NONEQUILIBRIUM THERMODYNAMICS OF FLUID MIXTURES: PRINCIPLES, PERTURBATION METHODS, AND PARAMETER ESTIMATION

Thesis for the Degree of Ph. D.
MICHIGAN STATE UNIVERSITY
JOHN LESTER BARTELT
1968

This is to certify that the

thesis entitled

NONEQUILIBRIUM THERMODYNAMICS OF FLUID MIXTURES:
PRINCIPLES, PERTURBATION METHODS, AND PARAMETER
ESTIMATION

presented by

John Lester Bartelt

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Chemistry

Frederick H. Horne

Major professor
Frederick H. Horne

Date 11 November 1968

O-169

ABSTRACT

NONEQUILIBRIUM THERMODYNAMICS OF FLUID MIXTURES: PRINCIPLES, PERTURBATION METHODS, AND PARAMETER ESTIMATION

By

John Lester Bartelt

A fundamental nonequilibrium thermodynamic theory and powerful, accurate methods of exploiting it have been developed to deal with the intricate problems encountered when various, interacting transport phenomena occur simultaneously. Critical examination of the fundamental theory has led to a reformulation which embodies a new approach to the specification of phenomenological relations through the rational use of the entropy inequality and proper enumeration of independent variables. The approach resolves most of the ambiguities in the earlier theory with regard to validity of a Gibbsian differential equation in nonequilibrium situations, pressure and mechanical equilibrium criteria, kinetic energy of diffusion, and the appropriateness of the Newtonian stress formula for mixtures. A perturbation expansion method has been developed to facilitate the solutions to a wide range of problems in transport theory. Coupled with the weighted residual method and finite transform method, this approach is shown to be an extremely versatile technique for handling such difficult problems as the solution to partial differential equations with variable coefficients and the convection problem of pure thermal diffusion. Some practical formulas are derived for the latter case. A detailed theory of estimation of nonlinearly interacting parameters from data with correlated errors is presented together with a computational algorithm which has distinct advantages over the ordinary least squares method.

NONEQUILIBRIUM THERMODYNAMICS OF FLUID MIXTURES: PRINCIPLES, PERTURBATION METHODS, AND PARAMETER ESTIMATION

By

John Lester Bartelt

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1968

To Brooks

ACKNOWLEDGMENTS

I would like to express my thanks to the Dow Chemical Company, the Lubrizol Foundation, and the National Institutes of Health for the fellowships which provided my financial support.

I am grateful to my colleagues Dr. T. G. Anderson and Mr. V. A. Nicely for the many hours of fruitful discussion and for the numerous suggestions and comments which helped to make this thesis a reality. I would also like to thank Mr. D. Knirk for making his plotting program available and for his interest in the computer aspects of this work.

I wish especially to express my sincere appreciation to Dr. F. H. Horne, whose counsel and guidance have been of immeasurable value. He has been encouraging, critical, and above all a conscientious teacher.

Finally, I am deeply grateful to my wife Brooks, who endured my difficult times, and whose understanding and encouragement were unlimited.

TABLE OF CONTENTS

Page

LIST OF FIGURES

Figure Page

CHAPTER I

INTRODUCTION

The mathematician has often been described as one who neither knows what he is talking about nor cares whether what he says is true. The physical scientist often prides himself on his practical understanding, thoroughness, and insatiable curiosity. Between such extremes of abstraction and realism it would hardly seem possible that there should be much progress. Yet the trend has been quite otherwise and today the scientist is increasingly aware of his need for mathematical insight and the mathematician proves more and more the stimulation of physical problems. The progress of the moment, at any rate in the science of materials, lies in the regions where mathematics and physical science have common interests.

If the mathematician has little care whether what he says is true, it is only in the sense that his primary concern is with inner consistency and deductive consequences of an axiomatic theory. He is content with certain undefined quantities and his satisfaction lies in the structure into which they can be built. If the scientist regards himself as dedicated to the progression of understanding, then he cannot rest content with particular details. It is his understanding of the common features of diverse problems that allows him to progress and hence he must be concerned with abstraction and generalization. It is the business of mathematical theory to provide just such an abstraction and generalization, but it will do it in its own fashion and use the axiomatic method. From what at first seem rather farfetched abstractions and assumptions, it will produce a coherent body of consequences. Insofar as these consequences correspond to the observable behavior of the materials the scientist handles, he will have confidence in the mathematical theory and its foundations. The theory itself will have been used to design the critical experiments and to interpret their results. If there is complete discordance between the valid expectations of the theory and the results of critically performed experiments, the theory may be rejected. Some measure of disagreement may suggest modification of the theory. Agreement within the limits of experimental error gives confidence in the mathematical model and opens the way for further progress. In particular nonequilibrium thermodynamics provides a model of the real world in which the scientist can have a high degree of confidence.

Although the early steps in the development of the theory of irreversible processes took place over a hundred years ago, the cornerstone of the modern theory was laid in 1931 by Onsager. Over the past twenty-five years a coordinated theory based on the fundamental work of Onsager has been developed by Prigogine (1947, 1955), de Groot (1945, 1955), de Groot and Mazur (1962), Meixner and Reik (1959), Kirkwood and Crawford (1952), Fitts (1962), and many others. It is also clear that over the last decade there has been a renaissance of interest in thermodynamics and rational mechanics in the mathematical world. It has been fairly widespread and attracted the attention of many mathematicians whose abilities are of the first order. If a few names are to be singled out, it would probably not be unfair to the others to select those of Truesdell and Toupin (1960) and Coleman and Noll (1963); their scholarship and extensive writing on the foundations of continuum mechanics have been of great influence.

Even though the development of the theory has been extensive, the fact remains that, because of the diversity of phenomena and range of material behaviors that come within the scope of nonequilibrium thermodynamics, it is unlikely that every possible area for study has been examined. The investigation of one such area initiated most of the research in this thesis: convection in pure thermal diffusion experiments.

Convection in liquids due to temperature, density, or composition gradients is an extremely delicate phenomenon. The pure thermal diffusion experiments of Thomaes (1951) and of Agar and Turner (1960), among others, indicate that proper interpretation of their results can only be made if the convection that is apparently present can be accounted for. Because of its simplicity and sensitivity the pure thermal diffusion method has the potential, if the convection problem can be solved or eliminated, of being an important source of transport parameters of interest not only to physicists and chemists but engineers and biologists as well. Unfortunately, it appears that the rule of thumb in the past has been to neglect convection and its effects whenever possible. Because of the paucity of theoretical and practical work on convection (hydrodynamicists had never considered convection under conditions appropriate to the thermal diffusion experiments), it was impossible to establish the convective behavior of a fluid mixture in a thermal diffusion experiment without a re-examination of the theory and without new (or better) mathematical methods.

Besides convection, there were and are many other unsolved transport problems. Throughout the research which has led to this thesis, the emphasis has been on the development of a generalized theory and of generalized methods of using it. Most of the ambiguities of the previous theory have now been resolved, and powerful methods have been obtained for applying the theory to particular experiments. Although examples are given only for pure thermal diffusion, the theory and methods are sufficiently general that a great variety of other problems may be solved.

A reformulation of the nonequilibrium thermodynamic theory of fluid mixtures is presented in Chapter II. The questions of theoretical interest which are dealt with in this chapter are: (1) validity of a Gibbsian differential equation in nonequilibrium situations; (2) neglect of inertial and viscous terms in the phenomenological equations; (3) neglect of the kinetic energy of diffusion; (4) definition of mechanical equilibrium; and (5) appropriateness of the Newtonian stress tensor for mixtures. The resolution of each of these problems is accomplished in this chapter through the development of a phenomenological theory for "ordinary" fluid mixtures.

Chapter III is concerned with the development of the methodology required to solve the extremely complex transport equations deduced in Chapter II. In particular it is shown that the perturbation expansion method is an extremely versatile technique for handling such difficult problems as the solution to partial differential equations with variable coefficients and the convection problem of pure thermal diffusion. Some practical formulas are presented for the interpretation of pure thermal diffusion experiments including the possibility of convection and variable phenomenological coefficients.

CHAPTER II

A THERMODYNAMIC THEORY OF FLUID MIXTURES

1. Introduction

The success of the thermodynamic theory of irreversible processes in its application to a wide variety of problems in the physics and chemistry of materials has led to a renewal of interest in the fundamentals of the theory. The material presented in this chapter is in fact a result of the need for better understanding of the principal assumptions and approximations made in the theory. The purpose here is not the derivation of a new theory; it is instead a reformulation in which the nature of these assumptions is clarified. Moreover, the reformulation has uncovered many new features of the theory which previously were buried in assumptions too casually accepted.

There is an extensive literature for the thermodynamics of irreversible processes (TIP) or nonequilibrium thermodynamics (NET) and its applications. Although a literature survey is not intended here, a reference to TIP or NET as it is currently practiced is generally meant to be a reference to the works of Fitts (1962), de Groot and Mazur (1962), Hasse (1963), and Meixner and Reik (1959). There is in addition a large volume of material in the technical journals, much of which can probably be found most easily by consulting the extensive bibliography of Fitts; specific articles of particular importance from the literature will be cited individually as the need arises.

The objectives of this chapter are (1) the development of a set of macroscopic transport equations from basic principles which describe the behavior of a liquid mixture, with an attempt at each stage of the development to indicate clearly the introduction of any necessary assumptions or approximations; and (2) the comparison of the differences between the results obtained here and those of the earlier theory (see Horne, 1966). In view of these objectives it will be necessary in the remainder of this section to give a concise exposition of TIP and to indicate at each opportunity the need for a more rigorous or objective approach. There is no doubt that in such a short exposition the case for TIP may not be presented as fairly as possible and where matters of opinion are involved it might be wise to consult the original sources.

Typically, TIP begins with the fundamental principles of conservation of mass, momentum, and energy. These basic postulates are usually given in integral form, and, in regions where the field variables are sufficiently smooth, the integral balance or conservation equations may be replaced by local differential equations. The conservation of mass condition leads to the differential equation usually called the equation of continuity,

$$\frac{\partial \rho_i}{\partial t} + \underset{\sim}{\nabla} \cdot (\rho_i \underset{\sim}{u}_i) = 0 \;, \qquad (1.1)$$

where ρ_i is the local density of component i, $\underset{\sim}{u}_i$ is the velocity of the local center of mass of component i, and it assumed that there are no sources of mass (i.e., chemical reactions). The conditions of conservation of linear and angular momentum lead to an equation of motion for the fluid,

$$\frac{\partial \rho \underset{\sim}{u}}{\partial t} + \underset{\sim}{\nabla} \cdot (\rho \underset{\sim}{u}\underset{\sim}{u}) = \rho \underset{\sim}{X} + \underset{\sim}{\nabla} \cdot \underset{\approx}{\sigma} \qquad (1.2)$$

where ρ is the total local density,

$$\rho \equiv \sum_{i=1}^{r} \rho_i \;, \qquad (1.3)$$

and $\underset{\sim}{u}$ is the local center of mass or convective velocity

$$\rho \underset{\sim}{u} \equiv \sum_{i=1}^{r} \rho_i \underset{\sim}{u}_i \qquad (1.4)$$

The quantity $\underset{\sim}{X}$ in (1.2) is the external force per unit mass acting on the fluid system, and the tensor $\underset{\approx}{\sigma}$ is the stress tensor, the negative of the pressure tensor, which gives the surface force acting on a fluid element. Finally, conservation of energy is expressed by

$$\frac{\partial \rho \bar{E}_T}{\partial t} + \underset{\sim}{\nabla} \cdot \underset{\sim}{J}_E = 0 \ , \tag{1.5}$$

where $\bar{E}_T$ is the total specific energy and $\underset{\sim}{J}_E$ is the total flux of the total energy.

It should be mentioned that the theory is already informationally deficient. Unless the external force, the stress tensor, and the total energy flux are independently specified there are more unknowns than equations. The procedure in TIP is to provide phenomenological relations (sometimes called constituitive relations) for these quantities, although the origin of these phenomenological relations is not determined with certainty. In some formulations of TIP a prescription is given for obtaining these phenomenological equations as will be seen later, but it is not clear that these prescriptions are more than arbitrary. The development given in this chapter approaches the determination of phenomenological relations in a more systematic if not more reasonable fashion.

Another source of consternation is that TIP generally fails to consider the possibility of determining equations of motion for the individual components of the mixture. Clearly momentum is not conserved for each component of the mixture since there is exchange between components. This is not a disadvantage however, since it will be shown that equations of motion for the individual components can be formulated by the use of componentwise or partial stress tensors without loss of information and with great increase in the scope and the generality of the theory. This single aspect has led to many of the new results produced in this reformulation.

At this point TIP makes a transition from the hydrodynamic stage represented by equations (1.1), (1.2), and (1.5) to the thermodynamic stage. This is usually accomplished by introducing the assumption of local equilibrium. For example Fitts (1962) uses the following postulate:

> 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.

The concepts defining the thermodynamic functions of state are not generally so restrictive as to exclude the possibility of extending the definitions to nonequilibrium situations. It is another matter, however, to assume that the same functional relations exist outside of the domain for which they were established. Some attempt should be made to investigate the resonableness of this claim. Prigogine (1949) in fact made such an investigation and found that the postulate was reasonable for mixtures of monatomic gases sufficiently close to equilibrium. Little else is known about the validity of the postulate except by comparison of the results which come from it with experiment. In this respect the postulate has performed very well for systems whose gradients of the thermodynamic functions are small and evolve slowly.

Despite these practical successes, there are still some inconsistencies which require clarification. One in particular was the stimulus for much of this research. According to the postulate of local equilibrium the specific internal energy, $\bar{E}$, is related to the specific entropy, $\bar{S}$, by the equation of Gibbs;

$$d\bar{E} = Td\bar{S} - pd\left(\frac{1}{\rho}\right) + \sum_{i=1}^{r} \mu_i d\left(\frac{\rho_i}{\rho}\right), \tag{1.6}$$

where $\left(\frac{1}{\rho}\right)$ is the specific volume, μ_i are the specific chemical potentials, and $\left(\frac{\rho_i}{\rho}\right)$ are concentrations (mass fractions). With regard to the quantity p Fitts makes the statement:

> For a nonequilibrium system, the pressure p (in equation (1.6)) is the same function $p(\rho,E)$ as for an equilibrium system. In this case, p is not the pressure in the usual sense; i.e., p is not the normal force per unit are exerted by the fluid.

In hydrodynamics the pressure or force per unit area is given in terms of the trace of the stress tensor. It seems strange that after stating a postulate to the contrary, Fitts reaches the conclusion that the quantity p in equation (1.6) is no longer the pressure normally used while the temperature, chemical potentials, etc. all correspond to the concepts typically associated with them. Furthermore TIP in general fails to discuss the correspondence between the quantity p and the trace of the stress tensor. This makes any critical analysis of the criterion for mechanical equilibrium within the context of TIP nearly impossible.

At this juncture of the thermodynamic stage of TIP an entropy balance equation is deduced from the energy equation (1.6). It is always possible to write this balance equation in the form

$$\frac{\partial \rho \bar{S}}{\partial t} + \underset{\sim}{\nabla} \cdot \underset{\sim}{J}_S = \frac{\Phi}{T} , \tag{1.7}$$

where $\underset{\sim}{J}_S$ is the entropy flux and Φ is the internal entropy production. It is important to note that the separation of terms in this equation between a flux and source is fairly arbitrary. Furthermore the introduction of this equation to the list of transport equations does not increase its information content. The real need for this equation is for application of the second law of thermodynamics. The form of the second law most appropriate for nonequilibrium thermodynamics is

$$\Phi \geqslant 0 . \tag{1.8}$$

In TIP the entropy production and the inequality (1.8) play a far less important role than in the theory to be presented here. The inequality does serve to place restrictions on the phenomenological equations which are obtained according to the following _ad hoc_ procedure:

After the energy equation (1.6), the equation of motion (1.2) and the equations of continuity (1.1) for the fluid have been introduced into the entropy balance equation and the resulting terms arbitrarily separated into flux and source terms, the entropy production can be written as,

$$\Phi = \underset{\approx}{F} : \underset{\approx}{J} + \sum_{i=0}^{r} \underset{\sim}{F}_i \cdot \underset{\sim}{J}_i \,, \tag{1.9}$$

where terms represented by the symbols F are called forces and those represented by J are called fluxes. This classification into fluxes and forces is often arbitrary and it is impossible to show that any given assignment is correct. One of the more common assignments is

$$\underset{\approx}{F} = (\underset{\approx}{\sigma} + p\underset{\approx}{1}) \,, \qquad \underset{\approx}{J} = \underset{\sim}{\nabla}\underset{\sim}{u} \,, \tag{1.10}$$

$$\underset{\sim}{F}_0 = \underset{\sim}{\nabla} \ell n \, T \,, \qquad \underset{\sim}{J}_0 = - \underset{\sim}{q} \,, \tag{1.11}$$

$$\underset{\sim}{F}_i = \nabla_T \underset{\sim}{u} \,, \qquad \underset{\sim}{J}_i = - \rho_i (\underset{\sim}{u}_i - \underset{\sim}{u}) \,, \tag{1.12}$$

where

$$\underset{\sim}{\nabla}_T \mu_i^1 = \underset{\sim}{\nabla} \mu_i - \underset{\sim}{X}_i + \overline{S}_i \underset{\sim}{\nabla} T \,, \tag{1.13}$$

and where the heat flux $\underset{\sim}{q}$ is related to the total energy flux of equation (1.5) by

$$\underset{\sim}{q} = \underset{\sim}{J}_E - \rho \overline{E} \underset{\sim}{u} + \sum_{i=1}^{r} J_i \overline{H}_i \,. \tag{1.14}$$

Also, $\overline{H}_i$ and $\overline{S}_i$ are the partial specific enthalpy and entropy respectively. The linear relations for the fluxes of (1.10-13) are generally written

$$(\underset{\approx}{\sigma} + p\underset{\approx}{1}) = (\phi - 2/3\eta)\ (\underset{\sim}{\nabla}\cdot\underset{\sim}{u})\underset{\approx}{1} + 2\eta\ \mathrm{sym}(\underset{\sim}{\nabla}\underset{\sim}{u}) \qquad (1.15)$$

where η is called the shear viscosity and ϕ is called the bulk or volume viscosity,

$$-\ q = \Omega_{00}\nabla \ell nT + \sum_{j=1}^{r} \Omega_{0j}\nabla_T\mu_j^1 \qquad (1.16)$$

and

$$+\ J_i = \Omega_{i0}\nabla \ell nT + \sum_{j=1}^{r} \Omega_{ij}\nabla_T\mu_j^1 \quad i=1,\ldots r\ . \qquad (1.17)$$

The coefficients Ω_{ij} are called phenomenological or Onsager coefficients. The number of independent phenomenological coefficients is limited because of the linear dependence of the diffusion fluxes

$$\sum_{i=1}^{r} J_i = 0 \qquad (1.18)$$

and is further restricted by the entropy inequality (1.8). See Appendix A for a derivation of these restrictions. It should be made clear that the phenomenological expressions given here are not unique and that TIP generally considers many transformations among the forces and fluxes. The procedure is quite constant however: the phenomenological relations are always determined in terms of those particular quantities appearing in the expression for the entropy production.

It is certainly obvious that phenomenological relations must be used in order to make the theory deterministic and that it is convenient to write out the source terms of the entropy balance equation in order to make use of the second law inequality (1.8) for the entropy production. It is not so obvious, however, that the phenomenological relations are to be written only for those quantities called fluxes in the expression for the entropy production or that they are only determined by linear combinations of only those forces of the same tensorial order. For example, TIP suggests that the same expression used for the stress tensor in a pure fluid is also appropriate for a mixture of fluids. Furthermore it is not obvious that the heat flux should be independent of the velocities of the components. The motivation for this ad hoc procedure for obtaining phenomenological expressions in TIP needs to be examined and at the same time the possibility for making the system deterministic by other procedures should be considered.

The theory of mixtures to be developed in this chapter uses the thermodynamic methods of Coleman and Noll (1963) and Coleman and Mizel (1963, 1964). This approach combines the rational use of the entropy inequality (1.8) and the principle of equipresence (An independent variable present in one phenomenological equation for a material should be so present in all, unless its presence is in direct contradiction with the assumed symmetry of the material or the laws of thermodynamics.) to obtain a system of transport equations consistent with ordinary thermostatics but without the need for the second part of the assumption of local equilibrium. This approach to non-equilibrium thermodynamics, after careful extension to mixtures, eliminates the inconsistencies and removes most of the criticisms mentioned above.

Coleman, Noll, and Mizel considered single thermoelastic materials, and the extension of their methods has been attempted by only a few workers. Green and Naghdi (1965, 1967), Ingram and Erigen (1967), and Bowen (1967) have made such an extension, but have failed to produce a theory which is both well motivated physically and also consistent with classical thermostatics. Stimulated by the shortcomings of these authors, Müller (1968) succeeded in formulating a thermodynamic theory of mixtures of fluids which is consistent with both thermostatics and TIP in those circumstances in which they can be compared. Müller's major contribution was to show that the form of the entropy production could be deduced from the principles set forth by Coleman and Noll. The theory of this chapter extends Müller's work in such a way that the comparison to TIP is easily made and so as to make the resolution of the inconsistencies mentioned above most obvious.

The development of the theory will be along the following lines: The conservation laws are introduced in the standard fashion to obtain the equations of continuity for each species, the energy balance equation, and in distinction with TIP, equations of motion for each component in terms of partial stress tensors. The entropy inequality and balance equation for entropy are introduced next. The energy balance, equations of continuity and motion, and the entropy balance equation are all used to write the entropy inequality in great detail. The (Helmholtz) free energy is introduced as the energy variable at this stage of the formulation for convenience in writing the results. In order to make the information content explicit (with respect to number of unknowns versus number of equations) the concept of thermodynamic process is introduced at this point. It is obvious that the theory at this stage can not be developed further without phenomenological assumptions about the fluid. Having introduced particular constitutive assumptions of an extremely general form (in particular not linear) the consequences of the entropy inequality are deduced. One result for this particular mixture is the establishment of the validity of the thermostatic functional relations applied in nonequilibrium situations. Further results are obtained by restricting the class of constitutive relations to those linear in the independent variables. Such a linear fluid is called an "ordinary" fluid mixture. After a considerable amount of algebra and careful application of the entropy inequality, it is found that the equations of transport for the "ordinary" fluid mixture are surprisingly similar to those generally found in TIP. There are differences however; for example, the diffusion fluxes are determined from equations of motion rather than directly from phenomenological equations. There are some differences due to the fact that terms involving the kinetic energy of diffusion are included here but are usually neglected in TIP (although not necessarily). Finally a complete review of the problems brought out in this introduction is made to show that a better understanding of the nature of nonequilibrium thermodynamics for mixtures has been achieved.

2. Kinematics and Equations of Balance[1]

In this section the kinematics of motion and the axioms of balance of mass, linear momentum, moment of momentum, and energy for a mixture of ν components are considered. Nothing new is presented in this section;

---

[1] Cartesian tensor notation will be 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 will also be used i.e.,

$$v_i t_{ij} \equiv \sum_{i=1}^{3} v_i t_{ij}$$

reference could simply be made to the papers of Müller (1968), Bowen (1967), or Truesdell (1957, 1960) were it not for the fact that notation and some of the well-known relations need to be introduced to the reader. Accordingly, the derivation of the balance laws is only sketched here.

Every place in space, x_n, is assumed to be occupied simultaneously by "particles" of all ν components. The density of component α is denoted ρ_α, and v_i^α is the component velocity relative to some frame of reference. The total density of the mixture is defined as[2]

$$\rho = \sum_{\alpha=1}^{\nu} \rho_\alpha \tag{2.1}$$

while the barycentric velocity is defined as

$$\rho v_i = \sum_{\alpha} \rho_\alpha v_i^\alpha \tag{2.2}$$

The diffusion velocity of component u_i^α is defined as

$$u_i^\alpha = v_i^\alpha - v_i \tag{2.3}$$

---

[2] For the remainder of this chapter the summation over all species $\sum_{\alpha=1}^{\nu}$ will be denoted $\sum_{\alpha}$.

The material, substantial, or convected time derivative, $\frac{d}{dt}$, i.e., the time rate of change an observer would detect if he moved through the mixture with velocity v_i, is related to the time derivative at a fixed point, $\frac{\partial}{\partial t}$, by

$$\frac{d}{dt} = \frac{\partial}{\partial t} + v_i \frac{\partial}{\partial x_i} \qquad (2.4)$$

<u>The general balance equation</u>.--The balance or conservation laws will be postulated as integral equations. In regions where the field variables are sufficiently smooth the integral balance equations may be replaced by local differential equations. The integral equations of all the balance laws considered in this chapter are special cases of the general balance law

$$\frac{d}{dt}\int_V \rho_\alpha \psi_\alpha dV = -\int_S F_i^\alpha dS_i + \int_V \rho_\alpha \sigma_\alpha dV , \qquad (2.5)$$

where V is a fixed volume with bounding surface S, F_i^α is the influx of ψ_α through S, σ_α is a volume supply of α within V, and ψ_α can be any component of a tensor, vector, or scalar.

In regions where $\rho_\alpha, \psi_\alpha, v_i^\alpha, \frac{\partial \rho_\alpha}{\partial t}, \frac{\partial \psi_\alpha}{\partial t}, \sigma_\alpha, \frac{\partial F_i^\alpha}{\partial x_j}, \frac{\partial v_i^\alpha}{\partial x_j}$ are continuous, (2.5) may be replaced by the differential equation

$$\frac{\partial}{\partial t} \rho_\alpha \psi_\alpha + \frac{\partial}{\partial x_j} (\rho_\alpha \psi_\alpha v_j^\alpha + f_j^\alpha) = \rho_\alpha \sigma_\alpha , \qquad (2.6)$$

where the convective contribution to the influx has been accounted for separately according to

$$F_i^\alpha = f_j^\alpha + \rho_\alpha \psi_\alpha v_j^\alpha \ . \tag{2.7}$$

By summing the integral equation of balance for an individual species over all species the total equation of balance is obtained,

$$\frac{d}{dt} \int_V \rho\psi dV = - \int_S F_i dS_i + \int_V \rho S dv \ , \tag{2.8}$$

where the following definitions are used:

$$\rho\psi = \sum_\alpha \rho_\alpha \psi_\alpha \tag{2.9}$$

$$F_i = \sum_\alpha (f_i^\alpha + \rho_\alpha \psi_\alpha u_i^\alpha) \tag{2.10}$$

$$\rho S = \sum_\alpha \rho_\alpha \sigma_\alpha \ . \tag{2.11}$$

The differential equation associated with (2.8) is

$$\frac{\partial}{\partial t} \rho\psi + \frac{\partial}{\partial x_j} F_j = \rho S \ . \tag{2.12}$$

Since appropriate F_j and S may always be defined for any given ψ, it may be said that all quantities ψ may be balanced, by definition. There remains, however, some indeterminacy in the definitions of the influx and volume source since any arbitrary solenoidal field may be included in the influx without affecting the balance equation. Even so the general balance equation is still useful since in many cases the influx or source may be given a priori, or special forms for these quantities may be derived from information about ψ.

The conservation of mass.--In the absence of chemical reactions the mass of an individual component is assumed to be conserved. Thus the equation of balance of mass of species α is postulated to be

$$\frac{d}{dt} \int_V \rho_\alpha dV = - \int_S \rho_\alpha v_j^\alpha dS_j \quad (\alpha=1,\ldots\nu) \ . \tag{2.13}$$

This is a special case of (2.5) with

$$\psi_\alpha = 1,\ f_i^\alpha = 0,\ \sigma_\alpha = 0 \ . \tag{2.14}$$

Substitution of (2.14) into (2.6) gives

$$\frac{\partial \rho_\alpha}{\partial t} + \frac{\partial}{\partial x_j} \rho_\alpha v_j^\alpha = 0 \quad (\alpha=1,\ldots\nu) \ . \tag{2.15}$$

Summation of (2.15) over all species results in

$$\frac{\partial \rho}{\partial t} + \frac{\partial \rho v_j}{\partial x_j} = 0 \ . \tag{2.16}$$

An alternative form of (2.15) can be obtained by introducing the rate of change with respect to the barycentric velocity. Using (2.4), (2.15) may be written in the form

$$\frac{d\rho_\alpha}{dt} + u_j^\alpha \frac{\partial \rho_\alpha}{\partial x_j} + \rho^\alpha \frac{\partial v_j^\alpha}{\partial x_j} = 0 \quad (\alpha=1,\ldots\nu) \ . \qquad (2.17)$$

<u>The conservation of linear momentum</u>.--The equation of balance of linear momentum of species α is postulated to be

$$\frac{d}{dt}\int_V \rho_\alpha v_i^\alpha dV = -\int_S (\rho_\alpha v_i^\alpha v_j^\alpha - S_{ij}^\alpha) dS_j + \int_V (\rho m_i^\alpha + \rho_\alpha b_i^\alpha) dV (\alpha=1,\ldots\nu) . \quad (2.18)$$

This is a special case of (2.5) with

$$\psi_\alpha = v_i^\alpha \ , \ f_j^\alpha = - S_{ij}^\alpha \ , \ \rho_\alpha \sigma_\alpha = \rho m_i^\alpha + \rho_\alpha b_i^\alpha \ . \qquad (2.19)$$

Equation (2.6) becomes

$$\frac{\partial \rho_\alpha v_i^\alpha}{\partial t} + \frac{\partial}{\partial x_j} (\rho_\alpha v_i^\alpha v_j^\alpha - S_{ij}^\alpha) = \rho m_i^\alpha + \rho_\alpha b_i^\alpha (\alpha=1,\ldots\nu) \qquad (2.20)$$

The source term here has been split into two parts. The external body force density $\rho_\alpha b_i^\alpha$ gives the part of the linear momentum source which would be calculated if the fluid consisted of only component α. The remainder, ρm_i^α, represents a force density due to interaction of component α with the other components. S_{ij}^α is the partial stress tensor of component α.

Clearly the total linear momentum should not be affected by internal interactions; thus,

$$\sum_{\alpha} m_i^{\alpha} = 0 \ . \tag{2.21}$$

Summation of (2.20) over all species yields by use of

$$\sum_{\alpha} \rho_{\alpha} u_i^{\alpha} = 0 \tag{2.22}$$

and (2.21) the following equation expressing the balance of total linear momentum:

$$\rho \frac{dv_i}{dt} - \frac{\partial}{\partial x_j}\left(\sum_{\alpha} S_{ij}^{\alpha} - \sum_{\alpha} \rho_{\alpha} u_i^{\alpha} u_j^{\alpha}\right) = \sum_{\alpha} \rho_{\alpha} b_i^{\alpha} \ . \tag{2.23}$$

The quantity in brackets corresponds to the total stress tensor for the fluid as a whole:

$$T_{ij} = \sum_{\alpha} (S_{ij}^{\alpha} - \rho u_i^{\alpha} u_j^{\alpha}) \ . \tag{2.24}$$

The conservation of moment of momentum.--The results needed here are completely embodied in Truesdell's (1960, p. 546) derivation of Cauchy's second law of motion, expressed by

> When there are no assigned couples and no couple-stresses, a necessary and sufficient condition for the balance of moment of momentum in a body where linear momentum is balanced is

$$T_{ij} = T_{ji} \ ; \tag{2.25}$$

> i.e., the stress tensor is symmetric.

Hence from (2.24) one concludes that the sum of partial stresses is also symmetric, although the partial stresses themselves need not be.

The conservation of total energy.--The balance equation of total energy is postulated to be

$$\frac{d}{dt} \int_V \rho E_T dV = - \int_S (q_u - v_i T_{ij} + E_T v_j) dS_j + \int_V (\rho r + \sum_\alpha \rho_\alpha v_i^\alpha b_i^\alpha) dV, \quad (2.26)$$

where E_T is the total energy density, q_j is the heat flux vector, and r is the heat supply density. Equation (2.6) becomes

$$\rho \frac{dE_T}{dt} + \frac{\partial}{\partial x_j} (q_j - v_i T_{ij}) = \rho r + \sum_\alpha \rho_\alpha v_i^\alpha b_i^\alpha . \quad (2.27)$$

The internal energy is defined as the difference between the total and kinetic energy:

$$E_I = E_T - \frac{1}{2\rho} \sum_\alpha \rho_\alpha v_i^\alpha v_i^\alpha . \quad (2.28)$$

A balance equation for the kinetic energy is obtained by using equations (2.15), (2.20), (2.22) and (2.16):

$$\rho \frac{d}{dt} \left(\frac{1}{2\rho} \sum_\alpha \rho_\alpha v_i^\alpha v_i^\alpha\right) = \frac{\partial}{\partial x_j} \left[\sum_\alpha v_i^\alpha (S_{ij}^\alpha - \rho_\alpha u_i^\alpha u_j^\alpha) + \frac{1}{2} \sum_\alpha \rho_\alpha u_i^\alpha u_i^\alpha u_j^\alpha\right] - \sum_\alpha S_{ij}^\alpha \frac{\partial v_i^\alpha}{\partial x_j} + \rho \sum_\alpha m_i^\alpha u_i^\alpha + \sum_\alpha \rho_\alpha v_i^\alpha b_i^\alpha \quad (2.29)$$

Subtraction of (2.29) from (2.27) with the use of (2.28) yields a balance equation for the internal energy:

$$\rho \frac{dE_I}{dt} + \frac{\partial h_i}{\partial x_j} = \rho r - \rho \sum_{\alpha} m_i^{\alpha} u_i^{\alpha} + \sum_{\alpha} S_{ij}^{\alpha} \frac{\partial v_i^{\alpha}}{\partial x_j} , \tag{2.30}$$

where a new heat flux vector has been defined,

$$h_j = q_j + \sum_{\alpha} u_i^{\alpha} \left(S_{ij}^{\alpha} - \rho_{\alpha} u_i^{\alpha} u_j^{\alpha}\right) + \frac{1}{2} \sum \rho_{\alpha} u_i^{\alpha} u_i^{\alpha} u_j^{\alpha} . \tag{2.31}$$

3. The Clausius-Duhem Inequality

The mathematical statement of the second law of thermodynamics takes the form of the Clausius-Duhem inequality or the entropy inequality. The form of the inequality used by Coleman and Noll for single materials is not sufficiently general. Even the various entropy inequalities proposed in works of TIP include an influx of entropy different from that for single materials. Perhaps some of the shortcomings of the earlier theories of Green and Naghdi, Ingram and Eringen, and Bowen are due to their particular choices for the form of the entropy production. Müller (1967, 1968), in fact, showed that the form of the entropy production could be derived explicitly within the domains of the principles set forth by Coleman and Noll.

According to the remarks made in the previous section any quantity can be balanced. Thus, the balance of entropy will be postulated to be

$$\frac{d}{dt}\int_V \rho\eta dV = -\int_S (\Phi_j+\rho\eta v_j)dS_j + \int_V \left(\rho\gamma+\rho\frac{r}{\theta}\right)dV \ , \quad (3.1)$$

where $\rho\eta$ is the entropy density, θ is the temperature, γ is the entropy production due to dissipative effects in V, and Φ_j is the entropy flux through the surface. The main point in this formulation is that, in contrast to all previous work, the entropy flux is not to be specified in advance. The entropy flux, Φ_j, is to be regarded as a quantity for which a constitutive relation has to be formulated, just as is usually done with the heat flux and the stress tensor.

From (3.1) and (2.4), the result corresponding to (2.6) is

$$\rho\frac{d\eta}{dt} = -\frac{\partial}{\partial x_j}\Phi_j + \rho\gamma + \rho\frac{r}{\theta} \ . \quad (3.2)$$

The second law of thermodynamics is made mathematically precise by the following postulate:

$$\gamma \geqslant 0 \ . \quad (3.3)$$

This postulate places restrictions on constitutive equations of the type to be introduced in the next section.

It will be convenient for examining these restrictions to write the entropy production, γ, in detail using the following definitions and substitutions:

The (Helmholtz) free energy is defined by

$$\psi_I = E_I - \theta\eta \ . \qquad (3.4)$$

The difference between the entropy flux for mixtures and that normally used for single materials (viz., the heat flux divided by temperature) is defined by

$$k_j = \Phi_j - \frac{h_j}{\theta} \ . \qquad (3.5)$$

Substitution of (3.4) and (3.5) into (3.2) yields, upon rearrangement,

$$\rho\theta\gamma = \rho \frac{dE_I}{dt} + \frac{\partial h_j}{\partial x_j} - \rho r - \rho \frac{d\psi_I}{dt} - \rho\eta \frac{d\theta}{dt} + \theta \frac{\partial k_j}{\partial x_j} - \frac{h_j}{\theta} \frac{\partial\theta}{\partial x_j} \ . \qquad (3.6)$$

The equation of balance of internal energy (2.30) is inserted into (3.6) to give

$$\rho\theta\gamma = - \rho \frac{d\psi_I}{dt} - \rho\eta\frac{d\theta}{dt} + \theta\frac{\partial k_j}{\partial x_j} - \frac{h_j}{\theta} \frac{\partial\theta}{\partial x_j} - \rho\sum_\alpha m_j^\alpha u_j^\alpha + \sum_\alpha S_{ij}^\alpha \frac{\partial v_i^\alpha}{\partial x_j} \ . \qquad (3.7)$$

The partial stresses can now be decomposed into symmetric and antisymmetric tensors according to

$$S_{ij}^\alpha = t_{ij}^\alpha + \tau_{ij}^\alpha \qquad (3.8)$$

$$t_{ij}^\alpha = \frac{1}{2} (S_{ij}^\alpha + S_{ji}^\alpha) \qquad (3.9)$$

$$\tau^{\alpha}_{ij} = \frac{1}{2} (s^{\alpha}_{ij} - s^{\alpha}_{ji}) \ , \tag{3.10}$$

which allows (3.7) to be written

$$\begin{aligned} \rho\theta\gamma = &- \rho \frac{d\psi_I}{dt} - \rho\eta \frac{d\theta}{dt} + \theta \frac{\partial k_j}{\partial x_j} - \frac{h_j}{\theta} \frac{\partial\theta}{\partial x_j} - \rho \sum_{\alpha} m^{\alpha}_j u^{\alpha}_j \\ &+ \sum t^{\alpha}_{ij} d^{\alpha}_{ij} + \sum_{\alpha} \tau^{\alpha}_{ij} \omega^{\alpha}_{ij} \ . \end{aligned} \tag{3.11}$$

In (3.11) the two quantities

$$d^{\alpha}_{ij} = \frac{1}{2} \left(\frac{\partial v^{\alpha}_i}{\partial x_j} + \frac{\partial v^{\alpha}_j}{\partial x_i} \right) \tag{3.12}$$

and

$$\omega^{\alpha}_{ij} = \frac{1}{2} \left(\frac{\partial u^{\alpha}_i}{\partial x_j} - \frac{\partial u^{\alpha}_j}{\partial x_i} \right) + \frac{1}{2\rho} \sum_{\beta} \left(u^{\beta}_i \frac{\partial \rho_{\beta}}{\partial x_j} - u^{\beta}_j \frac{\partial \rho_{\beta}}{\partial x_i} \right) \tag{3.13}$$

have been introduced with the help of the relation

$$\sum_{\alpha} \tau^{\alpha}_{ij} = 0 \ , \tag{3.14}$$

which is a result of the symmetry of the total stress tensor.

Equation (3.11) now gives the entropy production in a convenient form for use in the entropy inequality (3.3).

4. Thermodynamic Processes

By a generalization of the definition of Coleman and Noll (1963), a thermodynamic process for a mixture is defined as follows:

A process is a thermodynamic process if it can be described by a set of $(5\nu + 6)$ functions

$$\begin{array}{lll} \rho_\alpha = \rho_\alpha\,(x_i,t) & S^\alpha_{ij} = S^\alpha_{ij}\,(x_i,t) & h_i = h_i\,(x_i,t) \\ v^\alpha_i = v^\alpha_i\,(x_i,t) & E_I = E_I\,(x_i,t) & \eta = \eta\,(x_i,t) \\ m^\alpha_i = m^\alpha_i\,(x_i,t) & \theta = \theta\,(x_i,t) & \Phi_i = \Phi_i\,(x_i,t) \\ b^\alpha_i = b^\alpha_i\,(x_i,t) & r = r\,(x_i,t) & \end{array} \tag{4.1}$$

for each α, $\alpha=1,\dots\nu$, which satisfy

a) the balance of mass for each component

$$\frac{\partial \rho_\alpha}{\partial t} + \frac{\partial}{\partial x_j}(\rho_\alpha v^\alpha_j) = 0 \qquad (\alpha=1,\dots\nu) \tag{2.15}$$

b) the balance of linear momentum for each component

$$\frac{\partial \rho_\alpha v^\alpha_i}{\partial t} + \frac{\partial}{\partial x_j}(\rho_\alpha v^\alpha_i v^\alpha_j - S^\alpha_{ij}) = \rho m^\alpha_i + \rho_\alpha b^\alpha_i \quad (\alpha=1,\dots\nu) \tag{2.20}$$

c) the balance of angular momentum for the mixture

$$\sum_\alpha \tau^\alpha_{ij} = 0 \tag{3.14}$$

d) the balance of energy for the mixture

$$\rho \frac{dE_I}{dt} + \frac{\partial h_j}{\partial x_j} = \rho r - \rho \sum_{\alpha} m_i^{\alpha} u_i^{\alpha} \quad \sum_{\alpha} S_{ij}^{\alpha} \frac{\partial v_i^{\alpha}}{\partial v_j} \qquad (2.30)$$

for all x_i and t. To specify a thermodynamic process it suffices to prescribe the $(4\nu + 5)$ functions $\rho_\alpha, v_i^\alpha, m_i^\alpha, S_{ij}^\alpha$, $E_I, \theta, h_i, \eta, \Phi_i$. The remaining $(\nu + 1)$ functions b_i^α and r are then determined from equations (2.20) and (2.30).

In the above definition no reference was made to the entropy inequality (3.3). Its part in the development will become clear in section 6.

5. Constitutive Assumptions for a Fluid Mixture

To illustrate the implications of the theory proposed in sections 2, 3, and 4, it is useful to consider a special mixture, namely, a mixture of elastic materials susceptible of diffusion and heat conduction. This case is sufficiently generaly to illustrate the important features of the theory, and it is important since it includes by further specialization the thermodynamic theory of single materials and the theory of TIP for mixtures with diffusion and heat conduction.

The equations of balance and the entropy inequality suggest that constitutive equations should be prescribed for $\psi_I, \eta, h_i, k_i, t_{ij}^\alpha, \tau_{ij}^\alpha, m_i^\alpha$ for each $\alpha, (\alpha=1,\ldots\nu)$. It is assumed that the history of the motions of the components and the history of the temperature within the body considered determine these quantities as functions of x_i and t. The functional relations that connect these functions with the histories of motion and temperature are called constitutive equations; their form characterizes a material.

If, in particular, the constitutive functionals reduce to ordinary function of

$$\rho_\beta\, , \frac{\partial \rho_\beta}{\partial x_j}\, , \theta\, , \frac{\partial \theta}{\partial x_j}\, , u_i^\beta\, , d_{ij}^\beta\, , \omega_{ij}^\beta \tag{5.1}$$

then for the purposes of this chapter, the material will be called a mixture of fluids.

The constitutive relations are then

$$\psi_I = \psi_I \quad (\rho_\beta, f_i^\beta, \, , g_i, u_i^\gamma, d_{ij}^\beta, \omega_{ij}^\gamma) \tag{5.2}$$

$$\eta = \eta \quad (\rho_\beta, f_i^\beta, \theta, g_i, u_i^\gamma, d_{ij}^\beta, \omega_{ij}^\gamma) \tag{5.3}$$

$$k_j = k_j \quad (\rho_\beta, f_i^\beta, \theta, g_i, u_i^\gamma, d_{ij}^\beta, \omega_{ij}^\gamma) \tag{5.4}$$

$$t_{ij}^\alpha = t_{ij}^\alpha \quad (\rho_\beta, f_i^\beta, \theta, g_i, u_i^\gamma, d_{ij}^\beta, \omega_{ij}^\gamma) \quad (\alpha=1,\ldots\nu) \tag{5.5}$$

$$\tau_{ij}^\alpha = \tau_{ij}^\alpha \quad (\rho_\beta, f_i^\beta, \theta, g_i, u_i^\gamma, d_{ij}^\beta, \omega_{ij}^\gamma) \quad (\alpha=1,\ldots\nu-1) \tag{5.6}$$

$$m_i^\alpha = m_i^\alpha \quad (\rho_\beta, f_i^\beta, \theta, g_i, u_i^\gamma, d_{ij}^\beta, \omega_{ij}^\gamma) \quad (\alpha=1,\ldots\nu-1) \tag{5.7}$$

$$q_i = q_i \quad (\rho_\beta, f_i^\beta, \theta, g_i, u_i^\gamma, d_{ij}^\beta, \omega_{ij}^\gamma) \tag{5.8}$$

where

$$f_j = \frac{\partial \rho_\beta}{\partial x_j}\quad , \quad g_j = \frac{\partial \theta}{\partial x_j}$$

and

$$\beta = 1,\ldots\nu \quad , \quad \gamma = 1,\ldots\nu-1$$

These constitutive equations satisfy the principle of equipresence, according to which the same independent variables should appear in all constitutive equations unless their presence contradicts the entropy inequality (3.3) or the assumed symmetry of the material. It should also be noted that the functions (5.2)-(5.8) depend only on objective combinations of the velocities and velocity gradients. This choice was made because the principle of material objectivity (Noll, 1958) restricts any description of a material property of a material to one which does not depend on the frame of reference of the observer, no matter how he moves.

An admissible thermodynamic process is defined as a thermodynamic process that is compatible with the constitutive relations (5.2)-(5.8). To every choice of the component densities ρ_α, component velocities v_i^α, and temperature θ consistent with the equations of balance of mass of the components (2.15) and with $\theta > 0$, there corresponds a unique admissible thermodynamic process. For when ρ_α, v_i^α and θ are known for all x_i and t, then clearly $f_i^\alpha, g_i, u_i^\alpha, d_{ij}^\alpha$, and w_{ij}^α are determined. The constitutive equations then determine $\psi_I, \eta, k_i, q_i, m_i^\alpha, t_{ij}^\alpha$, and τ_{ij}^α. Once these fields are known, then b_i^α and r are determined by the balance equations.

Thus, at a given time t, it is possible to specify arbitrarily not only ρ_α, v_i^α, and θ (subject to (2.15) and

$\theta > 0$) but also the derivatives $\frac{d\theta}{dt}$, $\frac{dg_\ell}{dt}$, $\frac{du_i^\alpha}{dt}$, $\frac{dd_{ij}^\alpha}{dt}$, $\frac{dw_{ij}}{dt}$, and $\frac{\partial g_i}{\partial x_\ell}$ at a point x_i and to be sure that there exists at least one admissible thermodynamic process corresponding to this choice.[1] It is not necessarily true, however, that for this choice the entropy inequality will be satisfied. Extending the idea of Coleman and Noll (1963), it will be required here that the entropy inequality (3.3) be satisfied for all admissible thermodynamic processes. In other words, the constitutive functions are subjected to the requirement that the entropy production be non-negative, identically in the independent variables. The next section will be concerned with deriving necessary and sufficient conditions that the constitutive functions must obey in order that the entropy inequality be satisfied for all admissible processes.

6. Consequences of the Entropy Inequality

According to the discussion in the previous section, it is necessary to find the restrictions imposed on the constitutive relations by the entropy inequality. The non-negativity requirement is most easily applied if the entropy inequality is written in terms of the independent quantities discussed in the previous section. From the assumed smoothness of ρ_α, v_i^α, and θ, it follows that

---

[1] It should be noted that $\frac{d\rho_\alpha}{dt}$ and $\frac{df_i^\alpha}{dt}$ are not independent because of the relations (2.15). This fact will be used explicitly in the next section.

$$- \rho \frac{d\psi_I}{dt} = - \sum_\alpha \rho \left(\frac{\partial\psi_I}{\partial\rho_\alpha}\right) \frac{d\rho_\alpha}{dt} - \sum_\alpha \rho \left(\frac{\partial\psi_I}{\partial f_i^\alpha}\right) \frac{df_i^\alpha}{dt}$$

$$- \rho \left(\frac{\partial\psi_I}{\partial\theta}\right) \frac{d\theta}{dt} - \rho \left(\frac{\partial\psi_I}{\partial g_i}\right) \frac{dg_i}{dt} - \sum_\alpha{}' \rho \left(\frac{\partial\psi_I}{\partial u_i^\alpha}\right) \frac{du_i^\alpha}{dt}$$

$$- \sum_\alpha \rho \left(\frac{\partial\psi_I}{\partial d_{ij}^\alpha}\right) \frac{dd_{ij}^\alpha}{dt} - \sum_\alpha{}' \rho \left(\frac{\partial\psi_I}{\partial\omega_{ij}^\alpha}\right) \frac{d\omega_{ij}^\alpha}{dt} \tag{6.1}$$

and

$$\theta \frac{\partial k_\ell}{\partial x_\ell} = \sum_\alpha \theta \left(\frac{\partial k_\ell}{\partial\rho_\alpha}\right) f_\ell^\alpha + \sum_\alpha \theta \left(\frac{\partial k_\ell}{\partial f_i^\alpha}\right) f_{i\ell}^\alpha + \theta \left(\frac{\partial k_\ell}{\partial\theta}\right) g_\ell$$

$$+ \theta \left(\frac{\partial k_\ell}{\partial g_i}\right) g_{i\ell} + \sum_\alpha{}' \theta \left(\frac{\partial k_\ell}{\partial u_i^\alpha}\right) \frac{\partial u_i^\alpha}{\partial x_\ell}$$

$$+ \sum_\alpha \theta \left(\frac{\partial k_\ell}{\partial d_{ij}^\alpha}\right) \frac{\partial d_{ij}^\alpha}{\partial x_\ell} + \sum_\alpha{}' \theta \left(\frac{\partial k_\ell}{\partial\omega_{ij}^\alpha}\right) \frac{\partial\omega_{ij}^\alpha}{\partial x_\ell} \tag{6.2}$$

where for convenience

$$f_{i\ell}^\alpha = \frac{\partial^2\rho_\alpha}{\partial x_i \partial x_\ell} \tag{6.3}$$

$$g_{i\ell} = \frac{\partial^2\theta}{\partial x_i \partial x_\ell} \tag{6.4}$$

$$\sum_\alpha{}' = \sum_{\alpha=1}^{\nu-1} \tag{6.5}$$

If now the first and third terms of (3.11) are replaced by (6.1) and (6.2) respectively, and terms containing the same independent quantities are collected, then

$$\begin{aligned}\rho\theta\gamma = &-\rho\left[\eta+\left(\frac{\partial\psi_I}{\partial\theta}\right)\right]\frac{d\theta}{dt}-\rho\left(\frac{\partial\psi_I}{\partial g_i}\right)\frac{dg_i}{dt}-\sum_\alpha{}'\rho\left(\frac{\partial\psi_I}{\partial u_i^\alpha}\right)\frac{du_i^\alpha}{dt}\\ &-\sum_\alpha\rho\left(\frac{\partial\psi_I}{\partial d_{ij}^\alpha}\right)\frac{dd_{ij}^\alpha}{dt}-\sum_\alpha{}'\rho\left(\frac{\partial\psi_I}{\partial\omega_{ij}^\alpha}\right)\frac{d\omega_{ij}^\alpha}{dt}+\theta\left(\frac{\partial k_\ell}{\partial g_i}\right)g_{i\ell}+\rho\theta\gamma_{red},\end{aligned}\tag{6.6}$$

where

$$\begin{aligned}\rho\theta\gamma_{red} = &-\sum_\alpha\rho\left(\frac{\partial\psi_I}{\partial\rho_\alpha}\right)\frac{d\rho_\alpha}{dt}-\sum_\alpha\rho\left(\frac{\partial\psi_I}{\partial f_i^\alpha}\right)+\left[\theta\left(\frac{\partial k_\ell}{\partial\theta}\right)-\frac{h_\ell}{\theta}\right]g_\ell\\ &+\sum_\alpha\theta\left(\frac{\partial k_\ell}{\partial\rho_\alpha}\right)f_\ell^\alpha+\sum_\alpha\theta\left(\frac{\partial k_\ell}{\partial f_i^\alpha}\right)f_{i\ell}^\alpha+\sum_\alpha{}'\theta\left(\frac{\partial k_\ell}{\partial u_i^\alpha}\right)\frac{\partial u_i^\alpha}{\partial x_\ell}\\ &+\sum_\alpha\theta\left(\frac{\partial k_\ell}{\partial d_{ij}^\alpha}\right)\frac{\partial d_{ij}^\alpha}{\partial x_\ell}+\sum_\alpha{}'\theta\left(\frac{\partial k_\ell}{\partial\omega_{ij}^\alpha}\right)\frac{\partial\omega_{ij}^\alpha}{\partial x_\ell}\\ &-\rho\sum_\alpha m_i^\alpha u_i^\alpha+\sum_\alpha t_{ij}^\alpha d_{ij}^\alpha+\sum_\alpha\tau_{ij}^\alpha\omega_{ij}^\alpha\end{aligned}\tag{6.7}$$

Since each of the quantities

$$\frac{d\theta}{dt},\ \frac{dg_i}{dt},\ \frac{du_i^\alpha}{dt},\ \frac{dd_{ij}^\alpha}{dt},\ \frac{d\omega_{ij}^\alpha}{dt},\ g_{i\ell}\tag{6.8}$$

can be chosen arbitrarily and independently of any other term in the inequality, the last with due respect to its symmetry, the argument given at the end of the last section implies that the necessary conditions for non-negative entropy production are:

$$\rho\theta\gamma = \rho\theta\gamma_{red} \geq 0\tag{6.9}$$

$$\eta = -\left(\frac{\partial \psi_I}{\partial \theta}\right) \tag{6.10}$$

$$\left(\frac{\partial \psi_I}{\partial g_i}\right) = 0 \tag{6.11}$$

$$\left(\frac{\partial \psi_I}{\partial u_i^\alpha}\right) = 0 \tag{6.12}$$

$$\left(\frac{\partial \psi_I}{\partial d_{ij}^\alpha}\right) = 0 \tag{6.13}$$

$$\left(\frac{\partial \psi_I}{\partial \omega_{ij}^\alpha}\right) = 0 \tag{6.14}$$

$$\left(\frac{\partial k_\ell}{\partial g_i}\right) + \left(\frac{\partial k_i}{\partial g_\ell}\right) = 0 \ . \tag{6.15}$$

The inequality (6.9) can be further reduced, but the results will not be needed until section 7.

Equation (6.10) is a well-known result of thermostatics, and its presence here means that it is also valid in non-equilibrium thermodynamics for a fluid mixture.

Equations (6.11)-(6.14) imply that the functional dependence of ψ_I may be written as

$$\psi_I = \tilde{\psi}_I(\rho_\alpha, \theta, f_i^\alpha) \qquad \alpha=1,\ldots\nu \tag{6.16}$$

In the next section, in which a linear theory is introduced, the free energy depends only on ρ_α and θ. This together with some results established by reference to the equilibrium state, yet to be defined, delineates precisely the domains of validity of the theory of nonequilibrium thermodynamics derived from the assumption of local equilibrium.

7. Ordinary Binary Fluid Mixtures (The Linear Theory)

Up to this point mixtures of ν components have been considered. However, subsequent formulas would be even longer and more complicated than they are anyway if more than two components were considered. Since there is no conceptual difficulty in extending the theory to a mixture of any finite number of components, the treatment will be restricted, without loss of generality, to binary systems.

The development of the theory is further restricted in this section to the special case of mixtures whose constitutive relations are linear in the variables

$$\frac{\partial \rho_1}{\partial x_\ell}\ ,\ \frac{\partial \rho_2}{\partial x_\ell}\ ,\ \frac{\partial \theta}{\partial x_\ell}\ ,\ u_\ell^1\ ,\ d_{ij}^1\ ,\ d_{ij}^2\ ,\ \omega_{ij}^1 \tag{7.1}$$

This special material will be called an ordinary binary fluid mixture. That such a material is special is obvious from the restrictions placed on the constitutive relations. A conviction that this material accurately represents the binary fluid mixtures commonly encountered by the chemist in his laboratory is the reason for the label "ordinary." The appropriateness of this label can only be determined by testing the ability of the constitutive relations to represent accurately the experimentally measured responses of the material to variations of the independent variables. It should be mentioned, however, that under special conditions, according to which it is possible to neglect the effects of the so called inertial and viscous terms in the equations of motion, the ordinary binary fluid mixture is precisely the same material that TIP claims to describe. This correspondence will be made explicit at the end of this section.

Material objectivity and linear representation theorems.--So far the principle of material objectivity has not been used to its full extent; material objectivity has been used only in the selection of independent variables. A further consequence of the principle of material objectivity is that the constitutive functions must be isotropic scalar, vector, or tensor functions. Representation theorems have been worked out for these isotropic functions (see Truesdell and Noll (1965) and Smith (1965)). These theorems will not be needed here in their full generality, but for the case of functions linear in the variables (7.1) the following relations must hold for scalars s, vectors w_i, and tensors t_{ij}:

$$s\,(\rho_\beta, f_i^\beta, \theta, g_i, u_i^1, d_{ij}^\beta, \omega_{ij}^1) = s(\rho_\beta, \theta) \qquad \beta = 1,2$$

$$w_i\,(\rho_\beta, f_\ell^\beta, \theta, g_\ell, u_\ell^1, d_{\ell j}^\beta, \omega_{\ell j}^1) = w_T g_i + \sum_{\beta=1}^{2} w_{\rho\beta} f_\ell^\beta + W_D u_i^1$$

$$t_{ij}^s\,(\rho_\beta, f_\ell^\beta, \theta, g_\ell, u_\ell^1, d_{\ell j}^\beta, \omega_{\ell j}^1) = -\,p\delta_{ij} + \sum_{\beta=1}^{2} \phi^\beta d_{nn}^\beta \delta_{ij} + \sum_{\beta=1}^{2} 2\eta^\beta \,\{d_{ij}^\beta\}$$

$$t_{ij}^a\,(\rho_\beta, f_\ell^\beta, \theta, g_\ell, u_\ell^1, d_{\ell j}^\beta, \omega_{\ell j}^1) = -\,\mu\omega_{ij}^1 \qquad (7.2)$$

The superscripts s and a on t_{ij} indicate the symmetric and antisymmetric parts of t_{ij} respectively. The coefficients w_T, $w_{\rho\beta}$, w_D, p, ϕ, η, and μ may depend on ρ_α and θ; $\{d_{ij}^\beta\}$ is the traceless part of d_{ij}^β.

The functional relations given in (7.2) are usually obtained in TIP by application of Curie's theorem: entities whose tensorial characters differ by an odd integer cannot interact in isotropic systems.[1] Interactions between quantities of different tensorial orders are well known in the kinetic theory of gases. The separation of effects described by the writers on TIP are simply those that follow by linearization of isotropic functions

---

[1] This theorem has been attributed to P. Curie (1894), although apparently he neither stated it in this form nor proved it.

and should be considered only within the context of the linear theory.

Constitutive relations in the linear theory.--In section 6 some general restrictive conditions on the constitutive relations (5.2)-(5.8) were obtained. These results are summarized in equations (6.9)-(6.15), and they will be applied now to the most general possible linear constitutive equations.

According to the representation theorems (7.2) the free energy in the linear theory does not depend on density gradients and thus for an ordinary binary fluid mixture

$$\psi_I = \psi_I\ (\rho_1, \rho_2, \theta) \tag{7.3}$$

Here, use of (6.11)-(6.14) has been made in leaving out the dependence on ψ_I on f_i^α, g_i, u_ℓ^α, d_{ij}^α, and ω_{ij}^α. This means that for an ordinary fluid the free energy has the same functional dependence as that assumed in TIP on the basis of the assumption of local equilibrium.

According to (7.2), the heat flux h_i in the linear theory must be a linear function of the vectorial quantities in (7.1). Hence

$$h_i = -\lambda_T g_i - C_1 f_i^1 - C_2 f_i^2 - Q u_j^1 \tag{7.4}$$

where the coefficients may depend on ρ_1, ρ_2, and θ.

Similarly, m_i^1 in the linear theory is given by

$$m_i^1 = - m_0 g_i - m_1 f_i^1 - m_2 f_i^2 - m_D u_i^1 , \tag{7.5}$$

where again the coefficients may depend on ρ_1, ρ_2, and θ.

A linear constitutive relation must also be formulated for the vectorial quantity k_j; hence, from (7.2) and the restriction (6.15) already found for k_i, the form

$$k_i = + K u_i^1 - \ell_1 f_i^1 - \ell_2 f_i^2 \tag{7.6}$$

is expected. However, by further rearrangement of the reduced entropy inequality (this possibility was mentioned previously) it will be shown later that k_i must be independent of density gradients also.

Again from (7.2) it follows that the antisymmetric tensor τ_{ij}^1 is proportional to ω_{ij}^1:

$$\tau_{ij}^1 = - \mu \omega_{ij}^1 \tag{7.7}$$

where μ may depend on ρ_1, ρ_2, and θ.

The symmetric tensor t_{ij}^α is given, according to (7.2), by

$$t_{ij}^\alpha = - p^\alpha \delta_{ij} + \sum_{\beta=1}^{2} \phi^{\alpha\beta} d_{nn}^\beta \delta_{ij} + \sum_{\beta=1}^{2} 2\eta^{\alpha\beta} \{d_{ij}^\beta\} \quad (\alpha=1,2) \tag{7.8}$$

Here again the coefficients p^{α}, $\phi^{\alpha\beta}$, and $\eta^{\alpha\beta}$ are in general functions of ρ_1, ρ_2, and θ; $\{d^{\alpha}_{ij}\}$ is the traceless part of d^{α}_{ij}.

Restrictions Imposed on the Linear Constitutive Relations by the Entropy Inequality.--In order that the entropy inequality be written in terms of independent quantities, the equations of balance of mass are introduced into the reduced entropy inequality in the form

$$\frac{d\rho_{\alpha}}{dt} = - u^{\alpha}_{i} f^{\alpha}_{i} - \rho_{\alpha} d^{\alpha}_{ij} \delta_{ij} \tag{7.9}$$

At the same time several of the derivatives which are zero for the linear case are eliminated and terms involving the same independent quantities are collected. The resulting entropy inequality is from (6.7)

$$\begin{aligned}
\rho\theta\gamma_{\text{red}} = {} & \rho\left(\frac{1}{\rho_1}\left(\frac{\partial\psi_I}{\partial\rho_1}\right) f^{1}_{i} - \frac{1}{\rho_2}\left(\frac{\partial\psi_I}{\partial\rho_2}\right) f^{2}_{i}\right)\rho_1 u^{1}_{i} + \left(\theta\left(\frac{\partial k_{\ell}}{\partial\theta}\right) - \frac{h_{\ell}}{\theta}\right) g_{\ell} \\
& + \sum_{\alpha} \theta \left(\frac{\partial k_{\ell}}{\partial \rho_{\alpha}}\right) f^{\alpha}_{\ell} + \sum_{\alpha} \theta \left(\frac{\partial k_{\ell}}{\partial f^{\alpha}_{i}}\right) f^{\alpha}_{i_{\ell}} - \rho\left(\frac{1}{\rho_1} m^{1}_{i} + \frac{1}{\rho_2} m^{1}_{i}\right)\rho_1 u^{1}_{i} \\
& + \theta\left(\frac{\partial k_j}{\partial u^{1}_{i}}\right)\omega^{1}_{ij} + \theta\left(\frac{\partial k_j}{\partial u^{1}_{i}}\right) d^{1}_{ij} + \sum_{\alpha}\rho\left(\frac{\partial\psi_I}{\partial\rho_{\alpha}}\right)\rho_{\alpha} d^{\alpha}_{ij}\delta_{ij} \\
& - \sum_{\alpha} \frac{\theta\rho_{\alpha}}{\rho}\left(\frac{\partial k_j}{\partial u^{1}_{i}}\right) d^{\alpha}_{ij} - \frac{\theta}{\rho}\left(\frac{\partial k_{\ell}}{\partial u^{1}_{i}}\right)\left(\frac{1}{\rho_1} f^{1}_{i} - \frac{1}{\rho_2} f^{2}_{i}\right)\rho_1 u^{1}_{i} \\
& + \sum_{\alpha} t^{\alpha}_{ij} d^{\alpha}_{ij} + \left(\frac{1}{\rho_1}\tau^{1}_{ij} + \frac{1}{\rho_2}\tau^{1}_{ij}\right)\rho_1\omega^{1}_{ij} \geqslant 0
\end{aligned} \tag{7.10}$$

where the identity

$$\frac{\partial u_i^\alpha}{\partial x_\ell} = \omega_{i\ell}^\alpha + d_{i\ell}^\alpha - \frac{1}{\rho}\sum_\beta \rho_\beta d_{i_\ell}^\beta - \frac{1}{\rho}\sum_\beta u_i^\beta f_\ell^\beta \tag{7.11}$$

has been used.

The quantities $f_{i\ell}^\alpha$ are independent of all other terms in the inequality (taking proper account of their symmetry) and in the same manner as in section 6 the following restriction is needed:

$$\left(\frac{\partial k_\ell}{\partial f_i^\alpha}\right) + \left(\frac{k_i}{\partial f_\ell^\alpha}\right) = 0 \tag{7.12}$$

This implies that ℓ_1 and ℓ_2 are both zero and thus the most general possible linear constitutive relation for k_i is

$$k_i = Ku_i^1 \tag{7.13}$$

Equilibrium properties.--Further conclusions may be drawn from the inequality (7.10) without assuming more particular constitutive equations. These conclusions refer to the equilibrium state, and they establish a consistency between this theory and thermostatics.

The material is said to be in equilibrium if the independent variables

$$X_A = (g_i, d_{ij}^1, d_{ij}^2, \omega_{ij}^1, u_j^1) \quad A=1,\ldots 21 \tag{7.14}$$

are all zero. In order to write the entropy inequality completely in terms of these quantities the linear relations are inserted into (7.10) to yield

$$
\begin{aligned}
\rho\theta\gamma_{red} = {} & \frac{\lambda_T}{\theta}\, g_\ell g_\ell + \frac{C_1}{\theta}\, g_\ell f^1_\ell + \frac{C_2}{\theta}\, g_\ell f^2_\ell + \rho\left(\frac{1}{\rho_1} + \frac{1}{\rho_2}\right) m_D \rho_1 u^1_\ell u^1_\ell \\
& + \left[\frac{\theta}{\rho_1}\left(\frac{\partial K}{\partial \theta}\right) + \frac{Q}{\rho_1 \theta} + \rho\left(\frac{1}{\rho_1} + \frac{1}{\rho_2}\right) m_0\right] \rho_1 u^1_\ell g_\ell \\
& + \left[\frac{\rho}{\rho_1}\left(\frac{\partial \psi_I}{\partial \rho_1}\right) + \frac{\theta}{\rho_1}\left(\frac{\partial K}{\partial \rho_1}\right) + \rho\left(\frac{1}{\rho_1} + \frac{1}{\rho_2}\right) m_1 - \frac{\theta K}{\rho \rho_1}\right] \rho_1 u^1_\ell f^1_\ell \\
& + \left[-\frac{\rho}{\rho_2}\left(\frac{\partial \psi_I}{\partial \rho_2}\right) + \frac{\theta}{\rho_1}\left(\frac{\partial K}{\partial \rho_2}\right) + \rho\left(\frac{1}{\rho_1} + \frac{1}{\rho_2}\right) m_2 + \frac{\theta K}{\rho \rho_2}\right] \rho_1 u^1_\ell f^2_\ell \\
& + \sum_\alpha \sum_\beta \phi^{\alpha\beta} d^\alpha_{\ell\ell} d^\beta_{nn} + \sum_\alpha \sum_\beta 2\eta^{\alpha\beta} \{d^\alpha_{ij}\}\{d^\beta_{ij}\} \\
& + \left(\frac{1}{\rho_1} + \frac{1}{\rho_2}\right) \frac{\mu}{\rho_1}\, \omega^1_{ij}\omega^1_{ij} + \left[\frac{\theta K \rho_2}{\rho} + \rho\rho_1\left(\frac{\partial \psi_I}{\partial \rho_1}\right) - p^1\right] d^1_{\ell\ell} \\
& + \left[\rho\rho_2\left(\frac{\partial \psi_I}{\partial \rho_2}\right) - \frac{\theta K \rho_2}{\rho} - p^2\right] d^2_{\ell\ell}
\end{aligned}
\qquad (7.15)
$$

The entropy production γ may thus be considered as a function of the variables (7.14), and from inspection of (7.15) it is seen that

$$\gamma\ (X_1, X_2, \ldots X_{21}) \geq 0 \qquad (7.16)$$

and

$$\gamma\ (0, 0, \ldots 0) = 0\ . \qquad (7.17)$$

Hence γ has a minimum value in equilibrium. A necessary condition for this is

$$\left(\frac{\partial\gamma}{\partial X_A}\right)_0 = 0 \tag{7.18}$$

where the subscript 0 indicates that the function to which it is attached is to be evaluated in equilibrium.

Application of (7.18) to (7.15) results in the following restrictions:

$$p^1 = \rho\rho_1\left(\frac{\partial\psi_I}{\partial\rho_1}\right) + \frac{\theta K\rho_2}{\rho} \tag{7.19}$$

$$p^2 = \rho\rho_2\left(\frac{\partial\psi_I}{\partial\rho_2}\right) - \frac{\theta K\rho_2}{\rho} \tag{7.20}$$

If the pressure is defined as

$$p = p^1 + p^2 \tag{7.21}$$

then from (7.19) and (7.20)

$$p = \rho \sum_\alpha \rho_\alpha \left(\frac{\partial\psi_I}{\partial\rho_\alpha}\right) \tag{7.22}$$

Eq. (7.22) is the usual definition of pressure in thermostatics, and thus provides another example of an equilibrium relation that carries over to nonequilibrium processes in an ordinary binary fluid mixture without need for local equilibrium assumptions.

If the chemical potential is defined as[1]

$$\mu_\alpha = \psi_I + \rho \left(\frac{\partial \psi_I}{\partial \rho_\alpha}\right) \tag{7.23}$$

then the relation

$$\sum_\alpha \rho_\alpha \mu_\alpha = \rho \psi_I + p \tag{7.24}$$

is easily obtained, from which the Gibbs-Duhem relation

$$\sum_\alpha \rho_\alpha \frac{\partial \mu_\alpha}{\partial x_i} = \frac{\partial p}{\partial x_i} - \rho \eta \frac{\partial \theta}{\partial x_i} \tag{7.25}$$

follows by use of (7.3).

The results of the theory given here for the ordinary binary fluid mixture are thus completely consistent with the thermostatic theory and all the formalism of the latter can be taken over for use in nonequilibrium situations.

There are still further consequences of non-negativeness for entropy production. If, for example, all variables in (7.14) are chosen to be zero except for ω^1_{ij}, then it is necessary that

$$\mu \geqslant 0 \tag{7.25}$$

In the same way, if all variables except d^α_{nn} are chosen to be zero then

---

[1] The symbol μ_α used here for the chemical potential should not be confused with the symbol μ used previously for the phenomeological coefficient for the antisymmetric part of the stress tensor in equation (7.7).

$$\phi^{11} \geqslant 0 \ , \quad \phi^{22} \geqslant 0 \ , \ \phi^{11}\phi^{22} - \frac{1}{4}\left(\phi^{12}+\phi^{21}\right) \geqslant 0 \qquad (7.26)$$

One also finds using the same technique

$$\eta^{11} \geqslant 0 \ , \ \eta^{22} \geqslant 0 \ , \ \eta^{11}\eta^{22} - \frac{1}{4}\left(\eta^{12}+\eta^{21}\right) \geqslant 0 \qquad (7.27)$$

If now the temperature gradient g_ℓ is chosen to be some arbitrary vector X_i, f^1_ℓ and f^2_ℓ are both chosen to be equal to some other arbitrary vector Y_i, and all other independent variables are taken to be zero, then it can be seen by completing the square that in order for the entropy production to remain non-negative for all choices of X_i and Y_i it is necessary that

$$\lambda_T \geqslant 0 \qquad (7.28)$$

and

$$C_1 + C_2 = 0 \qquad (7.29)$$

Furthermore, if the density gradient f^1_ℓ is chosen to be equal to some arbitrary vector X_i, g_ℓ and f^2_ℓ are both chosen to be equal to some other arbitrary vector Y_i, and all other independent variables are taken to be zero, then by completing the square, it is necessary that

$$C_1 = 0 \ . \qquad (7.30)$$

Eqs. (7.29) and (7.30) imply further

$$C_2 = 0 \ . \qquad (7.31)$$

Precisely the same technique used with the diffusive velocity u_ℓ^1, instead of the temperature gradient, and the two density gradients yields the three necessary conditions

$$\frac{\rho^2}{\rho_1\rho_2} m_1 + \frac{\theta}{\rho_1}\left(\frac{\partial K}{\partial \rho_1}\right) + \frac{1}{\rho_1^2}\, p^1 - \frac{\theta K}{\rho_1^2} = 0 \tag{7.32}$$

$$\frac{\rho^2}{\rho_1\rho_2} m_2 + \frac{\theta}{\rho_1}\left(\frac{\partial K}{\partial \rho_2}\right) - \frac{1}{\rho_2^2}\, p^2 = 0 \tag{7.33}$$

$$m_D \geqslant 0 \tag{7.34}$$

Finally if all the independent variables except for the temperature gradient g_ℓ and diffusive velocity u_ℓ^1 are taken to be zero, the non-negativeness of the entropy production requires

$$\frac{\rho^2 \lambda_T m_D}{\rho_2 \theta} - \frac{1}{4}\left(\theta\,\frac{\partial K}{\partial \theta} + \frac{Q}{\theta} + \frac{\rho^2}{\rho_2}\, m_0\right)^2 \geqslant 0 \,. \tag{7.35}$$

Summary of the linear constitutive relations.--A summary of the most general linear relations possible for an ordinary binary fluid mixture are

$$\psi_I = \psi_I\,(\rho_1, \rho_2, \theta) \tag{7.3}$$

$$h_i = -\,\lambda_T g_i - Q u_i^1 \tag{7.36}$$

$$m_i^1 = -\,m_0 g_i - m_1 f_i^1 - m_2 f_i^2 - m_D u_i^1 \tag{7.5}$$

$$k_i = Ku_i^1 \tag{7.13}$$

$$\tau_{ij}^1 = -\mu\omega_{ij}^1 \tag{7.7}$$

$$t_{ij}^{\alpha} = -p^{\alpha}\delta_{ij} + \sum_{\beta=1}^{2}\phi^{\alpha\beta}d_{nn}^{\beta}\delta_{ij} + \sum_{\beta=1}^{2}2\eta^{\alpha\beta}\{d_{ij}^{\beta}\}$$

$$\alpha=1,2 \tag{7.8}$$

where

$$p^1 = \rho\rho_1\left(\frac{\partial\psi_I}{\partial\rho_1}\right) + \frac{\theta K\rho_2}{\rho} \tag{7.19}$$

$$p^2 = \rho\rho\left(\frac{\partial\psi_I}{\partial\rho_2}\right) - \frac{\theta K\rho_2}{\rho} \tag{7.20}$$

$$\frac{\rho^2}{\rho_1\rho_2}m_1 = \frac{\theta K}{\rho_1^2} - \frac{\theta}{\rho_1}\left(\frac{\partial K}{\partial\rho_1}\right) - \frac{1}{\rho_1^2}p^1 \tag{7.32}$$

$$\frac{\rho^2}{\rho_1\rho_2}m_2 = -\frac{\theta}{\rho_1}\left(\frac{\partial K}{\partial\rho_2}\right) + \frac{1}{\rho_2^2}p^2 \tag{7.33}$$

$$\lambda_T \geq 0 \tag{7.28}$$

$$m_D \geq 0 \tag{7.34}$$

$$\frac{\rho^2\lambda_T m_D}{\rho_2\theta} - \frac{1}{4}\left[\theta\left(\frac{\partial K}{\partial\theta}\right) + \frac{Q}{\theta} + \frac{\rho^2}{\rho_2}m_0\right]^2 \geq 0 \tag{7.35}$$

$$\mu \geq 0 \tag{7.25}$$

$$\phi^{11} \geq 0\ ,\ \phi^{22} \geq 0\ ,\ \phi^{11}\phi^{22} - \frac{1}{4}\left(\phi^{12} + \phi^{21}\right)^2 \geq 0 \tag{7.26}$$

$$\eta^{11} \geq 0\ ,\ \eta^{22} \geq 0\ ,\ \eta^{11}\eta^{22} - \frac{1}{4}\left(\eta^{12} + \eta^{21}\right)^2 \geq 0 \tag{7.27}$$

These relations are necessary and sufficient for the entropy production always to remain non-negative for any admissible process in an ordinary binary fluid mixture.

8. The Transport Equations

This section is intended as a summary of the differential equations governing the evolution of the state of the ordinary binary fluid mixture in thermodynamic processes. No new results are derived here. The equations are rearranged and expressed in a form more convenient for applications. This includes replacing ρ_1 and ρ_2 in favor of w_1 and ρ as independent variables, where the mass fraction w_1 is given by

$$w_1 = \rho_1/\rho \tag{8.1}$$

The balance of mass.--The two independent equations of conservation of mass to be used here are

$$\frac{d\rho}{dt} = -\rho\frac{\partial v_i}{\partial x_i} \tag{8.2}$$

which follows from (2.16) upon use of (2.4), and

$$\rho\frac{dw_1}{dt} = -\frac{\partial j_i^1}{\partial x_i} \tag{8.3}$$

which follows from (2.15) upon use of (2.4) and the definition of the diffusion flux

$$j_i^1 = \rho_1 u_i^1 \tag{8.4}$$

The balance of momentum.--The overall equation of motion of the mixture is derived from equation (2.23):

$$\rho \frac{dv_i}{dt} = \sum_\alpha \rho_\alpha b_i^\alpha - \frac{\beta}{\beta'} \frac{\partial \theta}{\partial x_i} - \frac{1}{\rho\beta'} \frac{\partial \rho}{\partial x_i} - \frac{\rho(\bar{V}_1-\bar{V}_2)}{\beta'} \frac{\partial w_1}{\partial x_i} + \frac{\partial \pi_{ij}}{\partial x_j} \qquad (8.5)$$

where the viscous pressure tensor has been defined as

$$\pi_{ij} = \sum_\alpha (S_{ij}^\alpha - \rho_\alpha u_i^\alpha u_j^\alpha + p^\alpha \delta_{ij}) \qquad (8.6)$$

and the following thermodynamic identity has been used for the pressure gradient:

$$- \frac{\partial p}{\partial x_i} = - \frac{\beta}{\beta'} \frac{\partial \theta}{\partial x_i} - \frac{1}{\rho\beta'} \frac{\partial \rho}{\partial x_i} - \frac{\rho(\bar{V}_1-\bar{V}_2)}{\beta'} \frac{\partial w_1}{\partial x_i} , \qquad (8.7)$$

where β is the thermal expansivity,

$$\beta = - \frac{1}{\rho} \left(\frac{\partial \rho}{\partial T}\right)_{p,w_1} \qquad (8.8)$$

β' is the isothermal compressibility,

$$\beta' = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial p}\right)_{T,w_1} \qquad (8.9)$$

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

The equation of balance of linear momentum (2.20) is written more conveniently

$$
\begin{aligned}
-\frac{\rho}{\rho_1\rho_2}\frac{dj_i^1}{dt} = {} & D_1 j_i^1 + D_2\frac{\partial\theta}{\partial x_i} + \frac{\partial}{\partial x_i}(\mu_1-\mu_2)_T \\
& -\left[\frac{1}{\rho_1}\frac{\partial}{\partial x_j}(S_{ij}^1 + p^1\delta_{ij}) - \frac{1}{\rho_2}\frac{\partial}{\partial x_j}(S_{ij}^2 + p^2\delta_{ij})\right] \\
& + \frac{\rho}{\rho_1\rho_2}\left\{ j_i^1\frac{\partial v_i^1}{\partial x_j} + j_i^1\frac{\partial v_j}{\partial x_j} - \frac{1}{\rho_2}\frac{\partial}{\partial x_j} j_i^1 j_j^1 \right. \\
& \left. + j_i^1 j_j^1\left[\frac{1}{\rho_1\rho_2}\frac{\partial\rho}{\partial x_j} + \rho\left(\frac{\rho(\rho_2-\rho_1)+\rho_1\rho_2}{\rho_1^2\rho_2^2}\right)\frac{\partial w_1}{\partial x_j}\right]\right\} \qquad (8.10)
\end{aligned}
$$

where the coefficients D_1 and D_2 are related to m_0, m_D, and K by

$$D_1 = \frac{\rho^2 m_D}{\rho_1^2\rho_2^2} \qquad (8.11)$$

$$D_2 = \frac{\rho^2 m_0}{\rho_1^2\rho_2} + \frac{K}{\rho_1} + \frac{\theta}{\rho_1}\left(\frac{\partial K}{\partial\theta}\right) - (\overline{S}_1 - \overline{S}_2) \qquad (8.12)$$

The partial specific entropies, $\overline{S}_\alpha$, have been used in (8.12). The special derivative of chemical potential used in (8.10) is defined by

$$
\begin{aligned}
\frac{\partial}{\partial x_i}(\mu_1-\mu_2)_T = {} & \frac{\beta(\overline{V}_1-\overline{V}_2)}{\beta'}\frac{\partial\theta}{\partial x_i} + \left[\frac{\rho(\overline{V}_1-\overline{V}_2)^2}{\beta'} + \frac{\rho\mu_{11}}{\rho_2}\right]\frac{\partial w_1}{\partial x_i} \\
& + \frac{(\overline{V}_1-\overline{V}_2)}{\rho\beta'}\frac{\partial\rho}{\partial x_i} \qquad (8.13)
\end{aligned}
$$

where

$$\mu_{11} = \left(\frac{\partial\mu_1}{\partial x_1}\right)_{\theta,p} \qquad (8.14)$$

The heat flux.--A new heat flux is introduced by the definition

$$q_j^1 = q_j - (\bar{H}_1 - \bar{H}_2)\, j_j^1 \tag{8.15}$$

where H_α is partial specific enthalpy defined by

$$\bar{H}_\alpha = \theta \bar{S}_\alpha + \mu_\alpha + \frac{1}{2} u_i^\alpha u_i^\alpha \tag{8.16}$$

From the definition (2.31) of the heat flux h_i and the constitutive relation (7.36), q_j is seen to be

$$- q_j^1 = B_1 \frac{\partial \theta}{\partial x_j} + B_2 j_j^1 + \sum_\alpha u_i^\alpha (S_{ij}^\alpha + p^\alpha \delta_{ij}) \tag{8.17}$$

where the coefficients B_2 are related to λ_T and Q by

$$B_1 = \lambda_T \tag{8.18}$$

and

$$B_2 = Q/\rho_1 + \theta (\bar{S}_1 - \bar{S}_2) - \frac{\theta K}{\rho_1} \tag{8.19}$$

The temperature equation.--In section 5 it was determined that a thermodynamic process could be specified by the fields w_1, ρ, j_i^1, v_i, and θ. So far differential equations have been given for all of these except θ. The temperature equation can be obtained from the following thermodynamic identity:

$$\rho \bar{C}_V \frac{d\theta}{dt} = \rho\theta \frac{d\eta}{dt} + \frac{\beta\theta}{\rho\beta'} \frac{d\rho}{dt} - \rho\theta \left[(\bar{S}_1 - \bar{S}_2) - \frac{\beta(\bar{V}_1 - \bar{V}_2)}{\beta'} \right] \frac{dw_1}{dt} \tag{8.20}$$

The equations of balance of mass (8.2) and (8.3) will be substituted into the last two terms of (8.23) and the first term will be replaced by the entropy balance

$$\rho\theta \frac{d\eta}{dt} = - \frac{\partial}{\partial x_j} \theta\Phi_j + \Phi_j g_j + \rho\theta\gamma + \rho r \tag{3.2}$$

The entropy flux to be used in (3.2) is determined from the definition (3.5) of k_i together with the constitutive relation for k_i, the definition (2.31) of h_i and the definition (8.18) of q_i^1:

$$\theta\Phi_j = q_j^1 + \theta(\bar{S}_1 - \bar{S}_2)\, j_j^1 + \sum_\alpha u_i^\alpha \left(S_{ij}^\alpha + p^\alpha \delta_{ij}\right) \tag{8.21}$$

Similarly, from equation (7.10) for the entropy production, the relations (2.20), (7.12), (7.23), (7.19), and (7.20) may be used to write the entropy production in the more convenient form:

$$\rho\theta\gamma = - \Phi_j g_j - \left[\frac{\partial}{\partial x_j} (\mu_1 - \mu_2)\right] j_j^1 - \sum_\alpha \left(\rho m_i^\alpha - \frac{\partial p^\alpha}{\partial x_i}\right) u_i^\alpha$$

$$+ \sum_\alpha \left(S_{ij}^\alpha + p^\alpha \delta_{ij}\right) \frac{\partial v_i^\alpha}{\partial x_j} \tag{8.22}$$

Substitution of these last two results into (3.2) gives

$$\rho\theta \frac{d\eta}{dt} = - \frac{\partial}{\partial x_j} q_j^1 - \theta(\bar{S}_1 - \bar{S}_2) \frac{\partial}{\partial x_j} j_j^1 + \rho r$$

$$- j_j^1 \frac{\partial}{\partial x_j} (\bar{H}_1' - \bar{H}_2') + \pi_{ij} \frac{\partial v_i}{\partial x_j} \tag{8.23}$$

where the system has been restricted to external fields derivable from a potential

$$b_i^\alpha = - \frac{\partial \Omega_\alpha}{\partial x_i} \tag{8.24}$$

and where

$$\overline{H}'_\alpha = \overline{H}_\alpha + \Omega_\alpha \tag{8.25}$$

The final temperature equation is now completed by inserting (8.26), (8.2) and (8.3) into equation (8.23). The result is

$$\begin{aligned}\rho \overline{C}_V \frac{d\theta}{dt} = &- \frac{\partial}{\partial x_j} q_j^1 - \frac{\theta\beta(\overline{V}_1 - \overline{V}_2)}{\beta'} \frac{\partial}{\partial x_j} j_j^1 + \rho r \\ &- \frac{\beta\theta}{\beta'} \frac{\partial v_i}{\partial x_i} - j_i^1 \frac{\partial}{\partial x_i} (H_1' - H_2') + \pi_{ij} \frac{\partial v_i}{\partial x_j}\end{aligned} \tag{8.26}$$

Summary of transport equations.--The complete set of equations which are necessary to describe any admissible thermodynamic process in an ordinary binary fluid mixture are equations (8.2), (8.3), (8.5), (8.6), (8.10), (8.17), and (8.26) together with the appropriate boundary conditions.

9. Discussion

It is not surprising that the transport equations for the ordinary fluid mixture bear striking resemblances to the transport equations of TIP (see Horne, 1966) since hopefully they describe the same material. Briefly, a comparison of the equations yields: (1) The equations of continuity of mass, (8.2-3), are identical with those of TIP; (2) The temperature equation (8.23) (derived from the energy balance equation) is identical in form to that of TIP except that the possibility of external sources of radiation has been included; (3) The phenomenological equation for the heat flux (8.17) contains viscous terms and a kinetic energy of diffusion not found in TIP; (4) The overall equation of motion (8.5) is identical in form to that of TIP; (5) The viscous pressure tensor (8.6) appearing in the equation of motion contains a contribution from the kinetic energy of diffusion; (7) The phenomenology of the partial stress tensors (7.7-8) provides completely new expressions for the determination of stress; and (8) The equation for the diffusion flux (8.10), usually given as a phenomenological equation in TIP, is determined here from the componentwise equations of motion. If the inertial and viscous terms of (8.10) are neglected, the equation is identical with that of TIP.

On the surface it appears that the major differences between the two formulations arise because of the use of the partial stress tensors and componentwise equations of motion. It should be apparent, however, that many of the underlying inconsistencies have also been eliminated. For example, the careful application of Coleman's thermodynamic methods has eliminated the need for the local equilibrium assumption as it is commonly used.

An extension of Müller's work has made it possible to determine the entropy flux by derivation rather than by making an arbitrary separation of flux and source terms as is done in TIP. It has been shown that the entropy production may be written as a quadratic form which allows the second law entropy inequality to be used with maximum effectiveness. Finally, the equivalence of the pressure appearing in the Gibbisian equation for the energy and the negative trace of the stress tensor has been established.

One result of the identification of pressure and the ability to write the entropy production in a quadratic form is that is is now possible, for the first time to give an unequivocal criterion for mechanical equilibrium: A system is in mechanical equilibrium if and only if

$$d^1_{ij} = d^2_{ij} = \omega^1_{ij} = \frac{dv_i}{dt} = 0$$

These restrictions also imply that at mechanical equilibrium the external forces are completely balanced by the pressure gradient in the fluid.

CHAPTER III

PERTURBATION EXPANSION METHODS

1. Introduction

The particular stimulus for the research in this thesis has been the need for a better understanding and interpretation of the results of pure thermal diffusion experiments. The previous chapter is the culmination of an effort to better understand the fundamental theory of irreversible processes in liquid mixtures. The following quote from Bellman (1964, p. 1) sets the tone for this chapter:

> . . ., one of the major problems confronting the mathematician, after he has passed the first hurdle of achieving a reasonable analytic formulation of a physical process, is that of deriving useful and meaningful approximations to the solutions of the equations describing the process. In some cases, analytic ingenuity, alone or abetted by digital computers, will furnish the desired expressions; in other cases, a combination of "low cunning" and physical intuition will provide the essential key.
>
> In still other cases, a completely new interpretation and formulation of the physical situation is required. A major obstacle at the start of any research is ignorance of where the real difficulties lie. The greater part of the time, only perseverance and plodding effort yield this vital information.

Indeed, there is no reason to believe that the research reported here has been any different.

In this section, prior to a discussion of particular problems, the simplest and most useful of all approximation techniques will be presented: the expansion of a solution as a power series in a parameter--the classical perturbation technique upon which much of the edifice of science rests.

The basic idea of the perturbation technique can be exhibited most easily in abstract terms. The introduction by Bellman (1964) is probably the best starting point: Suppose that we are required to solve the equation

$$N(u) = v \tag{1.1}$$

which for any of a variety of reasons, is inconvenient to tackle in its original form. It may, for example be nonlinear, be linear but of high dimension, or possess variable coefficients.

Let

$$L(u) = v \tag{1.2}$$

be an auxiliary equation that possesses a useful explicit solution

$$u = T(v) \tag{1.3}$$

in general, the unique solution of (1.2). In practice, this means that $L(u)$ is a linear operation on u. Let us henceforth assume that L is linear.

Returning to (1.1), we write it in the form

$$L(u) = v + R(u) \tag{1.4}$$

where the function R has been defined as

$$R(u) = L(u) - N(u). \tag{1.5}$$

To facilitate our discussion of particular solutions of (1.4), we introduce a parameter ε and consider the new equation

$$L(u) = v + \varepsilon R(u) \tag{1.6}$$

In some situations, the introduction of ε is solely a mathematical artifice that permits us to do various types of "bookkeeping" in a systematic fashion. For example, it allows us to group terms of comparable degrees of approximation in a methodical and convenient fashion. In a large number of situations, however, this parameter occurs naturally, representing some physical quantity. In the application to pure thermal diffusion experiments we shall have use for both interpretations.

It is quite natural and sensible to begin with the study of those equations where ε is close to zero. Let us then look for a solution of (1.6) having the form

$$u = u_0 + \varepsilon u_1 + \varepsilon^2 u_2 + \ldots, \tag{1.7}$$

a power series in ε with coefficients that are independent of ε. Clearly, the leading term u_0, obtained by setting $\varepsilon = 0$, is a solution of the linear approximation

$$L(u_0) = v \tag{1.8}$$

a solution that we shall write as $u_0 = T(v)$.

To obtain the subsequent coefficients, u_1, u_2, ..., in a systematic fashion, we substitute u as given by (1.7) into (1.6) and equate terms, obtaining thereby

$$L(u_0 + \varepsilon u_1 + \varepsilon^2 u_2 + \ldots) = v + \varepsilon R(u_0 + \varepsilon u_1 + \ldots) \tag{1.9}$$

Since L is by assumption a linear operator, the left side becomes

$$L(u_0) + \varepsilon L(u_1) + \varepsilon^2 L(u_2) + \ldots \tag{1.10}$$

Assuming that R(u) is analytic in u so that we can expand the right side of (1.9) as a power series in ε, we have

$$\begin{aligned} R(u_0 + \varepsilon u_1 + \varepsilon^2 u_2 + \ldots) &= R(u_0) + \varepsilon R_1(u_0, u_1) \\ &\quad + \varepsilon^2 R_2(u_0, u_1, u_2) + \ldots \end{aligned} \tag{1.11}$$

where, as indicated, the coefficient of u_k depends only upon the quantities u_n, $n \leqslant k$. Combining the expansions of (1.10) and (1.11), and equating coefficients of ε, the single equation of (1.6) gives rise to the infinite system of equations

$$
\begin{aligned}
L(u_0) &= v \\
L(u_1) &= R(u_0) \\
L(u_2) &= R_1(u_0, u_1) \qquad (1.12) \\
&\vdots \\
L(u_{k+1}) &= R_k(u_0, u_i, \ldots, u_k)
\end{aligned}
$$

and so on.

The important point to observe is that this system of equations can be solved recursively; that is, the determination of u_k involves a knowledge of u_n, $n \leqslant k$. The first equation yields

$$u_0 = T(v). \qquad (1.13)$$

From the second, we derive the relation

$$u_1 = T(R(u_0)) = T(R(T(v))). \qquad (1.14)$$

Continuing in this way, we see that we can express each u_k solely in terms of v.

The infinite series in (1.7), whose coefficients are determined in the foregoing fashion is called a formal solution of the original equation in (1.6). To obtain a formal solution of (1.4), we need only set $\varepsilon = 1$.

Pure thermal diffusion experiments.--Historically, the application of nonequilibrium thermodynamics to the problem of interpreting pure thermal diffusion experiments has been made by considering the magnitude and variability of the terms in the transport equations. Among the assumptions that have been made in formulating working equations in the past are: (1) constant phenomenological coefficients; (2) a one-dimensional temperature gradient; (3) a density independent of composition; (4) no convective motion; (5) no viscous effects; and (6) dilute solutions. Undoubtedly there is some validity to these approximations in some cases, and their use sometimes provides an adequate first order theory. However, it has been impossible to provide corrections to the theory for the cases in which there is significant deviation from these assumptions and it has thus been impossible to interpret properly the experimental results. The use of the perturbation technique not only provides these corrections but at the same time facilitates the solution to the transport equations.

It will be seen from the description of the pure thermal diffusion experiment in the next section that two characteristics stand out as natural possibilities for the application of the perturbation method: (1) The phenomenological coefficients are fairly constant and any variation might be taken as a perturbation. (2) No steady state convection is expected if it is possible to minimize heat losses; convective corrections are therefore introduced by the use of a heat loss parameter. In fact, as will be seen in section 3, we employ a double perturbation expansion to account for both effects simultaneously.

2. The Experiment

The experimental device used in studies of pure thermal diffusion is usually described as a sandwich-type cell consisting of two thermostated, horizontal metal plates with an arrangement for containing a homogeneous binary liquid solution of known initial composition between the plates. A temperature difference is maintained between the plates by the external thermostatting mechanism with the warmer plate situated above in order to minimize convective effects. The temperature gradients which are thus present in the liquid result in more than just heat conduction. The two components in the mixture will tend to separate or demix under the influence of the temperature gradient (thermal diffusion). Of course the resulting concentration gradient produced by this effect immediately induces ordinary diffusion which tends to remix the components. The total diffusion flux will be observed as the resultant sum of these two opposing fluxes. The fundamental measurement in the pure thermal diffusion experiment is the composition distribution in the cell under steady state conditions (all local time derivatives are zero) for which the thermal diffusion and ordinary diffusion fluxes are as closely balanced as possible (total diffusion flux approaching zero) and convective effects are at a minimum.

The boundary conditions.--Ideally the boundary conditions to be used with the temperature equation would consist of the temperatures at the top and bottom of the cell, together with a condition that the heat flux at the side walls is zero. Practically these boundary conditions cannot always be obtained and any observations of convection in the cell are probably for this reason. For the purpose of this treatment it will be assumed that the temperatures of the top and bottom plate can be controlled as accurately as desired, but that there is a slight heat loss at the side walls. There are two principal reasons for the constant temperature choice. First, the primary objective of this chapter is to show how a perturbation theory can be formulated for the heat loss problem, and the variable temperature problem only complicates the situation. Second, there are many practical experiments that can be done for which the constant temperature assumption is quite good. In any case if the inclusion of variable temperature at the horizontal surfaces is required, the procedure will not be very much different from that which will be introduced for handling the heat loss problem. With these considerations in mind the boundary conditions for the temperature equation are:

$$\theta = T_m + 1/2\ (\Delta T) \qquad \text{at } z = h \tag{2.1}$$

$$\theta = T_m - 1/2\ (\Delta T) \qquad \text{at } z = 0 \tag{2.2}$$

and

$$\frac{\partial \theta}{\partial r} = \varepsilon (T_r - \theta) \qquad \text{at } r = a \tag{2.3}$$

where it has been assumed that the z axis is vertical, with the height of the cell given by h, and that the fluid is contained between the plates by a cylindrical surface of radius a. The difference between the temperature at the top and at the bottom has been denoted by (ΔT) while the average of these two temperatures has been denoted by T_m. The heat loss coefficient is given above as ε, and the system is assumed to be radiating heat into surroundings which are at a temperature of T_r. Finally, we take it as an assumption that all of the properties of the fluid are axially symmetric; i.e., they depend only on the vertical position in the cell and on the distance from the center.

Although ε is a parameter which depends on the apparatus and must be determined experimentally in each individual case, it is helpful to have an order of magnitude estimate. If the fluid is assumed to be contained within glass walls (thermal conductivity = 0.0028 cal/(sec)(cm^2)(°C/cm)) and to lose heat through a stagnant layer of air (thermal conductivity = 0.000053 cal/(sec)(cm^2)(°C/cm)) of thickness 0.5 cm, then ε is given by $(0.000053)/(0.5 \cdot 0.0028) = 0.038\text{cm}^{-1}$. (See Carslaw and Jaeger (1959) for more details concerning the use of heat loss boundary conditions.)

In the absence of chemical reactions, the boundary conditions for density and mass fraction are simply statements of the conservation of mass:

$$\int_0^{2\pi} \int_0^h \int_0^a \rho(r,z)\ r dr dz d\psi = M \tag{2.4}$$

and

$$\int_0^{2\pi} \int_0^h \int_0^a \rho(r,z)\ w_1\ (r,z)\ r dr dz d\psi = M_1 \tag{2.5}$$

where M is the total mass contained in the cell and M_1 is the total mass of component one. These two masses are easily obtained by weighing or density determinations at the beginning of the experiment.

Boundary conditions for the velocity and diffusion flux are easily written to insure that no material either flows or diffuses through a rigid wall. These conditions are

$$u_z = j_{1z} = 0 \qquad \text{at } z = 0,\ h \tag{2.6}$$

$$u_r = j_{1r} = 0 \qquad \text{at } r = a \tag{2.7}$$

It will be further assumed that the fluid sticks to all rigid walls. This is the usual assumption in all hydrodynamic treatments. This leads to the further conditions

$$u_r = 0 \qquad \text{at } z = 0,\ h \tag{2.8}$$

$$u_z = 0 \qquad \text{at } r = a \tag{2.9}$$

Under certain circumstances it might be possible that the number of boundary conditions is insufficient in order to determine properly all the solutions to the differential equations. If these circumstances arise, it will always be possible to ask the experimenter to provide the additional measurements of concentration or concentration gradient at one or more points in the cell.

3. Pure Thermal Diffusion Transport Equations[1]

The equations to be used for the description of the pure thermal diffusion experiment are those listed at the end of Chapter II. There are a few modifications and specializations of these equations which make them more appropriate for pure thermal diffusion. The equations are written here in such a way as to make the comparison with the standard treatments of nonequilibrium thermodynamics convenient. In particular this involves the following major assumptions: (1) The viscous terms in both the phenomenological equation for the heat flux and the equation of motion which gives the diffusion flux are neglected. (2) The viscous stress tensor is assumed to be given by the Newtonian formula; *i.e.*, the stress depends only on the convective motion. The following simplifications have also been included: (1) Since the description is to be of a steady phenomena, all local time derivatives are set equal to zero. (2) The only external force to be considered is gravity. (3) It is assumed that there are no external sources of radiation.

---

[1] For the remainder of this chapter direct, as distinguished from Cartesian or component, tensor notation will be used. Vectors are denoted $\underset{\sim}{v}$, tensors by $\underset{\approx}{t}$, and the gradient operator by $\underset{\sim}{\nabla} = \frac{\partial}{\partial \underset{\sim}{x}}$.

The steady state equations of transport, modified as above, are

$$\underset{\sim}{v} \cdot \underset{\sim}{\nabla}\rho + \rho\underset{\sim}{\nabla} \cdot \underset{\sim}{v} = 0 \tag{3.1}$$

$$\rho\underset{\sim}{v} \cdot \underset{\sim}{\nabla}w_1 - \underset{\sim}{\nabla} \cdot \underset{\sim}{j}_1 = 0 \tag{3.2}$$

$$\frac{\rho}{\rho_1\rho_2}\underset{\sim}{v} \cdot \underset{\sim}{\nabla}\underset{\sim}{j}_1 + D_1\underset{\sim}{j}_1 + \underset{\sim}{\nabla}_T(\mu_1 - \mu_2) + \left[\frac{\rho(\overline{V}_1-\overline{V}_2)gh}{\Delta T} - \frac{\rho\mu_{11}\sigma}{\rho_2}\right]\underset{\sim}{\nabla}\theta = 0 \tag{3.3}$$

$$\rho\underset{\sim}{v} \cdot \nabla\underset{\sim}{v} + \underset{\sim}{\nabla}p - \rho g\underset{\sim}{\lambda} - \underset{\sim}{\nabla} \cdot \underset{\approx}{\pi} = 0 \tag{3.4}$$

$$\rho\overline{C}_V\underset{\sim}{v} \cdot \nabla\theta + \underset{\sim}{\nabla} \cdot \underset{\sim}{q}' + \frac{\beta\theta}{\beta'}\underset{\sim}{\nabla} \cdot \underset{\sim}{v} - \underset{\approx}{\pi} : \underset{\sim}{\nabla}\underset{\sim}{v} + \frac{\theta\beta(\overline{V}_1-\overline{V}_2)}{\beta'}\underset{\sim}{\nabla} \cdot \underset{\sim}{j}_1 + \underset{\sim}{j}_1 \cdot \nabla(\overline{H}_1'-\overline{H}_2') = 0 \tag{3.5}$$

$$- \underset{\sim}{q}' = B_1\underset{\sim}{\nabla}\theta + B_2\nabla\underset{\sim}{j}_1 \tag{3.6}$$

$$\underset{\approx}{\pi} = (\phi - 2/3\eta)(\underset{\sim}{\nabla} \cdot \underset{\sim}{u})\,\underset{\approx}{1} + 2\eta\ \mathrm{sym}\ (\underset{\sim}{\nabla}\underset{\sim}{u}) \tag{3.7}$$

Notice that the phenomenological coefficient D_2 of equation (II.8.10) has been eliminated in favor of the coefficient σ which is defined by

$$\sigma = \frac{\rho_2(\overline{V}_1-\overline{V}_2)gh}{\mu_{11}(\Delta T)} - \frac{\rho_2 D_2}{\rho\mu_{11}} \tag{3.8}$$

The coefficient σ will be called the thermal diffusion parameter. It is related to the thermal diffusion factor α_1 used in many nonequilibrium thermodynamic studies of thermal diffusion. For example, from the phenomenological equations given by Horne and Bearman (1967) it is easy to see that

$$\frac{w_1 w_2 \alpha_1}{\theta} = \sigma - \frac{\rho_2(\overline{V}_1-\overline{V}_2)gh}{\mu_{11}(\Delta T)} \tag{3.9}$$

The last term in this equation is typically very much smaller than σ, and the behaviors of σ and α_1 are therefore very strongly correlated. Notice also that in equation (3.7) the common coefficient of shear viscosity, η, and the coefficient of bulk or volume viscosity, ϕ, have been used. Finally, in the equation of motion (3.4) the external gravitational field has been assumed to be of magnitude g and to act in the direction $\underset{\sim}{\lambda}$. In all that follows, it is assumed that this direction is vertical and

$$\underset{\sim}{\lambda} = (0, 0, -1) \tag{3.10}$$

For completeness, the thermodynamic expansions for the pressure gradient and chemical potential gradient needed in equations (3.3) and (3.4) are repeated from the previous chapter:

$$\underset{\sim}{\nabla} p = \frac{\beta}{\beta'} \underset{\sim}{\nabla} \theta + \frac{1}{\rho\beta'} \underset{\sim}{\nabla} \rho + \frac{\rho(\overline{V}_1-\overline{V}_2)}{\beta'} \underset{\sim}{\nabla} w_1 \tag{3.11}$$

$$\underset{\sim}{\nabla}_T(\mu_1-\mu_2) = \frac{\beta(\overline{V}_1-\overline{V}_2)}{\beta'}\underset{\sim}{\nabla}\theta + \frac{(\overline{V}_1-\overline{V}_2)}{\rho\beta'}\underset{\sim}{\nabla}p + \left[\frac{\rho(\overline{V}_1-\overline{V}_2)^2}{\beta'} + \frac{\rho\mu_{11}}{\rho_2}\right]\underset{\sim}{\nabla}w_1 \tag{3.12}$$

4. The Perturbation Expansions

In this section the beginnings of the perturbation method for the pure thermal diffusion method are developed. In the introduction to this chapter it was suggested that in a typical pure thermal diffusion experiment the diffusion flux is small, that if there is only a small heat loss the convective velocity is small, and finally that the variability of the phenomenological coefficients is very slight. While it might be true that the phenomenological coefficients are fairly constant in experiments in which the gradients of temperature, pressure and composition are small, the neglect of their variation in the transport equations constitutes a serious introduction of systematic error in many cases. Of course the differential equations are much easier to solve if they have constant coefficients and not infrequently it might be suspected that the criterion of constancy is more strongly influenced by the reduction of work in solving the equations rather than by any physical evidence of constancy.

In any case, the perturbation method is particularly well suited to handle problems of this type. Its use focuses attention on the major processes while at the same time making possible corrections for the minor effects of variable coefficients. This is accomplished by expanding each of the coefficients in a thermodynamic series in the manner of Hurle, Mullin, and Pike (1965) and introducing the parameter γ for the purpose of ordering the terms. The typical coefficient is expanded in the following manner:

$$L = L_0 + \gamma[L_T(\theta-\theta_0)+L_C(w_1-w_{10})+L_\rho(\rho-\rho_0)] + O(\gamma^2) \tag{4.1}$$

Where

$$L_0 = L(\theta_0,w_{10},\rho_0) \tag{4.2}$$

$$L_T = \left(\frac{\partial L}{\partial \theta}\right)_{\theta=\theta_0,w_1=w_{10},\rho=\rho_0} \tag{4.3}$$

$$L_C = \left(\frac{\partial L}{\partial w_1}\right)_{\theta_0,w_{10},\rho_0} \tag{4.4}$$

and

$$L_\rho = \left(\frac{\partial L}{\partial \rho}\right)_{\theta_0,w_{10},\rho_0} \tag{4.5}$$

Corresponding to the ordering of terms by the parameter γ, each of the independent variables is given by a power series expansion in γ, so that the contribution of each term in the series to the total is proportional to the effects of the perturbation at that order.

It is easy to see that if the differential equations are solved with the parameter γ set equal to zero, then the solution is that for constant coefficients, whereas if γ equals one, then the full variability of the coefficients is taken into account. This same analysis can be applied to the heat loss ε as a parameter. If all the independent variables are expanded in a power series in ε, then the solutions to the differential equations with ε equal to zero correspond to the zero convection problem. The perturbation expansions for the independent variables thus become double power series expansions in γ and ε of the following form:

$$\theta = T_r + \sum_{i=0}^{\infty} \sum_{k=0}^{\infty} \varepsilon^i \gamma^k T_{ik} \tag{4.6}$$

$$\rho = \frac{M}{a^2 \pi h} + \sum_{i=0}^{\infty} \sum_{k=0}^{\infty} \varepsilon^i \gamma^k d_{ik} \tag{4.7}$$

$$w_1 = \frac{M_1}{M} + \sum_{i=0}^{\infty} \sum_{k=0}^{\infty} \varepsilon^i \gamma^k c_{ik} \tag{4.8}$$

$$\underset{\sim}{j}_1 = \sum_{i=1}^{\infty} \sum_{k=0}^{\infty} \varepsilon^i \gamma^k \underset{\sim}{J}_{ik} \tag{4.9}$$

$$\underset{\sim}{v} = \sum_{i=1}^{\infty} \sum_{k=0}^{\infty} \varepsilon^i \gamma^k \underset{\sim}{v}_{ik} \tag{4.10}$$

where the first term on the right in (4.6), (4.7), and (4.8) has been introduced for the purpose of making the boundary conditions homogeneous. The summations on i in (4.9) and (4.10) begin with one in order to indicate that in the case of zero heat loss no convective or diffusive effects are expected.

The phenomenological coefficients to be used are expanded according to (4.1) in the following way:

$$\sigma = \sigma_0 + \gamma[\sigma_T(\theta-T_0)+\sigma_C(w_1-w_{10})+\sigma_\rho(\rho-\rho_0)] + O(\gamma^2) \tag{4.11}$$

$$D_1 = D_0 + \gamma[D_T(\theta-T_0)+D_C(w_1-w_{10})+D_\rho(\rho-\rho_0)] + O(\gamma^2) \tag{4.12}$$

$$B_1 = K_0 + \gamma[K_T(\theta-T_0)+K_C(w_1-w_{10})+K_\rho(\rho-\rho_0)] + O(\gamma^2) \tag{4.13}$$

$$B_2 = Q_0 + \gamma[Q_T(\theta-T_0)+Q_C(w_1-w_{10})+Q_\rho(\rho-\rho_0)] + O(\gamma^2) \tag{4.14}$$

$$\rho(\bar{V}_1-\bar{V}_2) = V_0 + \gamma[V_T(\theta-T_0)+V_C(w_1-w_{10})+V_\rho(\rho-\rho_0)] + O(\gamma^2) \tag{4.15}$$

$$(\bar{H}_1'-\bar{H}_2') = H_0 + \gamma[H_T(\theta-T_0)+H_C(w_1-w_{10})+H_\rho(\rho-\rho_0)] + O(\gamma^2) \tag{4.16}$$

$$\beta = \beta_0 + \gamma[\beta_T(\theta-R_0)+\beta_C(w_1-w_{10})+\beta_\rho(\rho-\rho_0)] + O(\gamma^2) \tag{4.17}$$

$$\rho\beta' = \beta_0' + \gamma[\beta_T'(\theta-T_0)+\beta_C'(w_1-w_{10})+\beta_\rho'(\rho-\rho_0)] + O(\gamma^2) \tag{4.18}$$

$$C_V = C_{V0} + \gamma[C_{VT}(\theta-T_0)+C_{VC}(w_1-w_{10})+C_{V\rho}(\rho-\rho_0)] + O(\gamma^2) \tag{4.19}$$

$$\frac{\rho\mu_{11}}{\rho_2} = \mu_0 + \gamma[\mu_T(\theta-T_0)+\mu_C(w_1-w_{10})+\mu_\rho(\rho-\rho_0)] + O(\gamma^2) \tag{4.20}$$

$$\eta = \eta_0 + \gamma[\eta_T(\theta-T_0)+\eta_C(w_1-w_{10})+\eta_\rho(\rho-\rho_0)] + O(\gamma^2) \tag{4.21}$$

$$\phi = \phi_0 + \gamma[\phi_T(\theta-T_0)+\phi_C(w_1-w_{10})+\phi_\rho(\rho-\rho_0)] + O(\gamma^2) \tag{4.22}$$

5. The Perturbation Equations

The analysis of the pure thermal diffusion experiment begins with the transport equations listed in section 3. The expansions (4.6) to (4.22) are substituted into each of the equations in section 3 and into the boundary conditions of section 2. Terms of the same order in ε and γ for each i and k are collected and separated. The equations at each order may then be solved independently of the solutions of any higher order.

<u>The zeroth-order equations</u>.--After the substitutions indicated above, the terms of the equations containing neither parameter are rearranged to give

$$\nabla^2 T_{00} = 0 \tag{5.1}$$

$$\underset{\sim}{\nabla} C_{00} = \sigma_0 \underset{\sim}{\nabla} T_{00} - \frac{hgV_0}{(\Delta T)\mu_0}\left[\underset{\sim}{\nabla} T_{00} + \left(\frac{\Delta T}{h}\right)\underset{\sim}{\lambda}\right] \tag{5.2}$$

$$\begin{aligned}\underset{\sim}{\nabla} d_{00} = {} & \left(d_{00} + \frac{M}{a^2\pi h}\right)\left[\beta_0' g \underset{\sim}{\lambda} - (V_0\sigma_0 + \beta_0)\underset{\sim}{\nabla} T_{00}\right] \\ & + \frac{V_0^2 gh}{\mu_0(\Delta T)}\left(d_{00} + \frac{M}{a^2\pi h}\right)\left[\underset{\sim}{\nabla} T_{00} + \left(\frac{\Delta T}{h}\right)\underset{\sim}{\lambda}\right]\end{aligned} \tag{5.3}$$

The boundary conditions become

$$T_{00} = T_m - T_r + \frac{1}{2}(\Delta T) \qquad \text{at } z = h \tag{5.4}$$

$$T_{00} = T_m - T_r - \frac{1}{2}(\Delta T) \qquad \text{at } z = 0 \tag{5.5}$$

$$\frac{\partial T_{00}}{\partial r} = 0 \qquad \text{at } r = a \tag{5.6}$$

for temperature, and

$$\int_0^{2\pi}\int_0^{h}\int_0^{a} d_{00}\, r\,dr\,dz\,d\psi = 0 \tag{5.7}$$

and

$$\int_0^{2\pi}\int_0^{h}\int_0^{a}\left(d_{00} + \frac{M}{a^2\pi h}\right) C_{00} r\,dr\,dz\,d\psi = 0 \tag{5.8}$$

for composition and density.

The zeroth-order solutions.--The zeroth-order equations have been arranged so that the composition and density distributions may be easily found from the temperature distribution. The equation for temperature to zeroth-order (5.1) has a general solution consisting of linear terms together with periodic terms appropriate to the boundary conditions (5.4-6). The nature of these boundary conditions eliminates the possibility of periodic solutions to (5.1). The temperature can therefore be given by a linear function which according to (5.4-6) is

$$T_{00} = \frac{(\Delta T)}{h}(z - h/2) + (T_m - T_r) \tag{5.9}$$

The gradient of the zeroth-order temperature solution is most conveniently written

$$\underset{\sim}{\nabla} T_{00} = - \left(\frac{\Delta T}{h}\right) \underset{\sim}{\lambda} \tag{5.10}$$

The density distribution is next determined from equation (5.3). The solution is easily seen to be an exponential which satisfies the boundary condition (5.7). This solution is

$$d_{00} = \frac{M}{a^2 \pi h} \left[\frac{hA}{2 \sinh \frac{Ah}{2}} \exp\,[A(z - h/2)] - 1 \right] \tag{5.11}$$

where

$$A = \beta_0' g - (V_0 \sigma_0 + \beta_0) \left(\frac{\Delta T}{h} \right) \tag{5.12}$$

Finally, if the temperature solution is substituted into equation (5.2) and the density solution used in the boundary condition (5.8) the following solution can be found for the composition distribution:

$$C_{00} = \frac{\sigma_0 (\Delta T)}{h} \left[(z - h/2) + \frac{1}{A} - \frac{h}{2} \coth \left(\frac{Ah}{2} \right) \right] \tag{5.13}$$

In most practical problems the quantity A has a magnitude of about 10^{-2}, and the hyperbolic functions can conveniently be replaced by their expansions:

$$\sinh \left(\frac{Ah}{2} \right) = \left(\frac{Ah}{2} \right) + \frac{1}{6} \left(\frac{Ah}{2} \right)^3 + \ldots \tag{5.14}$$

$$\coth \left(\frac{Ah}{2} \right) = \left(\frac{Ah}{2} \right)^{-1} + \frac{1}{3} \left(\frac{Ah}{2} \right) - \frac{1}{45} \left(\frac{Ah}{2} \right)^3 + \ldots \tag{5.15}$$

In using these expressions the cubic terms (as well as all higher terms) are negligible with respect to the first. Insertion of (5.14) into (5.12) and (5.15) into (5.13) yields

$$d_{00} = \frac{M}{a^2 \pi h} \left[\exp\,[A(z - h/2)] - 1 \right] \tag{5.16}$$

and

$$C_{00} = \frac{\sigma_0 (\Delta T)}{h} \left[(z - h/2) - \frac{Ah^2}{12} \right] \tag{5.17}$$

after the higher order terms of the expansions have been dropped. It must be remembered that these are only approximate expressions for use in practical calculations where the magnitude of A is small.

Equations first order in γ.--After the perturbation expansions have been introduced into the transport equations the terms of these equations which multiply γ represent the corrections to the basic processes due to variability of phenomenological coefficients. The introduction of the perturbation expansions (4.6) to (4.10) into the thermodynamic expansions (4.1) of the phenomenological coefficients gives for the typical coefficient

$$L = L_0 + \gamma L_1 + \mathcal{O}(\gamma^2) \tag{5.18}$$

where L_1 has been introduced for compactness of notation and is defined as

$$L_1 = L_T(T_{00} + T_r - T_0) + L_C \left(C_{00} + \frac{M_1}{M} - w_{10} \right) + L_\rho \left(d_{00} + \frac{M}{a^2 \pi h} - \rho_0 \right) \tag{5.19}$$

The transport equations of first order in γ are

$$\nabla^2 T_{01} = - \left(\frac{\Delta T}{h} \right) \frac{1}{K_0} \frac{dK_1}{dz} \tag{5.20}$$

$$\underset{\sim}{\nabla} C_{01} = \sigma_1 \underset{\sim}{\nabla} T_{00} + \left[\sigma_0 - \frac{hgV_0}{(\Delta T)\mu_0} \right] \underset{\sim}{\nabla} T_{01} \tag{5.21}$$

$$\underset{\sim}{\nabla} d_{01} = - A d_{01} \underset{\sim}{\lambda} + \left(d_{00} + \frac{M}{a^2 \pi h}\right)\left[\beta_1' g \underset{\sim}{\lambda} - \left(V_0 \sigma_0 + \beta_0 - \frac{V_0^2 g h}{\mu_0 (\Delta T)}\right) \underset{\sim}{\nabla} T_{01} \right.$$

$$\left. - (V_1 \sigma_0 + V_0 \sigma_1 + \beta_1) \underset{\sim}{\nabla} T_{00} \right] \qquad (5.22)$$

From (2.1) to (2.8) the corresponding boundary conditions are

$$T_{01} = 0 \qquad \text{at } z = 0 \qquad (5.23)$$

$$T_{01} = 0 \qquad \text{at } z = h \qquad (5.24)$$

$$\frac{\partial T_{01}}{\partial r} = 0 \qquad \text{at } r = a \qquad (5.25)$$

for temperature and

$$\int_0^{2\pi} \int_0^{h} \int_0^{a} d_{01} r dr dz d\psi = 0 \qquad (5.26)$$

$$\int_0^{2\pi} \int_0^{h} \int_0^{a} \left[C_{00} d_{01} + \left(d_{00} + \frac{M}{a^2 \pi h}\right) C_{01} \right] r dr dz d\psi = 0 \qquad (5.27)$$

for density and composition.

<u>Solutions first order in γ</u>.--In the same way as in the zeroth-order case the boundary conditions on temperature admit no periodic solutions to (5.20). Under these conditions the only possible solution for the temperature is

$$T_{01} = \left(\frac{\Delta T}{h}\right) \frac{K_\rho}{K_0} \frac{M}{a^2 \pi h} z - \left(\frac{\Delta T}{h}\right)^2 \frac{1}{2K_0} \{K_T + K_C \sigma_0\} z(z-h)$$

$$+ \left(\frac{\Delta T}{h}\right) \frac{K_\rho M e^{-A\frac{h}{2}}}{2K_0 a^2 \pi \sinh A\frac{h}{2}} \left(1 - e^{Az}\right) \qquad (5.28)$$

while the gradient is most conveniently written

$$\underset{\sim}{\nabla}T_{01} = -\left[\left(\frac{\Delta T}{h}\right)\frac{K_\rho}{K_0}\,\frac{M}{a^2\pi h} - \left(\frac{\Delta T}{h}\right)^2 \frac{1}{K_0}\,\{K_T + K_C\sigma_0\}\left(z - \frac{h}{2}\right)\right.$$

$$\left. - \left(\frac{\Delta T}{h}\right)\frac{K_\rho M A e^{-A\frac{h}{2}}}{2K_0 a^2 \pi \sinh A\frac{h}{2}}\, e^{Az}\right]\underset{\sim}{\lambda} \tag{5.29}$$

Substitution of this expression for the temperature gradient into equation (5.22) for the density together with the detailed expressions for the phenomenological coefficients, allows equation (5.22) to be written

$$\frac{dd_{01}}{dz} = Ad_{01} + \left[B + 2Cz + ADe^{Az}\right]\left(d_{00} + \frac{M}{a^2\pi h}\right) \tag{5.30}$$

where A has been defined in (5.21) and

$$B = \left[\beta_T' g - \left(\frac{\Delta T}{h}\right)(\sigma_0 V_T + \sigma_T V_0 + \beta_T)\right]\left[T_m - T_0 - \left(\frac{\Delta T}{h}\right)\frac{h}{2}\right]$$

$$+ \left[\beta_C' g - \left(\frac{\Delta T}{h}\right)(\sigma_0 V_C + \sigma_C V_0 + \beta_C)\right]\left[\sigma_0\left(\frac{\Delta T}{h}\right)\left(-\frac{h}{2} + \frac{1}{A} - \frac{h}{2}\coth A\frac{h}{2}\right) + \frac{M_1}{M} - w_{10}\right]$$

$$- \left[V_0\sigma_0 + \beta_0 - \frac{V_0^2 gh}{\mu_0 \Delta T}\right]\left[\left(\frac{\Delta T}{h}\right)\frac{K_\rho}{K_0}\,\frac{M}{a^2\pi h} + \left(\frac{\Delta T}{h}\right)^2 \frac{h}{2K_0}\,(K_T + K_C\sigma_0)\right]$$

$$- \left[\beta_\rho' g - \left(\frac{\Delta T}{h}\right)(\sigma_0 V_\rho + \sigma_\rho V_C + \beta_\rho)\right]\rho_0 \tag{5.31}$$

$$C = \left[\left[V_0\sigma_0 + \beta_0 - \frac{V_0^2 gh}{\mu_0(\Delta T)}\right]\left[\left(\frac{\Delta T}{h}\right)\frac{1}{K_0}\,(K_T + K_C\sigma_0)\right] + [\beta_T' + \beta_C'\sigma_0]g\right.$$

$$\left. + \left(\frac{\Delta T}{h}\right)[\beta_T + \beta_C\sigma_0 - \sigma_0(V_T + V_C\sigma_0) + V_0(\sigma_T + \sigma_C\sigma_0)]\right]\frac{\Delta T}{2h} \tag{5.32}$$

$$D = \frac{1}{A}\left[\frac{MAe^{-A\frac{h}{2}}}{2a^2\pi\ \sinh\ A\frac{h}{2}}\right]\left[\beta'_\rho g + \left(V_0\sigma_0 + \beta_0 - \frac{V_0^2 gh}{\mu(\Delta T)}\right)\left(\frac{\Delta T}{h}\right)\left(\frac{K_\rho}{K_0}\right)\right.$$
$$\left. - \left(\frac{\Delta T}{h}\right)(\sigma_0 V_\rho + V_0\sigma_\rho + \beta_\rho)\right] \tag{5.33}$$

Note that the zeroth-order solutions have also been used.

The solution to equation (5.30) which satisfies the boundary condition (5.26) is easily found to be

$$d_{01} = \left\{\frac{B}{A} - \frac{2C}{A^2} + Bz + Cz^2 + De^{Az}\right.$$
$$\left. + \left[D\cosh\left(A\frac{h}{2}\right) - \frac{h}{2}\left(B - \frac{2C}{A} + Ch\right)\operatorname{sech}\left(\frac{Ah}{2}\right)\right]e^{A\frac{h}{2}}\right\}\left(d_{00} + \frac{M}{a^2\pi h}\right) \tag{5.34}$$

Finally the substitution of the temperature gradient and the complete expression for σ_1 into equation (5.21) for the composition gives

$$\frac{dC_{01}}{dz} = E + 2Fz + G\left(d_{00} + \frac{M}{a^2\pi h}\right) \tag{5.35}$$

where

$$E = \left(\frac{\Delta T}{h}\right)\left[\sigma_T\left(T_m - T_0 - \left(\frac{\Delta T}{h}\right)\frac{h}{2}\right) + \sigma_C\left(\sigma_0\left(\frac{\Delta T}{h}\right)\left(-\frac{h}{2} + \frac{1}{A} - \frac{h}{2}\coth\left(A\frac{h}{2}\right)\right)\right.\right.$$
$$\left.\left. + \frac{M_1}{M} - w_{10}\right) - \sigma_\rho\rho_0\right] + \left(\sigma_0 - \frac{hgV_0}{\mu_0(\Delta T)}\right)\left[\left(\frac{\Delta T}{h}\right)\frac{K_\rho}{K_0}\ \frac{M}{a^2\pi h}\right.$$
$$\left. + \left(\frac{\Delta T}{h}\right)^2 \frac{h}{2K_0}(K_T + K_C\ \sigma_0)\right] \tag{5.36}$$

$$F = \frac{1}{2}\left(\frac{\Delta T}{h}\right)^2\left[\sigma_T + \sigma_C\sigma_0 - \left(\sigma_0 - \frac{hgV_0}{\mu_0(\Delta T)}\right)\frac{1}{K_0}(K_T + K_C\sigma_0)\right] \tag{5.37}$$

$$G = \left(\frac{\Delta T}{h}\right)\left[\sigma_\rho - \left(\sigma_0 - \frac{hgV_0}{\mu_0(\Delta T)}\right)\frac{K_\rho}{K_0}\right] \tag{5.38}$$

Equation (5.35) when integrated gives the following expression for the composition:

$$C_{01} = R + Ez + Fz^2 + \frac{G}{A}\left(d_{00} + \frac{M}{a^2\pi h}\right) \tag{5.39}$$

where R is a constant of integration. The constant R is found by substitution of (5.39) into the boundary condition (5.27) and using the previously found solutions for C_{00}, d_{00}, and d_{01}. It is

$$\begin{aligned} R = {} & \frac{\left(E+\sigma_0\left(\frac{\Delta T}{h}\right)Q\right)}{A}\left[1 - \frac{Ahe^{A\frac{h}{2}}}{2\sinh A\frac{h}{2}}\right] \\ & - \frac{\left(F+\sigma_0\left(\frac{\Delta T}{h}\right)B\right)}{A^2}\left[2 - \frac{(Ah-2)Ahe^{A\frac{h}{2}}}{2\sinh A\frac{h}{2}}\right] \\ & + \frac{\sigma_0\left(\frac{\Delta T}{h}\right)C}{A^3}\left[6 - \frac{(A^2h^2-3Ah+6)Ahe^{A\frac{h}{2}}}{2\sinh A\frac{h}{2}}\right] \\ & + \frac{\sigma_0\left(\frac{\Delta T}{h}\right)D}{2A}\left[e^{A\frac{h}{2}}\cosh A\frac{h}{2} - \frac{Ahe^{3A\frac{h}{2}}}{2\sinh A\frac{h}{2}}\right] \\ & - \frac{MG}{2a^2\pi}\coth A\frac{h}{2} \end{aligned} \tag{5.40}$$

where Q is

$$Q = \left[D\cosh\left(A\frac{h}{2}\right) - \frac{h}{2}\left(B - \frac{2C}{A} + Ch\right)\operatorname{sech}\left(A\frac{h}{2}\right)\right]e^{A\frac{h}{2}} \tag{5.41}$$

Equations first order in ε[1].--The convective corrections due to heat loss first enter in the terms of the transport equations which are first order in ε. When the terms of order ε are equated, the following equations are obtained:

$$\underset{\sim}{v}_{10} \cdot \underset{\sim}{\nabla} d_{00} + \left(d_{00} + \frac{M}{a^2\pi h}\right) \underset{\sim}{\nabla} \cdot \underset{\sim}{v}_{10} = 0 \tag{5.42}$$

$$\left(d_{00} + \frac{M}{a^2\pi h}\right) \underset{\sim}{v}_{10} \cdot \nabla C_{00} - \underset{\sim}{\nabla} \cdot \underset{\sim}{J}_{10} = 0 \tag{5.43}$$

$$\begin{aligned} \underset{\sim}{\nabla} d_{10} + A d_{10} \underset{\sim}{\lambda} + \left(d_{00} + \frac{M}{a^2\pi h}\right) (\beta_0 \underset{\sim}{\nabla} T_{10} + V_0 \underset{\sim}{\nabla} C_{10}) \\ = \beta_0' \eta_0 \nabla^2 \underset{\sim}{v}_{10} + \beta_0' \left(\frac{1}{3}\eta_0 + \phi_0\right) \underset{\sim}{\nabla} (\underset{\sim}{\nabla} \cdot \underset{\sim}{v}_{10}) \end{aligned} \tag{5.44}$$

$$\begin{aligned} K_0 \nabla^2 T_{10} = \left(d_{00} + \frac{M}{a^2\pi h}\right) \left[\frac{\beta_0 (T_r + T_{00}) A}{\beta_0'} - C_{V0} \left(\frac{\Delta T}{h}\right) \right. \\ \left. - \sigma_0 \left(\frac{\Delta T}{h}\right) \left[\frac{(T_r + T_{00}) \beta_0 V_0}{\beta_0'} - Q_0 \right] \right] (\underset{\sim}{\lambda} \cdot \underset{\sim}{v}_{10}) \end{aligned} \tag{5.45}$$

$$\begin{aligned} D_0 \underset{\sim}{J}_{10} + \left[\frac{V_0 gh}{\Delta T} - \mu_0 \sigma_0 + \frac{\beta_0 V_0}{\beta_0'} \right] \underset{\sim}{\nabla} T_{10} \\ + \left[\frac{V_0^2}{\beta_0'} + \mu_0 \right] \underset{\sim}{\nabla} C_{10} + \frac{V_0}{\beta_0'} \left(d_{00} + \frac{M}{a^2\pi h}\right)^{-1} \underset{\sim}{\nabla} d_{10} \\ = \frac{V_0}{\beta_0'} \left(d_{00} + \frac{M}{a^2\pi h}\right)^{-2} d_{10} \underset{\sim}{\nabla} \left(d_{00} + \frac{M}{a^2\pi h}\right) \end{aligned} \tag{5.46}$$

---

[1] For the remainder of this section it will be assumed that the quantities r and z have been scaled in such a way that a and h may be taken to be unity. This greatly simplifies the analysis to follow without any loss in generality.

It should be clear that some of the zeroth order solutions have been used in these equations where convenient.

The boundary conditions for this order are

$$T_{10} = 0 \qquad \text{at } z = 0 \tag{5.47}$$

$$T_{10} = 0 \qquad \text{at } z = 1 \tag{5.48}$$

$$\frac{\partial T_{10}}{\partial r} = - T_{00} \qquad \text{at } r = 1 \tag{5.49}$$

for temperature,

$$\int_0^{2\pi} \int_0^1 \int_0^1 d_{10} r dr dz d\psi = 0 \tag{5.50}$$

$$\int_0^{2\pi} \int_0^1 \int_0^1 \left[C_{00} d_{10} + \left(d_{00} + \frac{M}{a^2 \pi h}\right) C_{10}\right] r dr dz d\psi = 0 \tag{5.51}$$

for density and composition, and

$$v_{10z} = v_{10r} = J_{10z} = 0 \quad \text{at } z = 0,1 \tag{5.52}$$

$$v_{10z} = v_{10r} = J_{10r} = 0 \quad \text{at } r = 1 \tag{5.53}$$

for the velocity and diffusion flux.

Solutions first order in ε.--The increased number and complexity of the equations for the convective corrections necessitate a different approach from that used in the previous two cases. In this case it is convenient to begin with the solution for velocity. It is possible, by introducing a velocity potential Φ which determines the velocities according to

$$v_{10r} = \frac{1}{r}\left(d_{00} + \frac{M}{a^2\pi h}\right)^{-1} \frac{\partial\Phi}{\partial z} \tag{5.54}$$

and

$$v_{10z} = -\frac{1}{r}\left(d_{00} + \frac{M}{a^2\pi h}\right)^{-1} \frac{\partial\Phi}{\partial r}\,, \tag{5.55}$$

to satisfy the continuity equation (5.42) identically.

Although at first sight the equation of motion (5.44) appears formidable, it can be used to obtain a single partial differential equation for the potential Φ alone. The curl of equation (5.44) has only one component:

$$\begin{aligned} A\,\frac{\partial d_{10}}{\partial r} + A\left(d_{00} + \frac{M}{a^2\pi h}\right)\left[\beta_0\,\frac{\partial T_{10}}{\partial r} + v_0\,\frac{\partial C_{10}}{\partial r}\right] \\ = \beta_0'\eta_0\nabla^2\left(\frac{\partial v_{10r}}{\partial z} - \frac{\partial v_{10z}}{\partial r}\right) \end{aligned} \tag{5.56}$$

while the divergence of the equation of motion may be written

$$\begin{aligned} \left(\nabla^2 - A\,\frac{\partial}{\partial z}\right) d_{10} + \left(d_{00} + \frac{M}{a^2\pi h}\right)\left(\nabla^2 + A\,\frac{\partial}{\partial z}\right)\left(\beta_0 T_{10} + v_0 C_{10}\right) \\ = \beta_0'\left(\frac{4}{3}\eta_0 + \phi_0\right) A\nabla^2 v_{10z} \end{aligned} \tag{5.57}$$

If equation (5.56) is operated on by $\nabla^2 - \frac{1}{r^2} - A\frac{\partial}{\partial z}$ and equation (5.57) is operated on by $\frac{\partial}{\partial r}$, then each of the left hand sides are equal and may be eliminated between the two equations. This gives the following equation for the velocities alone:

$$\left[\nabla^2 - \frac{1}{r^2} A \frac{\partial}{\partial z} \nabla^2\right]\left(\frac{\partial v_{10r}}{\partial z} - \frac{\partial v_{10z}}{\partial r}\right) = A^2\left(\frac{4}{3} + \frac{\phi_0}{\eta_0}\right)\left(\nabla^2 - \frac{1}{r^2}\right)\frac{\partial v_{10z}}{\partial r} \qquad (5.58)$$

With the introduction of the velocity potential Φ, equation (5.58) becomes the following sixth-order partial differential equation:

$$\left(\nabla^2 - \frac{1}{r^2} - A \frac{\partial}{\partial z}\right)\nabla^2 \frac{1}{r} e^{-Az}\left(r\frac{\partial}{\partial r}\frac{1}{r}\frac{\partial}{\partial r} + \frac{\partial^2}{\partial z^2} - A \frac{\partial}{\partial z}\right)\Phi$$

$$+ A^2\left(\frac{4}{3} + \frac{\phi_0}{\eta_0}\right)\left(\nabla^2 - \frac{1}{r^2}\right)e^{-Az} \frac{\partial}{\partial r}\frac{1}{r}\frac{\partial}{\partial r} \Phi = 0 \qquad (5.59)$$

It is obvious that this equation is far too complex to be amenable to exact analysis. There are however several possibilities for approximations. If the terms of (5.59) are expanded in detail, factors of the type $(1 + A^2 f + A^4 g + \ldots)$ occur very frequently. It was pointed out earlier that A is typically on the order of 10^{-2}. For this reason the higher order terms in A are ignored wherever they occur. This allows equation (5.59), after a great deal of algebraic manipulation, to be written in the compact form

$$\sum_{n=1}^{6} \sum_{\substack{j=0 \\ \text{even}}}^{n} L_{nj} \frac{(-1)^n}{r^{7-n}} \frac{\partial^n \Phi}{\partial r^{n-j} \partial z^j} + \sum_{n=1}^{6} \sum_{\substack{j=0 \\ \text{odd}}}^{n} L_{nj} \frac{(-1)^n A}{r^{6-n}} \frac{\partial^n \Phi}{\partial r^{n-j} \partial z^j} = 0 \qquad (5.60)$$

where the matrix L_{nj} is defined as

$$L_{nj} = \begin{pmatrix} 60 & 8 & 0 & 0 & 0 & 0 & 0 \\ 60 & 26 & 8 & 0 & 0 & 0 & 0 \\ 30 & 22 & 15 & 4 & 0 & 0 & 0 \\ 10 & 12 & 11 & 12 & 1 & 0 & 0 \\ 3 & 60 & 6 & 12 & 3 & 6 & 0 \\ 1 & 0 & 3 & 0 & 3 & 0 & 1 \end{pmatrix} \qquad (5.61)$$

Although equation (5.60) is still too complicated to allow an exact analysis, an approximate solution will be sought in the form

$$\Phi^* = r(r-1)z^2(z-1)^2\left[r(r-1) + \sum_{i=0}^{N}\sum_{j=1}^{M} C_{ij}z^i \sin \pi jr\right] \qquad (5.62)$$

The approximating function has been chosen in such a way that all the boundary conditions (5.53-53) are automatically satisfied. Furthermore, each term is a member of a complete set of functions and thus independent of every other term. There are a great many techniques and criteria for the determination of the coefficients C_{ik}, but very little information available which would allow a choice to be made from among them. The method of weighted residuals (Finlayson and Scriven, 1965 or Ames, 1965) has been successful in solving a large number of complicated problems and was selected for use in determining the C_{ik}'s.

The method of weighted residuals proceeds as follows: Let the function R represent the residual obtained from the substitution of the approximating function (5.62) into the differential equation (5.60). The residual is given by

$$R = \sum_{\substack{n=1 \\ \text{even}}}^{6} \sum_{j=0}^{n} L_{nj} \frac{(-1)^n}{r^{7-n}} \frac{\partial^n \Phi^*}{\partial r^{n-j} \partial z^j} + \sum_{\substack{n=1 \\ \text{odd}}}^{6} \sum_{j=0}^{n} L_{nj} \frac{(-1)^n A}{r^{6-n}} \frac{\partial^n \Phi^*}{\partial r^{n-j} \partial z^j} \qquad (5.63)$$

The residual R is a measure of the extent to which the function Φ^* satisfies the differential equation. As the number of approximating functions is increased in successive approximations, it is hoped that the residual will become smaller; the exact solution is obtained when the residual is identically zero. As an approximation to this ideal, the weighted integrals of the residual are set equal to zero:

$$\int_0^1 \int_0^1 W_j R\,dr\,dz = 0 \qquad j = 1, \ldots NM \qquad (5.64)$$

If Φ^* is the exact solution, equation (5.64) is satisfied regardless of the choice of weighting functions.

The weighting functions, W_j, can be chosen in several different ways, and each choice corresponds to a different criterion in the method of weighted residuals. The least squares method, which apparently was first presented for this type of application by Picone (1928), uses the weighting functions $\frac{\partial R}{\partial C_{ik}}$. The corresponding interpretation is that the mean square residual

$$I = \int_0^1 \int_0^1 R^2 drdz \tag{5.65}$$

is minimized with respect to the constants C_{ik}. (See Mikhlin, 1964), for a discussion of the least squares method.)

In practice the C_{ik}'s are determined by a direct minimization of the integral (5.65) using a computer routine developed in connection with least squares statistical problems. Of course the numerical values of the C_{ik}'s depend on the specific problem, in particular on the value of A. In Appendix C, numerical values calculated for a typical value of A are presented together with plots of the velocity profiles resulting from equations (5.54-55).

Inspection of the temperature equation (5.45) reveals that once the velocity is determined, the only dependent variable in the equation is the temperature correction T_{10}. Introduction of the velocity potential from equation (5.55) yields the following equation for the temperature corrections:

$$\frac{1}{r}\frac{\partial}{\partial r} r \frac{\partial T_{10}}{r} + \frac{\partial^2 T_{10}}{\partial z^2} = (p_1 z + p_2)\frac{1}{r}\frac{\partial \Phi^*}{\partial r} \tag{5.66}$$

where

$$p_1 = \frac{\beta_0(\Delta T)}{K_0\beta_0'}\left(A - \sigma_0 V_0(\Delta T)\right) \tag{5.67}$$

and

$$p_2 = \frac{1}{K_0}\left[(\sigma_0 Q_0 - C_{V0})(\Delta T) + \frac{\beta_0}{\beta_0'}\left(T_m - \frac{1}{2}(\Delta T)\right)\left(A-\sigma_0 V_0(\Delta T)\right)\right] \tag{5.68}$$

The z dependence of T_{10} is most easily determined by taking a finite sine transform of equation (5.66) and the associated boundary conditions (5.47-49). Multiplication of (5.66) by $\sin(\pi nz)$ and integration over z from 0 to 1 yields

$$\left[\frac{1}{r}\frac{d}{dr}\,r\,\frac{d}{dr} - n^2\pi^2\right]\tau_n(r) = T_{hn}(r) \tag{5.69}$$

after two integrations by parts and use of the boundary conditions. The sine transform of T_{10}, denoted by τ_n in (5.69) is defined as

$$\tau_n(r) = \int_0^1 T_{10}(r,z)\sin n\pi z dz \tag{5.70}$$

while the inhomogeneous term T_{hn} is given by the following integral:

$$T_{hn}(r) = \int_0^1 (p_1 z + p_2)\,\frac{1}{r}\frac{\partial\Phi^*}{\partial r}\sin n\pi z dz \tag{5.71}$$

The boundary condition (5.49) is transformed into

$$\frac{\partial \tau_n}{\partial r} = \frac{1}{n\pi} \left[(T_r - T_m + 1/2\ \Delta T)(1 - (-1)^n) + (-1)^n \right] \qquad (5.72)$$

Finally, because of the completeness and othogonality of the sine functions on the interval 0 to 1, T_{10} is determined from the transforms τ_n, by the sine series

$$T_{10}\ (r,z) = \sum_{n=1}^{\infty} \tau_n\ (r) \sin\ (n\pi z) \qquad (5.73)$$

The homogeneous part of equation (5.69) is immediately seen to be a special case of the modified Bessel equation. The general solution can be written as

$$\tau_n\ (r) = C_1 I_0\ (n\pi r) + C_1 K_0\ (n\pi r) \qquad (5.74)$$

where I_0 and K_0 are the modified Bessel functions of order zero, of the first and second types, respectively. The function K_0 (r) can be approximated by -ln (r) for small r, and thus increases without limit as r approaches zero. Consequently the coefficient C_2 will be set to zero. A particular solution to equation (5.69) is much more difficult to obtain. One procedure which works well in an approximate sense is to write the inhomogeneous term as a power series in r which is easily derived from the expansion of the sine functions in Φ^*. If this series is represented by

$$T_{hn} = \sum_{\ell=0}^{\infty} H_{n\ell} r^{\ell} \qquad (5.75)$$

then a particular solution may be written

$$\tau_{np} = \sum_{\ell=0}^{\infty} G_{n\ell} r^{\ell} \qquad (5.76)$$

where

$$G_{n0} = G_{n1} = 0 \qquad (5.77)$$

and

$$(\ell + 2)^2 \, G_{n,\ell+2} - n^2 \pi^2 G_{n,\ell} = H_{n,\ell} \qquad (5.78)$$

The first few coefficients of (5.75) are

$$H_{n0} = 2 \, (p_1 K_{1,n} + p_2 K_{0,n}) \qquad (5.79)$$

$$H_{n1} = \sum_{i=0}^{N} \sum_{j=1}^{M} \pi j C_{ij} \, (p_1 K_{i+1,n} + p_2 K_{in}) - 6 (p_1 K_{1,n} + p_2 K_{0,n}) \qquad (5.80)$$

$$H_{n2} = - \sum_{i=0}^{N} \sum_{j=1}^{M} \frac{(\pi j)^3}{3} C_{ij} (p_1 K_{i+1,n} + p_2 K_{in}) + 4 (p_1 K_{1,n} + p_2 K_{0,n}) \qquad (5.81)$$

where the matrix $K_{m,n}$ is defined as

$$K_{m,n} = (-1)^{m+1} \sum_{j=0} (-1)^j \, (2j)! \, (m\pi)^{-2j-1} \left[\binom{n+4}{2j} - 2 \binom{n+3}{2j} + \binom{n+2}{2j} \right] \qquad (5.82)$$

The coefficient C_1 is to be determined from the boundary condition (5.72) and has the following value:

$$C_1 = \frac{1}{(n\pi)^2 I_1(n\pi)} \left[(T_r - T_m + 1/2\ \Delta T)(1-(-1)^n) + (-1)^n - n\pi \sum_{\ell} \ell G_{n\ell} \right] \tag{5.83}$$

The temperature correction has thus been completely specified and may be calculated for any particular set of conditions. In Appendix C the temperature profiles have been calculated and graphed for the same conditions under which the velocity corrections were calculated.

If the potential Ψ for the diffusion flux is defined according to

$$\underset{\sim}{J}_{10} = \underset{\sim}{\nabla}\Psi \tag{5.84}$$

then the equation of continuity (5.43) becomes

$$\nabla^2\Psi = -\sigma_0 \ (\Delta T) \frac{1}{r} \frac{\partial \Phi^*}{\partial r} \tag{5.85}$$

This equation is virtually identical to equation (5.66) for the temperature. The solution to (5.85) is therefore

$$\Psi = \sum_{n=1}^{\infty} f_n(r) \sin(n\pi z) \tag{5.86}$$

where

$$f_n(r) = B_1 I_0(n\pi r) + \sum_{\ell=2}^{\infty} G'_{n\ell} r^{\ell} \tag{5.87}$$

where the equations (5.77-82) are again used to determine $G'_{n\ell}$ but with p_1 equal to zero and $p_2 = -\sigma_0\ (\Delta T)$. The constant B_1 is determined from the boundary condition (5.53) and is equal to

$$B_1 = \frac{-1}{I_0(n\pi)} \sum_{\ell=2}^{\infty} G'_{n\ell} \tag{5.88}$$

With the velocity, temperature, and diffusion flux corrections completely determined, it is now possible to obtain solutions for the composition and density corrections from the diffusion flux equation (5.46) and the equation of motion (5.44). It is a simple matter to rearrange and eliminate terms between these two equations to yield the following two equations:

$$\begin{aligned}(\underset{\sim}{\nabla} + A\underset{\sim}{\lambda})\, d_{10} = {} & \left(d_{00} + \frac{M}{a^2 \pi h}\right)\left[\frac{V_0 D_0}{\mu_0}\ \underset{\sim}{J}_{10} + \left(\frac{V_0^2 g h}{\mu_0 \Delta T} - V_0\sigma_0 - \beta_0\right)\underset{\sim}{\nabla} T_{10}\right] \\ & + \left(\frac{V_0^2}{\mu_0} + \beta'_0\right)\left[\eta_0 \nabla^2 \underset{\sim}{v}_{10} + (1/3\ \eta_0 + \phi_0)\,\underset{\sim}{\nabla}(\underset{\sim}{\nabla}\cdot\underset{\sim}{v}_{10})\right]\end{aligned} \tag{5.89}$$

$$\begin{aligned}\underset{\sim}{\nabla} C_{10} = {} & \left(\sigma_0 - \frac{V_0 g h}{\mu_0 \Delta T}\right)\ \underset{\sim}{\nabla} T_{10} - \frac{D_0}{\mu_0}\ \underset{\sim}{J}_{10} \\ & - \frac{V_0\left(d_{00} + \dfrac{M}{a^2 \pi h}\right)^{-1}}{\mu_0}\left[\nabla^2 \underset{\sim}{v}_{10} + (1/3\ \eta_0 + \phi_0)\,\underset{\sim}{\nabla}(\underset{\sim}{\nabla}\cdot\underset{\sim}{v}_{10})\right]\end{aligned} \tag{5.90}$$

The right hand sides of both of these equations are now completely known and it is an easy matter to integrate the equations. However, the major interest in the thermal diffusion experiments usually centers on the gradients, and it is therefore deemed unnecessary to go further.

This completes the solution to the convective heat loss equations at first order. It is obvious that the same process could be carried on to higher orders, but inasmuch as the corrections at the first order are already quite small, the corrections from higher orders are expected to be negligibly small.

6. Summary

It has been shown in this chapter that the perturbation expansion method can be a useful and valid technique for the solution of complex partial differential equations under a variety of difficult conditions. Corrections to account for convection due to heat loss in a thermal diffusion cell are now available for the first time, as well as corrections for the variability of phenomenological coefficients. It is doubtful that another technique could have achieved the same results without much greater effort. Finally, because of the simplicity of the approach, it seems reasonable to expect that it can be applied easily to countless other difficult problems.

CHAPTER IV

PARAMETER ESTIMATION

1. Introduction

The preceding chapters have been concerned with the problem of determining theoretical descriptions for experiments on liquid mixtures. The approach has been as rigorous as possible even though practical necessities have at times required approximation methods such as the perturbation technique. Once the differential equations appropriate to a particular experiment have been formulated and solved, the next step is to compare the solutions with actual experimental data.

Much of modern experimental physical science is concerned with the assignment of numerical values to quantities which occur in physical theories. This assignment is never absolutely accurate. No matter how well a measuring device is designed, there will always be limitations inherent in the materials, methods of construction, or human observation which will make the reproducibility of a measurement impossible at some level.

The inability to make precise measurements is only one of the problems which arises when the results of experiments are to be tested against physical theories. Another problem which is becoming more and more important as the sophistication of experiments and theories increases, arises in the fact that the quantities which can be most conveniently measured are not the quantities of basic interest in the theory. Mathematical relationships must be used to go from one to the other; these relationships may be simple or complex. In any case, if the quantity A has been measured with a given precision, we will want to know how well we know the value of a derived quantity B. A more general problem arises when a multitude of quantities A_1, A_2, ..., A_n have been measured, and it is necessary to determine the values of a set of theoretical parameters B_1, B_2, ..., B_m all of which are interrelated, each being dependent on all the A_i.

How are the best values of the B_i to be determined and is it possible to make a reliable estimate of the uncertainty in each estimated parameter? In fact is it possible that some of the parameters are not determined at all from the data? The solutions to these and related problems are the concern of statistical analysis. The comparison of experimental and theoretical descriptions can only be made after an attempt to answer some of these questions by statistical analysis.

In cases for which the relations between the experimental data and the parameters to be estimated are linear, standard techniques of multiple regression analysis have been developed to answer some of the questions above. If the random errors involved are normally distributed, then many of the standard statistical tests (F test, Student's t test, etc.) provide very powerful methods for testing hypotheses on the parameters. Unfortunately, the nonlinear problem occurs quite frequently, and typically the distribution of errors is unknown. In these cases statistical analysis has provided very few methods of general applicability.

In this chapter a generalization of the least squares or minimum variance parameter estimation technique is presented (see Hamilton, 1964, or Wentworth, 1965). The present approach is novel in several respects: (1) No assumptions are made about the data being uncorrelated; (2) It is not necessary to assume that the experimental errors are normally distributed; (3) No assumption of linearity in either the data or the parameters is necessary.

Finally, two examples which arose in the study of pure thermal diffusion experiments and which illustrate the methods and the computer techniques necessary to implement them are presented. Of particular interest in these examples is the difference between results obtained from the new approach and those obtained by the ordinary least squares method.

2. Generalized Least Squares Adjustment of Data

It will be supposed that in a given experiment or set set of experiments the n quantities

$$Z_1, Z_2, \ldots, Z_n \tag{2.1}$$

are measured and further that each of these n observables is known to depend on a set of m parameters

$$Y_1, Y_2, \ldots, Y_m \tag{2.2}$$

as represented by the function

$$f(Z_1^*, \ldots, Z_n^*, Y_1^*, \ldots, Y_m^*) = 0 \ . \tag{2.3}$$

The symbol * in (2.3) denotes the true or theoretical value. The value of the i^{th} observable for the k^{th} observation will be denoted by Z_{ik}. Thus the data for a series of N experiments or N repetitions of an experiment can be represented as

$$Z_{1i}, Z_{2i}, \ldots, Z_{ni} \ , \qquad i = 1, \ldots, N \tag{2.4}$$

It will be assumed that the errors or deviations of the experimental measurements from their theoretical values are random variables having a joint distribution with zero means, and that the variance-covariance matrices

$$(M^{i\ell})^{-1}_{kj} = E \quad (Z_{ki} - Z^*_{ki})(Z_{j\ell} - Z^*_{j\ell}) \qquad (2.5)^1$$

are of rank n. Thus one of the basic assumptions of this approach is that the errors in the observations are drawn from populations with finite second moments. It may be noted at this point that this is the only requirement, and that the theory of least squares does not depend on the assumption that the errors follow a normal distribution, although the latter assumption is commonly and mistakenly believed to be necessary.

A good measure of precision is usually taken to be inversely proportional to the dispersion or variance of a random variable. Thus one method of adjusting the data might be to choose the estimates of the theoretical data points, Z^*_{ij}, in such a way that the total sample variance

---

[1] Consider a sample space, a random variable x defined over this space, and some function of x: f(x). The expected value of f(x) is defined as

$$E \{f(x)\} = \Sigma f(x) P(x)$$

if the sample space is discrete, with probability measure P(x); the sum is over all points of the sample space. If the sample space is continuous with probability density function $\phi(x)$, the expected value is defined as

$$E \{f(x)\} = \int_{-\infty}^{\infty} f(x)\phi(x)\, dx$$

In either case, the expected value is defined only if the sum or integral exists.

$$S = \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{k=1}^{n} \sum_{=1}^{n} (Z_{ki} - Z^{*}_{ki})\, M^{ij}_{k\ell}\, (Z_{\ell j} - Z^{*}_{\ell j}) \qquad (2.6)$$

is a minimum. Note that in calculating the total sample variance the experimental points have been weighted in inverse proportion to their variances. Unfortunately, the estimates Z^{*}_{ij} cannot all be varied independently in the minimization of (2.6) since they are related to each other and to the parameters by the equations

$$f_i\ (Z^{*}_{1i}, Z^{*}_{2i}, \ldots Z^{*}_{ni}, Y^{*}_{1}, \ldots Y^{*}_{m}) = 0\ . \qquad (2.7)$$

It is usually convenient, when minimizing under a constraint like (2.7) to introduce Lagrangian multipliers, λ_i, and to minimize

$$S' = S + \sum_{i=1}^{N} \lambda_i f_i \qquad (2.8)$$

instead of (2.6). Equating to zero the λ_r, Y^{*}_{k}, and Z^{*}_{pr} derivatives of S' yields the minimum conditions

$$f_r = 0 \qquad r=1,\ldots N \qquad (2.9)$$

$$\sum_{r=1}^{N} \lambda_r \left(\frac{\partial f_r}{\partial Y^{*}_{k}}\right) = 0 \qquad k=1,\ldots m \qquad (2.10)$$

and

$$\frac{1}{2}\lambda_r \left(\frac{\partial f_r}{\partial Z^{*}_{pr}}\right) = \sum_{i=1}^{N} \sum_{k=1}^{n} M^{ri}_{pk}\, (Z_{ki} - Z^{*}_{ki}) \qquad r=1,\ldots N \quad p=1,\ldots n \qquad (2.11)$$

Note that the symmetry of M_{ik} has been used in simplifying equation (2.11).

Equations (2.9-11) are N(n + 1) + m conditions for the determination of the N(n + 1) + m unknowns λ_r, Y^*_k, and Z^*_{ij}. Unless the equations of (2.9) are linear, these are the most difficult to solve. In the nonlinear case the standard technique of Newton's method may be used, resulting in an iterative procedure. Newton's method for (2.9) consists of expanding each equation in a Taylor series about some initial guess for the parameters and truncating after first derivatives:

$$f_r = f_r^0 - \sum_{j=1}^{m} \left(\frac{\partial f_r}{\partial Y_j^*}\right) (Y_j^0 - Y_j^*) - \sum_{j=1}^{n} \left(\frac{\partial f_r}{\partial Z_{jr}^*}\right) (Z_{jr} - Z_{jr}^*) = 0 \quad (2.12)$$

If the differences $(Y_j^0 - Y_j^*)$ obtained from the solution of (2.10-12) are sufficiently small, then the Y_j^0's may be taken as the least squares estimates of the parameters Y_j^*. If the differences are not small enough, then new estimates of the parameters can be found by subtracting the differences from the original estimates and re-solving the equations. This procedure may be continued until the differences are as small as desired.

Terms containing the differences $(Z_{jr} - Z^*_{jr})$ will be eliminated from equation (2.12) by using the solution to equation (2.11). Equation (2.11) yields

$$(Z_{jr} - Z^*_{jr}) = \frac{1}{2} \sum_{i=1}^{N} \sum_{k=1}^{n} H^{ri}_{jk} \lambda_i \left(\frac{\partial f_i}{\partial Z^*_{ki}}\right) \qquad \begin{matrix} j=1,\ldots n \\ r=1,\ldots N \end{matrix} \tag{2.13}$$

where H^{ri}_{jk} is determined from the conditions

$$\sum_{j=1}^{n} \sum_{r=1}^{N} M^{\ell}_{mj} H^{ri}_{jk} = \delta_{i\ell}\delta_{km} \qquad \begin{matrix} \ell=1,\ldots N \\ m=1,\ldots n \end{matrix} \tag{2.14}$$

If equation (2.13) is introduced into (2.12) one obtains

$$f^0_r - \sum_{j=1}^{m} \left(\frac{\partial f_r}{\partial Y^*_j}\right) (Y^0_j - Y^*_j) = \frac{1}{2} \sum_{i=1}^{N} (W^{-1})_{ri} \lambda_i \tag{2.15}$$

where for convenience the following definition has been made:

$$(W^{-1})_{ri} = \sum_{j=1}^{n} \sum_{k=1}^{n} \left(\frac{\partial f_r}{\partial Z_{jr}}\right) H^{ri}_{jk} \left(\frac{\partial f_i}{\partial Z_{ki}}\right) \qquad \begin{matrix} i=1,\ldots N \\ r=1,\ldots N \end{matrix} \tag{2.16}$$

Equation (2.15) may be written in matrix form as follows:

$$\underset{\sim}{F}^0 - \underset{\sim}{A}\Delta Y = \frac{1}{2} W^{-1} \underset{\sim}{\lambda} \tag{2.17}$$

where

$$(F^0)_k = f^0_k \tag{2.18}$$

$$(\Delta Y)_k = (Y^0_k - Y^*_k) \tag{2.19}$$

$$(A)_{ij} = \left(\frac{\partial f_i}{\partial Y^*_j}\right) \tag{2.20}$$

and the matrix W has been defined in (2.16). Equation (2.10) in matrix notation becomes

$$A^T \underset{\sim}{\lambda} = 0 \tag{2.21}$$

Multiplication of (2.17) by A^TW and use of (2.21) yields

$$\underset{\sim}{\Delta Y} = (A^TWA)^{-1}\ A^TW\underset{\sim}{F}{}^0 \tag{2.22}$$

which corresponds to the normal equations usually obtained in the ordinary least squares method. Thus to obtain estimates of the deviations of the parameter guesses from their true values, it is only necessary to perform matrix inversions and multiplications.

Suppose now that $(M^{ij})^{-1}_{k\ell}$ is known only to within a scale factor:

$$(M^{ij})^{-1}_{k\ell} = \sigma^2\ (N^{ij})^{-1}_{k\ell} \tag{2.23}$$

It therefore follows that W is determined to within a constant:

$$W = \frac{1}{\sigma^2} P \tag{2.24}$$

where P is determined from (2.14) and (2.16). Using (2.24) in (2.22) gives

$$\underset{\sim}{\Delta Y} = (A^TPA)^{-1}\ A^TP\underset{\sim}{F}{}^0 \tag{2.25}$$

and the normal equations are thus seen to be independent of the scale of the weight matrix P.

Errors in the parameter estimates.--Once the best least squares values have been obtained as solutions to (2.25), it is necessary to determine the variance-covariance or moment matrix for the parameters. The desired matrix is

$$Q = \varepsilon \{ (\underset{\sim}{\Delta Y}) (\underset{\sim}{\Delta Y})^T \} \qquad (2.26)$$

By use of the normal equations (2.25), (2.26) may be written

$$Q = (A^TWA)^{-1} \; A^TW\varepsilon \; \{\underset{\sim}{F}^0 \underset{\sim}{F}^{0^T}\} WA(A^TWA)^{-1} \qquad (2.27)$$

Now if the iterative procedure has converged so that the deviations are small then

$$\varepsilon \; \{\underset{\sim}{F}\underset{\sim}{F}^T\} = W^{-1} \qquad (2.28)$$

Use of (2.28) in (2.27) gives

$$Q = (A^TWA)^{-1} = \sigma^2 \; (A^TPA)^{-1} \qquad (2.29)$$

To obatin the moment matrix for the parameters, it is thus necessary either to know σ^2, in which case Q is completely determined, or to make an unbiased estimate for σ^2, in which case only an unbiased estimate of the moment matrix is available. It will now be shown that an unbiased estimate of σ^2 is indeed available from the results of the least squares treatment.

The value of S in equation (2.6) at the least squares solution is found by substitution of (2.13) into (2.6), with the result

$$S = (\utilde{F}^0 - A\Delta\utilde{Y})^T W (\utilde{F}^0 - A\Delta\utilde{Y}) \ . \tag{2.30}$$

Use of the normal equations (2.22) in (2.30) gives

$$S = \utilde{F}^{0^T} W\utilde{F}^0 - (\Delta\utilde{Y})^T (A^T WA)(\Delta\utilde{Y}) \tag{2.31}$$

Because of (2.28-9) the expected value of (2.31) is

$$\varepsilon\{S\} = N - m \tag{2.32}$$

From (2.32) and (2.24) it is clear that an unbiased estimate of σ^2 may be obtained from

$$\sigma^2 = (N - m)^{-1} (\utilde{F}^0 - A\Delta\utilde{Y})^T P (\utilde{F}^0 - A\Delta\utilde{Y}) \tag{2.33}$$

which means finally that an unbaised estimate of the moment matrix of the parameters may be obtained from

$$Q = (N - m)^{-1} (\utilde{F}^0 - A\Delta\utilde{Y})^T P (\utilde{F}^0 - A\Delta\utilde{Y}) (A^T PA)^{-1} \tag{2.34}$$

3. An Alternative Approach

It happens very often that the iterative procedure suggested in the previous section fails to converge because the initial parameter estimates are not good enough. This is typical behavior for analogues of Newton's method. Several procedures have been suggested for improving the

convergence of the least squares method. Box (1958), Hartley (1961), and Strand, Kohl, and Bonham (1963) have all suggested the introduction of a parameter t into the normal equations

$$\underset{\sim}{\Delta Y} = t\ (A^T WA)^{-1}\ A^T W\underset{\sim}{F}^0 \tag{3.1}$$

A value for t is then chosen which makes the variance S of equation (2.6) as small as possible. While this procedure extends the range of convergence of the method, divergence is still obtained for a large number of practical problems, which necessitates even further refinement of the method.

The method of damped least squares as suggested by Levenberg (1944) and subsequently modified by Meiron (1965) has been one of the most successful improvements in the basic least squares method from the standpoint of convergence. (See the comparisons of Pitha and Jones (1966).) This method requires that the changes of the variables $\underset{\sim}{\Delta Y}^T G \underset{\sim}{\Delta Y}$ be minimized simultaneously with S. This keeps the method from taking steps outside of the region of validity of the Taylor series expansions, one of the more important reasons for the divergence of the ordinary least squares method. Meiron's particular choice of G was to take the diagonal elements of $(A^T WA)$. The parameters are then determined from

$$\underset{\sim}{\Delta Y} = (A^T WA + tG)^{-1} A^T W\underset{\sim}{F}^0 \qquad (3.2)$$

where again the parameter t is to be chosen so as to make S as small as possible. While the damped least squares method extends the range of application of the least squares technique, it suffers from two computational disadvantages: (1) The derivative matrices must be calculated at each step of the procedure. (2) A large number of matrix inversions are required not only in determining the parameter estimates, but also in determining the optimum values of the parameter t. These disadvantages can often increase significantly the amount of time required for convergence to be obtained.

For these reasons an alternative approach was sought which would eliminate some of the convergence and computational difficulties encountered in the ordinary or damped least squares methods. An approach which was found to be successful is summarized as follows: The minimization of the quantity

$$S'' = \underset{\sim}{F}'^T W \underset{\sim}{F}' \qquad (3.3)$$

with respect to Y_k^* results in the following minimum conditions

$$\left(\frac{\partial \underset{\sim}{F}'}{\partial Y_h^*}\right)^T W \underset{\sim}{F}' = 0 \ , \qquad (3.4)$$

where W is the matrix defined in (2.16) and $\underset{\sim}{F}'$ is obtained from the Taylor series

$$f_i'(Z_{1i},Z_{2i},\ldots Z_{ni},Y_1^*,\ldots Y_m^*) = \sum_{j=1}^{n} \left(\frac{\partial f_i'}{\partial Z_{ji}}\right)(Z_{ji} - Z_{ji}^*) + \ldots \quad . \tag{3.5}$$

If the behavior of the function F' near the minimum can be represented accurately by the approximation

$$\underset{\sim}{F}' = \underset{\sim}{F}^0 + A\Delta\underset{\sim}{Y} \tag{3.6}$$

then the values of the parameters Y_k^* which give a minimum for S " are the same values as those predicted by the normal equations of the least squares method.

The minimum conditions (3.4) are not used in this case for the determination of the minimum. Instead a one dimensional searching technique, which operates directly on the function (3.3) and which produces a sequence of conjugate directions for the searches as it proceeds, is used. This method, first introduced by Powell (1964), requires no derivative evaluation or matrix inversion. Furthermore, because of the use of conjugate directions the method can find the minimum of any quadratic function of n variables in exactly n searches. The algorithm given by Powell has been programed and the listing of the program and directions for its use are given in Appendix B.

The next two sections illustrate the use of the method on two nonlinear functions of importance in analyzing pure thermal diffusion experiments. It is important to note the effects of different choices for the weight matrix W.

4. Fringe Shape Analysis

In his experimental determination of thermal diffusion constants for the $CCl_4 - C_6H_{12}$ system using wavefront-shearing interferometery, Anderson (1968) observed interference fringes of skewed parabolic shape. The curvature of these fringes is due principally to the temperature dependence of the index of refraction of the $CCl_4 - C_6H_{12}$ mixture. This curvature is also found when a temperature gradient is applied to either pure component. The problem then is one of relating the curvature of the fringes to the temperature dependence of the index of refraction.

The curvature of the fringes is related to the index of refraction by the following formula:

$$x = A\,(n(z + b_1) - n(z - b_1)) + B \qquad (4.1)$$

where A and B are constants, n is the index of refraction, x is the displacement of the fringe measured from an arbitrary vertical plane, z corresponds to a vertical distance in the thermal diffusion cell, and b_1 is a shearing distance introduced by the interferometer.[1]

---

[1] The formula derived by Bryngdahl (1963) and subsequently used by Anderson (1968) has the same appearance as (4.1). However, the constant A, as they define it, makes their equation dimensionally inconsistent. The correct definition is $A = a \cdot d_f/\lambda$, where a is the path length through the cell, d_f is the distance between fringes, and λ is the wavelength of light used.

The temperature distribution in the cell is almost always well known. For example in the case of a pure component, the temperature is given by

$$T = \frac{1}{2} \Delta Tz + T_m - \frac{1}{8} \kappa_T (\Delta T)^2 (z^2 - 1) \tag{4.2}$$

when a temperature difference ΔT is applied between the horizontal planes bounded by $z = -1$ and $z = 1$. The average of the temperatures on the two planes is T_m, and κ_T denotes the temperature variation of thermal conductivity, κ:

$$\kappa_T = \frac{1}{\kappa} \left(\frac{\partial \kappa}{\partial T}\right)_{T_m} \tag{4.3}$$

It has also been assumed that the thermal conductivity depends only linearly on temperature and that the temperature variation is entirely vertical. The index of refraction will be represented by the following series:

$$n\ (z) = \sum_{k=0}^{\infty} u_k \left(\frac{T-T_m}{\Delta T}\right)^k \tag{4.4}$$

The derivatives of index of refraction with respect to temperature are determined from

$$\left(\frac{\partial^i n}{\partial T^i}\right)_{T_m} = \frac{i!}{(\Delta T)^i} u_i \tag{4.5}$$

once the coefficients u_i are known.

Substitution of the index of refraction-temperature expansion (4.4) into the interferometer equation (4.1) gives the final working equation for the least squares analysis:

$$f_i = x_i - A \sum_{k=0}^{\infty} u_k (\Delta T)^{-k} \; (T(z_i+b_1)-T_m)^k - (T(z_i-b_1)-T_m)^k - B \quad (4.6)$$

where the f_i has been written to correspond to the notation of the previous sections. It will be assumed that the data, x_i and z_i, are uncorrelated and of equal weight for all i. Although experience with the measuring technique is limited, nothing has been observed to date which would invalidate this assumption.

The coefficients are determined according to the least squares analysis from the minimization of the quantity

$$Q = \sum_{i=1}^{N} \sum_{j=1}^{N} f_i W_{ij} f_j = \underset{\sim}{F}^T W \underset{\sim}{F} \qquad (4.7)$$

It is particularly important to determine the weight matrix W carefully according to equation (2.16). One finds all too often that in problems where the data are uncorrelated and of equal weight, the weight matrix has been taken to be the identity matrix. This can result in serious systematic errors in the estimates of the coefficients for some problems; the fringe analysis problem provides a good illlustration of errors that can result from improper weighting.

Analysis of the fringe shapes has been done automatically using the computer routines FRNGFIT and FRNGSTAT in conjunction with the MINIMIZE routine. These programs are listed in Appendix B together with instructions for their use. Analysis of the fringes observed for the C_6H_{12} system maintained at a mean temperature of 24.2°C with a 3.382°C temperature difference gives the estimates

$$\begin{aligned} u_2 &= -1.9 \times 10^{-5} \\ u_3 &= 8.1 \times 10^{-5} \\ u_4 &= 7.1 \times 10^{-5} \\ u_5 &= 5.2 \times 10^{-5} \end{aligned} \tag{4.8}$$

under the assumption of unit weights, while use of weights calculated from (2.16) gives the following estimates

$$\begin{aligned} u_2 &= -2.2 \times 10^{-5} \\ u_3 &= 9.0 \times 10^{-5} \\ u_4 &= 3.5 \times 10^{-5} \\ u_5 &= -1.5 \times 10^{-5} \; . \end{aligned} \tag{4.9}$$

Estimates of the standard deviations of these coefficients are

$$\begin{aligned} \sigma_2 &= 1.1 \times 10^{-6} \\ \sigma_3 &= 3.6 \times 10^{-6} \\ \sigma_4 &= 1.1 \times 10^{-5} \\ \sigma_5 &= 2.6 \times 10^{-5} \end{aligned} \tag{4.10}$$

The first coefficient u_1 is determined in a separate experiment and is therefore not estimated here.

It is apparent from the magnitudes of the standard deviations that only the first two coefficients are determined with satisfactory precision from the fringe shapes. Even for these two estimates, however, the difference between the estimates in the two cases is on the order of three or four standard deviations, which clearly demonstrates the need for proper weighting.

5. Time Constant Analysis

The preceding example illustrated the need for careful choice of the weight matrix. However, the fringe shape equation (4.6) is liinear in the coefficients and thus does not illustrate the advantage of the MINIMIZE procedure over the analogues of Newton's method. In this section another least squares problem from the analysis of thermal diffusion experiments is presented. In this case the working equations are not linear in the parameters and therefore provide a good test of the MINIMIZE routine.

Anderson (1968) observed that during the course of a thermal diffusion experiment the fringes moved horizontally with time. The time dependence is exponential and the fringe shift with time can be expressed by

$$d = ae^{-bt} + c \qquad (5.1)$$

where d is the fringe shift measured from an arbitrary initial reference plane, t is time, and a, b, and c are constants to be determined by least squares analysis.

Anderson showed that the ordinary diffusion constant could be calculated from the value of b while the thermal diffusion factor could be calculated from the value of a. The computer routines EXPO and EXPOSTAT listed in Appendix B were written for the purpose of estimating the constants a, b, and c from the experimentally measured fringe shift with time according to the equation

$$f_i = d_i - ae^{-bt_i} - c \ . \tag{5.2}$$

To illustrate the power of the method, the fringe shift data reported by Anderson (1968, p. 158, Table 5j) was analyzed with these routines. The minimum was easily found to within 0.01 percent in only four or five iterations, using at most four seconds of computer time. The estimates found are

$$\begin{aligned} a &= -\ 7.11 \\ b &= 1.81 \times 10^{-2} \\ c &= 1.01 \times 10^{1} \end{aligned} \tag{5.3}$$

and the estimated standard deviations are

$$\begin{aligned} \sigma_a &= 1.5 \times 10^{-1} \\ \sigma_b &= 5.6 \times 10^{-4} \\ \sigma_c &= 3.3 \times 10^{-2} \ . \end{aligned}$$

The smallness of the standard deviations indicates that the analysis of the time shift behavior can produce reliable estimates of both the ordinary diffusion constant and the thermal diffusion factor.

6. Summary

It is apparent from the results of the last two sections of this chapter that the problem of estimating the values of interrelated theoretical parameters from correlated experimental data is within the means of most physical scientists. The general theory of parameter estimation set forth in Section 2 has been reduced to practice and made efficient by the use of a novel minimization scheme. The method can provide estimates for a wide range of complicated problems and, simultaneously gives estimates of standard deviations and goodness of fit information.

CHAPTER V

CONCLUSION

In the preceding chapters a general approach to the principles and practices of nonequilibrium thermodynamics of fluid mixtures has been presented. Examination of previously existing theories of irreversible processes revealed many inconsistencies, especially with regard to phenomenology and convective behavior. The reformulation of the theory given in Chapter II embodies a new approach to the specification of phenomenological relations through the rational use of the entropy inequality. One of the most significant improvements in this respect is the proper enumeration of independent variables. The approach also resolves such questions as (1) validity of a Gibbsian differential equation in nonequilibrium situations, (2) neglect of inertial and viscous terms in the phenomenological equations, (3) neglect of the kinetic energy of diffusion, (4) definition of mechanical equilibrium, and (5) appropriateness of the Newtonian stress tensor for mixtures.

A particularly interesting and novel result is the requirement that the phenomenological equations for diffusion fluxes are determined by componentwise equations of motion. The latter contain the partial stress tensors, which are phenomenologically related to the componentwise velocity gradients by as many as ten viscosity coefficients for a binary mixture. Snell and Spangler (1967) have also deduced a more general relation between stress and velocity gradients for mixtures. Although their macroscopic treatment is less extensive and uses friction coefficients rather than viscosity coefficients, the conclusion that a more general relation than the Newtonian stress formula is appropriate for mixtures is substantially the same as that reached here. This is a promising area for new experimental study. Hopefully, the viscosity coefficients (or the relaxation times to which they are related) can be determined from light scattering or ultrasonic measurements on mixtures under the influence of temperature and concentration gradients. Moreover, there are interesting aspects of microscopic theory (Bearman and Kirkwood, 1958; Snell, Aranow, and Spangler, 1967) to reconsider now that there is a firm macroscopic foundation for the existence of partial stress-strain relations.

In order to make use of the partial differential transport equations derived in Chapter II it was necessary to develop better mathematical techniques for their solution. Chapter III introduces the simple but powerful pertubation expansion method and illustrates its use in the solution to convection and variable phenomenological coefficient problems of pure thermal diffusion experiments. Even though this application of the method is fairly specific for illustrative purposes, it should be clear that the method is general enough to be applied to a vast number of other problems.

Besides the perturbation method, the method of weighted residuals (in the least squares form) and the finite transform method were used effectively in the determination of the velocity and temperature profiles for the heat loss problem of pure thermal diffusion. The use of these three methods in tandem provides an approach so powerful that the solutions to any complicated system of partial differential equations are now within reach.

It should be mentioned that the approximating functions, expansion parameters, and transform functions used in Chapter III are in some sense arbitrary. It requires a great deal of experience and cleverness to make the choices which give optimum results. For this reason the results should not be thought of as final, but subject to refinement by a better choice of procedures. Also, in order to give practical answers, some of the expansions used in Chapter III were truncated without investigation of the convergence of the series, perhaps resulting in inaccuracies. These areas for improvement are mentioned only in the hope that future application of these methods will be even more successful.

Finally the important subject of parameter estimation and comparison of theory with experiment has been treated in Chapter IV. For the first time a detailed account of the theory of estimation of nonlinearly interacting parameters from data with correlated experimental errors has been presented. The reduction of the estimation theory to practice has been accomplished with the introduction of a minimization scheme which is computationally more convenient than the usual least squares method with its associated matrix inversion problems. The illustrative examples from pure thermal diffusion experiments do not test the full power of the method, and it is certain that much more difficult problems can be easily solved. Convergence of the computational algorithm is probably the most difficult remaining problem in the parameter estimation field and any contribution to the state of the art in this matter will be extremely valuable. The interesting new approach of Kizner (1964) may ultimately lead to improvements in the method described here.

BIBLIOGRAPHY

BIBLIOGRAPHY

Agar, J. N. and J. C. R. Turner. Proc. Roy. Soc. (London) 225A, 307 (1960).

Ames, W. F. Nonlinear Partial Differential Equations in Engineering (Academic Press, New York, N.Y., 1965).

Anderson, T. G. Ph.D. Thesis, Michigan State University, East Lansing, Michigan, 1968.

Bearman, R. J. and J. G. Kirkwood. J. Chem. Phys. 28, 136 (1958).

Bellman, R. Perturbation Techniques in Mathematics, Physics, and Engineering (Holt, Rinehart, and Winston, Inc., New York, N.Y., 1964).

Bowen, R. M. Arch. Rational Mech. Anal. 24, 370 (1967).

Box, G. E. P. Bull. Inst. Intern. Statistique 36, 215 (1958).

Bryngdahl, O. J. Opt. Soc. Am. 53, 571 (1963).

Coleman, B. D. and W. Noll. Arch. Rational Mech. Anal. 13, 167 (1963).

________ and V. J. Mizel. Arch Rational Mech. Anal. 13, 245 (1963).

________ and V. J. Mizel, J. Chem. Phys. 40, 1116 (1964).

Curie, P. Journal de Physique, 3d series, 3, 393 (1894.

de Groot, S. R. L'Effect Soret (North Holland Pub. Co., Amsterdam, 1945).

________. Thermodynamics of Irreversible Processes (North Holland Pub. Co., Amsterdam, 1952).

________ and P. Mazur. Nonequilibrium Thermodynamics (North Holland Pub. Co., Amsterdam, 1962).

Finlayson, B. A. and L. E. Scriven. Chem. Eng. Sci. 20, 395 (1965).

Fitts, D. D. Nonequilibrium Thermodynamics (McGraw-Hill, New York, N.Y., 1962).

Green, A. E. and P. M. Naghdi. Arch. Rational Mech. Anal. 24, 243 (1963).

________. Int. J. Eng. Sci. 3, 231 (1965).

Haase, R. Thermodynamick der Irreversiblen Prozesse (Steinkopf Verlag, Darmstadt, Germany, 1963).

Hamilton, W. C. Statistics in Physical Science (Ronald Press, New York, N.Y., 1964).

Hartley, H. O. Technometrics 3, 269 (1961).

Horne, F. H. J. Chem. Phys. 45, 3069 (1966).

________ and R. J. Bearman. J. Phys. Chem. 46, 4128 (1967).

Hurle, D. T. J., J. B. Mullin, and E. R. Pike. J. Chem. Phys. 42, 1651 (1965).

Ingram, J. D. and A. C. Eringen. Int. J. Eng. Sci. 5, 289 (1967).

Kirkwood, J. G. and B. Crawford, Jr. J. Phys. Chem. 56, 1048 (1952).

Kizner, W. J. Soc. Ind. Appl. Math. 12, 424 (1964).

Levenberg, K. Quart. Appl. Math. 2, 164 (1944).

Meiron, J. J. Opt. Soc. Am. 55, 1105 (1965).

Meixner, J. and H. G. Reik. Handbuch der Physik, Vol. III/2, S. Flugge, Ed. (Springer-Verlag, Berlin, 1960).

Mikhlin, S. G. Variational Methods in Mathematical Physics (Pergamon Press-MacMillan, New York, 1964).

Müller, I. Arch. Rational Mech. Anal. 28, 1 (1968).

________. Arch. Rational Mech. Anal. 26, 118 (1967).

Noll, W. Arch. Rational Mech. Anal. 2, 197 (1958).

Onsager, L. Phys. Rev. **37**, 405, **38**, 2265 (1931).

Picone, M. Rend. Circ. mat. Palermo **52**, 225 (1928).

Pitha, J. and R. N. Jones. Cand. J. Chem. **44**, 3031 (1966).

Powell, M. J. D. The Computer Journal **7**, 155 (1965).

Prigogine, I. *Étude Thermodynamique des Phénomènes Irreversible* (Éditions Desoer, Liége, 1947).

________. *Introduction to Thermodynamics of Irreversible Processes* (C. C Thomas, Springfield, Ill, 1955).

________. Physica **15**, 272 (1949).

Smith, G. F. Arch. Rational Mech. Anal. **18**, 182 (1965).

Snell, F. M. and R. A. Spangler. J. Phys. Chem. **71**, 2503 (1967).

________, R. Aranow, and R. A. Spangler. J. Chem. Phys. **47**, 4959 (1967).

Strand, T. G., D. A. Kohl, and R. A. Bonham. J. Chem. Phys. **39**, 1307 (1963).

Thomaes, G. Physica **17**, 885 (1951).

Truesdell, C. Rend. Lincei (8) **22**, 33 (1957).

________ and R. A. Toupin, *Handbuch der Physik*, Vol. III/1, S. Flugge, Ed. (Springer-Verlag, Berlin, 1960).

________ and W. Noll, *Handbuch der Physik*, Vol. III/3, S. Flugge, Ed. (Springer-Verlag, Berlin, 1965).

Wentworth, W. E. J. Chem. Ed. **42**, 96 (1965).

APPENDICES

APPENDIX A

RESTRICTIONS ON PHENOMENOLOGICAL COEFFICIENTS IMPOSED BY POSITIVE ENTROPY PRODUCTION

It was suggested in Chapter II that the requirements of non-negativity of entropy production imposed by the second law of thermodynamics not only restricted the magnitudes of the phenomenological coefficients, but in addition served to limit the number of independent coefficients.

It is usual in the theory of nonequilibrium thermodynamics to write the entropy production in a bilinear form:

$$\sigma = \sum_{\alpha=0}^{\pi} \underset{\sim}{J}_{\alpha} \cdot \underset{\sim}{X}_{\alpha} \geqslant 0 \qquad \text{(A1)}$$

and to write phenomenological relations for the fluxes $\underset{\sim}{J}_{\alpha}$, and the forces $\underset{\sim}{X}_{\alpha}$, in the following way:

$$\underset{\sim}{J}_{\alpha} = \sum_{\beta=0}^{\pi} \Omega_{\alpha\beta} \underset{\sim}{X}_{\beta} \qquad \alpha=0,\ldots\pi \ , \qquad \text{(A2)}$$

where the $(\pi+1)^2$ quantities $\Omega_{\alpha\beta}$ are the phenomenological coefficients. Often it is possible to show that a relation of the type

$$\sum_{\alpha=1}^{\nu} \Omega_{\alpha\beta} = 0 \ , \qquad \beta=0,\ldots\pi \ , \qquad \text{(A3)}$$

exists among the coefficients. This implies that only $\pi\ (\pi+1)$ of the original $(\pi+1)^2$ coefficients are independent. One important example of this occurs when the fluxes $\underset{\sim}{J}_\alpha$, $\alpha=1,\ldots\nu$, are the diffusion fluxes, related by

$$\sum_{\alpha=1}^{\nu} \underset{\sim}{J}_\alpha = \underset{\sim}{0} \ , \tag{A4}$$

and all the forces are independent. This can be seen by summing equation (A2), which results in (A3).

The purpose of this appendix is to show that if the phenomenological coefficients are related by (A3), then (A1) requires

$$\sum_{\beta=1}^{\nu} \Omega_{\alpha\beta} = 0, \qquad \alpha=0,\ldots\pi \ . \tag{A5}$$

Thus only π^2 of the original $(\pi+1)^2$ coefficients are independent. de Groot (1952) first noticed the possibility of (A5) for a simple case, but failed to provide any generalization of (A5) or its proof.

Two lemmas will be used in establishing (A5):

<u>Lemma I</u>. The quadratic form

$$q(\underset{\sim}{Y}) = \underset{\sim}{Y}^T A \underset{\sim}{Y} = \begin{pmatrix} Y_1 & Y_2 \end{pmatrix} \begin{pmatrix} a_{11} & a_{12} \\ a_{12} & a_{22} \end{pmatrix} \begin{pmatrix} Y_1 \\ Y_2 \end{pmatrix} \tag{A6}$$

is positive ($q \geqslant 0$) for any $\underset{\sim}{Y}$ if and only if both

$$a_{11} \geqslant 0 \tag{A7}$$

and

$$a_{11}\,a_{22} - a_{12}^2 \geqslant 0\ . \tag{A8}$$

Proof. Equation (A6) may be rearranged to give

$$q = a_{11}\left(Y_1 + \frac{a_{12}}{a_{11}} \cdot Y_2\right)^2 + \left(a_{22} - \frac{a_{12}^2}{a_{11}}\right) Y_2^2\ . \tag{A9}$$

Thus if for any Y_1 and Y_2, $a_{11} \geqslant 0$ and $a_{11}a_{22} - a_{12} \geqslant 0$ then $q \geqslant 0$. On the other hand if $q \geqslant 0$ for any $\underset{\sim}{Y}$, and $Y_2 = 0$, then $a_{11} \geqslant 0$, while if $\left(Y_1 + \frac{a_{12}}{a_{11}} Y_2\right) = 0$ then $a_{11}a_{22} - a_{12}^2 \geqslant 0$.

Definition. Let

$$B_\delta \equiv \sum_{\alpha=1}^{\nu} \Omega_{\alpha\delta} \qquad \delta=0,\ldots\pi \tag{A10}$$

and

$$C_\delta \equiv \sum_{\alpha=1}^{\nu} \Omega_{\delta\alpha} \qquad \delta=0,\ldots\pi\ . \tag{A11}$$

Lemma II.

$$\Omega_{\delta\delta} \sum_{\varepsilon=1}^{\nu} B_\varepsilon \geqslant \frac{1}{4}\left(B_\delta + C_\delta\right)^2 \qquad \delta=0,\ldots\pi \tag{A12}$$

Proof. For each δ, $\delta=0,\ldots\pi$, choose

$$\underset{\sim}{X}_0 = \underset{\sim}{X}_\alpha = 0 \;, \qquad \alpha > \nu \;,$$

$$\underset{\sim}{X}_\alpha = \underset{\sim}{X}_\gamma \;, \qquad \alpha=1,\ldots\nu,\ \gamma \neq \delta,\ \alpha \neq \delta \;. \tag{A13}$$

Then by use of (A10-11)

$$\sigma = \begin{pmatrix} X_\delta & X_\gamma \end{pmatrix} \begin{pmatrix} \Omega_{\delta\delta} & \frac{1}{2}\,(B_\delta + C_\delta) - \Omega_{\delta\delta} \\ \frac{1}{2}\,(B_\delta + C_\delta) - \Omega_{\delta\delta} & \sum\limits_{\varepsilon=1}^{\nu} B_\varepsilon + \Omega_{\delta\delta} - B_\delta - C_\delta \end{pmatrix} \begin{pmatrix} X_\delta \\ X_\gamma \end{pmatrix} . \tag{A14}$$

Use of Lemma I and (A1) requires

$$\Omega_{\delta\delta} \sum_{\varepsilon=1}^{\nu} B_\varepsilon \geqslant \frac{1}{4}\,(B_\delta + C_\delta)^2 \;, \qquad \delta=0,\ldots\pi \;. \tag{A12}$$

The final theorem which gives (A5) is now:

<u>Theorem</u>. Given a scalar, invariant, positive, bilinear function σ, defined by

$$\sigma \equiv \sum_{\alpha=0}^{\pi} \underset{\sim}{J}_\alpha \cdot \underset{\sim}{X}_\alpha \geqslant 0 \;, \tag{A1}$$

where the $\underset{\sim}{X}_\alpha$ are a linearly independent set of vectors which determine the vectors $\underset{\sim}{J}_\alpha$ uniquely according to the linear relations

$$\underset{\sim}{J}_\alpha = \sum_{\beta=0}^{\pi} \Omega_{\alpha\beta} \underset{\sim}{X}_\beta \;, \qquad \alpha=0,\ldots\pi \;, \tag{A2}$$

then if

$$\sum_{\alpha=1}^{\nu} \Omega_{\alpha\beta} = 0 \;, \qquad \beta=0,\ldots\pi \;, \tag{A3}$$

(A1) requires

$$\sum_{\beta=1}^{\nu} \Omega_{\alpha\beta} = 0, \qquad \alpha=0,\ldots\pi \ . \tag{A5}$$

<u>Proof</u>. By hypothesis

$$B_{\delta} = 0 \ , \qquad \delta=0,\ldots\pi \ , \tag{A13}$$

and therefore

$$\sum_{\varepsilon=1}^{\nu} B_{\varepsilon} = 0 \ . \tag{A14}$$

Use of (A14) in (A12) of Lemma II yields

$$- C_{\delta}^{2} \geqslant 0 \ , \qquad \delta=0,\ldots\pi \ , \tag{A15}$$

or

$$\sum_{\beta=1}^{\nu} \Omega_{\alpha\beta} = 0 \ , \qquad \alpha=0,\ldots\pi \ . \tag{A5}$$

APPENDIX B

PARAMETER ESTIMATION PROGRAMS

1. Subroutine MINIMIZE

The subroutine described here was written in FORTRAN for use with a CDC3600 digital computer. It is designed to minimize a function of up to ten variables by choosing conjugate search directions. This assures that a quadratic function of n variables will be minimized in at most n steps. (If the number of variables exceeds ten, the program must be redimensioned.) For a theoretical description see the article by Powell (1964), "An efficient method for finding the minimum of a function of several variables without calculating derivatives."

There are three considerations for the use of the subroutine which must be tailored to the individual purpose.

1. Calling statement. The subroutine may be called from a FORTRAN program by means of the following statement:

```
CALL MINIMIZE(X,N,EPS,ENDNORM,ITMAX,IPRINT,SUCCESS,FNORM)
```

2. Parameters.

   a. X = A linear array dimensioned for the number of variables. The program should be called with a set of initial guesses for the variables stored in X. The solution will be returned in X.

b. N = The number of variables (less than ten).

c. EPS = A convergence criterion parameter. The change in each variable from the last step is compared with EPS times the current value, and convergence is assumed if the change is smaller.

d. ENDNORM = A convergence criterion parameter. The function value at the current point must be less than ENDNORM to obtain convergence.

e. ITMAX = The maximum desired number of iterations.

f. IPRINT = An option. If IPRINT equals unity, the program will cause the results to be printed. If IPRINT is zero, no results will be printed.

g. SUCCESS = A logical variable to indicate convergence. If success is unity, the process has converged. If SUCCESS is zero, the method has failed to converge, and a statement will be written to indicate the reason for termination. (SUCCESS must be declared TYPE LOGICAL in the calling program.)

h. FNORM = The name of the function subroutine which calculates the function to be minimized. (See the next section. FNORM must be declared EXTERNAL in the calling program.)

3. Required subroutines.

a. QUADMIN. This is a routine required by MINIMIZE and a listing is given together with MINIMIZE.

b. FNORM. This is a subprogram in which the function to be minimized is calculated. It must have the following form:

```
FUNCTION FNORM(X,N)
DIMENSION X(N)
     .
     .
     .
        (any necessary calculations)
     .
     .
     .
FNORM = f(X(1), X(2), ..., X(N))
RETURN
END
```

where f is the function to be minimized, and X and N have their previously indicated meanings.

Listing of MINIMIZE and QUADMIN

```
      SUBROUTINE MINIMIZE(X,N,EPS1,EPS2,ITMAX,IPRINT,SUCCESS,FNORM)
      DIMENSION X(N),X0(10),Y(10),P(10,10)
      COMMON/MIN/LASTNORM,KOUNT
      EXTERNAL FNORM
      TYPE REAL NORM, LASTNORM
      TYPE LOGICAL SUCCESS
      IF(N.GT.10)GO TO 5000
      ITER=0
      KOUNT=0
      DO1 I=1,N
      X0(I)=X(I)
      P(I,I)=0.1*X0(I)
      IF(X0(I).LT.(1.0E-7))P(I,I)=0.01
      L=I+1
      DO 1 J = L,N
 1    P(I,J)=P(J,I) =0.0
      LASTNORM = FNORM(X,N)
      KOUNT=KOUNT+1
      NM=N-1
      IF(IPRINT)PRINT 100,LASTNORM,X
 100  FORMAT(1H1,*THE INITIAL VALUES ARE*,//,5X,*NORM*,10X,*X0(1).....X0(N)*,
     1(N)*,//,9E15.6,/,(15X,8E15.6))
      IF(IPRINT)PRINT 110
 110  FORMAT(1H6,*ITER  INC*,5X,*NORM*,10X,*X(1).....X(N)*,//)
 1000 ITER =ITER+1
      IF(ITER.GT.ITMAX)GO TO 3000
 95   DELTA=1.0E-100
      M=0
      F1=LASTNORM
      DO 2000 I=1,N
      DO 2 J=1,N
 2    Y(J)=P(J,I)
      CALL QUADMIN(X,Y,NORM,N,FNORM)
      IF(IPRINT)PRINT 101,ITER,I,NORM,X
 101  FORMAT(2I5,8E15.6,/,(25X,7E15.6))
      IF((LASTNORM-NORM).GE.DELTA)3,4
 3    M=I
      DELTA = LASTNORM-NORM
 4    LASTNORM = NORM
 2000 CONTINUE
 2004 F2=NORM
      IF(ITER.GT.N)15,16
 15   IF(NORM.GT.EPS2)16,17
 17   IF(ABS(F1-F2).GT.ABS(EPS1*F2))16,19
 19   DO 18 I=1,N
      IF(ABS(X(I)-X0(I)).GT.ABS(EPS1*X(I)))16,18
 18   CONTINUE
      GO TO 4000
 16   DO 5 I=1,N
 5    Y(I)=2.0*X(I)-X0(I)
```

```
      F3=FNORM(Y,N)
      KOUNT=KOUNT+1
      IF((F3.GE.F1).OR.(((F1-2.0*F2+F3)*(F1-F2-DELTA)**
     12).GE.(DELTA*((F1-F2)**2)/2.0)))6,7
 6    DO 8 I=1,N
 8    XO(I)=X(I)
      GO TO 1000
 7    DO 9 I=1,N
 9    Y(I) =X(I)-XO(I)
      CALL QUADMIN(X,Y,NORM,N,FNORM)
      DO 10 I=1,N
 10   XO(I)=X(I)
      DO 11 I=M,NM
      DO 11 J=1,N
 11   P(J,I)=P(J,I+1)
      DO 12 I=1,N
 12   P(I,N)=Y(I)
      LASTNORM = NORM
      GO TO 1000
 3000 PRINT 102
 102  FORMAT(1H4,*THE MAXIMUM NUMBER OF ITERATIONS HAS BEEN EXCEEDED*)
      SUCCESS =0
      PRINT 5004,KOUNT
      RETURN
 4000 PRINT 103,ITER
 103  FORMAT(1H4,*THE PROCESS HAS CONVERGED IN*,I6,3X,*ITERATIONS*)
      SUCCESS =1
      PRINT 5004,KOUNT
 5004 FORMAT(1H-,*THE NUMBER OF FUNCTIONAL EVALUATIONS WAS*,I10)
      RETURN
 5000 PRINT 5001
 5001 FORMAT(1H4,*MORE THAN 10 VARIABLES.  PLEASE REDIMENSION.*)
      SUCCESS=0
      RETURN
      END
      SUBROUTINE QUADMIN(X,P,NORM,N,FNORM)
      DIMENSION PHI(3),VT(3),X(N),P(N)
      COMMON/MIN/LASTNORM,KOUNT
      TYPE INTEGER UPPER
      TYPE REAL NORM ,LASTT, LASTNORM
      DO 9 I=1,N
9     X(I) =X(I) +P(I)
      LASTT = 1.0
      T=0.0
      ITER =0
10    ITER = ITER + 1
      NORM = FNORM(X,N)
      KOUNT=KOUNT+1
      IF((ABS(T-LASTT).GT.(.01*ABS(T)).AND.ITER.LE.20).OR.(ITER.EQ.2))
     111,12
```

```
11    IF(ITER.EQ.1)13,14
13    VT(1)=0.0
      VT(3) =1.0
      PHI(1) =LASTNORM
      PHI(3) =NORM
      IF(PHI(1).GT.PHI(3))1,2
1     T=2.0
      LOWER=1
      MID=3
      UPPER=2
      K=2
      GO TO 1000
2     T=-1.0
      LOWER=2
      MID=1
      UPPER=3
      K=2
      GO TO 1000
14    PHI(II)=NORM
      XW =VT(2)-VT(3)
      XX=VT(3)-VT(1)
      XY =VT(1)-VT(2)
      XW =-(PHI(1)*XW+PHI(2)*XX+PHI(3)*XY)/(XW*XX*XY)
      XX=(PHI(1)-PHI(2))/XY-XW*(VT(1)+VT(2))
      LASTT =T
      IF(XW.GT.0.0)15,16
15    T=-XX/(2.0*XW)
      GO TO 19
16    IF(PHI(UPPER).GT.PHI(LOWER))17,18
17    T=3.0*VT(LOWER)-2.0*VT(MID)
      GO TO 19
18    T=3.0*VT(UPPER)-2.0*VT(MID)
19    IF(T.GT.VT(UPPER))20,21
20    I=LOWER
      LOWER =MID
      MID = UPPER
      UPPER =I
      K=UPPER
      GO TO 1000
21    IF(T.LT.VT(LOWER))22,23
22    I=UPPER
      UPPER =MID
      MID =LOWER
      LOWER=I
      K=LOWER
      GO TO 1000
23    IF(T.GT.VT(MID))24,25
24    I=LOWER
       LOWER =MID
      MID=I
```

```
      K=MID
      GO TO 1000
25    I =UPPER
      UPPER =MID
      MID=I
      K=MID
1000  II=K
      VT(K)=T
      DO 1001 J=1,N
1001  X(J)=X(J)+(T-LASTT)*P(J)
      GO TO 10
12    IF(NORM.LE.LASTNORM)RETURN
      NORM=LASTNORM
      DO 7 I=1,N
7     X(I)=X(I)-LASTT*P(I)
      RETURN
      END
```

2. Program FOTOFIT

The fringe shape analysis described in section 4 of Chapter IV is performed by the program FOTOFIT and its associated subroutine FRNGFIT and FRNGSTAT. FOTOFIT is an executive routine which handles the reading of data, transformation of data, and calling of auxiliary programs. The actual calculations of fringe shape and weight functions are done in FRNGFIT while the estimates of standard deviation are made from the moment matrix calculated by the subroutine FRNGSTAT. Of course the minimization of the difference between the calculated and experimental fringe shapes is done by the routine MINIMIZE which must accompany these routines.

The data input format is given by FORMAT statement 3 in the listing that follows. The first card of the data deck contains an identification code, the number of data cards to be read, the number of derivatives to be estimated, and the parameters A, b_1, κ_T, and u_1 as specified in equation (4.6) of Chapter IV. The remaining data cards are read according to FORMAT statement 2 and each card contains one (x_i, z_i) point. As many fringes as desired may be analyzed at one time. The only requirement is that a blank card be placed at the end of the data deck.

Listing of FOTOFIT, FRNGFIT, and FRNGSTAT

```
      PROGRAM FOTOFIT
      DIMENSION X(10)
      COMMON/TRNS/Z(2,100),NOPT,B1,A,TK,UT1,WT(100),F(100),TEMP,FOTOLBL
      TYPE LOGICAL SUCCESS
      EXTERNAL FRNGFIT,WTFIT
1000  READ 3,FOTOLBL,NOPT,N,A,B1,TK,UT1
3     FORMAT(A8,2I5,4E15.6)
      IF(NOPT.EQ.0)GO TO 999
      DO 1 I=1,NOPT
      READ 2,Z(1,I),Z(2,I)
2     FORMAT(F6.3,F5.3)
      Z(1,I)=2.0*(Z(1,I)+0.35)/4.4
1     CONTINUE
      DO 10 I=1,N
10    X(I)=0.0
      CALL MINIMIZE(X,N,0.001,1.0,25,1,SUCCESS,FRNGFIT)
      CALL MINIMIZE(X,N,0.0001,1.0,50,1,SUCCESS,WTFIT)
      CALL FRNGSTAT(X,N)
      GO TO 1000
999   CONTINUE
      END
      FUNCTION FRNGFIT(X,N)
      DIMENSION X(N)
      COMMON/TRNS/Z(2,100),NOPT,B1,A,TK,UT1,WT(100),F(100),TEMP,FOTOLBL
      DO 1 I=1,NOPT
1     WT(I)=1.0
      LUSE=1
      GO TO 2
      ENTRY WTFIT
      LUSE=0
2     CONTINUE
      M=N-1
      DO 3 I=1,NOPT
      YP=Z(1,I)+B1
      YL=YP-2.*B1
      TP=TK*(YP**2-1.0)/4.+YP/2.
      TM=TK*(YL**2-1.0)/4.+YL/2.
      IF(LUSE)GO TO 5
      TEMP=A*UT1*TK+B1
      DO 4 J=1,M
4     TEMP=TEMP+A*X(J)*(J+1)*(TP**J*(TK*YP+1.)-TM**J*(TK*YL+1.))/2.
      WT(I)=1.0/(1.0+TEMP**2)
5     CONTINUE
      DN=UT1*(TP-TM)
      DO 6 K=1,M
6     DN=DN+X(K)*(TP**(K+1)-TM**(K+1))
3     F(I)=X(N)-Z(2,I)+A*DN
      TEMP=0.0
      DO 7 I=1,NOPT
7     TEMP=TEMP+WT(I)*F(I)**2
```

```
      FRNGFIT=TEMP
      RETURN
      END
      SUBROUTINE FRNGSTAT(X,N)
      DIMENSION X(N),D(10,10),S(10,100)
      COMMON/TRNS/Z(2,100),NOPT,B1,A,TK,UT1,WT(100),F(100),TEMP,FOTOLBL
      M=N-1
      DO 1 I=1,NOPT
      S(N,I)=1.
      DO 1 J=1,M
      YP=Z(1,I)+B1
      YL=YP-2.*B1
      TP=TK*(YP**2-1.0)/4.+YP/2.
      TM=TK*(YL**2-1.0)/4.+YL/2.
 1    S(J,I)=(TP**(J+1)-TM**(J+1))*A
      DO 2 K=1,N
      DO 2 J=1,N
      D(K,J)=0.0
      DO 2 I=1,NOPT
 2    D(K,J)=S(K,I)*WT(I)*S(J,I)+D(K,J)
      CALL INVERSE(D,N,N,1.E-7,DET,10,10)
      IF(DET.EQ.0.0)PRINT 3
 3    FORMAT(1H6,*MATRIX IS SINGULAR*)
      PRINT 2102,(IOP,IOP=1,N)
 2102 FORMAT(/25X,*SIGMA MATRIX*/I6,12I10)
      PHI=NOPT-N
      BV=TEMP/PHI
      DO 3000 I=1,N
      DO 3000 J=1,N
 3000 D(I,J)=D(I,J)*BV
      DO 2106 J=1,N
 2106 PRINT 2101,J,(D(J,I),I=1,N)
 2101 FORMAT(* *,I2,13E10.2)
      DO 3001 I=1,N
 3001 S(I,1)=SQRT(D(I,I))
      PRINT 3002,FOTOLBL
 3002 FORMAT(1H-,*FINAL RESULTS FOR RUN*,A8,//,*PARAMETER NUMBER*,5X,*ES
     1TIMATE*,13X,*STD. DEV.*)
      DO 301 I=1,N
 301  PRINT 3003,I,X(I),S(I,1)
 3003 FORMAT(1H ,5X,I5,5X,E15.6,5X,E15.3)
      BV=SQRT(BV)
      PRINT 211,BV,PHI
 211  FORMAT(* STANDARD ERROR OF Y   *,E15.6,*   DEGREES OF FREEDOM   *,
     1F8.2)
      PRINT 9076,(I,F(I),I=1,NOPT)
 9076 FORMAT(4(4H FO(I3,3H) =E15.7,5X))
      RETURN
      END
C6H12294   29     5     2.394998E+5     2.272727E-1     1.200610E-3   -1.8500C
-1.4001.504
```

```
-1.3001.257
-1.2001.062
-1.1000.894
-1.0000.745
-0.9000.619
-0.8000.514
-0.7000.405
-0.6000.333
-0.5000.264
-0.4000.183
-0.3000.104
-0.2000.034
-0.1000.014
00.0000.000
 0.1000.009
 0.2000.025
 0.3000.074
 0.4000.159
 0.5000.225
 0.6000.324
 0.7000.460
 0.8000.569
 0.9000.691
 1.0000.845
 1.1001.046
 1.2001.215
 1.3001.524
01.4001.834
```

3. Program EXPCURVE

EXPCURVE is a program similar in nature to the FOTOFIT program and used for the time constant analysis of pure thermal diffusion experiments. Again the program is simply an executive routine which reads data and calls on the auxiliary routines EXPO and EXPOSTAT. The exponential functions are calculated together with weighting functions in EXPO while the subroutine EXPOSTAT handles the statistical calculations.

The data input is as follows: The first card to be read contains the number of data points in the time series to be analyzed. The second card contains the initial estimates of the parameters a, b, and c in equation (5.2) of Chapter IV. Each subsequent card is punched with one (d_i, t_i) data point which is to be read according to FORMAT statement 103. As listed the routines analyze only one set of data at a time, but they may be easily reprogrammed to handle multiple data decks.

Listing of EXPCURVE, EXPO, and EXPOSTAT

```
      PROGRAM EXPCURVE
      DIMENSION X(3)
      COMMON/TRNS/Z(2,100),NOPT,TEMP,WT(100)
      EXTERNAL EXPO,WTEXPO
      TYPE LOGICAL SUCCESS
      READ 101,NOPT
101   FORMAT(I2)
      READ 102,(X(I),I=1,3)
102   FORMAT(F6.2,F4.3,F5.2)
      DO 1 I=1,NOPT
1     READ 103,Z(2,I),Z(1,I)
103   FORMAT(F7.2,F5.2)
      CALL MINIMIZE(X,3,0.0001,0.5,10,1,SUCCESS,EXPO)
      CALL MINIMIZE(X,3,0.0001,0.5,10,1,SUCCESS,WTEXPO)
      CALL EXPOSTAT(X,N)
      END
      FUNCTION EXPO(X,N)
      DIMENSION X(N),F(100)
      COMMON/TRNS/Z(2,100),NOPT,TEMP,WT(100)
      DO 1 I=1,NOPT
1     WT(I)=1.0
      LUSE=1
      GO TO 2
      ENTRY WTEXPO
      LUSE=0
2     CONTINUE
      DO 3 I=1,NOPT
      S=X(1)*EXP(-X(2)*Z(2,I))
      IF(LUSE)GO TO 4
      WT(I)=1./(1.+(X(2)*S)**2)
4     F(I)=Z(1,I)-S-X(3)
3     CONTINUE
      TEMP=0.0
      DO 5 I=1,NOPT
5     TEMP=TEMP+WT(I)*F(I)**2
      EXPO=TEMP
      RETURN
      END
      SUBROUTINE EXPOSTAT(X,N)
      DIMENSION D(3,3),X(N),S(3,100)
      COMMON/TRNS/Z(2,100),NOPT,TEMP,WT(100)
      DO 1 I=1,NOPT
      S(1,I)=-EXP(-X(2)*Z(2,I))
      S(2,I)=Z(2,I)*X(1)*EXP(-X(2)*Z(2,I))
1     S(3,I)=-1.0
      DO 2 K=1,3
      DO 2 J=1,3
      D(K,J)=0.0
      DO 2 I=1,NOPT
2     D(K,J)=S(K,I)*WT(I)*S(J,I)+D(K,J)
```

```
      CALL INVERSE(D,3,3,1.E-7,DET,3,3)
      IF(DET.EQ.0.0)PRINT 3
 3    FORMAT(1H6,*MATRIX IS SINGULAR*)
      PRINT 2102,(IOP,IOP=1,3)
 2102 FORMAT(/25X,*SIGMA MATRIX*/I6,12I10)
      PHI=NOPT-3
      BV=TEMP/PHI
      DO 3000 I=1,3
      DO 3000 J=1,3
 3000 D(I,J)=D(I,J)*BV
      DO 2106 J=1,3
 2106 PRINT 2101,J,(D(J,I),I=1,3)
 2101 FORMAT(* *,I2,13E10.2)
      DO 3001 I=1,3
 3001 S(I,1)=SQRT(D(I,I))
      PRINT 3002
 3002 FORMAT(1H-,*FINAL RESULTS*,/,*PARAMETER NUMBER*,5X,*ESTIMATE*,5X,*
     1STD. DEV.*)
      DO 301 I=1,3
 301  PRINT 3003,I,X(I),S(I,1)
 3003 FORMAT(1H ,5X,I5,5X,E15.6,5X,E15.3)
      BV=SQRT(BV)
      PRINT 211,BV,PHI
 211  FORMAT(* STANDARD ERROR OF Y   *,E15.6,*   DEGREES OF FREEDOM   *,
     1F8.2)
      RETURN
      END
33    F6D37.06833.032-0.2501.7500.9766934.950
-05.50.01610.07
0025.0005.71
0030.0005.97
0035.0006.22
0040.0006.54
0045.0006.75
0050.0007.13
0055.0007.30
0060.0007.63
0065.0007.90
0071.0008.16
0075.0008.39
0080.0008.45
0090.0008.66
0100.0008.78
0110.0009.11
0120.0009.31
0130.0009.41
0140.0009.46
0150.0009.74
0160.0009.58
0170.0009.82
```

```
0180.0009.72
0190.0009.85
0200.0010.07
0212.0009.99
0222.0009.82
0240.0009.84
0252.0009.97
0266.0009.96
0280.0010.01
0300.0009.99
0314.0010.07
0364.0010.07
```

APPENDIX C

VELOCITY AND TEMPERATURE PROFILES FOR THE CONVECTIVE HEAT LOSS PROBLEM

1. Velocity Profiles

The detailed solutions for the vertical and radial velocity components in a pure thermal diffusion experiment with radial heat loss have been given in Chapter III, section 5. It is shown there that the velocities are determined by the potential Φ according to

$$v_{10r} = \left[d_{00} + \frac{M}{\pi}\right]^{-1} \frac{1}{r} \frac{\partial \Phi}{\partial z} \qquad (C.1)$$

$$v_{10z} = -\left[d_{00} + \frac{M}{\pi}\right]^{-1} \frac{1}{r} \frac{\partial \Phi}{\partial r} \qquad (C.2)$$

where r and z have been scaled to unit length and where, by equation (III.5.16),

$$\left[d_{00} + \frac{M}{\pi}\right]^{-1} = \frac{\pi}{M} \exp\,[A(1/2 - z)] \qquad (C.3)$$

The potential Φ is given in equation (III.5.62) as

$$\Phi = r(r-1)z^2(z-1)^2\ r(r-1) + \sum_{i=0}^{N} \sum_{j=1}^{M} C_{ij} z^i \sin \pi jr \qquad (C.4)$$

The coefficients C_{ij} have been determined by the minimization of the integral in equation (III.5.65) using the MINIMIZE routine (see Appendix B). It is clear that their values depend only on the magnitude of the quantity A. The numerical values determined with A equal to 0.01 are

$$C_{ij} = \begin{pmatrix} 0.12007 & -0.00597 & 0.00105 \\ -0.17734 & -0.00409 & 0.00197 \\ 0.17785 & -0.00396 & 0.00201 \end{pmatrix} \qquad (C.5)$$

Having determined these coefficients, one can easily calculate v_{10r} and v_{10z} for any r and z. The vertical velocity v_{10z} has been plotted versus r for z equal to 0.5 and is shown in Figure 1. For other values of z the vertical velocity has the same shape but decreases in magnitude almost parabolically from the center towards the horizontal plates.

The radial velocity v_{10r} has been plotted versus r for z = 0.25 and the results are shown in Figure 2. Again the shape of v_{10r} remains essentially the same for all values of z. The magnitude of v_{10r} decreases as z approaches 0.5, where v_{10r} changes sign, and then increases in magnitude.

It should be recognized that the signs on the velocities as they have been plotted are not absolute, but should be multiplied by the sign of the heat loss coefficient. Thus if there is a heat loss, the fluid

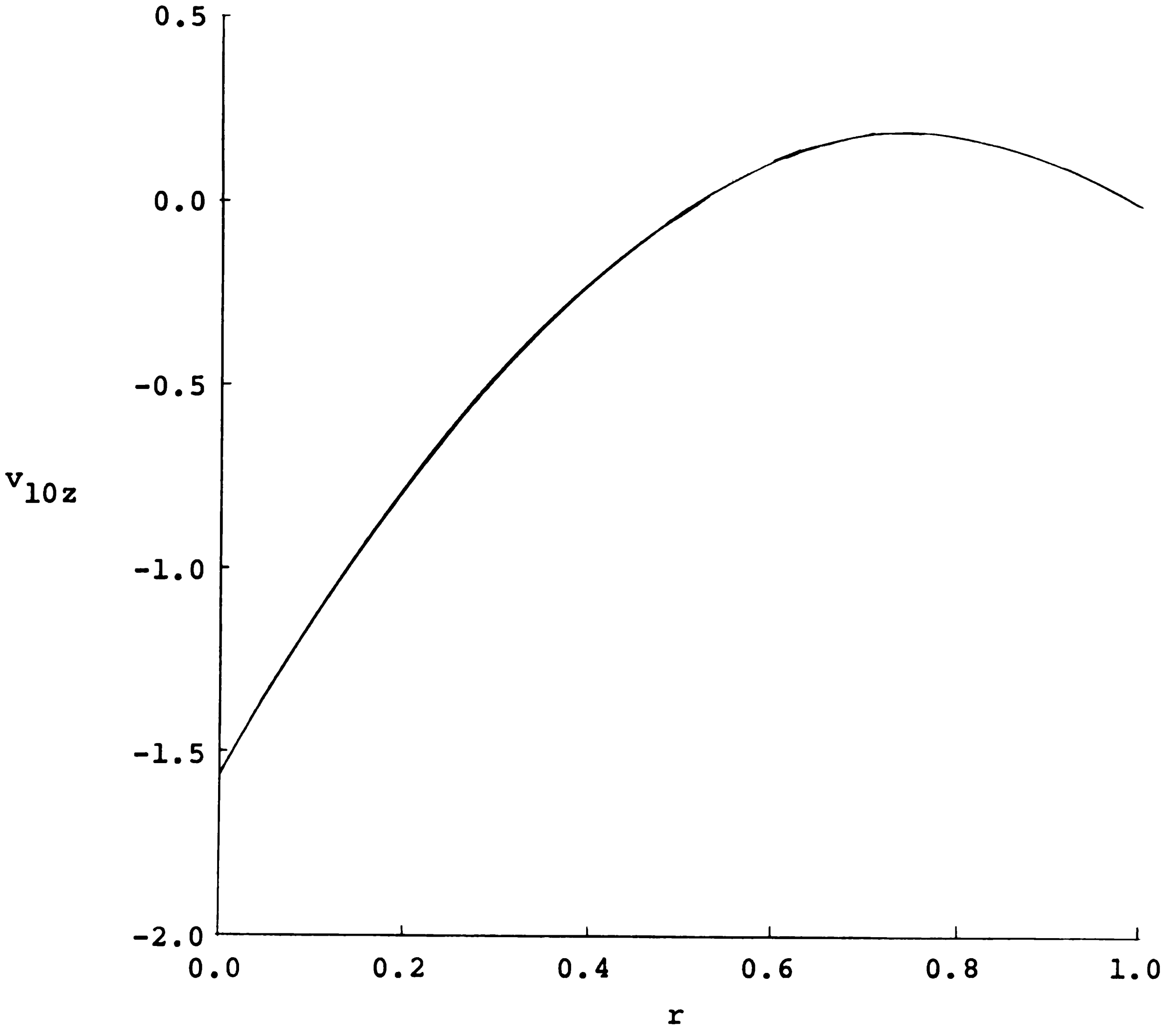

Figure 1.--Vertical velocity as a function of r at the center of the cell (z = 0.5).

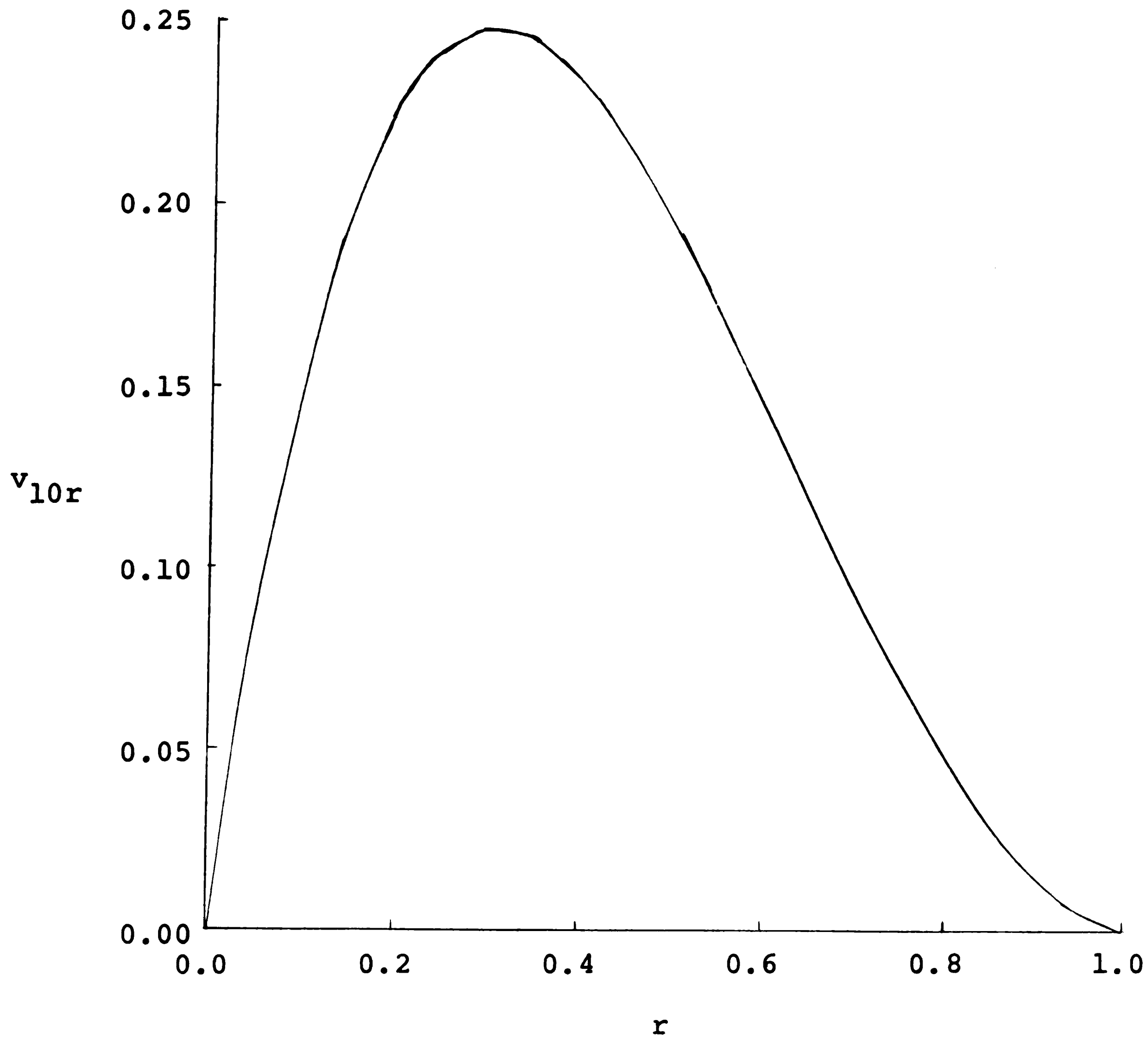

Figure 2.--Radial velocity as a function of r at z = 0.25.

near the wall will be relatively more dense than that in the center and the velocity near the wall will be downward.

2. Temperature Profiles

The temperature correction, T_{10} (r,z), for the convective heat loss problem is determined according to equation (III.5.73) by

$$T_{10}\,(r,z) = \sum_{n=1}^{\infty} \tau_n(r)\,\sin\,(n\pi z) \tag{C.6}$$

where

$$\tau_n(r) = C_1 I_0\,(n\pi r) + \tau_{np}\,(r) \tag{C.7}$$

and the coefficient C_1 is given by equation (III.5.83). The zeroth order modified Bessel function has been denoted by I_0 ($n\pi r$). The particular solution, τ_{np} (r), is given by

$$\tau_{np}\,(r) = \sum_{\ell=0}^{\infty} G_{n\ell} r^{\ell} \tag{C.8}$$

and the coefficients $G_{n\ell}$ are given by equations (III.5.77-8).

The temperature correction depends on the phenomenological coefficients for the system through the three parameters A, p_1, and p_2. The coefficient A is again taken to be 0.01 while p_1 is taken to be 100 and p_2 to be 500. These are values typical to common liquids. The shape of T_{10} is also affected by the value of the quantity

$(T_r - T_m + 1/2\ \Delta T)$ which enters through the boundary conditions. The sign of this quantity determines whether there is an overall heat loss or heat gain (- and + respectively).

The temperature correction has been plotted versus r at the center of the cell ($z = 0.5$) under the three conditions $(T_r - T_m + 1/2\ \Delta T) = -5.0$, 0.0, and 5.0 in the Figures 3, 4, and 5 respectively.

It is interesting to note that the slope of T_{10} versus r has the same sign as $(T_r - T_m + 1/2\ \Delta T)$ as r approaches 1.0 indicating heat loss or gain as the case may be. The temperature corrections appear to be largest near the center of the cell ($z = 0.5$) and to decrease in either direction towards the horizontal plates.

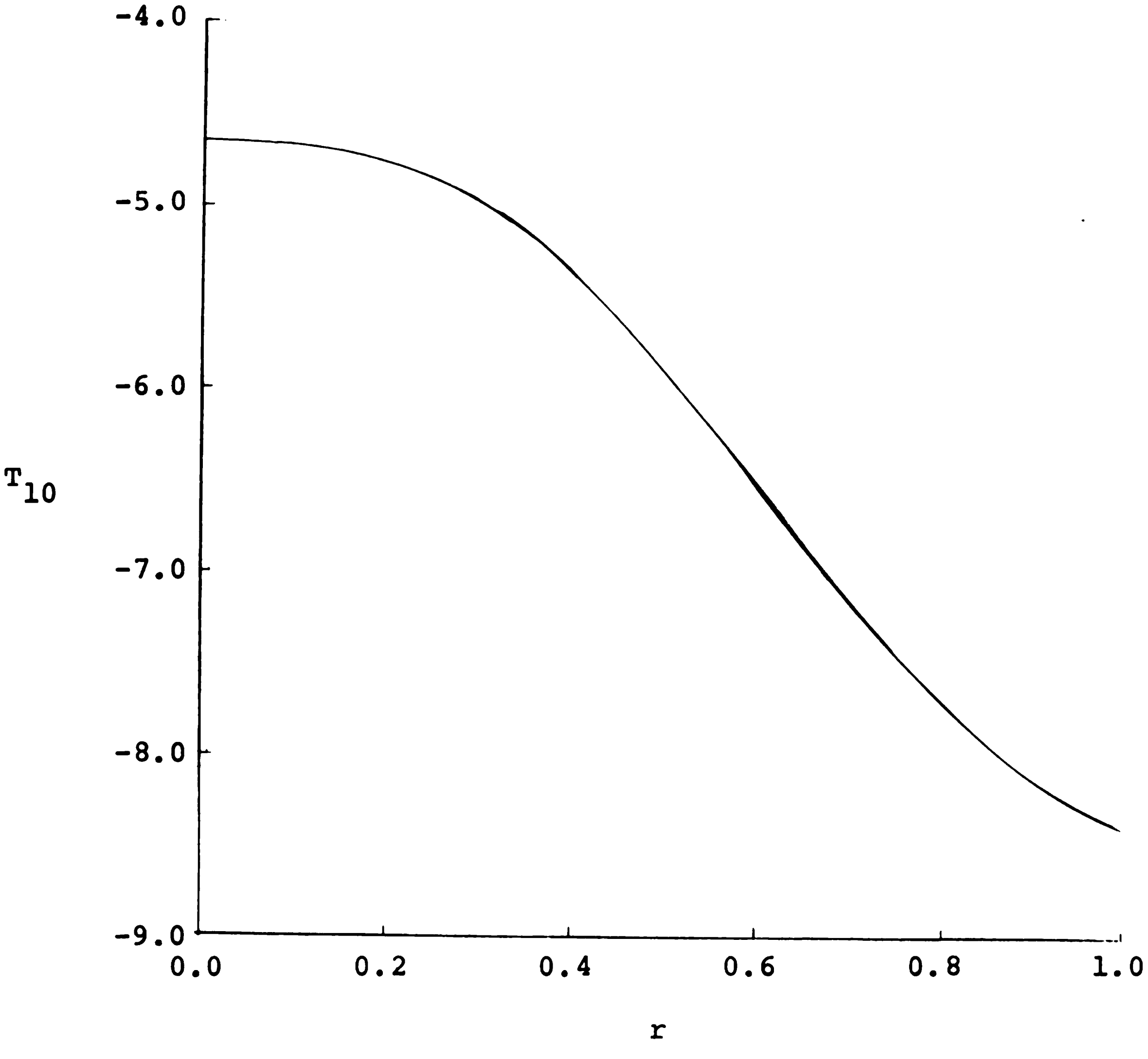

Figure 3.--Temperature correction versus r at z = 0.5 for (T_r - T_m + 1/2 ΔT) = - 5.0.

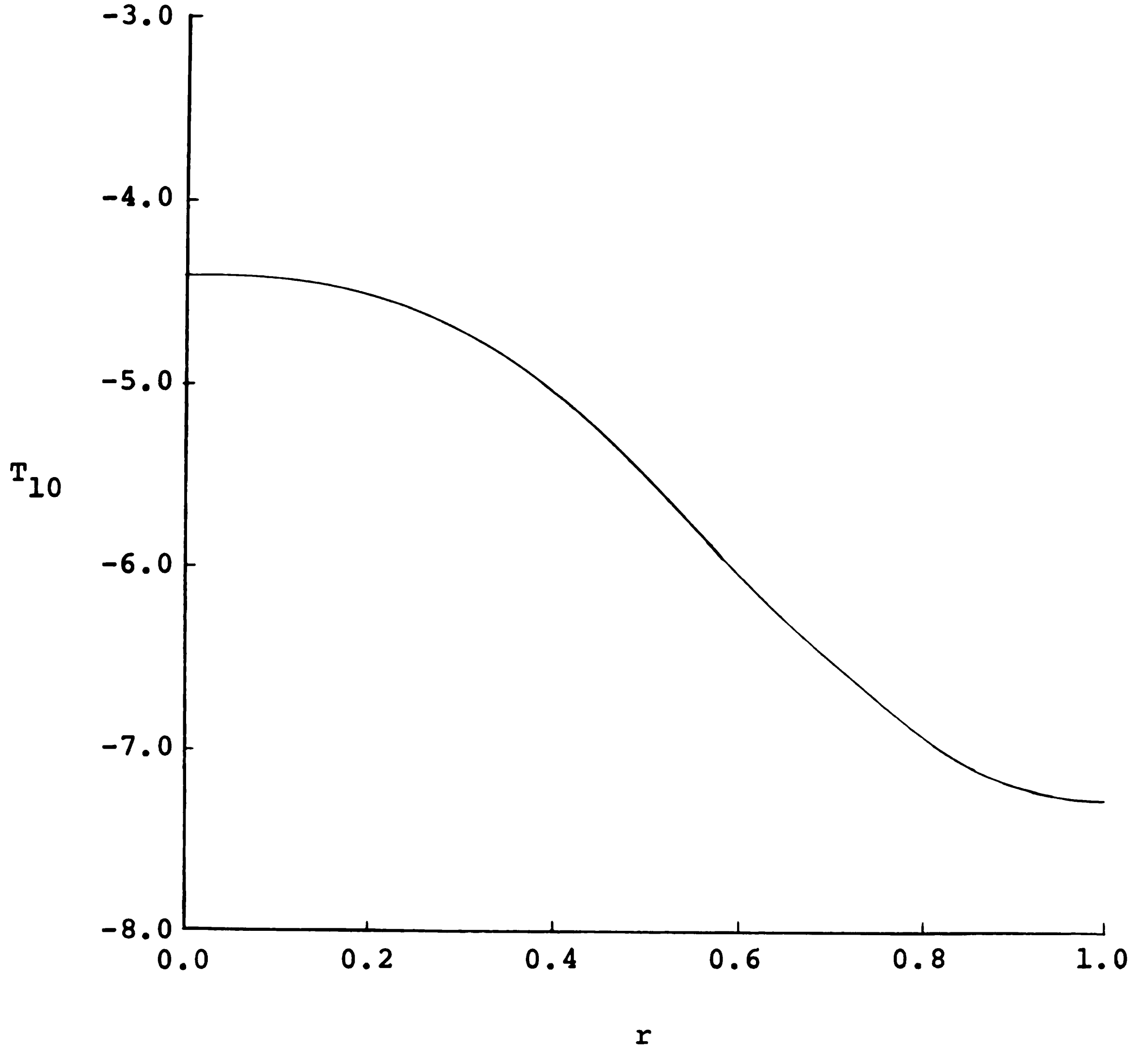

Figure 4.--Temperature correction versus r at z = 0.5 for ($T_r - T_m + 1/2\ \Delta T$) = 0.0.

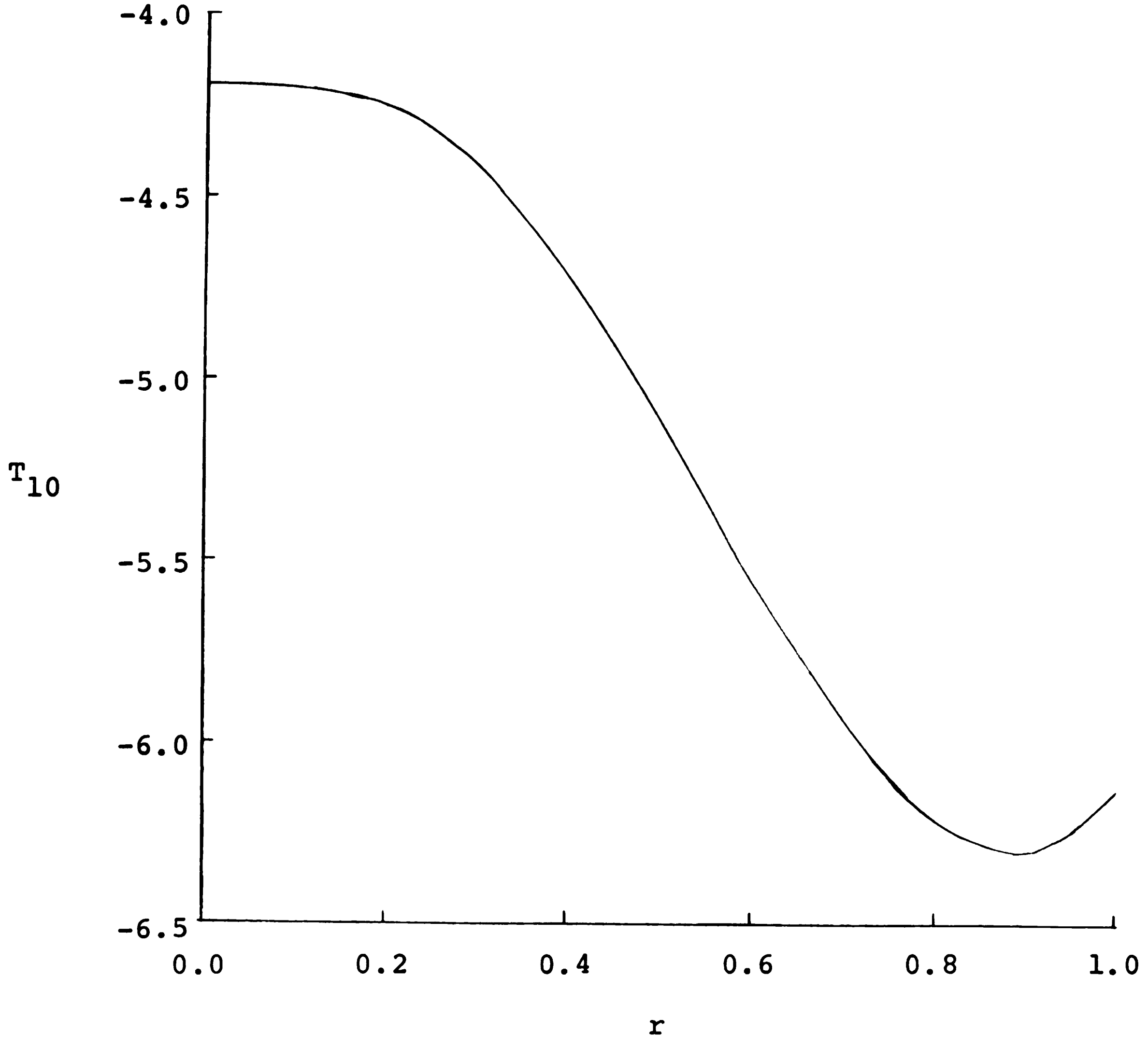

Figure 5.--Temperature correction versus r at z = 0.5 for $(T_r - T_m + 1/2\ \Delta T) = 5.0$.