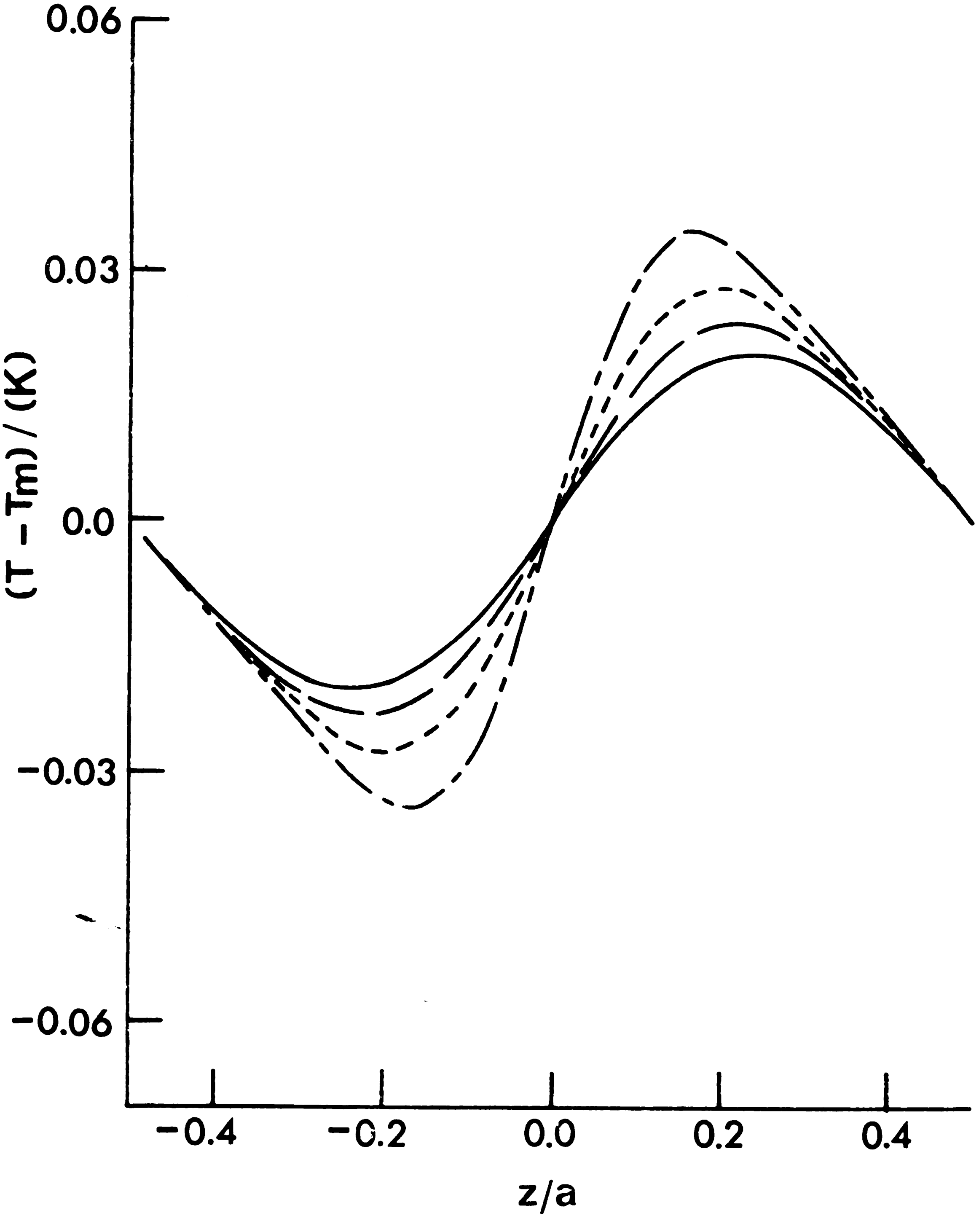

Figure 9

case. Halving the thermal conductivity again almost doubles the observable temperature difference as seen by comparison of Figures 9 and 10. The introduction of a heat of mixing in Figure 11 changes the temperature distributions little from the original curves of Figure 9. The curves are raised only a few hundredths of a degree due to rapid replacement of the heat of mixing through the end walls so that the overall temperature of the cell cannot rise appreciably. Figure 12 better emphasizes the greatly reduced effect of the heat of mixing, especially compared to Figure 6. That the diffusionist needs worry even less about difficulties arising from temperature fluctuations in a diathermic cell than about those in an adiabatic cell is attested to by Figure 14.

8. Discussion

We have attained temperature solutions both for adiabatic cells and for cells with diathermic ends when initially a sharp concentrations boundary exists in the center of an initially isothermal cell. From these solutions we find that the Dufour effect is measurable, that an adiabatic cell produces larger temperature differences than a cell with diathermic ends, that high heats of mixing do not cause significant variations in temperature changes due to the Dufour effect in a cell with diathermic ends, that low thermal conductivities and low heats of

Figure 10--Temperature variations in a cell with diathermic ends for $\Delta\bar{H}_m = 0.0$, $\rho D Q_1^* = 3 \times 10^{-2}$ J m^{-1}s^{-1}, $\kappa = 1 \times 10^{-1}$ J m^{-1}s^{-1}K^{-1}, and $\omega_1^o = 0.8$ at $(t/\Theta) = 0.05$ (—— – ——-), $(t/\Theta) = 0.09$ (– – – – – –-), $(t/\Theta) = 0.13$ (—— ——), and $(t/\Theta) = 0.17$ (————).

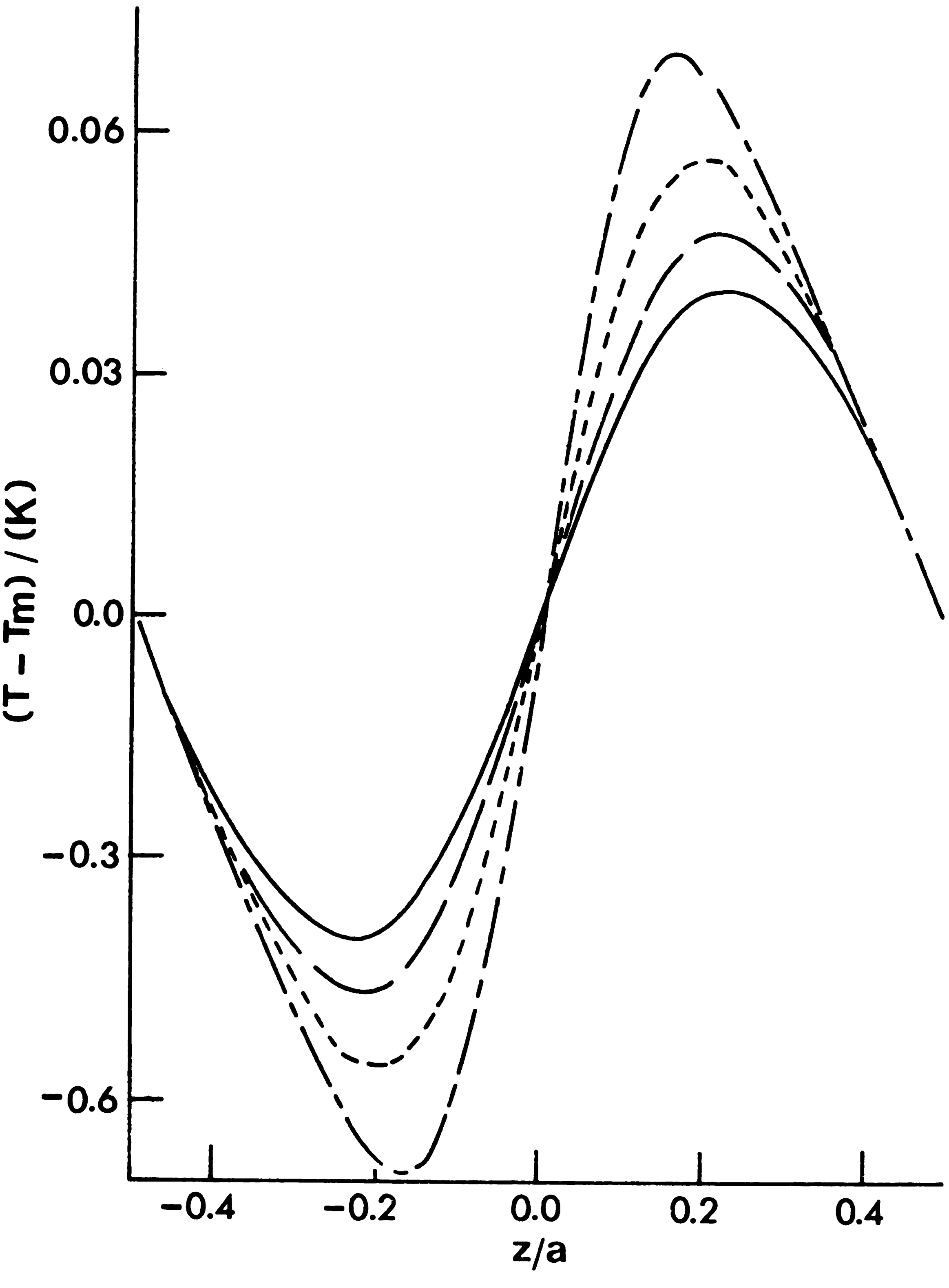

Figure 10

Figure 11--Temperature variations in a cell with diathermic ends for $\Delta\bar{H}_m = -6.5 \times 10^3$ J kg^{-1}, $\rho D Q_1^* = 3 \times 10^{-2}$ J m^{-1}s^{-1}, $\kappa = 2 \times 10^{-1}$ J m^{-1}s^{-1}K^{-1}, and $\omega_1^o = 0.8$ at $(t/\Theta) = 0.05$ (——— – ———), $(t/\Theta) = 0.09$ (– – – – – – –), $(t/\Theta) = 0.13$ (——— ———), and $(t/\Theta) = 0.7$ (—————).

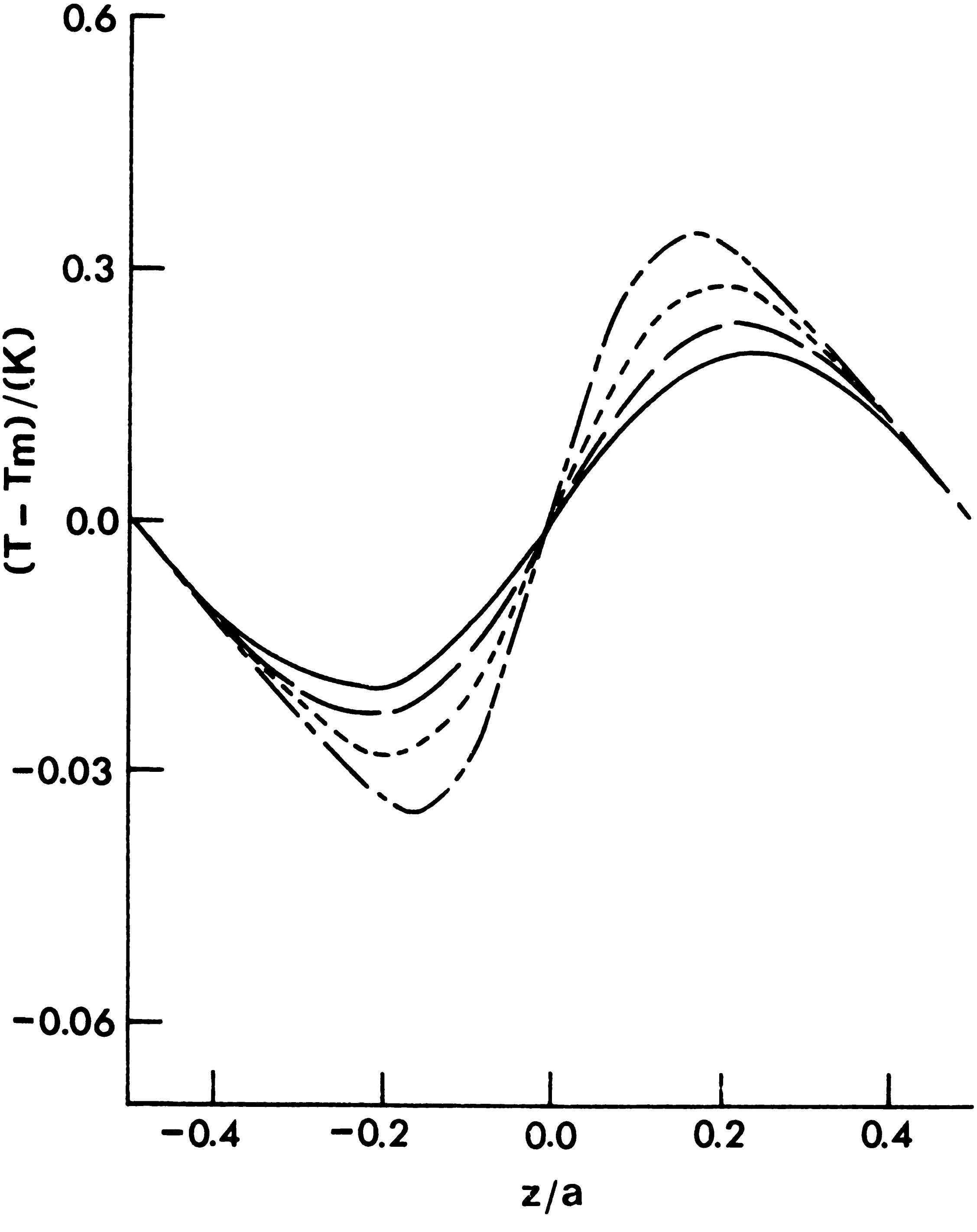

Figure 11

Figure 12--Temperature variations in a cell with diathermic ends for $(t/\Theta) = 0.1$, $\rho D Q_1^* = 3 \times 10^{-2}$ J $m^{-1}s^{-1}$, $\kappa = 2 \times 10^{-1}$ J $m^{-1}s^{-1}K^{-1}$, and $\omega_1^o = 0.8$ with $\Delta\bar{H}_m = -\ 19.5 \times 10^3$, $-\ 6.5 \times 10^3$, 0.0, and 6.5×10^3 J kg^{-1}. The curves are indistinguishable.

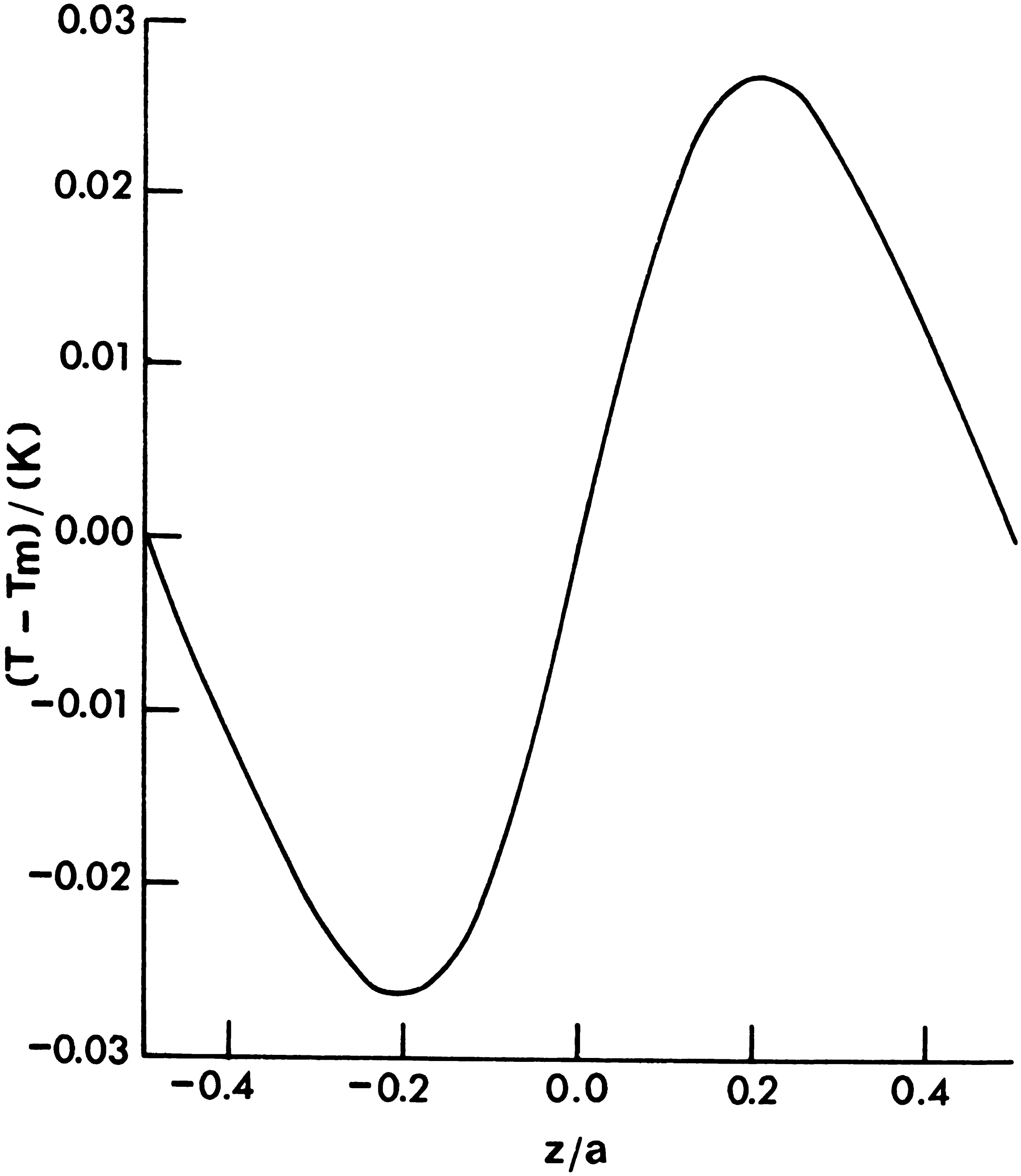

Figure 12

Figure 13--Temperature variations in a cell with diathermic ends for $(t/\Theta) = 0.1$, $\Delta\bar{H}_m = -6.5 \times 10^3$ J kg^{-1}, $\kappa = 2 \times 10^{-1}$ J m^{-1}s^{-1}K^{-1}, and $\omega_1^o = 0.8$ with $\rho DQ_1^* = 6 \times 10^{-2}$ (——— ———), 3×10^{-2} (—— – ——), 3×10^{-3} (————————), and -3×10^{-2} J m^{-1}s^{-1} (– – – – – –).

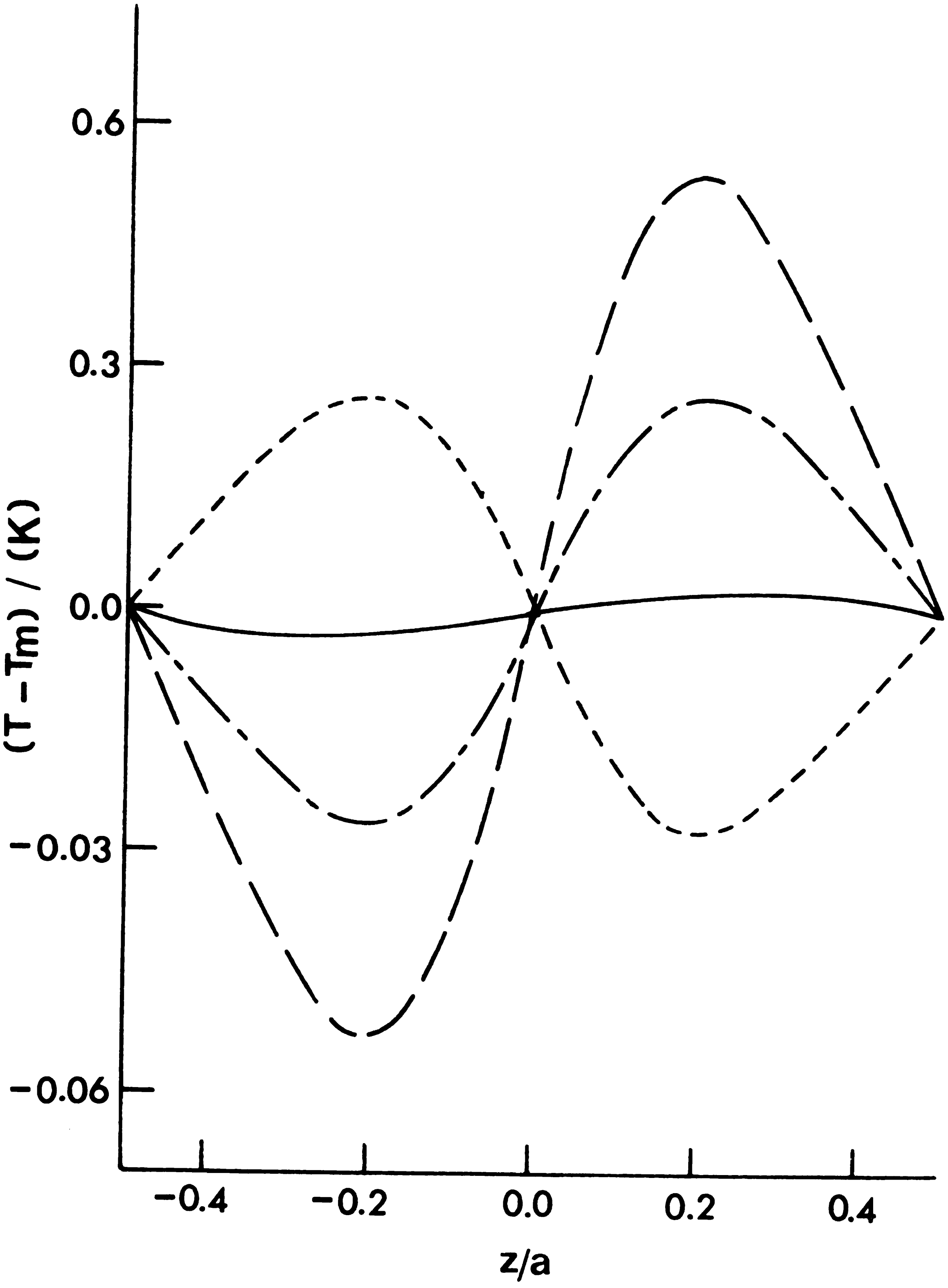

Figure 13

Figure 14--Temperature variations in a cell with diathermic ends for $(t/\Theta) = 0.1$, $\Delta\bar{H}_m = -6.5 \times 10^3$ J kg^{-1}, $\kappa = 2 \times 10^{-1}$ J m^{-1}s^{-1}K^{-1}, and $\rho D Q_1^* = 6 \times 10^{-2}$ J m^{-1}s^{-1} with $\omega_1^o = 0.8$ (● ● ● ● ● ●), 0.5 (—— - —— -), 0.2 (- - - - - -), 0.05 (—— ——), and 0.01 (————).

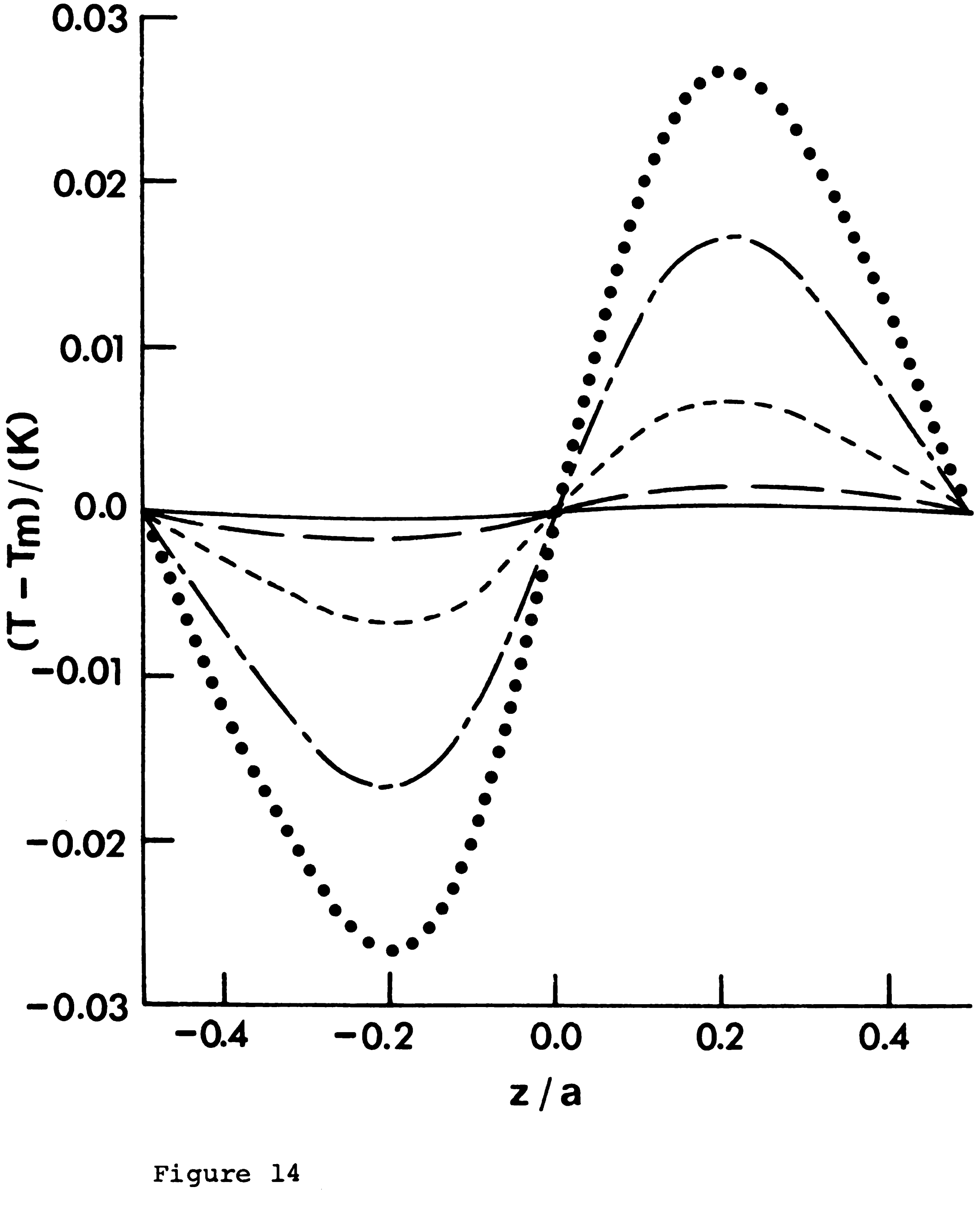

Figure 14

mixing are conducive to easier measurement of the Dufour effect, and that the Dufour effect becomes very small as the initial concentration difference decreases.

Using our results we can analyze the work of Rastogi et al. (1965, 1969, 1970). First, they neglected heat of mixing. We find this a very poor assumption in that the temperature at all points of the adiabatic cell depends strongly on the heat of mixing. However, our results do show that, if the points between which the temperature difference is measured are symmetric about $z = 0$, the heat of mixing does not appreciably affect the temperature difference measured. The assumption by Rastogi et al. that coefficients are constant is not correct but does not introduce large errors. Their cell design is not really comparable with our idealized cell in that their initially sharp concentration boundary was achieved by a stop cock whose diameter was only half that of the cell. This constriction was not taken into account in their results. Their cell was 23 cm long and measurement was made at $z/a = \pm 0.24$. This falls in the region which does not attain a steady temperature difference as discussed in Section 7. The maximum temperature difference between these two points was reached at very low reduced time; and the concentration difference between the points was assumed to be the initial concentration difference. From Figures 3 and 4 we observe that the maximum temperature difference varies with the z/a used while the assumption that the concentration difference is the initial one is still reasonable. Rastogi and Yadava (1970) recognized this and took the variations into account with their experimentally determined parameter δ. Unfortunately their results are incomprehensible because one given distance between their thermocouple and stop cock is greater than the given half length of the cell. As we have shown, it is the value z/a, not z, which is important to the temperature distribution.

We hope that the results of our work will provide a useful guide to the experimentalist. The solutions given are such that, if all diffusion coefficients, heat capacities, *etc.*, are known, they can be substituted into the temperature equation, and the heat of transport can be adjusted to fit the measured temperature variations. Our results also indicate that the Dufour effect causes no complications in diffusion experiments with very small concentration differences.

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APPENDICES

APPENDIX A

SOME EQUATIONS OF THERMOSTATICS

$$A_I = E_I - TS \tag{A.1}$$

$$dE_I = TdS - Pd(1/\rho) + (\mu_1 - \mu_2)dw_1 \tag{A.2}$$

$$H_I = E_I + VP \tag{A.3}$$

$$- dP + w_1 d(\mu_1 - \mu_2) + SdT = 0 \tag{A.4}$$

$$\rho H_I = \sum \rho_\alpha \overline{H}_\alpha \tag{A.5}$$

$$\overline{H}_\alpha = \mu_\alpha + T\overline{S}_\alpha \tag{A.6}$$

$$S = - \partial A_I/\partial T \tag{A.7}$$

$$\sum w_\alpha \mu_\alpha = A_I + P/\rho \tag{A.8}$$

$$\mu_\alpha = A_I (1 - w_\alpha)(\partial A_I/\partial w_1)_{\rho,T} + \rho^2 (\partial A_I/\partial \rho)_{w_1,T} \tag{A.9}$$

$$\mu_\alpha = A_I + \rho(\partial A_I/\partial \rho_\alpha)_{\rho_\beta,T} \tag{A.10}$$

$$\begin{aligned}(\mu_1 - \mu_2/\rho) &= (\partial A_I/\partial \rho_1)_{\rho_2,T} - (\partial A_I/\partial \rho_2)_{\rho_1,T} \\ &= 1/\rho(\partial A_I/\partial w_1)_{T,\rho}\end{aligned} \tag{A.11}$$

$$\begin{aligned}P &= \rho\rho_1(\partial A_I/\partial \rho_1)_{\rho_2,T} + \rho\rho_2(\partial A_I/\partial \rho_2)_{\rho_1,T} \\ &= \rho^2(\partial A_I/\partial \rho)_{w_1,T}\end{aligned} \tag{A.12}$$

APPENDIX B

A RATIONAL MECHANICAL DEVELOPMENT OF THE TIP THEORY

The heuristic but very successful TIP results of nonequilibrium thermodynamics have often been criticized for their lack of mathematical rigor by the proponents of rational mechanics. It is, however, quite possible to derive the results of TIP with the formalism of rational mechanics by redefinition of thermodynamic process for a mixture in such a way that there is no difference between the specific partial stress tensors and there are no internal forces among components. The thermodynamic process is then defined by the $3\nu + 5$ functions which satisfy the balance of mass for each component, the balance of linear momentum for the mixture as a whole, and the balance of energy. Now we can further assume that the external forces, b_i^α, may be solved for using the linear momentum balance equation. There are no interaction forces. With this limited definition of a mixture, the TIP results are immediately derivable from a linear rational mechanical formalism.

Our balance of energy equation is

$$\rho(dE/dt) = (\partial v_i/\partial x_j)T_{ij} - (\partial q_j^*/\partial x_j) + \rho r$$
$$+ (\rho_1\rho_2/\rho)u_i(b_i^1 - b_i^2). \quad \text{(B.1)}$$

This can be placed in the entropy balance equation using the thermodynamic identity

$$A = E - TS. \quad \text{(B.2)}$$

The entropy balance equation which results is

$$\rho T(dS/dt) = -\rho(dA/dt) - \rho S(dT/dt) + (\partial v_i/\partial x_j)T_{ij}$$
$$- (\partial q_j^*/\partial x_j) + (\rho_1\rho_2/\rho)u_i(b_i^1 - b_i^2). \quad \text{(B.3)}$$

Until this point we have not needed to distinguish among the independent variables and the functionals determined by constitutive equations. Studying our definition of thermodynamic process and those terms which appear in the energy balance equation we let our independent variables be

$$\rho_1,\ \rho_2,\ T,\ \frac{\partial\rho_1}{\partial x_j},\ \frac{\partial\rho_2}{\partial x_j},\ \frac{\partial T}{\partial x_j},\ \frac{\partial v_i}{\partial x_j}, \quad \text{(B.4)}$$

and our constitutive relations in terms of these variables will define

$$u_i,\ T_{ij},\ q_i^*,\ f_i,\ A,\ S. \quad \text{(B.5)}$$

Following the principle of equipresence in the linear limit, we obtain constitutive relations of the form

$$A = A(\rho_1, \rho_2, T) \tag{B.6}$$

$$T_{ij} = - P\delta_{ij} + \phi(\partial v_k/\partial x_k)\delta_{ij} + 2\eta(\partial v_j/\partial x_i) \tag{B.7}$$

$$q_j^* = - C''_{q1}(\partial\rho_1/\partial x_j) - C''_{q2}(\partial\rho_2/\partial x_j) - C''_{qT}(\partial T/\partial x_j) \tag{B.8}$$

$$k_j = - C''_{k1}(\partial\rho_1/\partial x_j) - C''_{k2}(\partial\rho_2/\partial x_j) - C''_{kT}(\partial T/\partial x_j) \tag{B.9}$$

$$u_j = - C''_{u1}(\partial\rho_1/\partial x_j) - C''_{u2}(\partial\rho_2/\partial x_j) - C''_{uT}(\partial T/\partial x_j), \tag{B.10}$$

where k_j is defined by

$$k_j = f_j - \frac{q_j^*}{T}. \tag{B.11}$$

The derivatives dA/dt and $\partial k_j/\partial x_j$ can be expanded in terms of the independent variables and $d\rho_\alpha/dt$ can then be replaced by the balance equations:

$$\begin{aligned}(d\rho_1/dt) &= - (\rho_2^2/\rho)u_j(\partial\rho_1/\partial x_j) - (\rho_1^2/\rho)u_j(\partial\rho_2/\partial x_j) \\ &\quad - \rho_1\rho_2(\partial u_j/\partial x_j) - \rho\rho_1(\partial v_j/\partial x_j) \\ (d\rho_2/dt) &= (\rho_2^2/\rho)u_j(\partial\rho_1/\partial x_j) + (\rho_1^2/\rho)u_j(\partial\rho_2/\partial x_j) \\ &\quad + \rho_1\rho_2(\partial u_j/\partial x_j) - \rho\rho_2(\partial v_j/\partial x_j).\end{aligned} \tag{B.12}$$

An immediate consequence of this formalism is

$$k_j = 0. \tag{B.13}$$

The total entropy production is readily rearranged to the form

$$\rho T\Phi = (\mu_1 - \mu_2)[\partial(\rho_1\rho_2/\rho)u_j/\partial x_j] + (T_{ij} + P)(\partial v_i/\partial x_j) + q_j^*(\partial T/\partial x_j) + (\rho_1\rho_2/\rho)u_i(b_i^1 - b_i^2). \tag{B.14}$$

The coefficient P is identified as the thermostatic pressure,

$$P = \rho[\rho_1(\partial A/\partial\rho_1) + \rho_2(\partial A/\partial\rho_2)] \tag{B.15}$$

and the usual thermostatic definition of chemical potential has been used. The result

$$S = -\,\partial A/\partial T \tag{B.16}$$

is a consequence of the Clausius-Duhem inequality. Rearrangement of the entropy balance equation (B.3), then leads to the TIP result

$$\rho T\Phi = \partial[(\mu_1' - \mu_2')\rho_1\rho_2 u_j/\rho]/\partial x_j - (\rho_1\rho_2/\rho)u_j[\partial(\mu_1' - \mu_2')/\partial x_j] + q_j^*(\partial T/\partial x_j) + (T_{ij} + P\delta_{ij})(\partial v_i/\partial x_j). \tag{B.17}$$

APPENDIX C

THE TEMPERATURE SOLUTION, T_1, FOR THERMAL CONDUCTIVITY OF A PURE FLUID IN A FLAT PLATE CELL

The solution of equation (III.3.13) for n = 1, subject to the conditions $\gamma = \gamma_u = \gamma_L$ and $T_U + T_L = 2T_M$, is

$$\begin{aligned} T_1(z,t) = {} & (4/\pi^3)(\Delta T)^2 \sum_{\ell=0}^{\infty} \Big[(\kappa_T/\kappa_o)(2\ell+1)^{-1} \\ & \Big((2\ell+1)^{-2}\{1 - \exp[-(2\ell+1)^2 t/\tau]\} \\ & - 2\chi[(2\ell+1)^2\chi-1]^{-1}\{\exp(-t/\gamma) \\ & - \exp[-(2\ell+1)^2 t/\tau]\} \\ & + \chi[(2\ell+1)^2\chi-2]^{-1}\{\exp(-2t/\gamma) - \exp[-(2\ell+1)^2 t/\tau]\}\Big) \\ & + \sum_1 + \sum_2\Big](-1)^{\ell}\cos[(2\ell+1)\pi z/a] \end{aligned} \tag{C.1}$$

where

$$\chi = \gamma/\tau, \tag{C.2}$$

$$\begin{aligned} \sum_1 = \sum_{n=1}^{\infty} & (4n^2\chi - 1)^{-1}\{2\beta_o(2\ell+1)^{-1} \\ & - [2(\kappa_T/\kappa_o) - \beta_o](2\ell+1)[2n+2\ell+1]^{-1}[2n-(2\ell+1)]^{-1} \\ & - [(\rho\bar{C}_p)_T/(\rho\bar{C}_p)_o - (\kappa_T/\kappa_o)] \end{aligned}$$

$$\times\ 16n(2\ell+1)\,[2n+2\ell+1]^{-2}[2n-(2\ell+1)]^{-2}\}$$

$$\times\ \Big|\chi[(2\ell+1)^{2}\chi - 1]^{-1}\{\exp(-t/\gamma) - \exp]-(2\ell+1)^{2}t/\tau]\}$$

$$-\ [(2\ell+1)^{2}-4n^{2}]^{-1}\{\exp[-4n^{2}t/\tau] - \exp[-(2\ell+1)^{2}t/\tau]\}$$

$$-\ \chi[(2\ell+1)^{2}\chi - 2]^{-1}\{\exp(-2t/\gamma) - \exp[-(2\ell+1)^{2}t/\tau]\}$$

$$+\ \chi\{[(2\ell+1)^{2}-4n^{2}]\chi - 1\}^{-1}\{\exp[-4n^{2}(t/\tau)-(t/\gamma)]$$

$$-\ \exp\ [-(2\ell+1)^{2}t/\tau]\}\Big| \qquad \text{(C.3)}$$

$$\sum_{2} = \sum_{n=1}^{\infty}\ \sum_{m=1}^{\infty}(4n^{2}\chi - 1)^{-1}(4m^{2}\chi - 1)^{-1}$$

$$\times\ \Big|4\beta_{o}[2n-(2\ell+1)]^{-1}[2n+(2\ell+1)]^{-1} + \{[(\kappa_{T}/\kappa_{o}) - \beta_{o}]4(2\ell+1)$$

$$\times\ [4n^{2}+4m^{2}+(2\ell+1)^{2}]$$

$$+\ [(\rho\overline{C}_{p})_{T}/(\rho\overline{C}_{p})_{o} - (\kappa_{T}/\kappa_{o})]32(2\ell+1)m^{2}\ \}$$

$$\times\ \{[2(n+m)+2\ell+1][2(n+m)-(2\ell+1)][2(n-m)+(2\ell+1)]$$

$$\times\ [2(n-m)-(2\ell+1)]\}^{-1}$$

$$\times\ \Big|\chi\{[(2\ell+1)^{2}-4m^{2}]\chi - 1\}^{-1}\{\exp[-4m^{2}(t/\tau)+4m^{2}(t/\gamma)]$$

$$-\ \exp[-2(2\ell+1)^{2}t/\tau]\}$$

$$-\ [(2\ell+1)^{2}-4(n^{2}+m^{2})]^{-1}\{\exp[-4(n^{2}+m^{2})t/\tau]$$

$$-\ \exp[-(2\ell+1)^{2}t/\tau]\}$$

$$-\ \chi[(2\ell+1)^{2}\chi-2]^{-1}\{\exp[-2t/\gamma] - \exp[-(2\ell+1)^{2}t/\tau]\}$$

$$+\ \chi\{[(2\ell+1)^{2}-4n^{2}]\chi - 1\}^{-1}\{\exp[-4n^{2}(t/\tau)-(t/\gamma)]$$

$$-\ \exp[-(2\ell+1)^{2}t/\tau]\} \qquad \text{(C.4)}$$

APPENDIX D

THE TEMPERATURE SOLUTIONS, $T_{\varepsilon\delta}$, FOR THE DUFOUR EFFECT IN ADIABATIC CELLS AND CELLS WITH DIATHERMIC ENDS

Adiabatic

In the adiabatic cell, the solution $T_{\varepsilon\delta}$ from Eqs. (IV.5.18) and (IV.4.17) has the form

$$T_{\varepsilon\delta} = 2\omega_1^{o2}\pi^{-2}\kappa_o^{-1} \sum_{\ell=0}^{\infty} [(2\ell+1)^{-2} B_1(\ell) + \sum_{m=1}^{\infty} (-1)^m B_2(\ell,m)\cos(2m\pi x/a)] \qquad \text{(D.1)}$$

where

$$B_1(\ell) = C_1(\ell) + C_2(\ell)$$

$$B_2(\ell,m) = C_3(\ell,m) + C_4(\ell,m) + C_5(\ell,m) + C_6(\ell,m) + C_7(\ell,m), \qquad \text{(D.2)}$$

with

$$\tau/\Theta = \gamma$$

$$C_1(\ell) = 0.5\{(\rho\bar{C}_p)_w(\rho DQ_1^*)_o[(\rho\bar{C}_p)_o\,\kappa_o(1-\gamma)]^{-1} + (\ell n\rho)_w(\rho DQ_1^*)_o[\kappa_o(1-\gamma)]^{-1} - (\rho D)_o(\bar{H}_1-\bar{H}_2)_w[(\rho\bar{C}_p)_o D_o]^{-1}\} \times \{\exp[-2(2\ell+1)^2(t/\Theta)] - 1\}$$

$$C_2(\ell) = \{-(\rho\bar{C}_p)_w(\rho DQ_1^*)_o\ [(\rho\bar{C}_p)_o(1-\gamma)]^{-1}$$

$$- (\ell n\rho)_w(\rho\bar{C}_p)_o\ (\rho DQ_1^*)_o\ [\kappa_o(1-\gamma)]^{-1}$$

$$\times \{\exp\ [-(2\ell+1)^2(\tau^{-1}+\Theta^{-1})t] - 1\}\ (1-\gamma)^{-1},$$

$$C_3(\ell,m) = \{(\rho D)_o(\bar{H}_1-\bar{H}_2)_w - (\rho\bar{C}_p)_o(\rho DQ_1^*)_o D_o(\ell n\rho)_w[\kappa_o(1-\gamma)]^{-1}$$

$$+ [2(\kappa_w/\kappa_o)(\rho DQ_1^*)_o(1-\gamma)^{-1}-2(\rho DQ_1^*)_w]m(2\ell+1-2m)^{-1}$$

$$- (\rho\bar{C}_p)_w D_o(\rho DQ_1^*)_o(2\ell+1)[\kappa_o(1-\gamma)(2\ell+1-2m)]^{-1}$$

$$- D_w(\rho DQ_1^*)_o 8m^3[4D_o(2\ell+1-2m)^2(2\ell+1)]^{-1}$$

$$+ (\ell n\rho)_w(\rho DQ_1^*)_o 4m^2[(2\ell+1-2m)(2\ell+1)]^{-1}\}$$

$$\times \{\exp[-(2\ell+1-2m)^2(t/\Theta) - (2\ell+1)^2(t/\Theta)] - \exp[-4m^2(t/\tau)]\}$$

$$\times \{4m^2 - \gamma[(2\ell+1-2m)^2 + (2\ell+1)^2]\}^{-1},$$

$$C_4(\ell,m) = \{(\rho D)_o(\bar{H}_1-\bar{H}_2)_w$$

$$- (\rho\bar{C}_p)_o(\rho DQ_1^*)_o D_o(\ell n\rho)_w[\kappa_o(1-\gamma)]^{-1}$$

$$- [2\kappa_w\kappa_o^{-1}(\rho DQ_1^*)_o(1-\gamma)^{-1}-2(\rho DQ_1^*)_w]m(2\ell+1+2m)^{-1}$$

$$- (\rho\bar{C}_p)_w D_o(\rho DQ_1^*)_o(2\ell+1)[\kappa_o(1-\gamma)(2\ell+1+2m)]^{-1}$$

$$+ D_w(\rho DQ_1^*)_o 8m^3[4D_o(2\ell+1+2m)^2(2\ell+1)]^{-1}$$

$$+ (\ell n\rho)_w(\rho DQ_1^*)_o 4m^2[(2\ell+1)(2\ell+1+2m)]^{-1}\}$$

$$\times \{\exp[-(2\ell+1+2m)^2(t/\Theta) - (2\ell+1)^2(t/\Theta)] - \exp[-4m^2(t/\tau)]\}$$

$$\times \{4m^2 - \gamma[(2\ell+1+2m)^2 + (2\ell+1)^2]\}^{-1},$$

$$C_5(\ell,m) = \{(\rho\bar{C}_p)_o D_o(\ell n\rho)_w(\rho DQ_1^*)_o[\kappa_o(1-\gamma)]^{-1}$$

$$- 2(\rho DQ_1^*)_w m[(1-\gamma)(2\ell+1-2m)]^{-1}$$

$$+ (\rho\overline{C}_p)_w(\rho DQ_1^*)_o(2\ell+1)[(\rho\overline{C}_p)_o(1-\gamma)(2\ell+1-2m)]^{-1}\}$$

$$\times \{\exp[-(2\ell+1-2m)^2(t/\Theta) - (2\ell+1)^2(t/\tau)] - \exp[-4m^2(t/\tau)]\}$$

$$\times \{4m^2-(2\ell+1)^2 - \gamma(2\ell+1-2m)^2\}^{-1},$$

$$C_6(\ell,m) = \{(\rho\overline{C}_p)_o D_o(\ell n\rho)_w(\rho DQ_1^*)_o[\kappa_o(1-\gamma)]^{-1}$$

$$+ 2(\rho DQ_1^*)_w m[(1-\gamma)(2\ell+1+2m)]^{-1}$$

$$+ (\rho\overline{C}_p)_w(\rho DQ_1^*)_o(2\ell+1)[(\rho\overline{C}_p)_o(1-\gamma)(2\ell+1+2m)]^{-1}\}$$

$$\times \{\exp[-(2\ell+1+2m)^2(t/\Theta) - (2\ell+1)^2(t/\tau)] - \exp[-4m^2(t/\tau)]\}$$

$$\times \{4m^2 - (2\ell+1)^2 - \gamma(2\ell+1+2m)^2\}^{-1},$$

$$C_7(\ell,m) = \{(D_w/D_o)(\rho DQ_1^*)_o 2m[(2\ell+1)^2-4m^2]^{-2}$$

$$+ 2(\ell n\rho)_w(\rho DQ_1^*)_o[(2\ell+1)^2-4m^2]^{-1}\}$$

$$\times \{\exp[-4m^2(t/\Theta)] - \exp[-4m^2(t/\tau)]\}(1-\gamma)^{-1}.$$

Diathermic

In the cell with diathermic ends and adiabatic walls, the solution $T_{\varepsilon\delta}$ from (IV.5.14) and (IV.6.2) has the form

$$T_{\varepsilon\delta} = 4\omega_1^{o2}\pi^{-3}\kappa_o^{-1}(\rho\overline{C}_p)_o \sum_{r=0}^{\infty}[\sum_{n=0}^{\infty}\sum_{\ell=0}^{\infty}(-1)^{\ell+n}E_1(r,\ell,n)$$

$$+ \sum_{m=1}^{\infty}\sum_{\ell=0}^{\infty}(-1)^m(\rho DQ_1^*)_o(\rho\overline{C}_p)_o^{-1}\, E_2(r,\ell,m)]\cos[(2r+1)\pi x/a] \tag{D.3}$$

where

$$
\begin{aligned}
E_1(r,\ell,n) &= F_1(r,\ell,n) + F_2(r,\ell,n) + F_3(r,\ell,n)\\
E_2(r,\ell,m) &= F_4(r,\ell,m) + F_5(r,\ell,m)
\end{aligned}
\qquad (D.4)
$$

with

$$
\begin{aligned}
F_1(r,\ell,n) = \Big|&(\rho D)_o(\bar{H}_1-\bar{H}_2)_w(\rho\bar{C}_p)_o^{-1}\{2(2r+1)[(2r+1)^2 - (2\ell-2n)^2]^{-1}\\
&- 2(2r+1)[(2r+1)^2-(2\ell+2n+2)^2]^{-1}\}\\
&+ (\rho DQ_1^*)_w(\rho\bar{C}_p)_o^{-1}(2n+1)^{-1}\{2(2n-2\ell)(2r+1)\\
&\times [(2r+1)^2-(2n-2\ell)^2]^{-1}-2(2n+2\ell+2)(2r+1)\\
&\times [(2r+1)^2 - (2n+2\ell+2)^2]^{-1}\}\\
&+ 2(\rho DQ_1^*)_o\kappa_o^{-1}(2\ell+1)(2n-2r)[(2n-2r)^2-(2\ell+1)^2]^{-1}\\
&\times [(2n-2r)^2-\gamma(2\ell+1)^2]^{-1}\\
&\times [(\rho\bar{C}_p)_w(\rho\bar{C}_p)_o^{-1}D_o(2\ell+1)^2(2n+1)^{-1} + D_o(\ell n\rho)_w(2n-2r)\\
&+ \kappa_w(\rho\bar{C}_p)_o^{-1}(2n-2r)(2r+1)(2n+1)^{-1}]\\
&+ 2(\rho DQ_1^*)_o\kappa_o^{-1}(2\ell+1)(2n+2r+2)[(2n+2r+2)^2 - (2\ell+1)^2]^{-1}\\
&\times [(2r+2n+2)^2 - \gamma(2\ell+1)^2]^{-1}\\
&\times [-(\rho\bar{C}_p)_w(\rho\bar{C}_p)_o^{-1}D_o(2\ell+1)^2(2n+1)^{-1} - D_o(\ell n\rho)_w(2n+2r+2)\\
&+ \kappa_w(\rho\bar{C}_p)_o^{-1}(2r+1)(2n+2r+2)(2n+1)^{-1}]\Big|\\
&\times \Big|\exp\{-[(2\ell+1)^2 + (2n+1)^2](t/\Theta)\} - \exp\{-(2r+1)^2(t/\tau)\}\Big|\\
&\times \{(2r+1)^2 - \gamma[(2\ell+1)^2 + (2n+1)^2]\}^{-1},
\end{aligned}
$$

$$
\begin{aligned}
F_2(r,\ell,m) = \;&2(\rho DQ_1^*)_o(2\ell+1)(2n-2r)^2\\
&\times \{\kappa_o[(2n-2r)^2-(2\ell+1)^2][(2n-2r)^2 - \gamma(2\ell+1)^2]\}^{-1}
\end{aligned}
$$

$$\times \{-D_o(\ell n\rho)_w - (\rho\bar{C}_p)_w\kappa_o(2n-2r)\,[(\rho\bar{C}_p)_o^2(2n+1)]^{-1}$$

$$- (2r+1)\kappa_w[(2n+1)(\rho\bar{C}_p)_o]^{-1}\}$$

$$\times \{\exp[-(2n+1)^2(t/\Theta) - (2n-2r)^2(t/\tau)] - \exp[-(2r+1)^2(t/\tau)]\}$$

$$\times \{(2r+1)^2 - \gamma[(2n+1)^2 + (2n-2r)^2]\}^{-1},$$

$$F_3(r,\ell,n) = 2(\rho DQ_1^*)_o(2\ell+1)(2n+2r+2)^2\{\kappa_o[(2n+2r+2)^2 - (2\ell+1)^2]$$

$$\times [(2n+2r+2)^2 - \gamma(2\ell+1)^2]\}^{-1}$$

$$\times \{D_o(\ell n\rho)_w + (\rho\bar{C}_p)_w\kappa_o(2n+2r+2)\,[(\rho\bar{C}_p)_o^2(2n+1)]^{-1}$$

$$- (2r+1)\kappa_w\,[(2n+1)(\rho\bar{C}_p)_o]^{-1}\}$$

$$\times \{\exp[-(2n+1)^2(t/\Theta) - (2n+2r+2)^2(t/\tau)]$$

$$- \exp\,[-(2r+1)^2(t/\tau)]\}$$

$$\times \{(2r+1)^2 - \gamma[(2n+1)^2 + (2n+2r+2)^2]\}^{-1},$$

$$F_4(r,\ell,m) = \{2(\ell n\rho)_w - 2mD_w[D_o(2\ell+1-2m)]^{-1}\}\,(2r+1)4m^2$$

$$\times \{(2\ell+1)[(2r+1)^2-4m^2]\,(2\ell+1-2m)\}^{-1}$$

$$\times \Big(\{\exp[-(2\ell+1)^2(t/\Theta) - (2\ell+1-2m)^2(t/\Theta)]$$

$$- \exp[-(2r+1)^2t/\Theta)]\}$$

$$\times \{(2r+1)^2 - \gamma[(2\ell+1)^2 + (2\ell+1-2m)^2]\}^{-1}$$

$$- \{\exp[-4m^2(t/\Theta)] - \exp[-(2r+1)^2(t/\Theta)]\}$$

$$\times [(2r+1)^2 - \gamma 4m^2]^{-1}\Big),$$

$$F_5(r,\ell,m) = \{2(\ell n\rho)_w + 2mD_w[D_o(2\ell+1+2m)]^{-1}\}\,(2r+1)4m^2$$

$$\times \{(2\ell+1)\,[(2r+1)^2 - 4m^2](2\ell+1+2m)\}^{-1}$$

$$\begin{aligned}
&\times \Big(\{\exp[-(2\ell+1)^2(t/\Theta) - (2\ell+1+2m)^2(t/\Theta)] \\
&- \exp\,[-(2r+1)^2(t/\tau)]\} \\
&\times \{(2r+1)^2 - \gamma[(2\ell+1)^2 + (2\ell+1+2m)^2]\}^{-1} \\
&- \{\exp[-4m^2(t/\Theta) - \exp[-(2r+1)^2(t/\tau)]\} \\
&\times [(2r+1)^2 - \gamma 4m^2]^{-1}\Big),
\end{aligned}$$

APPENDIX E

EQUATIONS FOR $T_{\varepsilon\delta\delta}$ AND THEIR SOLUTION IN AN ADIABATIC CELL

The right hand side of Eq. (IV.5.6) for $T_{\varepsilon\delta\delta}$ is

$$
\begin{aligned}
U_{\varepsilon\delta\delta} = & -[(\rho\bar{C}_p)_w/(\rho\bar{C}_p)_o]\omega_o(\partial T_{\delta\delta}/\partial t) - [(\rho\bar{C}_p)_w/(\rho\bar{C}_p)_o]\omega_\delta(\partial T_\delta/\partial t) \\
& - [(\rho\bar{C}_p)_T/(\rho\bar{C}_p)_o]T_\delta(\partial T_\delta/\partial t) \\
& + 2(\rho\bar{C}_p)_o^{-1}[(\rho D)_o(\bar{H}_1-\bar{H}_2)_w + (\rho DQ_1^*)_w](\partial\omega_\delta/\partial z)(\partial\omega_o/\partial z) \\
& + (\rho\bar{C}_p)_o^{-1}[(\rho D)_o(\bar{H}_1-\bar{H}_2)_T + (\rho DQ_1^*)_T](\partial T_\delta/\partial z)(\partial\omega_o/\partial z) \\
& + \kappa_w(\rho\bar{C}_p)_o^{-1}\omega_o(\partial^2 T_{\delta\delta}/\partial z^2) + \kappa_w(\rho\bar{C}_p)_o(\partial\omega_\delta/\partial z)(\partial T_\delta/\partial z) \\
& + \kappa_T(\rho\bar{C}_p)_o^{-1}(\partial T_\delta/\partial z)^2 + \kappa_w(\rho\bar{C}_p)_o^{-1}\omega_\delta(\partial^2 T_\delta/\partial z^2) \\
& + \kappa_T(\rho\bar{C}_p)_o^{-1}T_\delta(\partial^2 T_\delta/\partial z^2) + (\rho DQ_1^*)_o(\rho\bar{C}_p)_o^{-1}(\partial^2\omega_{\varepsilon\delta\delta}/\partial z^2) \\
& + (\rho DQ_1^*)_w(\rho\bar{C}_p)_o^{-1}\omega_o(\partial^2\omega_\delta/\partial z^2) + (\rho DQ_1^*)_w(\rho\bar{C}_p)_o\omega_\delta(\partial^2\omega_o/\partial z^2) \\
& + (\rho DQ_1^*)_T(\rho\bar{C}_p)_o^{-1}T_\delta(\partial^2\omega_o/\partial z^2) - v_\varepsilon(\partial T_{\delta\delta}/\partial z) - v_{\varepsilon\delta}(\partial T_\delta/\partial z).
\end{aligned}
\tag{E.1}
$$

After application of (IV.5.8), we have the greatly simplified form,

$$
\begin{aligned}
U_{\varepsilon\delta\delta} = & - [(\rho\bar{C}_p)_T/(\rho\bar{C}_p)_o]T_\delta(\partial T_\delta/\partial t) \\
& + (\rho DQ_1^*)_T(\rho\bar{C}_p)_o^{-1}T_\delta(\partial^2\omega_o/\partial z^2) \\
& + (\rho\bar{C}_p)_o^{-1}[(\rho D)_o(\bar{H}_1-\bar{H}_2)_T + (\rho DQ_1^*)_T](\partial T_\delta/\partial z)(\partial\omega_o/\partial z)
\end{aligned}
$$

$$+ \kappa_T(\rho\bar{C}_p)_o^{-1} T_\delta(\partial^2 T_\delta/\partial z^2) + \kappa_T(\rho\bar{C}_p)_o^{-1}(\partial T_\delta/\partial z)^2$$

$$- v_{\varepsilon\delta}(\partial T_\delta/\partial z). \qquad (E.2)$$

The equation for order $\varepsilon\delta^2$ corresponding to (IV.5.18) is

$$\partial g_{\varepsilon\delta\delta m}(t)/\partial t + (m^2/\tau) g_{\varepsilon\delta\delta m}(t) = (2/a) \int_0^a U_{\varepsilon\delta\delta} \cos(m\pi x/a) \qquad (E.3)$$

and solution of this equation under adiabatic conditions gives

$$T_{\varepsilon\delta\delta} = 2\omega_1^{o2}(\rho DQ_1^*)_o[\pi^2\kappa_o(1-\gamma)]^{-1} \, [\sum_{\ell=0}^{\infty} G_1(\ell)$$

$$+ (\rho DQ_1^*)_o\kappa_o^{-1} \sum_{m=1}^{\infty} \sum_{\ell=0}^{\infty} G_2(\ell,m)(-1)^m \cos(2m\pi x/a)], \qquad (E.4)$$

where

$$G_1(\ell) = H_1(\ell) + H_2(\ell)$$

$$G_2 = H_3(\ell,m) + H_4(\ell,m) + H_5(\ell,m) + H_6(\ell,m) + H_7(\ell,m), \qquad (E.5)$$

with

$$\gamma = \tau/\Theta$$

$$H_1(\ell) = \{(\rho\bar{C}_p)_T(\rho DQ_1^*)_o[(\rho\bar{C}_p)_o\kappa_o(1-\gamma)]^{-1}$$

$$- (\rho D)_o(\bar{H}_1-\bar{H}_2)_T[D_o(\rho\bar{C}_p)_o]^{-1}\}$$

$$\times \{1 - \exp[-2(2\ell+1)^2(t/\Theta)]\}[2(2\ell+1)^2]^{-1},$$

$$H_2(\ell) = \{(\rho\bar{C}_p)_T(\rho DQ_1^*)_o[(\rho\bar{C}_p)_o\kappa_o(1-\gamma)]^{-1}$$

$$+ (\rho D)_o(\bar{H}_1-\bar{H}_2)_T[\kappa_o(1-\gamma)]^{-1}\}$$

$$\times \{1 - \exp[-(2\ell+1)^2(\tau^{-1}+\Theta^{-1})t]\}(2\ell+1)^{-2},$$

$$H_3(\ell,m) = (\rho\bar{C}_p)_T(\rho DQ_1^*)_o[(\rho\bar{C}_p)_o\kappa_o(1-\gamma)]^{-1}$$

$$\times \{1 - \exp[-2(2\ell+1)^2(t/\tau)]\} \; [2(2\ell+1)^2]^{-1},$$

$$H_4(\ell,m) = \Big(D_o(\rho C_p)_T(2\ell+1)\,[\pi^2\kappa_o(1-\gamma)(2\ell+1-2m)]^{-1}$$

$$+ 2m(2\ell+1-2m)^{-1}\{(\rho DQ_1^*)_T(\rho DQ_1^*)_o^{-1} - \kappa_T[\kappa_o(1-\gamma)]^{-1}\}$$

$$- (\rho D)_o(\bar{H}_1-\bar{H}_2)_T(\rho DQ_1^*)_o^{-1} + (\ell n\rho)_T D_o(\rho\bar{C}_p)_o[\kappa_o(1-\gamma)]^{-1}\Big)$$

$$\times \Big(\{\exp[-(2\ell+1)^2(t/\Theta)-(2\ell+1-2m)^2(t/\Theta)] - \exp[-4m^2(t/\tau)]\}$$

$$\times \{4m^2-\gamma[(2\ell+1)^2+(2\ell+1-2m)^2]\}^{-1}$$

$$- \{\exp[-(2\ell+1)^2(t/\Theta)-(2\ell+1-2m)^2(t/\tau)] - \exp[-4m^2(t/\tau)]\}$$

$$\times \{4m^2-(2\ell+1-2m)^2-\gamma(2\ell+1)^2\}^{-1}\Big),$$

$$H_5(\ell,m) = \Big(D_o(\rho\bar{C}_p)_T(2\ell+1)\,[\kappa_o(1-\gamma)(2\ell+1+2m)]^{-1}$$

$$+ 2m(2\ell+1+2m)^{-1}\{\kappa_T[\kappa_o(1-\gamma)]^{-1} - (\rho DQ_1^*)_T(\rho DQ_1^*)_o^{-1}\}$$

$$- (\rho D)_o(\bar{H}_1-\bar{H}_2)_T(\rho DQ_1^*)_o^{-1} + (\ell n\rho)_T D_o(\rho\bar{C}_p)_o[\kappa_o(1-\gamma)]^{-1}\Big)$$

$$\times \Big(\{\exp[-(2\ell+1)^2(t/\Theta)-(2\ell+1+2m)^2(t/\Theta)] - \exp\,[-4m^2(t/\tau)]\}$$

$$\times \{4m^2-\gamma[(2\ell+1)^2+(2\ell+1+2m)^2]\}^{-1}$$

$$- \{\exp[-(2\ell+1)^2(t/\Theta)-(2\ell+1+2m)^2(t/\tau)] - \exp[-4m^2(t/\tau)]\}$$

$$\times \{4m^2-(2\ell+1+2m)^2-\gamma(2\ell+1)^2\}^{-1}\Big),$$

$$H_6(\ell,m) = \{-(\ell n\rho)_T(1-\gamma)^{-1} - (2\ell+1)(\rho\bar{C}_p)_T[(2\ell+1-2m)(\rho\bar{C}_p)_o(1-\gamma)]^{-1}$$

$$+ 2m\kappa_T[(2\ell+1-2m)\kappa_o(1-\gamma)]^{-1}\}$$

$$\times \Big(\{\exp[-(2\ell+1)^2(t/\tau)-(2\ell+1-2m)^2(t/\Theta)] - \exp[-4m^2(t/\tau)]\}$$

$$
\begin{aligned}
&\times \{4m^2-(2\ell+1)^2-\gamma(2\ell+1-2m)^2\}^{-1}\\
&- \{\exp[-(2\ell+1)^2(t/\tau)-(2\ell+1-2m)^2(t/\tau)] - \exp[-4m^2(t/\tau)]\}\\
&\times \{4m^2-(2\ell+1)^2-(2\ell+1-2m)^2\}^{-1}\Big) ,
\end{aligned}
$$

$$
\begin{aligned}
H_7(\ell,m) = {}&\{-(\ell n\rho)_T(1-\gamma)^{-1}-(2\ell+1)(\rho\bar{C}_p)_T[(2\ell+1+2m)(\rho\bar{C}_p)_o(1-\gamma)]^{-1}\\
&- 2m\kappa_T[(2\ell+1+2m)\kappa_o(1-\gamma)]^{-1}\}\\
&\times \{\exp[-(2\ell+1)^2(t/\tau)-(2\ell+1+2m)^2(t/\Theta)] - \exp[-4m^2(t/\tau)]\}\\
&\times \{4m^2-(2\ell+1)^2-\gamma(2\ell+1+2m)^2\}^{-1}\\
&- \{\exp[-(2\ell+1)^2(t/\tau)-(2\ell+1+2m)^2(t/\tau)] - \exp[-4m^2(t/\tau)]\}\\
&\times \{4m^2-(2\ell+1)^2-(2\ell+1+2m)^2\}^{-1}\Big) . \qquad \text{(E.6)}
\end{aligned}
$$

APPENDIX F

THE RELATIONSHIP OF HEAT OF MIXING TO $\partial(\bar{H}_1 - \bar{H}_2)/\partial w_1$

The measured heat of mixing of a binary mixture can easily be related to the derivative of the difference of the partial specific enthalpies with respect to the mass fraction if the mixture is assumed to be regular. This is a satisfactory assumption in our case since we need only an estimate of $\partial(\bar{H}_1 - \bar{H}_2)/\partial w_1$. This derivative can be rewritten using the Euler relation

$$w_1\bar{H}_1 + w_2\bar{H}_2 = 0 \tag{F.1}$$

so that

$$\partial(\bar{H}_1 - \bar{H}_2)/\partial w_1 = (1/w_2)(\partial\bar{H}_1/\partial w_1). \tag{F.2}$$

The mass fraction derivative is related to the mole fraction derivative by

$$(\partial/\partial w_1) = (w_1 w_2/x_1 x_2)(\partial/\partial x_1) = (M_1 M_2/\bar{M}^2)(\partial/\partial x_1), \tag{F.3}$$

where $\bar{M}$ is the average molecular weight, so with (F.3) we have

$$\partial(\bar{H}_1 - \bar{H}_2)/\partial w_1 = (M_1 M_2/\bar{M}^2 w_2)(\partial\bar{H}_1/\partial x_1). \tag{F.4}$$

We can replace the partial specific enthalpy by a partial molar enthalpy,

$$\bar{H}_1 = \bar{H}_1{}^M/M_1, \tag{F.5}$$

and thus

$$\begin{aligned}\partial(\bar{H}_1 - \bar{H}_2)/\partial w_1 &= (M_2/\bar{M}^2 w_2)(\partial\bar{H}_1{}^M/\partial x_1)\\ &= (1/\bar{M}x_2)(\partial\bar{H}_1{}^M/\partial x_1).\end{aligned} \tag{F.6}$$

For regular solutions (Rock, 1969; Lewis, Randall, Pitzer, and Brewer, 1961),

$$\partial\bar{H}_1{}^M/\partial x_1 = -\ 2\ x_2\ [w - T(\partial w/\partial T)] \tag{F.7}$$

where w is a constant independent of x_1. Thus,

$$\partial(\bar{H}_1 - \bar{H}_2)/\partial w_1 = -\ 2[w - T(\partial w/\partial T)]/\bar{M}. \tag{F.8}$$

Now, by regular solution theory

$$\Delta H_m{}^M = x_1 x_2 [w - T(\partial w/\partial T)]; \tag{F.9}$$

therefore,

$$\partial(\bar{H}_1 - \bar{H}_2)/\partial w_1 = -\ (2/x_1 x_2)\Delta H_m{}^M/\bar{M}, \tag{F.10}$$

where $\Delta H_m{}^M$ is the molar heat of mixing. Thus, for an equimolar mixture

$$\partial(\bar{H}_1 - \bar{H}_2)/\partial w_1 = -\ 8\Delta\bar{H}_m, \tag{F.11}$$

where $\Delta\bar{H}_m$ is the specific heat of mixing of the equimolar mixture.