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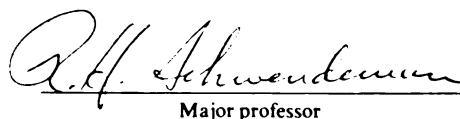
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Thermogravitational Thermal Diffusion
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Yuan Xu

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Major professor

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THERMOGRAVITATIONAL THERMAL DIFFUSION OF ELECTROLYTE SOLUTIONS

By

YUAN XU

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A B S T R A C T

THERMOGRAVITATIONAL THERMAL DIFFUSION OF ELECTROLYTE SOLUTIONS

BY

YUAN XU

Thermogravitational Thermal Diffusion (TGTD) is used to separate the components of fluid mixtures. The development of a set of macroscopic partial differential equations from nonequilibrium thermodynamics and hydrodynamics which describes the TGTD of electrolytes is presented here.

The goal of the research is the solution of the set of partial differential equations for TGTD columns with or without reservoirs at the ends. The solutions are obtained analytically under a variety of boundary and initial conditions. Through perturbation approaches, we obtain a complete set of temperature, velocity, and concentration distribution functions for binary electrolyte solutions in the TGTD

column for both the time-dependent regime and the steady state. The space derivatives of the steady state concentration function confirms previous results. However, the approach here is new and the results are more complete. The average steady state concentration distribution function along the TGTD column can be used to calculate the thermal diffusion factor of binary electrolyte solutions.

The time-dependent solution of the concentration equation allows us to estimate the relaxation time required to reach steady state, and the solution can be used as a guide for designing the TGTD column.

The reservoir theory of the TGTD column based on an isothermal diffusion model is also reported here. Due to the complexity of the theory, we obtain only a rough but simple formula to account for the reservoir effect on the TGTD column early in the experiment. The formula can be applied to calculate the thermal diffusion factor of electrolyte solutions while the concentration-time-dependence is still linear if the TGTD column is connected to reservoirs at the ends. We may also use the formula to guide the proper design of the reservoirs and to explain recent strange experimental results.

謹此博士論文獻給我的父母：

**徐 子 維 先生
謝 申 鉅 女士**

永遠銘記對兒的教誨及信任。

兒： 徐 源（永泳）

公元一九八八年五月記于密執安州立大學計算機中心。

美國密執安州，東蘭辛。

To my parents, Mr. Ziwei Xu, and Mrs. Shensu Xie,

who believed in education and in me.

and

a special gift for the 60's birthday of my father

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CHAPTER 1

INTRODUCTION

A. THERMAL DIFFUSION

Application of a temperature gradient to an electrolyte solution or to any multicomponent liquid or gas mixture causes redistribution of the components. The motion of the components leads to the establishment of a concentration gradient which ultimately achieves a constant value that depends on the thermodynamic and transport properties of the system. The final concentration distribution is not uniform.

Thermal diffusion in salt solutions was first demonstrated by Ludwig [1856] and was re-discovered by Soret [1879], who more thoroughly investigated the phenomenon. Thermal diffusion of aqueous salt solutions is often called the Soret Effect. Very few binary non-electrolyte solution (Wereide [1914]), aqueous electrolyte and non-electrolyte solution systems (Eilert [1914]), were studied before World War II. The Soret Effect has since been studied in liquid alloys (Winter and Drickamer [1955]), in mixtures of molten salts (Hirota, Matsunaga, and

Tunaka [1943]), and in solutions of macromolecules and polymers (Debye and Bueche [1954], Gaeta and Cursio [1969]). Several studies have been made of mixtures of organic liquids (Prigogine [1950], Rutherford, Dougherty, and Drickamer [1954], Horne and Bearman [1962-68], Turner, Butler, and Story [1967], Turner and Story [1969], Johnson and Beyerlein [1978], Ma and Beyerlein [1983]). Thermal diffusion in gases is well known and has been extensively investigated both experimentally and theoretically (Furry, Jones, and Onsager [1939], Bardeen [1940], Jones and Furry [1946], Grew and Ibbs [1952], Greene, Hoglund, and Halle [1966], Rutherford [1973], Santamaria, Saviron, and Yarza [1976], Navarro, Madariaga, and Saviron [1983]).

There are two major experimental thermal diffusion methods, thermogravitational thermal diffusion (TGTD) and pure thermal diffusion (PTD). PTD is characterized by a vertical temperature gradient directed so that there is no density induced convection (for most mixtures this requires that the system is heated from above). PTD is theoretically simpler since the steady state concentration gradient is proportional to the temperature gradient. The operational theory based on Onsager thermodynamics has been developed by deGroot [1947], Rutherford [1954], Bierlein [1955], Agar [1960], Horne and Anderson [1970], and Navarro et al. [1983] for both electrolyte and non-electrolyte solutions. A good summary of early work was given by Tyrrell [1961].

TGTD is experimentally quite different from PTD. In TGTD, the mixture is contained between two vertical plates or two cylindrical columns. The outer and inner surfaces are kept at different temperatures. Thermal diffusion takes place horizontally. In solutions of electrolytes, the solute usually moves towards the cold region and solvent to the warm region. Because of the density gradient produced in

the horizontal direction by thermal expansion under the temperature gradient, natural convection develops due to gravity. The solute enriched fluid nearer the cold wall descends to the bottom of the column, and the less concentrated solution near the hot wall ascends to the top of the column. Of the two vector components of the steady state concentration gradient, the vertical component is independent of the magnitude of the horizontal temperature gradient. The horizontal component of the steady state concentration gradient is smaller than what would be caused by PTD because convection reduces the concentration difference. Clusius and Dickel [1938] invented this technique and applied it to separate gaseous isotopes. The theory of TGTD for separation of gaseous isotopic materials was developed by Furry, Jones, and Onsager [1939], and reformulated by Furry and Jones [1946]. Uranium isotope separation by TGTD was of considerable interest in both Germany and the United States during World War II. Bardeen [1940] studied the time dependent theory of TGTD for gases.

The operational theory of TGTD for liquid mixtures was outlined by Debye [1939], Hibi and Wirtz [1940], deGroot [1945] and Prigogine [1950]. The theory was similar to that of gases. Horne and Bearman [1962, 1966, 1968] developed the detailed operational theory of TGTD for liquids at steady state. The phenomenon is a very complicated function of the geometric parameters of the column and the physical properties of the solution.

B. OBJECTIVES OF THE RESEARCH

Although the working theory of TGTD has been treated extensively, it has not previously been approached using a full, rigorous nonequilibrium

thermodynamic analysis including time as a variable. All previous approaches followed the general pattern of Furry, Jones and Onsager [1939], which was developed for gases. Only a few experimental TGTD studies of electrolyte solutions have been reported (Hiorta, Matsanaga, and Tanaka [1942, 1943, 1944, 1950], Gillespie [1941,1949], Alexander [1954], Longsworth [1957], Gaeta, Cursio, Perna, Scala, and Bellucci [1969, 1982], and Naokata and Kimie [1984]).

Thermal diffusion in electrolyte solutions has attracted a good deal of attention because the Soret coefficient and the heat of transport are important characteristics of ion-ion and ion-solvent interactions for nonequilibrium situations. Interest in electrolyte solutions has accelerated in recent years due to three developments: (1) increased, efficient use of TGTD as a means of separating liquid solution components (Naokata and Kimie [1984]); (2) improved approaches to the long sought but so far elusive goal of an explicit usable molecular theory of coupled mass and heat flows in mixtures (Wolynes [1980], Kahana and Lin [1981], Mauzerall and Ballard [1982], Calef and Deutsch [1983], Fries and Patey [1984], Petit, Hwang, and Lin [1986], and Kincaid, Cohen, and Lopez de Haro [1987]); and (3) the published reports of Gaeta, Perna, Scala, and Bellucci [1982], whose TGTD experiments appear to imply phase transition behavior in dilute sodium chloride and potassium chloride solutions. Petit, Renner, and Lin [1984], using a pure thermal diffusion technique, and Naokata and Kimie [1984], using a TGTD technique, did not find the behavior suggested by Gaeta, et al. Since Gaeta, et al. and other TGTD experimentalists used for their experimental calculations only the very approximate equations developed long ago for gas mixtures (Furry, Jones, and Onsager [1939]) and since the Gaeta, et al results are so intriguing, it is appropriate

to obtain accurate time-dependent equations for TGTd in electrolyte solutions. The results may be readily adapted to nonelectrolyte liquid mixtures and to gas mixtures.

The principal objective of the research reported here was to describe TGTd of electrolyte solutions by equations based on the thermodynamics of irreversible process and hydrodynamics. We formulate rigorously a set of partial differential equations and upon applying certain assumptions, we solve these differential equations analytically, where possible, to obtain the temperature, velocity, and concentration distributions in a cylindrical TGTd column.

The results presented here should lead to a greater understanding of TGTd in general. More specifically, it is hoped that these results lead to clarification of the recent contradictory experimental results and that the working equation derived from our theoretical results can be used to calculate Soret coefficients at both the steady state and at early time in a TGTd experiment in electrolytes.

C. PLAN OF THE DISSERTATION

Chapter 2 begins with some basic assumptions for the nonequilibrium thermodynamic and hydrodynamic equations of TGTd. On the basis of these fundamental assumptions, we formulate a set of TGTd transport equations, and we discuss, in detail, the physical significance of these transport equations. Because of the importance of boundary and initial conditions the entire chapter 3 is devoted to them. In chapter 4, we obtain the equation for the temperature distribution. The temperature equation is solved analytically by a perturbation scheme. We give, for the first

time, a complete time and space dependent temperature distribution function. Chapter 5 deals with the velocity distribution in the column. Chapter 6 describes the steady state concentration distribution. The concentration derivative with respect to the vertical variable agrees with previous results (Horne and Bearman [1967]). The result presented here is more complete than theirs.

We devote chapter 7 to the time dependent solution of the concentration equation of a column without reservoirs. It is found that the steady state result is independent of whether or not there are reservoirs, and the result agrees with the steady state solution derived in the previous chapter. Chapter 8 deals with the concentration distribution in top and bottom reservoirs. The partial differential equation for diffusion is solved, and it is seen that the concentration distribution in the two reservoirs is a very complicated function of reservoir dimensions and time. We show again that at steady state, the average concentrations in the reservoirs are the same as they would be at the two ends of a TGT column without reservoirs. For the rest of chapter 8, we derive a working equation from which the Soret coefficients can be determined, if the average concentration change with time in the two reservoirs can be measured. We also discuss the contradictory TGT experimental results.

Finally in the last chapter, we discuss the need for some numerical calculations to obtain a better working equation as well as some of the mathematical difficulties for deriving a limiting form for the sum of the infinite series at small times.

CHAPTER 2

FUNDAMENTAL EQUATIONS OF TGTD

A. INTRODUCTION

In this chapter, we use the set of basic hydrodynamic and thermodynamic equations to develop the theory of TGTD for liquids. These equations can be found in the literature of thermodynamics of irreversible processes and of fluid mechanics (de Groot and Mazur, [1962], Fitts, [1962], Horne [1966]).

After presenting the fundamental equations of nonequilibrium thermodynamics and of hydrodynamics, we transform the set of coupled partial differential equations to the Hittorf reference frame, the frame most suitable for electrolyte solutions. The transformed equations are then solved under experimental initial and boundary conditions appropriate to TGTD. In order to facilitate the solution, a number of carefully specified assumptions and simplifications are made.

B. BASIC ASSUMPTIONS

The "thermodynamics of irreversible processes" could also be called the "thermodynamic-phenomenological theory of irreversible processes", for it consists of both a thermodynamic and a phenomenological part. The thermodynamic part of the theory follows the terminology of classical thermodynamics extended to the nonequilibrium regime. The phenomenological part of the theory introduces a postulate new to macroscopic theory, the "phenomenological equations" or the "Onsager equations", which are mathematically expressed as

$$J_i = \sum_{j=1}^m \alpha_{ij} X_j ; \quad (i = 1, 2, 3 \dots)$$

These homogeneous linear relations are the phenomenological equations, where J_i is the i th generalized flux and X_j is the j th generalized driving force. The quantities α_{ij} are called phenomenological coefficients or Onsager coefficients. Thus the assumption is the linear dependence of the generalized fluxes on the generalized forces. The generalized fluxes and the generalized forces all individually vanish at equilibrium. The "Onsager reciprocal relations" $\alpha_{ij} = \alpha_{ji}$ are motivated by the molecular theoretical foundation (especially by the notion of microscopic reversibility), and have been proved correct in all experimental tests in near-equilibrium systems.

In general, matter in a gravitational, centrifugal, or electromagnetic field constitutes a continuous system in which properties such as concentration, density, pressure, temperature and the chemical potentials depend, even in equilibrium, on the space coordinates in a continuous way if we exclude the phase boundaries and

do not consider discontinuous fields. We restrict our derivations to the case of time-invariant (stationary) conservative force fields, as represented by the earth's gravitational field, the centrifugal field at constant angular speed, and the electrostatic field. We assume isotropic media and exclude the polarization of matter.

In a continuous system, intensive properties such as density, pressure, temperature, and concentration depend on the space coordinates in a continuous manner. Thus, those quantities are, in general, functions of time and position for irreversible processes. Only in the case of a steady state are intensive state functions constant in time, although they still may depend on the position coordinates. In summary, the general assumptions are:

- (1) The system is isotropic.
- (2) External force fields are constant in time.
- (3) Electric and magnetic polarization of the material do not appear.
- (4) For electrical phenomena, the Lorentz force which acts on moving charges in magnetic fields, can be neglected.
- (5) The irreversible processes take place near equilibrium.
- (6) Electrical fields can be neglected for TGTD of electrolyte solutions because of bulk electroneutrality.

C. MASS BALANCE

For a continuous, isotropic, nonreacting binary mixture, the equations of conservation of mass are

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (c_i \mathbf{v}_i) = 0, \quad i = 1, 2. \quad (2-1)$$

where c_i is the molar density of component i and $\mathbf{v}_i$ is its local vector velocity. The operator $\partial/\partial t$ denotes the derivative with respect to time at fixed position, so the equation is a local balance equation. The barycentric velocity $\mathbf{v}$ is the mass-fraction sum of the component velocities.

$$\mathbf{v} = w_1 \mathbf{v}_1 + w_2 \mathbf{v}_2, \quad (2-2)$$

with

$$w_i = \frac{x_i M_i}{\bar{M}} = c_i M_i / \rho, \quad i = 1, 2 \quad (2-3)$$

where w_i is mass fraction, x_i mole fraction, M_i is molar mass of component i , $\bar{M}$ is mean molar mass,

$$\bar{M} = x_1 M_1 + x_2 M_2, \quad (2-4)$$

and ρ is density,

$$\rho = \bar{M} / \bar{V}, \quad (2-5)$$

where $\bar{V}$ is the molar volume of the solution. The equation for conservation of total mass is obtained by summing Eq. (2-1, 2, and 3

), with the familar result

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 . \quad (2 - 6)$$

Eq. (2-6) is the local total mass balance equation, which is called the equation of continuity of matter in hydrodynamics. If we introduce the diffusion current density or diffusion flux

$$\mathbf{j}_i^B = c_i (\mathbf{v}_i - \mathbf{v}) , \quad i = 1, 2 \quad (2 - 7)$$

with $\mathbf{v}$ defined by Eq. (2-2), then Eq. (2-1) becomes

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (c_i \mathbf{v}) + \nabla \cdot (\mathbf{j}_i^B) = 0 . \quad (2 - 8)$$

D. MOMENTUM BALANCE

A general form for momentum balance is:

$$\rho \frac{\partial \mathbf{v}}{\partial t} + \rho \mathbf{v} \cdot \nabla \mathbf{v} + \nabla \cdot \mathbf{\Pi} - \sum c_i \mathbf{K}_i = 0 , \quad (2 - 9)$$

where $\mathbf{v}$ is the barycentric velocity, $\mathbf{K}_i$ is the molar external force acting on species i , and $\mathbf{\Pi}$ is the pressure tensor, which for viscous fluids is (Fitts, [1962]),

$$\Pi = \left[\left(\frac{2}{3}\eta - \phi \right) \nabla \cdot \mathbf{v} + P \right] \mathbf{1} - 2\eta \text{sym}(\nabla \mathbf{v}) , \quad (2-10)$$

where η and ϕ are, respectively, the shear and bulk viscosity, $\mathbf{1}$ is the unit tensor, P is pressure, and

$$\text{sym}(\nabla \mathbf{v}) = \frac{1}{2} (\nabla \mathbf{v} + \nabla \mathbf{v}^T) , \quad (2-11)$$

where $(\nabla \mathbf{v})^T$ is the transpose of $\nabla \mathbf{v}$. Eq.(2-9) becomes, with Eq.(2-10),

$$\rho \frac{\partial \mathbf{v}}{\partial t} + \rho \nabla \cdot \nabla \mathbf{v} + \nabla \cdot \left[\left(\frac{2}{3}\eta - \phi \right) \nabla \cdot \mathbf{v} + P \right] \mathbf{1} - 2\nabla \cdot \eta \text{sym}(\nabla \mathbf{v}) - \sum_i c_i \mathbf{K}_i = 0 , \quad (2-12)$$

The term $\sum c_i \mathbf{K}_i$ is the resultant of the force density of the external forces.

The equation of momentum balance for a Newtonian fluid subject to no external field except gravity leads to the equation of motion (Horne [1966]),

$$\rho \frac{\partial \mathbf{v}}{\partial t} + \nabla P + \rho \mathbf{g} + \nabla \cdot \left[\left(\frac{2}{3}\eta - \phi \right) \nabla \cdot \mathbf{v} \right] + \rho \nabla \cdot \nabla \mathbf{v} - 2\nabla \cdot \eta \text{sym} \nabla \mathbf{v} = 0 , \quad (2-13)$$

where $\mathbf{g}$ represents the gravitational field.

E. ENERGY BALANCE

The most useful form of the equation of energy transport for experimental purposes is (Horne [1966]),

$$\begin{aligned} \frac{\bar{C}_p}{\bar{V}} \frac{\partial T}{\partial t} + \frac{\bar{C}_p}{\bar{V}} \mathbf{v} \cdot \nabla T - \alpha \mathbf{v} \cdot \nabla P - \alpha \frac{\partial P}{\partial t} - (\Pi + P\mathbf{I}) : \nabla \mathbf{v} + \nabla \cdot \mathbf{q} \\ + \mathbf{j}_1^B \cdot \nabla [\bar{H}_1 - (M_1/M_2) \bar{H}_2] = 0 \end{aligned} \quad (2-14)$$

where $\bar{C}_p$ is the molar constant pressure heat capacity, T is the temperature, α is the thermal expansivity,

$$\alpha = \frac{(\partial \bar{V} / \partial T)_{P, x_1}}{\bar{V}} = - \frac{(\partial \rho / \partial T)_{P, x_1}}{\rho} \quad (2-15)$$

The thermal and mass flux terms in Eq.(2-4) contain the heat flux $\mathbf{q}$ and the molar diffusion flux $\mathbf{j}_i^B$ relative to the barycentric velocity, which is given by Eq.(2-7). Note by Eq.(2-2,3,and 7),

$$M_1 \mathbf{j}_1^B + M_2 \mathbf{j}_2^B = 0. \quad (2-16)$$

The last term on the left hand side of Eq.(2-14) contains the partial molar enthalpies $\bar{H}_1$ and $\bar{H}_2$; this term is proportional to the heat of mixing (Ingle and Horne [1973]; Rowley and Horne [1980]).

F. ONSAGER EQUATIONS

The Onsager equations that relate the heat and matter fluxes to the partial derivatives of temperature and chemical potential are:

$$\begin{aligned}
 - \mathbf{q} &= \Omega_{01} \nabla_T \mu_1 + \Omega_{02} \nabla_T \mu_2 + \Omega_{00} \nabla \ln T, \\
 - \mathbf{j}_1^B &= \Omega_{11} \nabla_T \mu_1 + \Omega_{12} \nabla_T \mu_2 + \Omega_{10} \nabla \ln T, \\
 - \mathbf{j}_2^B &= \Omega_{21} \nabla_T \mu_1 + \Omega_{22} \nabla_T \mu_2 + \Omega_{20} \nabla \ln T,
 \end{aligned}
 \tag{2 - 17}$$

with

$$\nabla_T \mu_i = \nabla \mu_i + \tilde{S}_i \nabla T,
 \tag{2 - 18}$$

where μ_i is the chemical potential of component i and $\tilde{S}_i$ is its partial molar entropy.

The Onsager coefficients Ω_{ij} are not all independent (Bartelt and Horne [1969]),

$$\begin{aligned}
 \sum_{i=1}^2 M_i \Omega_{0i} &= 0 = \sum_{i=1}^2 M_i \Omega_{i0} \\
 \sum_{i=1}^2 M_i M_j \Omega_{ij} &= 0 = \sum_{j=1}^2 M_i M_j \Omega_{ij}
 \end{aligned}
 \tag{2 - 19}$$

In the independent Onsager coefficients Ω_{02} , Ω_{12} , and Ω_{00} , Eqs.(2-17)

become

$$\begin{aligned}
& -q \left(\nabla_T \mu_2 - (M_2/M_1) \nabla_T \mu_1 \right) \Omega_{02} + \Omega_{00} \nabla \ln T \\
& -j_2^B - \left(\nabla_T \mu_2 - (M_2/M_1) \nabla_T \mu_1 \right) \Omega_{12} (M_1/M_2) + \Omega_{20} \nabla \ln T .
\end{aligned} \tag{2-20}$$

Now (Horne [1966]),

$$\begin{aligned}
\nabla_T \mu_1 &= \tilde{V}_1 \nabla P - (x_2/x_1) \mu_{22} \nabla x_2 - M_1 g \\
\nabla_T \mu_2 &= \tilde{V}_2 \nabla P - (x_2/x_1) \mu_{22} \nabla x_2 - M_2 g
\end{aligned} \tag{2-21}$$

where

$$\mu_{22} = (\partial \mu_{22} / \partial x_2)_{T,P} = (RT/x_2) \left[1 + (\partial \ln f_2 / \partial \ln x_2)_{T,P} \right] \tag{2-22}$$

and f_2 is the mole fraction based activity coefficient of the solute. In the experimentally measurable properties mole fraction, pressure, and temperature, Eqs.(2-20) become:

$$\begin{aligned}
& -q - \Omega_{02} \frac{\tilde{M} \mu_{22}}{x_1 M_1} \nabla x_2 + \Omega_{02} M_2 \left(\frac{\tilde{V}_2}{M_2} - \frac{\tilde{V}_1}{M_1} \right) \nabla P + \Omega_{00} \nabla \ln T \\
& -j_2^B - \Omega_{12} \frac{\tilde{M} \mu_{22}}{x_1 M_2} \nabla x_2 - \Omega_{12} M_1 \left(\frac{\tilde{V}_2}{M_2} - \frac{\tilde{V}_1}{M_1} \right) \nabla P + \Omega_{20} \nabla \ln T .
\end{aligned} \tag{2-23}$$

G PRACTICAL TRANSPORT EQUATIONS

Although Eqs.(2-1,13,14, and 23) suffice as the differential

equations for TGTD in a binary fluid system, they are not those used in practice. In this section we first convert to more common transport parameters such as the mutual diffusivity D , the Soret coefficient σ , and the thermal conductivity κ . In order to identify the Onsager coefficients of Eqs.(2-23) with conventionally tabulated parameters, it is necessary to define precisely the experimental conditions that underlie the various definitions. A particularly important result of this section is the identification of the Soret coefficient σ^* determined in TGTD experiments on electrolytes.

The thermal diffusion factor α_2 is defined(Horne and Bearman [1962]) by the experimental equation for the steady state of one-dimensional pure thermal diffusion experiment in the absence of a pressure gradient,

$$\frac{dx_2}{dz} = \alpha_2 x_1 x_2 \frac{d \ln T}{dz} \quad (2 - 24)$$

By Eqs.(2-27 and 28)

$$\alpha_2 = (\Omega_{20}/\Omega_{12}) \left(\frac{M_2}{\bar{M} x_2 \mu_{22}} \right) \quad (2 - 25)$$

Note that $\alpha_1 = -\alpha_2$ when α_1 is defined by the equation symmetric to Eq.(2-24). The Soret coefficient is simply (deGroot [1945], Haase [1969])

$$\sigma = \alpha_2 / T \quad (2 - 26)$$

The sedimentation coefficient s_2 is defined by the experimental

equation for the isothermal equilibrium one-dimensional composition gradient due to a pressure gradient,

$$\frac{dx_2}{dz} = -s_2 x_1 x_2 \frac{dP}{dz} \quad (2 - 27)$$

whence

$$s_2 = \left(\frac{M_1 M_2}{\bar{M} x_2 \mu_{22}} \right) \left(\frac{\bar{V}_2}{M_2} - \frac{\bar{V}_1}{M_1} \right). \quad (2 - 28)$$

Again, $s_1 = -s_2$ if s_1 is defined symmetrically. Note that s_2 is not a transport property since sedimentation is an equilibrium phenomenon.

To obtain the relationship between Ω_{12} and the mutual diffusion coefficient D defined by Fick's Law, consider the Fickian flux j_1^F defined relative to the volume velocity $\mathbf{v}^V$,

$$j_1^F = c_1 (\mathbf{v}_1 - \mathbf{v}^V), \quad \mathbf{v}^V = c_1 \bar{V}_1 \mathbf{v}_1 + c_2 \bar{V}_2 \mathbf{v}_2. \quad (2 - 29)$$

where $c_i \bar{V}_i = (x_i \bar{V}_i / \bar{V})$ is the volume fraction of component i . Fick's First Law is the experimental equation for the relationship between the one-dimensional Fickian diffusion flux j_1^F and the concentration gradient in a binary, isothermal, isobaric system,

$$-j_1^F = D (dc_i/dz) \quad (2 - 30)$$

By Eq.(2-33),

$$\bar{V}_1 j_1^F + \bar{V}_2 j_2^F = 0 \quad (2-31)$$

the definition of D in Eq.(2-30) is consistent with Eq.(2-31) and the general Gibbs-Duhem result for uniform temperature and pressure

$$\bar{V}_1 dc_1 + \bar{V}_2 dc_2 = 0 . \quad (2-32)$$

The relationship between the Fickian diffusion flux j_2^F and the barycentric molar diffusion flux j_2^B is

$$j_2^F = \rho (\bar{V}_1 / M_1) j_2^B , \quad (2-33)$$

where we have used Eqs.(2-7,16, and 29).

To complete the relationship between D and Ω_{12} , we need the relationship between dx_2 and dc_2 , which we obtain from $x_2 = c_2 \bar{V}$ and the chain rule for $d\bar{V}$

$$d\bar{V} = (\bar{V}_2 - \bar{V}_1) dx_2 + \alpha \bar{V} dT - \beta \bar{V} dP , \quad (2-34)$$

where β is the isothermal compressibility. Then

$$\bar{V} dc_2 = (\bar{V}_1 / \bar{V}) dx_2 - x_2 \alpha dT + x_2 \beta dP . \quad (2-35)$$

For the one dimensional, isothermal, isobaric Fick's experiment, from Eq.(2-34,36 and 38)

$$- j_2^B = [M_1/(\rho \tilde{V})] D[\tilde{V}_1/\tilde{V}^2] (dx_2/dz) , \quad (2 - 36)$$

or

$$- j_2^B = [M_1/(\tilde{M}\tilde{V})] D(dx_2/dz) ,$$

and by Eqs.(2-25 and 23),

$$D = - \Omega_{12} \left(\frac{\tilde{V}\tilde{M}^2 \mu_{22}}{x_1 M_1 M_2} \right) . \quad (2 - 37)$$

The heat of transport Q^* is experimentally obtained, in principle, by determining the heat flux due to matter flux under isothermal conditions. Thus (Bearman, Kirkwood, and Fixman [1958], Rowley and Horne [1980]), for $\nabla \ln T = 0$,

$$q = Q_i^* j_i \quad (2 - 38)$$

and by Eq.(2-24),

$$Q_2^* = - \left(\frac{M_2}{M_1} \right) \left(\frac{Q_{02}}{Q_{12}} \right) . \quad (2 - 39)$$

By Eqs.(2-16 and 42),

$$Q_1^* = - (M_1/M_2) Q_2^* , \quad (2 - 40)$$

With Eqs.(2-25 and 39) Onsager reciprocity implies

$$Q_2^* = - \left(\frac{\tilde{M}x_2\mu_{22}}{M_1} \right) \alpha_2 . \quad (2 - 41)$$

Two thermal conductivity parameters must be distinguished, in principle, in thermal diffusion experiments. At the beginning of the experiment, when no chemical potential gradient has developed, Fourier's First Law is

$$- q = \kappa_0 \nabla T \quad (2 - 42)$$

and, by the first of Eqs.(2-24).

$$\kappa_0 = \Omega_{00}/T \quad (2 - 43)$$

At the steady state of a thermal diffusion experiment, the diffusion flux vanishes and Fourier's Law in the form

$$- q = \kappa_\infty \nabla T, \quad (2 - 44)$$

combined with Eq.(2-20) yields

$$\kappa_\infty = \left[\Omega_{00} + (M_2/M_1) \left(\frac{\Omega_{02}\Omega_{20}}{\Omega_{12}} \right) \right] T^{-1} = \kappa_0 + (M_2/M_1) \left(\frac{\Omega_{02}\Omega_{20}}{T\Omega_{12}} \right)$$

$$= \kappa_0 + x_1 x_2 \left(\frac{M_1}{\bar{V}_M} \right) \sigma Q_2^* D . \quad (2 - 45)$$

With "practical" transport parameters replacing Onsager coefficients, the flux equations are

$$\begin{aligned} -j_2^B &= \left(\frac{M_1}{\bar{V}_M} \right) D \left(\nabla x_2 - x_1 x_2 \sigma \nabla T + x_1 x_2 s_2 \nabla P \right) \\ -q &= Q_2^* j_2^B + \kappa_\infty \nabla T . \end{aligned} \quad (2 - 46)$$

Following is a summary of the relationships between the Onsager coefficients and the practical transport parameters:

$$\begin{aligned} \Omega_{12} &= -x_1 x_2 \left(\frac{M_1 M_2}{x_2 \mu_{22} \bar{V}_M^2} \right) D , \quad \Omega_{20} = -x_1 x_2 \left(\frac{M_1 T}{\bar{V}_M} \right) \sigma D \\ \Omega_{02} &= x_1 x_2 \left(\frac{M_1^2}{x_2 \mu_{22} \bar{V}_M^2} \right) Q_2^* D , \quad \Omega_{00} = T \kappa_0 . \end{aligned} \quad (2 - 47)$$

Although the volume frame of reference is the basis of Fick's Law and is the reference frame of choice for concentrated electrolyte solutions and for non-electrolyte mixtures, the Hittorf frame, with the solvent velocity as reference velocity, is the better choice for dilute solutions. Moreover, the composition variable usually chosen for dilute solutions is the molar concentration c_2 rather than mole fraction x_2 .

With Eq.(2-34), the first of Eq.(2-45) becomes:

$$-j_2^B = \left(\frac{M_1 \bar{V}}{\bar{V}_1 \bar{M}} \right) D \left(\nabla c_2 - (c_1 c_2 \bar{V}_1 \sigma - c_2 \alpha) \nabla T + (c_1 c_2 \bar{V}_1 s_2 - c_2 \beta) \nabla P \right) . \quad (2 - 48)$$

The Hittorf diffusion flux is defined by

$$\mathbf{j}_2^H = c_2 (\mathbf{v}_2 - \mathbf{v}_1) . \quad (2-49)$$

To obtain the relationship between the Hittorf flux and the molar barycentric flux, it is useful to add and subtract $\mathbf{v}$ in Eq.(2-49), and to use Eq.(2-16), where

$$\begin{aligned} \mathbf{j}_2^H &= c_2 [\mathbf{v}_2 - \mathbf{v} - (\mathbf{v}_1 - \mathbf{v})] = \mathbf{j}_2^B - (c_2/c_1) \mathbf{j}_1^B \\ &= \mathbf{j}_2^B + \frac{c_2 M_2}{c_1 M_1} \mathbf{j}_2^B = [\tilde{M}/(x_1 M_1)] \mathbf{j}_2^B . \end{aligned} \quad (2-50)$$

Note, for later use, that

$$\mathbf{v} = w_1 \mathbf{v}_1 + w_2 \mathbf{v}_2 = w_1 (\mathbf{v}_2 - \mathbf{v}_1) + \mathbf{v}_2 = (w_1/c_2) \mathbf{j}_2^H + \mathbf{v}_2 \quad (2-51)$$

or

$$c_2 \mathbf{v}_2 = c_2 \mathbf{v} + \frac{x_1 M_1}{\tilde{M}} \mathbf{j}_2^H = c_2 \mathbf{v} + \frac{c_1 M_1}{\rho} \mathbf{j}_2^H . \quad (2-52)$$

By Eqs.(2-48 and 50),

$$-\mathbf{j}_2^H = D^* (\nabla c_2 - c_2 \sigma^* \nabla T + c_2 s_2^* \nabla P) , \quad (2-53)$$

where

$$D^* = D / (c_1 \tilde{V}_1)$$

$$\sigma^* = c_1 \bar{V}_1 \sigma - \alpha \quad (2-54)$$

$$s_2^* = c_1 \bar{V}_1 s_2 - \beta .$$

Note that $c_1 \bar{V}_1$ is the volume fraction of solvent and is nearly equal to unity. Even for 0.5 M sodium or potassium chloride solutions, however, the difference, $1 - c_1 \bar{V}_1 = c_2 \bar{V}_2$ is about 0.02, and for 1.0 M solutions is about 0.04. It is thus not prudent to replace $c_1 \bar{V}_1$ with 1 if 1% or better accuracy is desirable.

The equation of mass concentration for the solute is, from Eq.(2-1),

$$\frac{\partial c_2}{\partial t} + \nabla \cdot (c_2 \mathbf{v}_2) = 0 . \quad (2-55)$$

With Eqs.(2-52 and 53), this becomes

$$\frac{\partial c_2}{\partial t} - \nabla \cdot \left[\frac{DM_1}{\bar{V}_1 \rho} \left(\nabla c_2 - \sigma^* c_2 \nabla T + s^* c_2 \nabla P \right) - c_2 \mathbf{v} \right] = 0 . \quad (2-56)$$

Eq.(2-56) describes the concentration distribution in space and in time. Obviously, this equation cannot be solved alone because it is coupled with equations for temperature, pressure, and fluid velocity.

H. SIMPLIFYING ASSUMPTIONS

A typical TGT D apparatus is shown in Fig. 1. For the thermal steady state the constant temperature T_H of the inner cylinder, radius r_1 , is maintained hotter than the constant temperature T_C of the outer cylinder, radius r_2 (a cylindrical jacket surrounds the apparatus). To begin the experiment the apparatus is filled with a solution of concentration c_2^0 and is allowed to come to isothermal equilibrium, which is also the sedimentation equilibrium of Eq.(2-27). By Eq.(2-13)

$$\partial P / \partial z = - \rho g \quad (2 - 57)$$

at mechanical equilibrium (Bartelt and Horne [1970]), and the pressure is constant in both of the other two directions. By Eqs.(2-53 and 57)

$$\frac{\partial \ln c_2}{\partial z} = s_2^* \rho g \approx \frac{M_1 M_2}{\bar{V} RT} \left(\frac{\bar{V}_2}{M_2} - \frac{\bar{V}_1}{M_1} \right) \quad (2 - 58)$$

For KCl, $\left(\frac{\bar{V}_2}{M_2} - \frac{\bar{V}_1}{M_1} \right) \approx -0.7 \times 10^{-4} \text{ m}^3 \text{kg}^{-1}$ and $s_2^* \rho g \approx -3.0 \times 10^{-5} \text{ m}^{-1}$

(see table 2-1). Thus, c_2 varies by only 0.003% per meter. This is undetectably small in most thermal diffusion experiments. Similarly, for

NaCl, $\left(\frac{\bar{V}_2}{M_2} - \frac{\bar{V}_1}{M_1} \right) \approx -0.7 \times 10^{-4} \text{ m}^3 \text{kg}^{-1}$ and $s_2^* \rho g \approx -2.0 \times 10^{-5} \text{ m}^{-1}$. Thus,

for practical purposes, (1) the composition is uniform at the beginning of the thermal diffusion experiment and (2) pressure gradient contributions to the composition gradient are always negligible. An immediate consequence is that Eqs.(2-53 and 56) become

$$- \mathbf{j}_2^H = D^* (\nabla c_2 - c_2 \sigma^* \nabla T)$$

$$\frac{\partial c_2}{\partial t} - \nabla \cdot \left[\frac{DM_1}{V_1 \rho} \left(\nabla c_2 - \sigma^* c_2 \nabla T \right) - c_2 \mathbf{v} \right] = 0 . \quad (2 - 59)$$

I. VELOCITY EQUATION

The equation for the convective velocity in a gravitational field is Eq.(2-13). This equation, as it stands, cannot be solved exactly because it is nonlinear. Moreover, the quantities η and ϕ are functions of pressure and temperature and in general η and ϕ are not constant throughout the fluid. In most cases, however, the viscosity coefficients vary only slightly in a fluid which does not contain large temperature, composition, or pressure gradients, and they can then usually taken to be constants. We do this here.

The next simplification comes from the so-called incompressibility assumption. This is based on Eq.(2-6) and the chain rule equation for the pressure dependence of the density of a pure isothermal substance. At steady state,

$$\nabla \rho = \rho \beta \nabla P. \quad (2 - 60)$$

The conservation Eq.(2-6) can be rewritten as

$$\rho \nabla \cdot \mathbf{v} + \mathbf{v} \cdot \nabla \rho = 0 , \quad (2 - 61)$$

which, when combined with Eq.(2-64), yields

$$\nabla \cdot \mathbf{v} + \beta \mathbf{v} \cdot \nabla P = 0 . \quad (2 - 62)$$

Thus, if $\beta = 0$, then the fluid is incompressible and $\nabla \cdot \mathbf{v} = 0$. It is customarily assumed that the total density is constant throughout the system. This would be ludicrous for TGT D because the chief driving force is the thermal expansivity of the fluid. We do assume that the divergence of the velocity vanishes in the steady state and also for the time dependent state. Eq.(2-13) becomes

$$\rho \frac{\partial \mathbf{v}}{\partial t} + \rho \mathbf{v} \cdot \nabla \mathbf{v} - 2 \nabla \cdot \eta \text{sym}(\nabla \mathbf{v}) + \rho \mathbf{g} + \nabla \cdot P = 0 \quad (2 - 63)$$

For subsequent use, note that $\nabla \cdot \mathbf{v} = 0$ implies that the vertical component of $\mathbf{v}$ is independent of the vertical direction if the other components of $\mathbf{v}$ vanish.

J. THE TEMPERATURE EQUATION

The temperature equation has been discussed in great detail for both TGT D and PTD (Horne and Bearman [1967], Horne and Anderson [1970]). The chief simplifying result is that all terms but the first and $\nabla \cdot \mathbf{q}$ are very small in Eq.(2-14). The initial heat flow is caused by the temperature gradient. Since the steady temperature distribution is established very quickly, the flow of heat is dominated by thermal conduction rather than heat of transport or heat of mixing. Under these assumptions, Eq.(2-14) yields

$$\frac{\bar{C}}{\bar{V}}^p \frac{\partial T}{\partial t} + \mathbf{V} \cdot \mathbf{q} = 0 \quad (2-64)$$

or

$$\frac{\bar{C}}{\bar{V}}^p \frac{\partial T}{\partial t} - \mathbf{V} \cdot (\kappa \nabla T) = 0, \quad (2-65)$$

where $\kappa = -\Omega_{00}/T$. That is, we neglect both the contribution of the heat of transport term and the difference between κ_0 and κ_∞ . Eq.(2-65) is the well-known heat conduction equation of Fourier.

K. SUMMARY

In this chapter, we have obtained the three basic partial differential equations describing TGTd for binary electrolyte solutions. They are

$$\frac{\bar{C}}{\bar{V}}^p \frac{\partial T}{\partial t} - \mathbf{V} \cdot (\kappa \nabla T) = 0$$

$$\rho \frac{\partial \mathbf{v}}{\partial t} + \rho \mathbf{v} \cdot (\nabla \mathbf{v}) - 2 \nabla \cdot \eta \text{sym}(\nabla \mathbf{v}) - \rho \mathbf{g} + \nabla \cdot \mathbf{P} = 0$$

$$\frac{\partial c_2}{\partial t} - \nabla \cdot \left[\frac{DM_1}{\bar{V}_1 \rho} \left(\nabla c_2 - \sigma^* c_2 \nabla T \right) - c_2 \mathbf{v} \right] = 0 \quad (2-76)$$

These three equations will be solved under experimental boundary and initial conditions appropriate for TGTd.

Table 2-1

Approximate values of some thermodynamic and transport properties for 0.5M binary aqueous NaCl and KCl solutions at 25°C. Solute is component 2, solvent (H₂O) is component 1

Property	NaCl soln.	KCl soln.	References
$M_1/10^{-2}\text{kg.mol}^{-1}$	1.80	1.80	
$M_2/10^{-2}\text{kg.mol}^{-1}$	5.84	7.46	
$\bar{V}_1/10^{-5}\text{m}^3\text{mol}^{-1}$	1.8	1.8	a
$\bar{V}_2/10^{-5}\text{m}^3\text{mol}^{-1}$	1.81	1.97	a
$\rho/10^3\text{kg m}^{-3}$	1.02	1.02	b
$\rho^{-1}(\partial\rho/\partial c)_{T,P}/10^{-5}\text{m}^3\text{mol}^{-1}$	3.9	4.5	c
$\alpha/10^{-4}\text{K}^{-1}$	-2.29	-2.86	d
$\beta/10^{-10}\text{Pa}^{-1}$	4.92	4.48	d
$\bar{C}_p/10^3\text{J.kg}^{-1}\text{K}^{-1}$	4.03	4.1	e
$\kappa/10^{-1}\text{J.s}^{-1}\text{K}^{-1}\text{m}^{-1}$	6.04	5.99	f
$\kappa^{-1}(\partial\kappa/\partial T)_c/10^{-3}\text{K}^{-1}$	2.45	2.47	f
$\kappa^{-1}(\partial\kappa/\partial c)_T/10^{-5}\text{m}^3\text{mol}^{-1}$	-9.2	-2.25	f

Table 2-1 (continued)

$\eta/10^{-3}\text{kg.s}^{-1}\text{m}^{-1}$	0.93	0.9	g
$\eta^{-1}(\partial\eta/\partial T)_c/K^{-1}$	-0.02	-0.02	g
$\eta^{-1}(\partial\eta/\partial C)_T/10^{-6}\text{m}^3\text{mol}^{-1}$	0.9	3.5	g
$D/10^{-9}\text{m}^2\text{s}^{-1}$	1.47	1.85	d,h
$D^{-1}(\partial D/\partial c)_T/10^{-5}\text{m}^3\text{mol}^{-1}$	0.5	3.7	d,h
$D^{-1}(\partial D/\partial T)_c/K^{-1}$	0.02	0.02	i

M_1 , M_2 , $\bar{V}_1$, $\bar{V}_2$ are, respectively, the molar masses of water, salts, and partial molar volumes of water and salts, ρ the density, α thermal expansivity, β isothermal compressibility, $\bar{C}_p$ heat capacity, κ thermal conductivity, η shear viscosity and D diffusion coefficient of the salt solutions.

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- i) Estimated on assumption that the product ηD is independent of temperature

CHAPTER 3

BOUNDARY AND INITIAL CONDITIONS

A. GENERAL REMARKS

The set of partial differential equations that describe general TGTD cannot be solved without experimental boundary and initial conditions. The expression "experimental boundary and initial conditions" is intended to imply that the conditions may vary under different TGTD column designs and specific experimental operations. (Tyrell [1961], Horne and Bearman [1962], Gaeta et al [1982], Naokata and Kimie [1984]).

The apparatus in question here (Fig.3-1) consists of two vertical, concentric cylinders closed at both ends, and it contains an electrolyte solution. At the beginning of the experiment the system in the TGTD column is effectively homogeneous, which means that the temperature and concentration are uniform throughout the annulus and the fluid is static, and the convection velocity is zero. In fact, there is an initial concentration gradient in the column due to the gravitational force but this concentration gradient is experimentally undetectable, as

already discussed in chapter 2. We assume that the apparatus is cylindrically symmetric and that all physical properties are independent of the azimuthal coordinate.

B. BOUNDARY AND INITIAL CONDITIONS FOR TEMPERATURE

The experiment starts when a horizontal temperature difference is imposed by suddenly increasing the temperature of the inner wall relative to the outer wall. For a brief interval, the temperature of the fluid in the column remains uniform due to the time required for thermal conduction through the walls. This phenomenon is called the "warming-up effect" (Horne and Anderson, [1970]). There is also a slight lag because it is not possible experimentally to change the wall temperatures instantaneously.

It is, nevertheless, possible to determine empirically the time required for both the inner wall and the outer wall to reach their steady state temperatures. This time depends for both walls on the column material and thickness as well as the means of maintaining the temperatures of the inner and outer walls. A useful way to take account of the warming-up effect is (Horne and Anderson [1970])

$$\begin{aligned}
 T_H(r_1, t) &= T_M + \frac{1}{2}\Delta T(1 - e^{-t/\tau_H}) \\
 T_C(r_2, t) &= T_M - \frac{1}{2}\Delta T(1 - e^{-t/\tau_C}) ,
 \end{aligned}
 \tag{3 - 1}$$

where ΔT is $(T_H - T_C)$, the applied temperature difference, T_M is the

arithmetic mean temperature, and τ_H and τ_C are, respectively, the relaxation times at the hot and cold walls, best obtained experimentally. Usually the walls reach their steady state temperature distribution much sooner than the over-all system attains its steady temperature distribution. The initial condition for temperature is

$$T(r, t=0) = T_M . \quad (3 - 2)$$

Eqs.(3-1 and 2) are the boundary and initial conditions for the temperature equation given by Eq.(2-69).

C. BOUNDARY AND INITIAL CONDITIONS FOR VELOCITY

The initial condition for velocity stems from the requirement that at zero time, the system in the TGTD column is uniform, and there is no convection. Then the vertical and radial components of $\mathbf{v}$ are initially

$$v_z(r, z, 0) = 0 = v_r(r, z, 0) . \quad (3 - 3)$$

Because the fluid is contained within the column, all velocity components vanish at the cylinder boundaries:

$$v_r(r_1, z, t) = 0 = v_r(r_2, z, t),$$

$$v_r(r, 0, t) = 0 = v_r(r, L, t),$$

$$v_z(r_1, z, t) = 0 = v_z(r_2, z, t),$$

$$v_z(r,0,t) = 0 = v_z(r,L,t). \quad (3 - 4)$$

D. BOUNDARY AND INITIAL CONDITIONS FOR CONCENTRATION

For concentration, the experimental initial condition is that at the beginning the concentration is uniform when we ignore the sedimentation equilibrium concentration distribution.

$$c_2(r,z,0) = c_2^0. \quad (3 - 5)$$

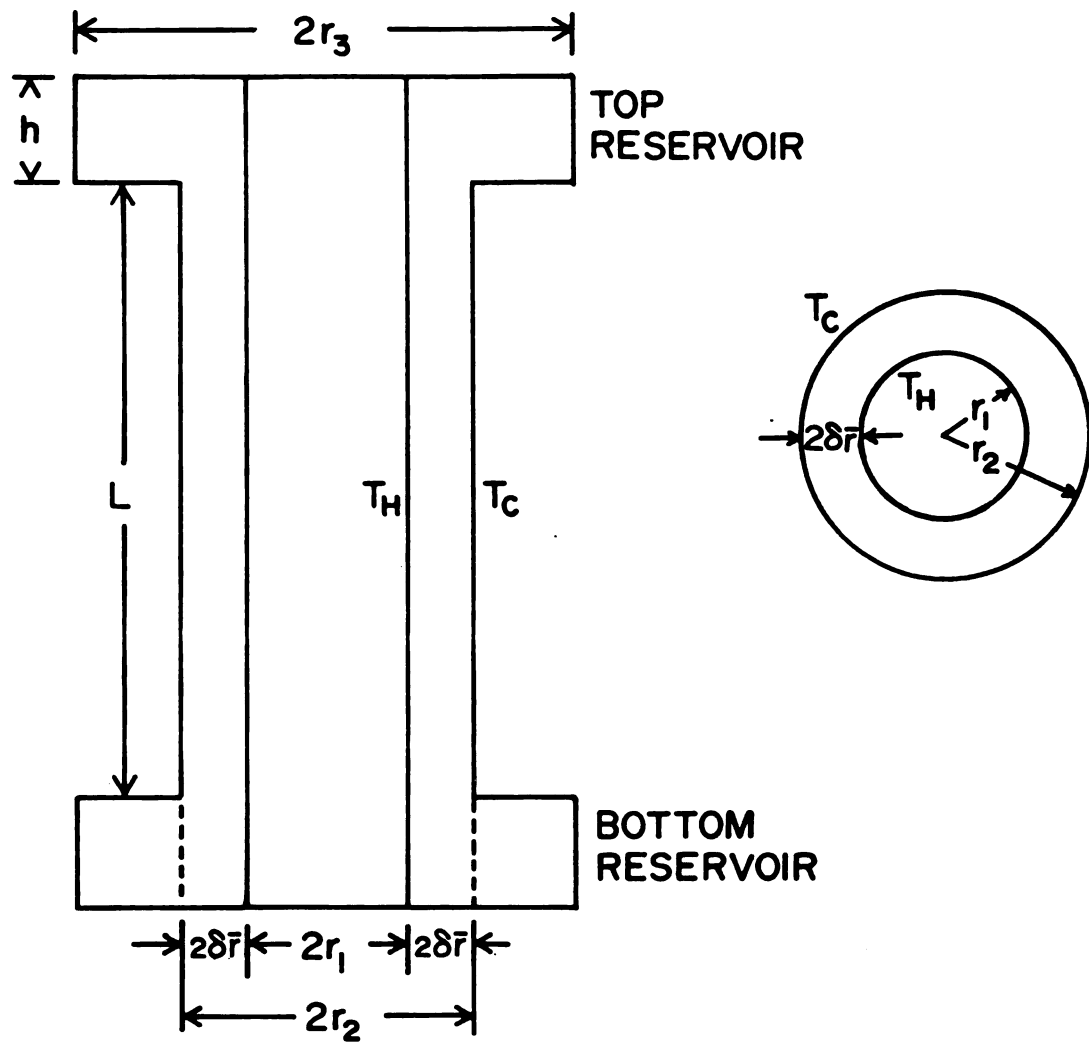
We can say nothing a priori about the concentration at the boundary at any time later than zero because the concentration varies at every point of the boundary. This causes no difficulty, however, because the theoretical boundary condition is that the diffusion flux perpendicular to the wall vanishes at the wall for all times. This is because neither the solvent nor the solute leaves the column. Thus the boundary conditions for concentration are

$$j_{2r}^H(r_1,z,t) = 0 = j_{2r}^H(r_2,z,t), \quad (3 - 6)$$

where j_{2r}^H is the radial component of the flux j_2^H . The vertical component of the flux vanishes at the top and bottom of the apparatus. The presence or absence of reservoirs determines the form of the corresponding equations. We deal with this in chapters 7 and 8.

Figure (3-1)

Schematic profile of TGTD apparatus (not to scale). Radius r_1 is maintained at higher constant temperature T_H , the outer cylinder radius r_2 is maintained at lower constant temperature T_C . $2\delta\bar{r}=a$ is the annular spacing and h is the height of the reservoirs. (We assume that the two reservoirs are identical).



C H A P T E R 4

TEMPERATURE DISTRIBUTION

A. PERTURBATION SCHEME

In general the thermodynamic and transport parameters are not constants, but instead, they depend on composition and temperature. To take into account the temperature and composition dependences of coefficients, we formally use the perturbation scheme of Horne and Anderson [1970], which is based on the fact that the thermodynamic and transport properties vary only slightly with composition and temperature. For any coefficient L , we write

$$\begin{aligned} \hat{L} = \bar{L} + \epsilon \left[(T - T_M) \bar{L}_T + (c_2 - c_2^0) \bar{L}_C \right] \\ + \epsilon^2 \left[\frac{1}{2} (T - T_M)^2 \bar{L}_{TT} + (T - T_M) (c_2 - c_2^0) \bar{L}_{TC} + \frac{1}{2} (c_2 - c_2^0)^2 \bar{L}_{CC} \right] \\ + O(\epsilon^3), \end{aligned} \quad (4 - 1)$$

where

$$\bar{L} = L(T_M, c_2^0),$$

$$\bar{L}_T = \left(\frac{\partial L}{\partial T} \right)_{T_M, c_2^0}, \quad \bar{L}_C = \left(\frac{\partial L}{\partial c_2} \right)_{T_M, c_2^0},$$

$$\bar{L}_{TT} = \left(\frac{\partial^2 L}{\partial T^2} \right)_{T_M, c_2^0}, \quad \bar{L}_{TC} = \left(\frac{\partial^2 L}{\partial T \partial c_2} \right)_{T_M, c_2^0}, \quad (4-2)$$

$$\bar{L}_{CC} = \left(\frac{\partial^2 L}{\partial c_2^2} \right)_{T_M, c_2^0},$$

with T_M the mean temperature, and c_2^0 the initial uniform concentration of solute. When $\epsilon = 1$, $\hat{L} = L$. Except for the ordering parameter ϵ , Eq.(4-1) is simply a Taylor's series expansion of a property L about the mean temperature and initial concentration. For the variables T and c_2 the perturbation expansions are

$$T = T_M + \theta, \quad \theta = \theta_0 + \epsilon \theta_1 + \epsilon^2 \theta_2 + \epsilon^3 \theta_3 + \dots \quad (4-3)$$

$$c_2 = c_2^0 + \gamma, \quad \gamma = \gamma_0 + \epsilon \gamma_1 + \epsilon^2 \gamma_2 + \epsilon^3 \gamma_3 + \dots$$

Substitution of Eqs.(4-3) into Eq.(4-1) yields

$$\begin{aligned} \hat{L} = & \bar{L} + \epsilon \left(\theta_0 \bar{L}_T + \gamma_0 \bar{L}_C \right) + \epsilon^2 \left(\frac{1}{2} \theta_0^2 \bar{L}_{TT} + \gamma_0 \theta_0 \bar{L}_{TC} + \frac{1}{2} \gamma_0^2 \bar{L}_{CC} + \theta_1 \bar{L}_T + \gamma_1 \bar{L}_C \right) \\ & + O(\epsilon^3). \end{aligned} \quad (4-4)$$

The partial differential equation for temperature, Eq.(2-69) becomes, in cylindrical coordinates,

$$\frac{\partial T}{\partial t} = \frac{\nu}{r} \frac{\partial}{\partial r} \left(\kappa r \frac{\partial T}{\partial r} \right), \quad (4-5)$$

where

$$\nu = (\bar{V}/\bar{C}_p) \text{ and } \kappa = \Omega_{00}/T.$$

Since mass diffusion is very slow compared with thermal conduction, the concentration terms in Eq.(4-4) have no effect on the temperature distribution at the outset. Moreover, neither ν nor κ is sufficiently dependent on concentration that the small concentration gradient at steady state has any discernible effect on the steady state temperature distribution. Substitution of Eqs.(4-3 and 4) into Eq.(4-5) yields, with neglect of concentration terms,

$$\begin{aligned} \frac{\partial \theta_0}{\partial t} + \epsilon \frac{\partial \theta_1}{\partial t} + \epsilon^2 \frac{\partial \theta_2}{\partial t} + O(\epsilon^3) = & \left[\bar{\nu} + \epsilon \nu_T \theta_0 + \epsilon^2 \left(\nu_T \theta_1 + \frac{1}{2} \nu_{TT} \theta_0^2 \right) \right] \\ & \times \frac{1}{r} \frac{\partial}{\partial r} \left\{ \left[\bar{\kappa} + \epsilon \kappa_T \theta_0 + \epsilon^2 \left(\kappa_T \theta_1 + \frac{1}{2} \kappa_{TT} \theta_0^2 \right) \right] \times \left[r \frac{\partial \theta_0}{\partial r} + \epsilon r \frac{\partial \theta_1}{\partial r} + \epsilon^2 r \frac{\partial \theta_2}{\partial r} \right] \right\} \\ & + O(\epsilon^3). \end{aligned} \quad (4-6)$$

The zeroth-order equation is

$$\frac{\partial \theta_0}{\partial t} = \bar{\nu} \bar{\kappa} \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \theta_0}{\partial r} \right), \quad (4-7)$$

with boundary and initial conditions

$$\begin{aligned} \theta_0(r_1, t) &= \frac{1}{2} \Delta T \left(1 - e^{-t/\tau} \right); \quad \theta_0(r_2, t) = \frac{1}{2} \Delta T \left(e^{-t/\tau} - 1 \right) \\ \theta_0(r, 0) &= 0, \end{aligned} \quad (4-8)$$

where we assume that the warming-up relaxation time $\tau = \tau_h - \tau_c$ is the same at the inner wall as it is at the outer. This assumption is experimentally testable, and may be removed, if necessary, without appreciable increase in complexity.

The first order equation is

$$\frac{\partial \theta_1}{\partial t} - \bar{\nu} \bar{\kappa} \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \theta_1}{\partial r} \right) + \nu_T \bar{\kappa} \frac{\theta_0}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \theta_0}{\partial r} \right) + \bar{\nu} \kappa_T \frac{1}{r} \frac{\partial}{\partial r} \left(r \theta_0 \frac{\partial \theta_0}{\partial r} \right) , \quad (4-9)$$

with boundary and initial conditions

$$\theta_1(r_1, t) = 0 = \theta_1(r_2, t); \quad \theta_1(r_2, 0) = 0 . \quad (4-10)$$

The second order equation is very similar, and like Eq.(4-9) contains terms involving lower order solutions. We shall demonstrate that the maximum contribution of θ_1 to the temperature distribution is negligible and shall then neglect θ_1 and all higher order contributions to the temperature distribution.

B. STEADY STATE TEMPERATURE DISTRIBUTION

We first solve the steady state problem for θ_0 and θ_1 . At steady state,

$$\frac{d}{dr} \left(r \frac{d\theta_0}{dr} \right) = 0 , \quad (4-11)$$

with

$$\theta_0(r_1) = \frac{1}{2}\Delta T; \quad \theta_0(r_2) = -\frac{1}{2}\Delta T. \quad (4-12)$$

The steady state problem for θ_1 is

$$\frac{d}{dr} \left(r \frac{d\theta_1}{dr} \right) + \frac{\kappa_T}{\kappa} \frac{d}{dr} \left(r \theta_0 \frac{d\theta_0}{dr} \right) = 0, \quad (4-13)$$

with boundary condition Eq.(4-10).

The solution of the zeroth order steady state equation is

$$\theta_0 = - \left(\frac{\Delta T}{\ln(r_2/r_1)} \right) \left(\ln(r/\sqrt{r_2 r_1}) \right). \quad (4-14)$$

For θ_1 the solution is

$$\theta_1 = -\frac{1}{2}(\kappa_T/\bar{\kappa}) \left(\frac{\Delta T}{\ln(r_2/r_1)} \right)^2 \left(\ln(r/r_2) \right) \ln(r/r_1) \quad (4-15)$$

The maximum contribution of θ_1 to T occurs at $\bar{r} = \sqrt{r_2 r_1}$, the geometric mean annular radius, and is

$$\theta_1(\bar{r}) = \frac{1}{8}(\kappa_T/\bar{\kappa})(\Delta T)^2 \quad (4-16)$$

For $(\kappa_T/\bar{\kappa}) = (\partial \ln \kappa / \partial T)_{T_M} \approx 0.002/K$ and $\Delta T \approx 10K$, $(\theta_1)_{\max} \approx 0.05K$.

This is negligible compared with $T_M \approx 300K$.

For thermal diffusion, the temperature gradient is more important than the temperature itself. It is therefore necessary to compare the derivative $r(d\theta_0/dr)$ with $r(d\theta_1/dr)$. By Eq.(4-14)

$$r \frac{d\theta_0}{dr} = -\Delta T / \ln(r_2/r_1) . \quad (4 - 17)$$

By Eq.(4-15)

$$r \frac{d\theta_1}{dr} = - (\kappa_T / \bar{\kappa}) \left(\frac{\Delta T}{\ln(r_2/r_1)} \right)^2 \ln(r / \bar{r}) . \quad (4 - 18)$$

Thus, in the steady state,

$$r \frac{dT}{dr} - r \frac{d\theta}{dr} - \left(\Delta T / \ln(r_2/r_1) \right) \left[1 + (\kappa_T / \bar{\kappa}) [\Delta T / \ln(r_2/r_1)] \ln(r/\bar{r}) \right] . \quad (4 - 19)$$

The maximum contribution of the first order term occurs at the walls, where the bracketed term in Eq.(4-19) becomes $\left(1 \pm \frac{1}{2} (\kappa_T / \bar{\kappa}) \Delta T \right)$.

For $(\kappa_T / \bar{\kappa}) = 0.002K^{-1}$ and $\Delta T = 10K$, the maximum contribution of θ_1 , to the gradient is less than 1%.

Further insight into the steady state temperature gradient is gained by converting the logarithmic radial dependence to a linear form by using a transformation similar to that of Horne and Bearman [1962].

$$r = \bar{r} e^s , \quad s = \ln(r / \bar{r}) ; \quad \bar{r} = \sqrt{r_2 r_1} , \quad s(r_1) = -\delta$$

$$s(r_2) = \delta, \quad s(\bar{r}) = 0, \quad (r_2/r_1) = e^{2\delta}, \quad (4-20)$$

$$r_2 - r_1 = \bar{r}(e^\delta - e^{-\delta}) = 2\bar{r} \sinh \delta \approx 2\bar{r} \delta = a,$$

then

$$\theta_0 = -s\left(\frac{\Delta T}{2\delta}\right); \quad \theta_1 = \frac{1}{2}\left(\kappa_T / \bar{\kappa}\right)(\delta^2 - s^2)\left(\frac{\Delta T}{2\delta}\right)^2 \quad (4-21)$$

and

$$\begin{aligned} T - T_M &= s\left(\frac{\Delta T}{2\delta}\right) + \frac{1}{2}\left(\kappa_T / \bar{\kappa}\right)(\delta^2 - s^2)\left(\frac{\Delta T}{2\delta}\right)^2 \\ &- T_M \frac{1}{2}(\Delta T)(s/\delta) + \frac{1}{8}\left(\kappa_T / \bar{\kappa}\right)(\Delta T)^2 \left[1 - (s/\delta)^2\right] \end{aligned} \quad (4-22)$$

Further,

$$\frac{\partial T}{\partial s} = -\left(\frac{\Delta T}{2\delta}\right) \left[1 + \frac{1}{2}\left(\kappa_T / \bar{\kappa}\right)(\Delta T)(s/\delta)\right] - \frac{1}{r} \frac{\partial T}{\partial r} \quad (4-23)$$

C. TIME DEPENDENT TEMPERATURE EQUATION

The zeroth order time dependent temperature problem with initial and boundary conditions is displayed in Eqs.(4-7 and 8). Since the first order contributions are negligible in the steady state, we henceforth retain only the zeroth order term. We solve the zeroth order time-dependent problem by Laplace transform. Multiplication of Eqs.(4-7 and 8) by e^{-pt} and integration from zero to infinity yields

$$\begin{aligned} \int_0^\infty e^{-pt} \frac{\partial \theta_0}{\partial t} dt &= \int_0^\infty e^{-pt} Q_r \frac{1}{r} \frac{\partial}{\partial r} \left[r \frac{\partial \theta_0}{\partial r} \right] dt, \\ \int_0^\infty \theta_0(r_1, t) e^{-pt} dt &= \int_0^\infty \frac{1}{2} \Delta T \left[e^{-t/\tau} - 1 \right] e^{-pt} dt, \end{aligned} \quad (4-24)$$

$$\int_0^{\infty} \theta_0(r_2, t) e^{-pt} dt = \int_0^{\infty} \frac{1}{2} \Delta T \left(1 - e^{-t/\tau} \right) e^{-pt} dt ,$$

where p is a complex number, $Q = \nu \kappa$, and we drop the subscript for θ . Integrating the left hand side of the first equation of Eqs.(4-24) by parts, and defining

$$\hat{\theta} = \int_0^{\infty} \theta e^{-pt} dt , \quad (4 - 25)$$

and then performing the integrations for the two boundary conditions, we obtain the transformed differential equation and boundary conditions.

$$\frac{d^2 \hat{\theta}}{dr^2} + \frac{1}{r} \frac{d\hat{\theta}}{dr} - Qp\hat{\theta} = 0 ,$$

$$\hat{\theta}(r_1, p) = - \frac{\Delta T}{2} \left[\frac{1}{p(p\tau + 1)} \right] , \quad (4 - 26)$$

$$\hat{\theta}(r_2, p) = \frac{\Delta T}{2} \left[\frac{1}{p(p\tau + 1)} \right] .$$

The transformed partial differential equation is an ordinary differential equation with two constant boundary conditions, which can be solved easily. The solution of Eqs.(4-26) is a linear combination of modified zeroth order Bessel functions of the first and second kinds (Watson [1958], Abramowitz and Stegun [1970]),

$$\hat{\theta}(r, p) = AI_0(\lambda r) + BK_0(\lambda r) ,$$

$$\lambda^2 = p/Q . \quad (4 - 27)$$

The two constants are obtained from the required boundary conditions, with the result

$$\hat{\theta}(r, p) = \frac{\Delta T}{2p(p\tau+1)[K_0(\lambda r_2)I_0(\lambda r_1) - K_0(\lambda r_1)I_0(\lambda r_2)]} \times \\ \left\{ K_0(\lambda r) \left[I_0(\lambda r_1) + I_0(\lambda r_2) \right] - I_0(\lambda r) \left[K_0(\lambda r_1) + K_0(\lambda r_2) \right] \right\} . \quad (4 - 28)$$

For greater simplicity of notation, we write

$$\hat{\theta}(r, p) = \frac{\Delta T}{2p(p\tau+1)} f(r, p) , \\ f(r, p) = \left\{ K_0(\lambda r) \left[I_0(\lambda r_1) + I_0(\lambda r_2) \right] - I_0(\lambda r) \left[K_0(\lambda r_1) + K_0(\lambda r_2) \right] \right\} G(r, p)^{-1} \\ G(r, p) = K_0(\lambda r_2)I_0(\lambda r_1) - K_0(\lambda r_1)I_0(\lambda r_2) . \quad (4 - 29)$$

To obtain the solution for $\theta(r, t)$, we must find the inverse transform of Eq.(4-29). That is, we must evaluate the inverse transform integral

$$\theta(r, t) = \frac{1}{2\pi i} \int_{\theta} e^{pt} \hat{\theta}(r, p) dp . \quad (4 - 30)$$

The integral is performed along any simple closed contour θ around p_0 , described in the positive sense, such that the integral is analytic on the contour θ and interior to it except at the point p_0 itself, where p_0 is a singular point inside the contour. The straightforward way to evaluate Eq.(4-30) is by Cauchy's residue theorem,

$$\theta(r, t) = \frac{1}{2\pi i} \int_{\theta} e^{+pt} \hat{\theta}_0(r, p) dp = \sum_n \rho_n(r, t), \quad (4 - 31)$$

where $\rho_n(r, t)$ is the n th residue of the integrand, at the n th isolated singular point of the integrand. From Eq.(4-29), this integrand is

$$\hat{\theta}(r, p)e^{pt} = \frac{\Delta T e^{pt}}{2p(p\tau + 1)} f(r, p). \quad (4 - 32)$$

The singular points for $\hat{\theta}(r, p)e^{pt}$ are those that make the denominator vanish. These singular points are those at $p = 0$, $p = -1/\tau$ as well as those such that

$$f(r, p) = \infty$$

or $G(r, p) = K_0(\lambda r_2)I_0(\lambda r_1) - K_0(\lambda r_1)I_0(\lambda r_2) = 0 \quad (4 - 33)$

The next step is to evaluate the residues (Spiegel [1964], Churchill, Brown, and Verhey [1974]). Because the integrand has a simple pole at $p=0$, the residue there is

$$\begin{aligned} \rho(r, t, 0) &= \lim_{p \rightarrow 0} p \hat{\theta}(p, r) e^{pt} = \lim_{p \rightarrow 0} \frac{p \Delta T e^{pt}}{2p(p\tau + 1)} f(r, p) \\ &= \lim_{p \rightarrow 0} \frac{\Delta T e^{pt}}{2(p\tau + 1)} f(r, p) \end{aligned} \quad (4 - 34)$$

or

$$\rho(r, t, 0) = \frac{\Delta T}{2} \lim_{p \rightarrow 0} \frac{K_0(\lambda r) \left[I_0(\lambda r_1) + I_0(\lambda r_2) \right] - I_0(\lambda r) \left[K_0(\lambda r_1) + K_0(\lambda r_2) \right]}{K_0(\lambda r_2)I_0(\lambda r_1) - K_0(\lambda r_1)I_0(\lambda r_2)}. \quad (4 - 35)$$

From Eq.(4-27), λ approaches zero as p approaches zero, and we can use the limiting forms for Bessel functions of small arguments.

$$I_\nu(z) \approx (z/2)^\nu / \Gamma(\nu + 1), \quad \nu \neq -1, -2, -3, \dots$$

$$K_0(z) \approx -\ln z, \quad (4-36)$$

where $\Gamma(\nu + 1)$ is the Gamma Function of order ν . Of course, $I_0(z) \rightarrow 1$ as $z \rightarrow 0$. Then

$$\begin{aligned} \rho(r, t, 0) &= \frac{\Delta T}{2} \lim_{p \rightarrow 0} \left[\frac{-2\ln(\lambda r) - \left[-\ln(\lambda r_1) - \ln(\lambda r_2) \right]}{[-\ln(\lambda r_2) + \ln(\lambda r_1)]} \right] \\ &= \frac{\Delta T}{2} \frac{\ln \left[\frac{r_1 r_2}{r^2} \right]}{\ln(r_1/r_2)} = \Delta T \frac{\ln(\tilde{r}/r)}{\ln(r_1/r_2)}. \end{aligned} \quad (4-37)$$

This is the residue at $p = 0$.

The pole at $p = -1/\tau$ is also a simple pole, so

$$\begin{aligned} \rho(t, -1/\tau) &= \lim_{p \rightarrow (-1/\tau)} (p + 1/\tau) \hat{\theta}(r, p) e^{pt} \\ &= \frac{\Delta T}{2} e^{-t/\tau} \lim_{p \rightarrow (-1/\tau)} \frac{(p + 1/\tau)}{p(p\tau + 1)} f(r, p) \\ &= -\frac{\Delta T}{2} e^{-t/\tau} \lim_{p \rightarrow (-1/\tau)} f(r, p). \end{aligned} \quad (4-38)$$

Now as $p \rightarrow (-1/\tau)$, then $\lambda \rightarrow i/\sqrt{\tau Q}$ by Eq.(4-27).

Let

$$\tilde{\lambda} = 1/(\sqrt{\tau Q}). \quad (4-39)$$

Then $\lambda \rightarrow i\bar{\lambda}$ as $p \rightarrow (-1/\tau)$. Some of the useful Bessel Function identities that permit conversion between real and complex arguments are

$$I_0(z) = J_0(iz) ,$$

$$J_0(z) = J_0(-z) ,$$

$$H_\nu^1(z) = J_\nu(z) + iY_\nu(z) ,$$

$$H_\nu^2(z) = J_\nu(z) - iY_\nu(z) , \quad (4 - 40)$$

$$K_\nu(z) = \frac{\pi}{2} i e^{\pi\nu i/2} H_\nu^1(iz)$$

$$H_\nu^1(ze^{m\pi i}) = \frac{\sin(1-m)\nu\pi}{\sin\nu\pi} H_\nu^1(z) - \frac{\sin m\nu\pi}{\sin\nu\pi} H_\nu^2(z) ,$$

where J_ν and Y_ν are, respectively, Bessel functions of the first and second kind of order ν , and $H_\nu^1(z)$ and $H_\nu^2(z)$ are, respectively, Hankel functions of the first and second kind of order ν .

Of specific use for evaluating $\rho(t, -1/\tau)$ from Eqs.(4-38 and 29) are

$$I_0(i\bar{\lambda}r) = J_0(\bar{\lambda}r) , \quad K_0(i\bar{\lambda}r) = -(\pi/2)iH_0^2(\bar{\lambda}r) . \quad (4 - 41)$$

These yield, for $G(-1/\tau)$

$$\begin{aligned} G(-1/\tau) &= K_0(i\bar{\lambda}r_2)I_0(i\bar{\lambda}r_1) - K_0(i\bar{\lambda}r_1)I_0(i\bar{\lambda}r_2) \\ &= \pi/2 \left[J_0(\bar{\lambda}r_2)Y_0(\bar{\lambda}r_1) - J_0(\bar{\lambda}r_1)Y_0(\bar{\lambda}r_2) \right] . \quad (4 - 42) \end{aligned}$$

Similarly, the numerator of $f(r, -1/\tau)$ is, from Eq.(4-29),

$$K_0(i\bar{\lambda}r) \left[I_0(i\bar{\lambda}r_1) + I_0(i\bar{\lambda}r_2) \right] - I_0(i\bar{\lambda}r) \left[K_0(i\bar{\lambda}r_1) + K_0(i\bar{\lambda}r_2) \right] - \\ \pi/2 \left\{ J_0(\bar{\lambda}r) \left[Y_0(\bar{\lambda}r_1) + Y_0(\bar{\lambda}r_2) \right] - Y_0(\bar{\lambda}r) \left[J_0(\bar{\lambda}r_1) + J_0(\bar{\lambda}r_2) \right] \right\}. \quad (4-43)$$

Then the residue at $-1/\tau$ is

$$\rho(r, t, -1/\tau) = -\frac{\Delta T}{2} e^{-t/\tau} f(r, -1/\tau), \quad (4-44)$$

$$f(r, -1/\tau) = \frac{J_0(\bar{\lambda}r) \left[Y_0(\bar{\lambda}r_1) + Y_0(\bar{\lambda}r_2) \right] - Y_0(\bar{\lambda}r) \left[J_0(\bar{\lambda}r_1) + J_0(\bar{\lambda}r_2) \right]}{\left[J_0(\bar{\lambda}r_2) Y_0(\bar{\lambda}r_1) - J_0(\bar{\lambda}r_1) Y_0(\bar{\lambda}r_2) \right]}.$$

The last set of singular points contains those that make $G(r, p)$ vanish. We must evaluate the residues at these singular points as p approaches any one of the roots of $G(r, p)$. In general, the procedure for evaluating residues at these roots is algebraically very tedious, and is not of great interest. In fact, we work out the residues here because of the absence of published results in the literature; the method, however is available (Bateman [1954], Roberts and Kaufman [1966]). We assume that there are no duplicate roots, that all roots are real, that all roots are isolated, and that the derivative of $G(r, p)$ exists as the argument approaches any one root. Rewrite Eq.(4-29),

$$\hat{\theta}(r, p) e^{pt} = \frac{\Delta T e^{pt}}{2p(p\tau + 1)} f(r, p) = \frac{N(r, t, p)}{D(r, p)}, \quad (4-45)$$

where the numerator is

$$N(r, t, p) = \left[K_0(\lambda r) \left[I_0(\lambda r_1) + I_0(\lambda r_2) \right] \right]$$

$$- I_0(\lambda r) \left[K_0(\lambda r_1) + K_0(\lambda r_2) \right] \Delta T e^{pt} , \quad (4 - 46)$$

and the denominator is

$$D(r,p) = 2p(p\tau+1)G(r,p) .$$

With these definitions, the residues can be evaluated

$$\rho_n(t,r) = \lim_{p \rightarrow -q_n^2} \frac{N(r,t,p)}{dD(r,p)/dp} , \quad (4 - 47)$$

where $-q_n^2$ is the n th root of $G(r,p)$, and $\rho_n(t,r)$ denotes the residue at the n th root of $G(r,p)$.

We evaluate $dD(r,p)/dp$ first.

$$\begin{aligned} dD/dp &= 2p(p\tau + 1) \left[r_2 K'_0(\lambda r_2) I_0(\lambda r_1) + r_1 K_0(\lambda r_2) I'_0(\lambda r_1) \right. \\ &\quad \left. - r_1 K'_0(\lambda r_1) I_0(\lambda r_2) - r_2 K_0(\lambda r_1) I'_0(\lambda r_2) \right] (d\lambda/dp) \Big|_{p = -q_n^2} \\ &= (Qp)^{1/2} p(p\tau+1) \left[r_2 K'_0(\lambda r_2) I_0(\lambda r_1) + r_1 K_0(\lambda r_2) I'_0(\lambda r_1) \right. \\ &\quad \left. - r_1 K'_0(\lambda r_1) I_0(\lambda r_2) - r_2 K_0(\lambda r_1) I'_0(\lambda r_2) \right]_{p=-q_n^2} . \quad (4 - 48) \end{aligned}$$

Here K'_0 and I'_0 denote respectively the derivatives of K_0 and I_0 with respect to λr . In deriving Eq.(4-47), we have used the fact that $D(r,p)$ vanishes for $p = -q_n^2$ and Eq.(4-33). Now define

$$\tilde{r} = r/\sqrt{Q} \quad (4 - 49)$$

and rewrite Eq.(4-48) with the help of Eq.(4-27)

$$\begin{aligned} dD/dp = \sqrt{p}(pr+1) & \left[\tilde{r}_2 \left\{ K'_0(\sqrt{p}\tilde{r}_2) I_0(\sqrt{p}\tilde{r}_1) - K_0(\sqrt{p}\tilde{r}_1) I'_0(\sqrt{p}\tilde{r}_2) \right\} \right. \\ & \left. + \tilde{r}_1 \left\{ K_0(\sqrt{p}\tilde{r}_2) I'_0(\sqrt{p}\tilde{r}_1) - K'_0(\sqrt{p}\tilde{r}_1) I_0(\sqrt{p}\tilde{r}_2) \right\} \right]_{p \rightarrow -q_n^2} . \quad (4 - 50) \end{aligned}$$

As $p \rightarrow -q_n^2$, one has to consider two cases for $\sqrt{p}$.

Case 1: $\sqrt{p} \rightarrow iq_n$.

Case 2: $\sqrt{p} \rightarrow -iq_n$.

For case 1 Eq.(4-47) is

$$\begin{aligned} dD/dp \Big|_{p \rightarrow -q_n^2 = -iq_n(-\tau q_n^2 + 1)} & \left[\tilde{r}_2 \left\{ K'_0(iq_n \tilde{r}_2) I_0(iq_n \tilde{r}_1) - K_0(iq_n \tilde{r}_1) I'_0(iq_n \tilde{r}_2) \right\} \right. \\ & \left. + \tilde{r}_1 \left\{ K_0(iq_n \tilde{r}_2) I'_0(iq_n \tilde{r}_1) - K'_0(iq_n \tilde{r}_1) I_0(iq_n \tilde{r}_2) \right\} \right] . \quad (4 - 51) \end{aligned}$$

Using the relations among Bessel functions

$$I'_0(z) = I_1(z) , \quad K'_0(z) = -K_1(z) , \quad (4 - 52)$$

then

$$\begin{aligned} dD/dp \Big|_{p \rightarrow -q_n^2 = -iq_n(-\tau q_n^2 + 1)} & \left[\tilde{r}_1 \left\{ K_0(iq_n \tilde{r}_2) I_1(iq_n \tilde{r}_1) + K_1(iq_n \tilde{r}_1) I_0(iq_n \tilde{r}_2) \right\} - \right. \\ & \left. \tilde{r}_2 \left\{ K_1(iq_n \tilde{r}_2) I_0(iq_n \tilde{r}_1) + K_0(iq_n \tilde{r}_1) I_1(iq_n \tilde{r}_2) \right\} \right] . \quad (4 - 53) \end{aligned}$$

To rewrite Eq.(4-50) in terms of the Bessel functions of the first and second kinds, we use

$$\begin{aligned}
 I_\nu(z) &= e^{-(\nu\pi i)/2} J_\nu(iz), \quad -\pi < \arg(z) \leq \pi/2 \\
 J_\nu(ze^{m\pi i}) &= e^{m\pi\nu i} J_\nu(z), \quad m = \pm 1, \pm 2, \dots \quad (4-54) \\
 Y_\nu(ze^{m\pi i}) &= e^{-m\pi\nu i} Y_\nu(z) + 2i \sin(m\nu\pi) \cos(\nu\pi) J_\nu(z).
 \end{aligned}$$

Making use of these relations and Eqs.(4-37), then

$$\begin{aligned}
 K_1(iq_n \tilde{r}_1) &= \pi/2 \left[J_1(q_n \tilde{r}_1) + iY_1(q_n \tilde{r}_1) \right], \\
 K_1(iq_n \tilde{r}_2) &= \pi/2 \left[J_1(q_n \tilde{r}_2) + iY_1(q_n \tilde{r}_2) \right], \quad (4-55) \\
 K_0(iq_n \tilde{r}_1) &= i\pi/2 \left[J_0(q_n \tilde{r}_1) + iY_0(q_n \tilde{r}_1) \right], \\
 K_0(iq_n \tilde{r}_2) &= i\pi/2 \left[J_0(q_n \tilde{r}_2) + iY_0(q_n \tilde{r}_2) \right].
 \end{aligned}$$

Thus we have converted, for case 1, the modified complex Bessel functions of the first and second kinds into the Bessel functions of the first and second kinds, which involve no complex arguments. The same work must be done for case 2, namely, for $\sqrt{p} = -iq_n$. Substituting $\sqrt{p} = -iq_n$ into Eq.(4-47) we derive

$$\begin{aligned}
 dD/dp = -iq_n(1-q_n^2 r) &\left[\tilde{r}_2 \left[K'_0(-iq_n \tilde{r}_2) I_0(-iq_n \tilde{r}_1) - K_0(-iq_n \tilde{r}_1) I'_0(-iq_n \tilde{r}_2) \right] + \right. \\
 &\left. \tilde{r}_1 \left[K_0(-iq_n \tilde{r}_2) I'_0(-iq_n \tilde{r}_1) - K'_0(-iq_n \tilde{r}_1) I_0(-iq_n \tilde{r}_2) \right] \right]_{p=-q_n^2}
 \end{aligned}$$

$$\begin{aligned}
& -iq_n(1-q_n^2\tau) \left[\tilde{r}_2 \left(-K_1(-iq_n\tilde{r}_2)I_0(-iq_n\tilde{r}_1) - K_0(-iq_n\tilde{r}_1)I_1(-iq_n\tilde{r}_2) \right) + \right. \\
& \left. \tilde{r}_1 \left(K_0(-iq_n\tilde{r}_2)I_1(-iq_n\tilde{r}_1) + K_1(-iq_n\tilde{r}_1)I_0(-iq_n\tilde{r}_2) \right) \right] \Big|_{p=-q_n^2} . \quad (4-56)
\end{aligned}$$

For case 2, we need to convert K_1 , K_0 , I_1 , I_0 into J_1 , J_0 , Y_1 , Y_0 . These relations can be worked out, but we omit the details and only list these relations

$$\begin{aligned}
I_0(-iq_n\tilde{r}) &= J_0(q_n\tilde{r}) , \quad I_1(-iq_n\tilde{r}) = -J_1(q_n\tilde{r}) , \\
K_0(-iq_n\tilde{r}) &= i\pi/2 \left[J_0(q_n\tilde{r}) + iY_0(q_n\tilde{r}) \right] , \\
K_1(iq_n\tilde{r}) &= i\pi/2 \left[J_1(q_n\tilde{r}) + iY_1(q_n\tilde{r}) \right] . \quad (4-57)
\end{aligned}$$

To obtain dD/dp , as $p \rightarrow -q_n^2$, in terms of J_0 , J_1 , Y_0 , Y_1 , we substitute Eqs.(4-52) into Eq.(4-50) and Eqs.(4-54) into Eq.(4-53). With lengthy algebraic operations and great care, the results are:

for $\text{Im}(q_n) > 0$,

$$\begin{aligned}
& \frac{(dD/dp)}{[iq_n(1-q_n^2\tau)]} \Big|_{p \rightarrow -q_n^2} - \frac{\pi i}{2} \left\{ \tilde{r}_1 \left[J_0(\tilde{r}_2 q_n) Y_1(\tilde{r}_1 q_n) - J_1(\tilde{r}_1 q_n) Y_0(\tilde{r}_2 q_n) \right] + \right. \\
& \left. \tilde{r}_2 \left[J_1(\tilde{r}_2 q_n) Y_0(\tilde{r}_1 q_n) - J_0(\tilde{r}_1 q_n) Y_1(\tilde{r}_2 q_n) \right] \right\} ; \quad (4-58)
\end{aligned}$$

for $\text{Im}(q_n) < 0$

$$\frac{(dD/dp)}{[-iq_n(1-q_n^2r)]} \Big|_{p \rightarrow -q_n^2} - \frac{\pi i}{2} \left\{ \tilde{r}_1 \left[J_0(\tilde{r}_2 q_n) Y_1(\tilde{r}_1 q_n) - J_1(\tilde{r}_1 q_n) Y_0(\tilde{r}_2 q_n) \right] + \right. \\ \left. \tilde{r}_2 \left[J_1(\tilde{r}_2 q_n) Y_0(\tilde{r}_1 q_n) - J_0(\tilde{r}_1 q_n) Y_1(\tilde{r}_2 q_n) \right] \right\} . \quad (4-59)$$

Because Eq.(4-58) is identical with Eq.(4-59), we conclude that as $p \rightarrow -q_n^2$, the function dD/dp is single valued even though two choices, $\sqrt{p} = \pm iq_n$, are made. In order to obtain the residues of Eq.(4-44), we evaluate the function $N(r,p)$ for the two cases $\sqrt{p} = \pm iq_n$.

For $\text{Im}(q_n) > 0$, from Eq.(4-43)

$$N(r,p) = (\pi/2) \Delta T e^{-q_n^2 t} \left\{ J_0(\tilde{r} q_n) \left[Y_0(\tilde{r}_1 q_n) + Y_0(\tilde{r}_2 q_n) \right] \right. \\ \left. - Y_0(\tilde{r} q_n) \left[J_0(\tilde{r}_1 q_n) + J_0(\tilde{r}_2 q_n) \right] \right\} . \quad (4-60)$$

For $\text{Im}(q_n) < 0$, from Eq.(4-43), then

$$N(r,p) = (\pi/2) \Delta T e^{-q_n^2 t} \left\{ J_0(\tilde{r} q_n) \left[Y_0(\tilde{r}_1 q_n) + Y_0(\tilde{r}_2 q_n) \right] \right. \\ \left. - Y_0(\tilde{r} q_n) \left[J_0(\tilde{r}_1 q_n) + J_0(\tilde{r}_2 q_n) \right] \right\} . \quad (4-61)$$

where $\tilde{r} = r/\sqrt{Q}$. Because Eqs.(4-60 and 61) are the same, we consider only $\text{Im}(q_n) > 0$, for evaluation of the residues at singular points q_n^2 for $n = 1, 2, 3, \dots$ from Eq.(4-47). Combining Eqs.(4-58,60) and Eq.(4-47), to give the residue at the n th singular point q_n ,

$$\begin{aligned}
\rho_n(r, t) = & \frac{\Delta T e^{-q_n^2 t}}{(q_n^2 r - 1) q_n} \times \left\{ J_0(\tilde{r} q_n) \left[Y_0(\tilde{r}_1 q_n) + Y_0(\tilde{r}_2 q_n) \right] \right. \\
& - Y_0(\tilde{r} q_n) \left[J_0(\tilde{r}_1 q_n) + J_0(\tilde{r}_2 q_n) \right] \Big\} + \\
& \left\{ \tilde{r}_1 \left[J_0(\tilde{r}_2 q_n) Y_1(\tilde{r}_1 q_n) - J_1(\tilde{r}_1 q_n) Y_0(\tilde{r}_2 q_n) \right] \right. \\
& \left. + \tilde{r}_2 \left[J_1(\tilde{r}_2 q_n) Y_0(\tilde{r}_1 q_n) - J_0(\tilde{r}_1 q_n) Y_1(\tilde{r}_2 q_n) \right] \right\} , \quad (4 - 62) \\
= & (\Delta T) e^{-q_n^2 t} (T_n/B_n) / [q_n (q_n^2 r - 1)]
\end{aligned}$$

where

$$\begin{aligned}
T_n = & \left\{ J_0(\tilde{r} q_n) \left[Y_0(\tilde{r}_1 q_n) + Y_0(\tilde{r}_2 q_n) \right] - Y_0(\tilde{r} q_n) \left[J_0(\tilde{r}_1 q_n) + J_0(\tilde{r}_2 q_n) \right] \right\} \\
B_n = & \tilde{r}_1 \left[J_0(\tilde{r}_2 q_n) Y_1(\tilde{r}_1 q_n) - J_1(\tilde{r}_1 q_n) Y_0(\tilde{r}_2 q_n) \right] + \tilde{r}_2 \left[J_1(\tilde{r}_2 q_n) Y_0(\tilde{r}_1 q_n) - \right. \\
& \left. J_0(\tilde{r}_1 q_n) Y_1(\tilde{r}_2 q_n) \right] . \quad (4 - 63)
\end{aligned}$$

In this equation $\tilde{r} = r/\sqrt{Q}$, $Q = \kappa \tilde{V}/\tilde{C}_p$, and $p = -q_n^2$ is the n th root of Eq.(4-33). In general there are infinitely many roots. The sum of these residues is

$$\rho(r, t) = \sum_{n=1}^{\infty} \rho_n(r, t) . \quad (4 - 64)$$

The complete inverse Laplace transform of Eq.(4-31) is

$$\theta(r, t) = \rho(r, t) \Big|_{p=0} + \rho(r, t) \Big|_{p=-1/r} + \sum_{n=1}^{\infty} \rho_n(r, t) \Big|_{p=-q_n^2} \quad (4 - 65)$$

$$\begin{aligned}
& -(\Delta T) \frac{\Delta T}{2} \frac{\ln \left(\frac{r_1 r_2}{r^2} \right)}{\ln(r_1/r_2)} + \frac{1}{2} A(\Delta T) e^{-t/\tau} + \sum_{n=1}^{\infty} \frac{T_n \Delta T e^{-q_n^2 t}}{(q_n^2 t - 1) q_n B_n}, \\
& A = \left\{ \frac{J_0(\bar{\lambda} r) \left[Y_0(\bar{\lambda} r_1) + Y_0(\bar{\lambda} r_2) \right] - Y_0(\bar{\lambda} r) \left[J_0(\bar{\lambda} r_1) + J_0(\bar{\lambda} r_2) \right]}{\left[J_0(\bar{\lambda} r_2) Y_0(\bar{\lambda} r_1) - J_0(\bar{\lambda} r_1) Y_0(\bar{\lambda} r_2) \right]} \right\}. \quad (4 - 66)
\end{aligned}$$

D. ASYMPTOTIC SOLUTION

For electrolyte solutions, $\kappa = 0.6 \text{ J.s.m}^{-1} \text{K}^{-1}$, $\bar{V} = 18 \times 10^{-6} \text{ m}^3 \text{mol}^{-1}$, $\bar{C}_p = 4 \times 10^3 \text{ J.kg}^{-1} \text{K}^{-1}$, and hence $Q = 1.5 \times 10^{-7} \text{ m}^2 \text{s}^{-1}$. For metal walls, $\tau \approx 60 \text{ sec}$ (Anderson and Horne [1970]), and $\bar{\lambda} = 1/\sqrt{(\tau Q)} = 333 \text{ m}^{-1}$. For $r_2 = 1.1 \text{ cm}$, and $r_1 = 1.0 \text{ cm}$, $\bar{\lambda} r \approx 3.3$, and we may use the asymptotic relations

$$J_0(z) = \left(\frac{2}{\pi z} \right)^{\frac{1}{2}} \left(\cos z - \frac{1}{4} \pi \right), \quad Y_0(z) = \left(\frac{2}{\pi z} \right)^{\frac{1}{2}} \left(\sin z - \frac{1}{4} \pi \right) \quad (4 - 67)$$

to simplify Eq.(4-66), with the result,

$$A = - (r_2 r_1 / r)^{\frac{1}{2}} \frac{\sin(\bar{\lambda}(r-r_1))/\sqrt{r_1} - \sin(\bar{\lambda}(r_2-r))/\sqrt{r_2}}{2 \sin(\bar{\lambda}(r_2-r_1))}, \quad (4 - 68)$$

where $\bar{\lambda} = 1/\sqrt{(Q\tau)}$. Note that $\bar{\lambda}(r_2-r_1) \approx 0.33$. Since the

argument of sin is small, we may simplify Eq.(4-66) by taking

$\sin(z) \approx z$ whence, after some algebra,

$$A = \frac{(r - \tilde{r})}{\sqrt{r}(\sqrt{r_2} - \sqrt{r_1})} . \quad (4 - 69)$$

To simplify the infinite sum term requires the roots of Eq.(4-33). To obtain these roots, we use

$$I_0(iz) = J_0(z), \quad K_0(iz) = (i\pi/2)[J_0(z) + iY_0(z)], \quad (4 - 70)$$

so that Eq.(4-33) becomes

$$G(r, p) = J_0(x_n)Y_0(\mu x_n) - J_0(\mu x_n)Y_0(x_n) , \quad (4 - 71)$$

where $x_n = q_n \tilde{r}_1$ and $\mu = (r_2 / r_1)$. The nth root of Eq.(4-71) is given by

(Abramowitz and Stegun [1970])

$$x_n = \frac{n\pi r_1}{r_2 - r_1} - \frac{r_2 - r_1}{8n\pi r_2} + \theta \left[\left(\frac{r_2 - r_1}{n\pi} \right)^3 \right] . \quad (4 - 72)$$

Retaining only the leading term of Eq.(4-72) since the rest of terms are much smaller, we have

$$x_n = \frac{n\pi r_1}{r_2 - r_1}, \quad \text{and} \quad q_n = \frac{n\pi/Q}{r_2 - r_1} . \quad (4 - 73)$$

Since $\tilde{r} = \frac{n\pi r_1}{r_2 - r_1}$, the arguments in T_n and B_n of Eq.(4-63) are about $10n\pi$

for $r_2 - r_1 = 0.1$. We may confidently use asymptotic expansions of Eqs.(4-

66) for all the Bessel functions, along with

$$Y_1(z) = -J_0(z), \quad J_1(z) = Y_0(z). \quad (4-74)$$

Then

$$T_n = \left[\frac{2(r_2 - r_1)}{n\pi^2 \bar{r} \sqrt{r}} \right] \left[(-1)^n \sqrt{r_1 + \sqrt{r_2}} \right] \sin[n\pi(r - r_1)/(r_2 - r_1)]$$

$$B_n = 2(-1)^n (r_2 - r_1)^2 / (n\pi^2 \bar{r}), \quad (4-75)$$

and

$$\rho_n(r, t) = -\frac{\Delta T (-1)^n e^{-n^2 t / \tau'}}{n\pi (n^2 \tau / \tau' - 1) \sqrt{r}} \left[(-1)^n \sqrt{r_1 + \sqrt{r_2}} \right] \sin \left[\left(\frac{n\pi}{r_2 - r_1} \right) (r - r_1) \right], \quad (4-76)$$

where

$$\tau' = (r_2 - r_1)^2 / (\pi^2 Q). \quad (4-77)$$

For $r_2 - r_1 = 0.1 \text{ cm}$ and $Q = 1.5 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$, $\tau' = 0.675 \text{ s}$, and ρ_n is better expressed as

$$\rho_n(r, t) = -\sum_{n=1}^{\infty} \frac{\Delta T (-1)^n e^{-n^2 t / \tau'}}{[n^3 \pi^3 \tau / (rQ)] (r_2 - r_1)^2} \left[(-1)^n \sqrt{r_1 + \sqrt{r_2}} \right] \sin \left[\left(\frac{n\pi}{r_2 - r_1} \right) (r - r_1) \right]$$

(4-78)

where we neglect τ' compared with $n^2 \tau$. The complete asymptotic solution is a combination of Eqs. (4-62, 65, 69 and 78).

$$\theta(r, t) \approx -\frac{(\Delta T) \ln(\bar{r}/r)}{\ln(r_1/r_2)} + \frac{(r - \bar{r})}{2\sqrt{r}(\sqrt{r_2} - \sqrt{r_1})} e^{-t/\tau}$$

$$+ \sum_{n=1}^{\infty} \frac{\Delta T (-1)^n e^{-n^2 t / \tau'}}{[(n^3 \pi^3 \tau \sqrt{rQ})]} (r_2 - r_1)^2 \left[(-1)^n / r_1 + \sqrt{r_2} \right] \sin \left[\left(\frac{n \pi}{r_2 - r_1} \right) (r - r_1) \right]$$

(4 - 79)

This solution satisfies the boundary and initial conditions. It is reduced considerably if we (1) neglect all but the first term of the infinite series, an excellent approximation for $t > 1$ sec., and (2) convert from the radial variable r to the linear variable s by using Eqs.(4-20); then

$$\theta(r, t) = \Delta T \left[\left(\frac{s}{2\delta} \right) (e^{-t/\tau} - 1) + \frac{\delta \tau}{\pi r} \sin \left(\frac{\pi(\delta + s)}{2\delta} \right) e^{-t/\tau'} \right] \quad (4 - 80)$$

and

$$T(r, t) = T_M + \theta(r, t) \quad (4 - 81)$$

Eq.(4-80) is of the form (Carslaw and Jaeger [1959], Horne and Anderson [1970]), usually found for one-dimensional cartesian system.

E. DISCUSSION OF THE SOLUTION

The general solution of $\theta(r, t)$ consists of two parts, the steady state and time dependent part. The time required to reach the steady state temperature distribution is controlled by two relaxation times. τ is the relaxation time which characterizes the time interval required for a column wall to reach its steady state temperature from the instant it is brought into contact with a reservoir of the desired temperature. τ is nearly the same for both the inner and the outer walls of the

column. Another relaxation time τ' is that of the fluid, which characterizes the time interval required for the fluid to achieve a steady state temperature gradient, after the temperature gradient is established at the walls. The relaxation time τ depends mainly on the thickness, heat capacity, and thermal conductivity of the column material. The relaxation time of the fluid depends on the thermal conductivity, heat capacity, density, and the square of the annular gap width a . The relaxation time ratio τ'/τ affects the time dependent temperature distribution significantly only for large values of a . After about at most 4τ of starting the experiment, the temperature distribution in a TGTD column is the steady state distribution. The steady state temperature gradient is established long before the concentration begins to change detectably. This has been taken as an assumption by many authors (Jones and Furry [1946], Tyrell [1961], Navarro et al [1983]). It is important to note that we assume here that the relaxation time of the walls is much larger than that of the fluid in the annulus. If, however, the column is made of non-metal the thermal conductivity of the material will be very small. This leads to a much larger relaxation time, and if it is much larger than one minute, then Eq.(4-66) cannot be simplified. Under such a situation one has a very complicated form for the temperature distribution and mass diffusion will develop before the steady state temperature is reached. This will in turn lead to a much more complicated situation for the velocity equation as well as for the concentration distribution.

In this chapter we solved both the steady state and the time dependent temperature equations. Our zeroth order solution for steady state agrees with previous results. The time dependent temperature distribution has not been obtained for the TGTD column before due to its

complicated form. The temperature distribution as a function of r and time is given in Fig.4.1. The equation used for the plot is Eq.(4-79). Numerically, except at short time, say $t < 0.5\tau$, Eq.(4-79) is in good agreement with Eq.(4-80).

Figure(4-1)

Temperature distribution in a TGTD column, for $r = 1.0\text{cm}$, $r_2 = 1.1\text{cm}$, $\Delta T = 10\text{K}$, $T_M = 298\text{K}$. The lines from top to bottom represent individually the temperature distributions at $t = \infty$, 100 sec., 60 sec., 30 sec., 10 sec., and 0 sec. Eq.(4-79) is used for the plot.

CHAPTER 5

VELOCITY DISTRIBUTION

A. PERTURBATION AND OTHER ASSUMPTIONS

If we neglect all v_r terms (Horne and Bearman [1962,1967]) and assume that the fluid is incompressible, then by Eq.(2-67)

$$\frac{\partial v}{\partial t} - \frac{\omega}{r} \frac{\partial}{\partial r} r \frac{\partial v}{\partial r} + \frac{1}{\rho} \frac{\partial p}{\partial z} + g = 0 , \quad (5 - 1)$$

with $v=v_z$, $\omega=(\eta/\rho)$ =constant, and homogeneous boundary and initial conditions

$$v(r_1, t) = 0 = v(r_2, t) ,$$

$$v(r, 0) = 0 . \quad (5 - 2)$$

Following the general perturbation expansions of the temperature and concentration given by Eqs.(4-1 to 4), the perturbation assumptions

here are

$$\begin{aligned} \hat{\rho} &= \bar{\rho} + \left(\bar{\rho}_T \theta_0 + \bar{\rho}_C \gamma_0 \right) + \\ &\quad \epsilon \left(\frac{1}{2} \theta_0^2 \bar{\rho}_{TT} + \theta_0 \gamma_0 \bar{\rho}_{TC} + \frac{1}{2} \gamma_0^2 \bar{\rho}_{CC} + \theta_1 \bar{\rho}_T + \gamma_1 \bar{\rho}_C \right) + O(\epsilon^2) , \\ v &= v_0 + \epsilon v_1 + \epsilon^2 v_2 + \dots \end{aligned} \quad (5-3)$$

where in order to accommodate both (1) the essential equivalence of $\partial p / \partial z$ and $-\rho g$ and (2) the physical requirement that convection in a temperature field is due to temperature-induced density differences, we have assumed $\bar{\rho}_T$ and $\bar{\rho}_C$ to be zeroth order. Thus,

$$\partial p / \partial z = -\bar{\rho} g . \quad (5-4)$$

The zeroth order velocity equation is then

$$\frac{\partial v_0}{\partial t} - \frac{\omega}{r} \frac{\partial}{\partial r} r \frac{\partial v_0}{\partial r} + g(\bar{\rho}_T \theta_0 / \bar{\rho} + \bar{\rho}_C \gamma_0 / \bar{\rho}) = 0 , \quad (5-5)$$

with

$$\bar{\rho}_T = \left[\left(\frac{\partial \rho}{\partial T} \right)_{P, c_2} \right]_{T_M, c_2^0} = -\alpha \bar{\rho} , \quad \bar{\rho}_C = \left[\left(\frac{\partial \rho}{\partial c_2} \right)_{T, P} \right]_{T_m, c_2^0} , \quad (5-6)$$

where α is the thermal expansivity evaluated at (T_M, c_2^0) .

Since $\rho = c_1 M_1 + c_2 M_2$,

$$\left(\frac{\partial \rho}{\partial c_2} \right)_{T, P} = \left(\frac{\partial c_1}{\partial c_2} \right)_{T, P} M_1 + M_2 = -(V_2 M_1 / V_1) + M_2$$

$$= \frac{M_1 M_2}{V_1} [(V_1/M_1) - (V_2/M_2)] , \quad (5-7)$$

and Eq.(5-5) becomes

$$\frac{\partial v_0}{\partial t} - \frac{\omega}{r} \frac{\partial}{\partial r} r \frac{\partial v_0}{\partial r} - g \alpha \theta_0 + g \frac{M_1 M_2}{\rho V_1} [(V_1/M_1) - (V_2/M_2)] \gamma_0 = 0 . \quad (5-8)$$

Since this equation contains the concentration term γ_0 , the velocity cannot be found unless γ_0 is known. On the other hand, by Eq.(2-63), γ_0 cannot be found unless v_0 is known.

The composition dependence of the density has been the object of much concern in thermal diffusion studies. Its effect on TGTD was called "l'effet oublie" - the forgotten effect-by deGroot [1945]. Horne and Bearman [1968] showed that the steady state effect on thermal diffusion is about 1% for liquid mixtures of carbon tetrachloride and cyclohexane, the system in which the effect should be maximal because of the great difference in densities of the two pure components. The forgotten effect should be considerably less important for electrolyte solutions.

In order to solve Eq.(5-8), we suppress the concentration term γ_0 in Eq.(5-8) and later evaluate its importance after determining γ_0 . With this suppression Eq.(5-8) reduces to

$$\frac{\partial v_0}{\partial t} - \frac{\omega}{r} \frac{\partial}{\partial r} r \frac{\partial v_0}{\partial r} - g \alpha \theta_0 = 0 . \quad (5-9)$$

We showed in chapter 4 that the steady state temperature

distribution is established within about 2 minutes after the beginning of the experiment. Convection starts as soon as the temperature difference is imposed but becomes established only after the temperature gradient is established. It is satisfactory for our purpose (determining γ) to use the steady state result for the temperature distribution. We shall see that the velocity distribution becomes steady very rapidly.

Since higher order perturbation contributions to the velocity depend on very small terms [see Eq.(5-3)], we obtain only the zeroth order result.

B. SOLUTION OF THE ZEROth ORDER EQUATION

The partial differential equation for the convective velocity $v_0 = v$ with boundary and initial conditions is

$$\frac{\partial v}{\partial t} - \omega \frac{\partial}{\partial r} r \frac{\partial v}{\partial r} - g\alpha\theta_0 = 0, \quad v(t, r_1) = 0, \quad v(t, r_2) = 0,$$

$$v(t=0, r) = 0. \quad (5-10)$$

Let

$$v(r, t) = \zeta(r) + \xi(r, t) \quad (5-11)$$

The $\zeta(r)$ term represents the steady state velocity. Furthermore, to satisfy the boundary and initial conditions, we require that $\xi(r, t)$ vanish as time goes to infinity. Both $\xi(r, t)$ and $\zeta(r)$ vanish at the walls. With Eq.(5-11), Eq.(5-10) yields

$$\omega \frac{d}{dr} r \frac{d\zeta}{dr} - g\alpha\theta_0 = 0, \quad (5-12)$$

$$\zeta(r_1) = 0 = \zeta(r_2) ,$$

and

$$\frac{\partial \xi}{\partial t} - \frac{\omega}{r} \frac{\partial}{\partial r} r \frac{\partial \xi}{\partial r} = 0 , \quad (5 - 13)$$

$$\xi(r_1, t) = 0 = \xi(r_2, t)$$

$$\xi(r, 0) = -\zeta(r) ,$$

where the $t=0$ condition for ξ takes the specified form because $v(r, 0)=0$.

From Eq.(4-14),

$$\theta_0(r) = -\Delta T \left[\frac{\ln(r/\bar{r})}{\ln(r_2/r_1)} \right] , \quad (5 - 14)$$

where $\bar{r} = \sqrt{(r_1 r_2)}$. Thus,

$$\frac{d}{dr} r \frac{d\zeta}{dr} = -\frac{g\alpha\Delta T}{\omega} r \left[\frac{\ln(r/\bar{r})}{\ln(r_2/r_1)} \right] . \quad (5 - 15)$$

Successive integration of Eq.(5-15) and imposition of the boundary conditions yield

$$\begin{aligned} \zeta(r) = & \frac{\bar{\rho} \Delta T \alpha g}{4\eta \ln(r_1/r_2)} \left[r^2 \left(\ln \frac{r}{\bar{r}} - 1 \right) - r_1^2 \left(\ln \frac{r}{r_2} \right) \left(\frac{1}{2} - \frac{1}{\ln(r_1/r_2)} \right) \right. \\ & \left. - r_2^2 \left(\ln \frac{r}{r_1} \right) \left(\frac{1}{2} - \frac{1}{\ln(r_2/r_1)} \right) \right] . \end{aligned} \quad (5 - 16)$$

To solve Eq.(5-13), we assume a solution of form

$$\xi(r,t) = W(t)X(r) . \quad (5 - 17)$$

Then

$$dW/dt + \lambda^2 W = 0 , \quad (5 - 18)$$

and

$$\frac{d^2 X}{dr^2} + \frac{1}{r} \frac{dX}{dr} + \frac{\lambda^2}{\omega} X = 0 , \quad (5 - 19)$$

$$X(r_1) = 0 = X(r_2) ,$$

where λ^2 is the separation constant. The solution for $W(t)$ is

$$W(t) = K e^{-\lambda^2 t} \quad (5 - 20)$$

where K is a constant of integration.

To solve Eq.(5-19), we make the independent variable transformation

$$z = \lambda r / \sqrt{\omega} ; \quad (5 - 21)$$

then Eq.(5-24) becomes

$$\frac{d^2 X}{dz^2} + \frac{1}{z} \frac{dX}{dz} + X = 0 , \quad (5 - 22)$$

$$X(z_1) = 0 = X(z_2) .$$

Eq.(5-22) is Bessel's differential equation of order zero, whose solution is a linear combination of zeroth-order Bessel functions of the first and second kinds.

$$X(z) = AJ_0(z) + BY_0(z) . \quad (5 - 23)$$

To satisfy the boundary conditions, we must have

$$\begin{aligned} A &= -BY_0(z_1)/J_0(z_1), \\ J_0(z_1)Y_0(z_2) - J_0(z_2)Y_0(z_1) &= 0 . \end{aligned} \quad (5 - 24)$$

One of the solutions is

$$X(z) = B \left[J_0(z_1)Y_0(z) - J_0(z)Y_0(z_1) \right] . \quad (5 - 25)$$

The general solution is

$$\xi(r, t) = \sum_{n=1}^{\infty} B_n X_n(\lambda_n r / \sqrt{\omega}) e^{-\lambda_n^2 t} , \quad (5 - 26)$$

where λ_n is proportional to the n th root of Eq.(5-24). Moreover,

$$\int_{r_1}^{r_2} r X_m(z) X_n(z) dr = \begin{cases} 0, & n \neq m \\ \frac{2}{\pi^2 \lambda_n^2 / \omega} \left(\frac{J_0^2(z_1)}{J_0^2(z_2)} - 1 \right), & n = m . \end{cases} \quad (5 - 27)$$

For simplicity of notation, we abbreviate by z , z_1 , and z_2 what are actually $z(n)$, $z_1(n)$ and $z_2(n)$, with

$$z(n) = \lambda_n r / \sqrt{\omega} . \quad (5 - 28)$$

The initial condition is, from Eq.(5-13),

$$\xi(r, t=0) = \sum_{n=1}^{\infty} B_n X_n(\lambda_n r/\sqrt{\omega}) = \zeta(r) \quad (5-29)$$

Using Eq.(5-27), we obtain from Eq.(5-29)

$$B_n(\lambda_n) = \frac{\int_{r_1}^{r_2} r \zeta(r) X_n(\lambda_n r/\sqrt{\omega}) dr}{\frac{2}{\pi^2 \lambda_n^2 / \omega} \left[\frac{J_0^2(z_1)}{J_0^2(z_2)} - 1 \right]} \quad (5-30)$$

The solution of Eq.(5-13) is Eq.(5-26), with the constants $B_n(\lambda_n)$ obtained from Eq.(5-30). The difficulty is evaluation of the integral

$$\int_{r_{1H}}^{r_2} r \zeta(r) X_n(\lambda_n r/\sqrt{\omega}) dr ,$$

with $\zeta(r)$ given by Eq.(5-16). The calculation is extremely complicated due to the combinations of Bessel functions and $r\zeta(r)$. With the help of Tranter [1968], after considerable work, we find that the integral has the very simple form

$$\int_{r_2}^{r_2} r \zeta(r) X_n(\lambda_n r/\sqrt{\omega}) dr = -\frac{\rho \alpha (\Delta T) \omega^2}{\pi \eta \lambda_n^4} \left\{ [Y_0(z_1)/Y_0(z_2)] + 1 \right\} \quad (5-31)$$

Then

$$B_n(\lambda_n) = \frac{\bar{\rho}\alpha\Delta T\pi\omega \left\{ [Y_0(z_1)/Y_0(z_2)] + 1 \right\}}{2\eta\lambda_n^2 \left\{ [J_0(z_1)/J_0(z_2)] - 1 \right\}}, \quad (5-32)$$

and

$$\begin{aligned} v_z(r, t) = & \sum_{n=1}^{\infty} \frac{\bar{\rho}\alpha\Delta T\pi\omega \left\{ [Y_0(z_1)/Y_0(z_2)] + 1 \right\}}{2\eta\lambda_n^2 \left\{ [J_0(z_1)/J_0(z_2)] - 1 \right\}} \left[J_0(z_1)Y_0(z) - J_0(z)Y_0(z_1) \right] e^{-\lambda_n^2 t} \\ & + \frac{\bar{\rho} \Delta T \alpha g}{4\eta \ln(r_1/r_2)} \left[r^2 \left(\ln \frac{r}{r_1} - 1 \right) - r_1^2 \left(\ln \frac{r}{r_2} \right) \left(\frac{1}{2} - \frac{1}{\ln(r_1/r_2)} \right) \right. \\ & \left. - r_2^2 \left(\ln \frac{r}{r_1} \right) \left(\frac{1}{2} - \frac{1}{\ln(r_2/r_1)} \right) \right], \quad (5-33) \end{aligned}$$

with λ_n proportional to the n th root of Eq.(5-24) and $z(n)$ given by Eq.(5-28).

C. ASYMPTOTIC FORM OF THE SOLUTION FOR LARGE ARGUMENT

This form of the velocity is very complicated. It simplifies quickly once we determine that the roots of Eq.(5-25) are large and therefore that the argument z is large enough to express the Bessel functions asymptotically.

By Abramowitz and Stegun [1970] the roots q_n of Eq.(5-25) can be written as a series expansion (this approach was also used in Chapter 4, Eq.(4-72),

$$q_n/\sqrt{\omega} = \beta_n + p/\beta_n + (g-p^2)/\beta_n^3 + \dots, \quad (5-34)$$

$$\beta_n = n\pi/[(r_2/r_1) - 1],$$

$$p = -1/[8(r_2/r_1)] ,$$

$$g = \frac{25 \left[(r_2/r_1)^3 - 1 \right]}{6(4r_2/r_1)^3(r_2/r_1 - 1)} .$$

Thus for $r_2/r_1 = 1.1$,

$$q_1/\sqrt{\omega} = 31.4 - (0.12/31.4) + (0.13/31.4^2) + \dots \approx 31.4$$

and

$$q_n/\sqrt{\omega} = 10n\pi . \quad (5 - 35)$$

Now $z(n) = r\lambda_n/\sqrt{\omega}$, with

$$\lambda_n = n\pi\sqrt{\omega}/(r_2 - r_1) , \quad (5 - 36)$$

and therefore

$$z(n) = rn\pi/(r_2 - r_1) . \quad (5 - 37)$$

Since $z \approx 10n\pi$, asymptotic Bessel function formulas can be used to simplify the expression for the time dependent part of the velocity. Repeated use of Eq.(4-65) yields

$$\xi(r, t) = \frac{\rho \alpha a^2 (\Delta T)}{\eta \pi^3 \sqrt{r}} \sum_{n=1}^{\infty} \frac{[(-1)^n \sqrt{r_2 + r_1}]}{\pi^3} \sin \frac{n\pi(r - r_1)}{a} e^{-n^2(\pi^2 \omega / a^2)t} \quad (5 - 38)$$

The viscous relaxation time $(\pi^2 \omega / a)$ is very large since $\omega = \eta / \rho \approx 10^{-6} \text{m}^2 \text{s}^{-1}$. Then $(\pi^2 \omega / a^2) = \pi^2 \text{s}^{-1}$ for $a = 0.1 \text{cm}$, and the convection steady state is attained about 0.4 second $(4/\pi^2)$ after the establishment of

the steady state temperature gradient. We may thus ignore the time-dependent part of the velocity equation.

Use of the steady state convection velocity function for the treatment of a TGT column has been taken as an assumption by previous authors (Jones and Furry [1946], Tyrrell [1961], and Navarro et al. [1983]). We here have established a solid foundation for the assumption by solving the time dependent velocity equation.

D. STEADY STATE VELOCITY PROFILE AND DISCUSSION

As discussed above, the time-independent part of the convective velocity suffices for solving the concentration equation. It is convection that brings about a measurable concentration gradient along the column. The steady state velocity distribution as a function of r is displayed in Figure(5-1). Clearly, $\zeta(r)$ vanishes at r_1 and r_2 and

effectively at $\bar{r}$. The vertical velocity is positive (upward) for the warmer portion of the annulus because the density there is smaller and the material rises against gravity; similarly, the velocity is negative in the cooler portion of the annulus.

Because the algebraic form of $\zeta(r)$ is $\ln(r)$ dependent and it is not easy to work with the logarithmic form in solving the concentration equation, we use the linear transformations given by Eqs.(4-20). Applying these transforms, and neglecting the time-dependent terms, Eq.(5-32) becomes

$$v(s) = -\frac{\bar{\rho} \alpha g \Delta T (\bar{r})^2}{8\eta\delta} \left[(1-s)(\cosh 2\delta - e^{2s}) + (s-\delta^2)\delta - \sinh 2\delta \right] \quad (5-39)$$

If we expand the hyperbolic functions and the exponential functions and truncate after the first order in δ , we find

$$v(s) \approx -\frac{\bar{\rho}\alpha\Delta Tg}{48\eta}a^2\left[1-(s/\delta)^2\right]\left\{(s/\delta)-\delta[1+(s/\delta)^2]+\theta(\delta^2)\right\}. \quad (5-40)$$

Ignoring the second and higher terms in the curly-bracketed part of this equation introduces as much as 10% error since $0.05 \geq \delta$, but yields a very simple form for the steady state vertical velocity,

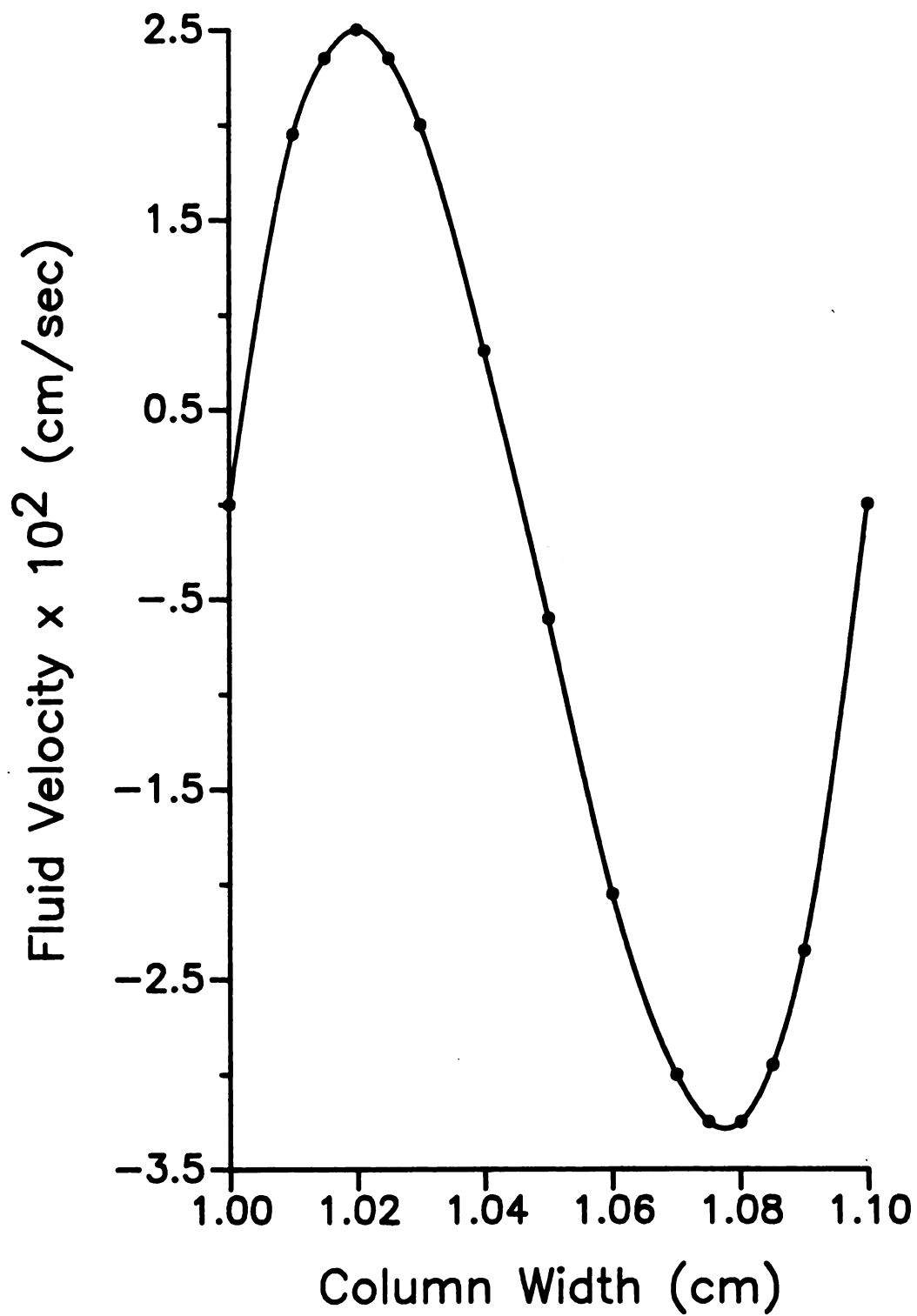
$$v(s) \approx -\frac{\bar{\rho}\alpha g \Delta T}{48\eta}a^2\left[1-(s/\delta)^2\right](s/\delta). \quad (5-41)$$

This equation has previously been derived by Jones and Furry [1946] and Horne and Bearman [1962]. For careful work, the second term in the curly brackets of Eq.(5-40) should be retained.

The vertical velocity is directly proportional to the gravitational constant, the thermal expansivity, the temperature difference, and the square of gap width, and is inversely proportional to the kinematic viscosity ($\eta/\bar{\rho}$).

Figure(5-1)

Steady state convection velocity profile. r and ΔT are the same as in Fig.(4-1). Eq.(5-16) is used for the plot. If Eq.(5-41) is plotted against s/δ , the diagram will be symmetric at $s=0$.



CHAPTER 6

STEADY STATE CONCENTRATION DISTRIBUTION

A. SOLUTION OF THE CONCENTRATION EQUATION

In this chapter, we establish the steady state concentration distribution by using a perturbation scheme based on the smallness of the Soret coefficient. The result here is of considerable use in finding the zeroth order time-dependent solution of the concentration equation in the next chapter.

To obtain the steady state radial concentration distribution, we use Eq.(2-76) for steady state,

$$\nabla \cdot \left[\frac{DM_1}{\bar{V}_1 \rho} \left(\nabla c_2 - \sigma^* c_2 \nabla T \right) - c_2 \mathbf{v} \right] = 0 . \quad (2 - 76)$$

For reasonably small temperature gradients, the properties represented by ρ , $\bar{V}_1$, and D are constants to be evaluated at the mean temperature

and initial composition. In that case,

$$D^* \nabla \cdot (\nabla c_2 - \sigma^* c_2 \nabla T) - \nabla \cdot (c_2 \mathbf{v}) = 0, \quad (6-1)$$

where,

$$D^* = \frac{DM_1}{V_1 \rho}. \quad (6-2)$$

Since $\nabla \cdot \mathbf{v}$, $\nabla^2 T$, and v_r are all zero, Eq.(6-1) becomes

$$D^* \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial c_2}{\partial r} - c_2 \sigma^* r \frac{\partial T}{\partial r} \right) + D^* \frac{\partial^2 c_2}{\partial z^2} - v_z \frac{\partial c_2}{\partial z} = 0, \quad (6-3)$$

where we have also taken σ^* to be constant. The wall boundary conditions are from Eq.(3-6),

$$\left[\left(\frac{\partial c_2}{\partial r} \right) - c_2 \sigma^* \frac{dT}{dr} \right]_{r_1, r_2} = 0. \quad (6-4)$$

Additional boundary conditions are required to obtain c_2 as a function of both r and z . These, too, stem from conservation requirements. By symmetry, the average value of c_2 at the vertical center plane must be the initial concentration. Thus,

$$\langle c_2 \left(\frac{L}{2} \right) \rangle_r = c_2^0, \quad (6-5)$$

with

$$\langle f \rangle = \frac{\int_{r_1}^{r_2} r f dr}{\int_{r_1}^{r_2} r dr} \quad (6-6)$$

In the steady state, Gauss' theorem requires that

$$\int_V (\nabla \cdot c_2 \mathbf{v}_2) dV = \int_S (c_2 \mathbf{v}_2) \cdot d\mathbf{s} \quad (6-7)$$

or, by Eqs.(6-3 and 4),

$$\int_{r_1}^{r_2} r \left(D^* \frac{\partial c_2}{\partial z} - c_2 v \right) dr = 0 \quad (6-8)$$

In the linear variable s defined by Eq.(4-20), Eqs.(6-3 and 4) become

$$\frac{\partial}{\partial s} \left(\frac{\partial c_2}{\partial s} + c_2 \sigma \frac{\Delta T}{2\delta} \right) - \frac{\tilde{r}^2}{D^*} e^{2s} \sqrt{\frac{\partial c_2}{\partial z}} - \tilde{r}^2 e^{2s} \frac{\partial^2 c_2}{\partial z^2} = 0$$

$$\left(\frac{\partial c_2}{\partial s} + c_2 \sigma \frac{\Delta T}{2\delta} \right)_{\pm \delta} = 0 \quad (6-9)$$

where we have used the steady state temperature result of Eq.(4-21),

$$\frac{dT}{ds} = -\frac{\Delta T}{2\delta} \quad (6-10)$$

Further simplification is obtained by defining

$$x=(s/\delta), \quad x(-\delta)=-1, \quad x(\delta)=1. \quad (6-11)$$

Then, with Eq.(5-41) for the velocity,

$$\begin{aligned} \frac{\partial}{\partial x} \left(\frac{\partial c_2}{\partial x} + \epsilon c_2 \right) &= -\theta(1-x^2) [x - \delta(1-x^2)] \frac{\partial c_2}{\partial z} - \frac{1}{4} a^2 (1+2\delta x) \frac{\partial^2 c_2}{\partial z^2}, \\ \left(\frac{\partial c_2}{\partial x} + \epsilon c_2 \right)_{\pm 1} &= 0. \end{aligned} \quad (6-12)$$

where

$$\epsilon = \sigma^* \Delta T / 2, \quad a = 2\delta \bar{r}, \quad \theta = \frac{\bar{\rho}^2 \alpha g \tilde{V}_1 a^4 \Delta T}{192 \eta M_1 D}. \quad (6-13)$$

If we neglect the terms of order δ and neglect the second z-derivative of c_2 , then

$$\frac{\partial}{\partial x} \left(\frac{\partial c_2}{\partial x} + \epsilon c_2 \right) = -\theta x(1-x^2) \frac{\partial c_2}{\partial z}, \quad \left(\frac{\partial c_2}{\partial x} + \epsilon c_2 \right)_{\pm 1} = 0. \quad (6-14)$$

Moreover, Eqs.(6-6 and 8) become

$$\begin{aligned} \frac{1}{2} \int_{-1}^1 c_2(x, L/2) dx &= c_2^0, \\ \int_{-1}^1 \left[\frac{1}{4} a^2 \frac{\partial c_2}{\partial z} + \theta x(1-x^2) c_2 \right] dx &= 0. \end{aligned} \quad (6-15)$$

Now assume that c_2 is separable according to

$$c_2 = e^{-Kz} \left[c_2^0 + U(x) \right] + \Phi(z) + R(x) , \quad (6 - 16)$$

where K is a constant and c_2^0 is the initial concentration. Substitution of Eq.(6-16) into Eqs.(6-12) yields

$$\begin{aligned} \frac{d}{dx} \left[\frac{dU}{dx} + \epsilon (c_2^0 + U) \right] - k\theta (c_2^0 + U) (1-x^2)x , \\ \left[\frac{dU}{dx} + \epsilon (c_2^0 + U) \right]_{\pm 1} = 0 , \end{aligned} \quad (6 - 17)$$

and

$$\begin{aligned} \frac{d^2}{dx^2} \left(\frac{dR}{dx} + \epsilon R \right) - \theta x (1-x^2) \frac{d\Phi}{dz} , \\ \left(\frac{dR}{dx} + \epsilon R \right)_{\pm 1} = 0 . \end{aligned} \quad (6 - 18)$$

In order to satisfy Eq.(6-18), $(d\Phi/dz)$ must be constant, or

$$\Phi = A + Bz , \quad (6 - 19)$$

where A and B are both constants.

Eqs.(6-18 and 19) are satisfied if

$$\frac{dR}{dx} + \epsilon R = [-B\theta x^2 (2-x^2)^2] / 4 . \quad (6 - 20)$$

This yields, through first order in ϵ ,

$$R = \frac{1}{60} B\theta [(15x - 10x^3 + 3x^5) - \frac{1}{2} \epsilon (15x^2 - 5x^4 + x^6)] + C(1 - \epsilon x) , \quad (6 - 21)$$

where B and C are to be determined by using Eq.(6-15). The Φ and R parts of the second of Eqs.(6-15) are

$$\int_{-1}^1 \left[\frac{a^2}{4} B + \frac{1}{60} B \theta^2 x(1-x^2)(15x-10x^3+3x^5) - \epsilon \theta C x^2(1-x^2) \right] dx = 0, \quad (6-22)$$

where only even terms appear because odd terms vanish upon integration.

This yields

$$B = \frac{21\epsilon}{4\theta} C \left(1 + \frac{315a^2}{32\theta^2} \right)^{-1}. \quad (6-23)$$

Since $(a/\theta) = 192\eta M_1 D / (\rho \alpha g V_1 a^3 \Delta T) \approx 0.01$ for $a=1\text{mm}$ and $\Delta T=10\text{K}$, we safely

neglect the second term in the denominator of Eq.(6-23), and

$$B = \frac{21\epsilon}{4\theta} C. \quad (6-24)$$

Note that $(\epsilon/\theta) = 96\sigma^* \eta M_1 D / (\rho \alpha g V_1 a^4) \approx 0.05\text{m}^{-1}$ for $\sigma^* = 10^{-3}/\text{K}$.

To solve Eqs.(6-17), we suppose that

$$\begin{aligned} U &= \epsilon u_0 + \epsilon^2 u_1 + \theta(\epsilon^3), \\ K\theta &= \epsilon k_0 + \epsilon^2 k_1 + \theta(\epsilon^3) \dots \end{aligned} \quad (6-25)$$

Then

$$\begin{aligned} \frac{d}{dx} \left(\frac{du_0}{dx} + c_2^0 \right) &= k_0 c_2^0 x(1-x^2), \\ \left(\frac{du_0}{dx} + c_2^0 \right)_{\pm 1} &= 0, \end{aligned}$$

$$\int_{-1}^1 x(1-x^2)u_0 dx = 0, \quad (6-26)$$

where the last of Eqs.(6-26) is from the second of Eqs.(6-15) with neglect of terms of order $(a/\theta)^2$ compared to the retained term. The results are

$$u_0 = -\frac{c_2^0}{80} (25x - 70x^3 + 21x^5) \quad (6-27)$$

$$k_0 = 21/4.$$

Thus, through terms of order ϵ ,

$$c_2 = \left[c_2^0 - \frac{\epsilon c_2^0}{80} (25x - 70x^3 + 21x^5) \right] \exp \left(-\frac{21\epsilon z}{4\theta} \right) + \frac{21\epsilon}{4\theta} C(z - L/2) + C$$

$$- \frac{\epsilon c_2^0}{80} x(25 - 70x^2 + 21x^4) \quad (6-28)$$

By the first of Eqs.(6-15),

$$C = c_2^0 - c_2^0 \exp \left(-\frac{21\epsilon}{4\theta} \frac{L}{2} \right), \quad (6-29)$$

and then

$$c_2 = c_2^0 + c_2^0 \left[\exp \left(-\frac{21\epsilon z}{4\theta} \right) - \exp \left(-\frac{21\epsilon}{4\theta} \frac{L}{2} \right) \right] + \frac{21\epsilon}{4\theta} c_2^0 \left[1 - \exp \left(-\frac{21\epsilon}{4\theta} \frac{L}{2} \right) \right] \left(z - \frac{L}{2} \right)$$

$$- \frac{\epsilon c_2^0}{80} x(25 - 70x^2 + 21x^4) \left[\exp \left(-\frac{21\epsilon z}{4\theta} \right) - \exp \left(-\frac{21\epsilon}{4\theta} \frac{L}{2} \right) \right]$$

$$- \frac{\epsilon c_2^0}{80} x(25 - 70x^2 + 21x^4) \quad (6-30)$$

B. DISCUSSION OF THE SOLUTION

Eq.(6-30) is the steady state concentration distribution function.

However, for practical application of Eq.(6-30) and because

$\epsilon/\theta \approx 0.05\text{m}^{-1}$, we expand all exponential terms to first order in ϵ . Then

$$\begin{aligned} c_2^0 - c_2^0 + \frac{21\epsilon}{4\theta} c_2^0 \left(1 - \frac{21\epsilon}{4\theta} \frac{L}{2} \right) \left(\frac{L}{2} - z \right) \\ - \frac{\epsilon c_2^0}{80} \{ x(25 - 70x^2 + 21x^4) \} \left[1 + \frac{21\epsilon}{4\theta} \left(\frac{L}{2} - z \right) \right] , \\ - c_2^0 \left[1 - \frac{\epsilon}{80} x(25 - 70x^2 + 21x^4) \right] \left[1 + \frac{21\epsilon}{4\theta} \left(\frac{L}{2} - z \right) \right] . \end{aligned} \quad (6-31)$$

and

$$\begin{aligned} \frac{\partial c_2^0}{\partial x} - \frac{\Delta T \sigma^*}{32} c_2^0 \left[\left(1 - \frac{42}{5} x^2 + \frac{21}{5} x^4 \right) \left\{ 1 + \frac{21\epsilon}{4\theta} \left(\frac{L}{2} - z \right) \right\} \right] \\ \approx - \frac{\Delta T \sigma^*}{32} c_2^0 \left(1 - \frac{42}{5} x^2 + \frac{21}{5} x^4 \right) , \end{aligned} \quad (6-32)$$

$$\begin{aligned} \frac{\partial c_2^0}{\partial z} - \frac{21\epsilon}{4\theta} c_2^0 \left(1 - \frac{\epsilon}{80} x(25 - 70x^2 + 21x^4) \right) \\ \approx - \frac{50}{\alpha \rho^2} \frac{4\eta D M_1 \sigma^*}{g \bar{V}_1 a^4} c_2^0 . \end{aligned} \quad (6-33)$$

Eqs.(6-32 and 33), the derivatives of our zeroth order solution of the steady state concentration Eq.(6-31), agree with the previous results (Horne and Bearman [1967, 1968]). The present result is more accurate at higher order, and for the first time we obtain explicitly the steady state concentration distribution itself rather than the first derivative. The previous results for the first order derivative cannot be integrated to obtain our results because the integration constant is

usually a function of z . This function is important also for the time dependent solution.

In chapter 5 , we assumed that the forgotten effect is not important for electrolyte solutions. We then neglected the composition dependence of the density in solving the velocity equation. This assumption can be verified if one knows the steady state concentration function. Since the concentration difference for TGTD reaches its maximum in the steady state, the forgotten effect should be maximal then. The effect is now easily estimated with the help of Eq.(6-31). The γ_0 in Eq.(5-8) is, from Eq.(6-31)

$$\gamma_0 = \frac{21\epsilon}{4\theta} c_2^0 \left(1 - \frac{21\epsilon}{4\theta} \frac{L}{2} \right) \left(\frac{L}{2} - z \right) ,$$

$$- \frac{\epsilon c_2^0}{80} (x(25 - 70x^2 + 21x^4)) \left[1 + \frac{21\epsilon}{4\theta} \left(\frac{L}{2} - z \right) \right] , \quad (6 - 34)$$

γ_0 has its maximum at $z=0$ and $x=1$ and $\gamma_0 \approx (21/8)c_2^0 L(\epsilon/\theta)$. Using the data given in table 1, for $c_2^0 = 0.5 \text{ mol dm}^{-3}$, $L = 0.1 \text{ m}$, and $\epsilon/\theta \approx 0.05 \text{ m}^{-1}$, then $\gamma_0 \approx 6.3 \text{ mol m}^{-3}$. The fourth and fifth terms of Eq.(5-8) are, then, respectively, for $\Delta T = 10\text{K}$ (and suppression of g in both terms),

$$\alpha\theta_0 \approx 1.5 \times 10^{-3} ,$$

$$\frac{M_1 M_2}{\rho V_1} [(V_1/M_1) - (V_2/M_2)] \gamma_0 \approx 0.28 \times 10^{-3} .$$

Thus, the fifth term is at most about 18% of the fourth term for KCl solutions, and at most about 12% for NaCl solutions. For higher

concentrations, longer tubes or smaller temperature differences, neglect of the concentration term in Eq.(5-8) must be re-examined.

CHAPTER 7

TIME DEPENDENT CONCENTRATION DISTRIBUTION IN THE COLUMN WITH TWO ENDS CLOSED

A. INTRODUCTION

Although the time dependent solution of the concentration equation for liquid mixtures is very important for both theoretical and practical purposes, an accurate time dependent solution has not previously been achieved. The TGTD experiments for binary liquid solutions involve a very long waiting period, usually several hours, to achieve the steady state concentration distribution. The time dependent equation usually used to calculate liquid thermal diffusion coefficients from non-steady state experimental data is based on the approximate theory of Furry and Jones [1946], derived for gaseous mixtures. An assumption in that theory is that the convection velocity profile is a step function. In this chapter we present the derivations of the time dependent concentration distribution in the annulus and of the working equations for both steady state and time dependent evaluation of Soret coefficients. The steady state working equation applies to a column with or without reservoirs,

but the time dependent working equation is applicable only to a column without reservoirs.

B. TIME DEPENDENT DIFFERENTIAL EQUATION

Our starting equation is Eq.(2-60)

$$\frac{\partial c_2}{\partial t} - \nabla \cdot \left[\frac{DM_1}{V_1 \rho} \left(\nabla c_2 - \sigma^* c_2 \nabla T \right) - c_2 \nabla \right] = 0 \quad (7-1)$$

In cylindrical coordinates, the equation is

$$D^* \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial c_2}{\partial r} - c_2 \sigma^* r \frac{\partial T}{\partial r} \right) + D^* \frac{\partial^2 c_2}{\partial z^2} - v_z \frac{\partial c_2}{\partial z} = \frac{\partial c_2}{\partial t} \quad (7-2)$$

As before, we assume that the temperature and convection velocity are both time independent. With the independent variable transformation relations Eqs.(4-20),

$$\frac{\partial}{\partial x} \left(\frac{\partial c_2}{\partial x} + \epsilon c_2 \right) + \theta (1-x^2) [x - \delta (1-x^2)] \frac{\partial c_2}{\partial z} + \frac{1}{4} a^2 (1+2\delta x) \frac{\partial^2 c_2}{\partial z^2} = \frac{\omega^2}{D^*} \frac{\partial c_2}{\partial t} \quad (7-3)$$

where we have made use of Eqs.(6-10,11, and 5-41). The initial condition is Eq.(3-3), but the boundary condition depends upon the design of the column. For a column without reservoirs, i.e. both ends closed, the boundary condition is

$$j_2^H(x, z, t) = 0, \quad x = \pm 1, \quad j_2^H(x, z, t) = 0, \quad z = 0, L. \quad (7-4)$$

To solve Eq.(7-3), we assume that the solution consists of two parts, Y and R:

$$c_2 = Y(x, z, t) + R(x, t). \quad (7-5)$$

We call R(x, t) the pure thermal diffusion effect in the TGTD column. Eq.(7-3) becomes, with Eq.(7-5)

$$\frac{\partial}{\partial x} \left(\frac{\partial Y}{\partial x} + \epsilon Y \right) + \theta(1-x^2)x \frac{\partial Y}{\partial z} + \omega^2 \frac{\partial^2 Y}{\partial z^2} - \frac{\omega^2 \partial Y}{D \partial t} + \frac{\partial^2 R}{\partial x^2} + \epsilon \frac{\partial R}{\partial x} - \frac{\omega^2 \partial R}{D \partial t} = 0, \quad (7-6)$$

$$\omega^2 = a^2/4, \quad (7-7)$$

where we ignore terms of order δ . We require that both Y and R must satisfy the following two equations as well as boundary and initial conditions:

$$\frac{\partial}{\partial x} \left(\frac{\partial Y}{\partial x} + \epsilon Y \right) + \theta(1-x^2)x \frac{\partial Y}{\partial z} + \omega^2 \frac{\partial^2 Y}{\partial z^2} - \frac{\omega^2 \partial Y}{D \partial t} = 0, \quad (7-8)$$

$$\left(\frac{\partial Y}{\partial x} + \epsilon Y \right)_{x=\pm 1} = 0; \quad Y(x, t=0) = 0,$$

$$\frac{\partial^2 R}{\partial x^2} + \epsilon \frac{\partial R}{\partial x} - \frac{\omega^2 \partial R}{D \partial t} = 0; \quad \left(\frac{\partial R}{\partial x} + \epsilon R \right)_{x=\pm 1} = 0, \quad (7-9)$$

$$R(x, t=0) = c_2^0.$$

Eq.(7-9) is easy to solve, but Eq.(7-8) is solvable only by use of a perturbation approach.

C. SOLUTIONS OF DIFFERENTIAL EQUATIONS.

The solution of Eq.(7-9) is

$$R(x, t) = \frac{2\epsilon c_2^0}{e^\epsilon - e^{-\epsilon}} e^{-\epsilon x} - 4\epsilon c_2^0 e^{-\epsilon x} \sum_{n=1}^{\infty} \frac{(n\pi)^2 [1 - (-1)^n e^\epsilon]}{[\epsilon^2 + (n\pi)^2]^2} \times \quad (7 - 10)$$

$$\left[\cos[(x+1)n\pi/2] - \frac{\epsilon}{n\pi} \sin[(x+1)n\pi/2] \right] \exp\left[-\frac{[(n\pi)^2 + \epsilon^2] D^* t}{a^2} \right] .$$

We call $R(x, t)$ the pure thermal diffusion effect in the TGTD column because $R(x, t)$ is analogous to the time dependent pure thermal diffusion results of Horne and Anderson [1970]. Note that $R \rightarrow c_2^0 + \theta(\epsilon)$

as $t \rightarrow \infty$.

To solve Eq.(7-8) we try

$$Y = e^{K(L/2 - z)} \left[c_2^0 + u(x, z, t) \right] , \quad (7 - 11)$$

then

$$\frac{\partial^2 u}{\partial x^2} + \epsilon \frac{\partial u}{\partial x} - \theta K x (1 - x^2) \left[c_2^0 + u \right] + \theta x (1 - x^2) \frac{\partial u}{\partial z}$$

$$+ \omega^2 \left[\frac{\partial^2 u}{\partial z^2} - 2K \frac{\partial u}{\partial z} + K^2 \left[c_2^0 + u \right] \right] - b^2 \frac{\partial u}{\partial t} = 0 , \quad b^2 = \omega^2 / D^* , \quad (7 - 12)$$

$$\left(\frac{\partial u}{\partial x} + \epsilon (c_2^0 + u) \right)_{x=\pm 1} = 0, \quad u(t=0) = -c_2^0.$$

We take $u(x, z, t)$ as a perturbation term because $u(x, z, t)$ is much smaller than initial concentration c_2^0 except at the boundaries, where it takes its extreme values. Thus, Eq.(7-12) becomes

$$\begin{aligned} & \frac{\partial^2 u}{\partial x^2} + \epsilon \frac{\partial u}{\partial x} - \theta K x (1-x^2) \left(c_2^0 + \lambda u \right) + \theta x (1-x^2) \frac{\partial u}{\partial z}, \\ & + \omega^2 \left[\frac{\partial^2 u}{\partial z^2} - 2K \frac{\partial u}{\partial z} + K^2 \left(c_2^0 + \lambda u \right) \right] - b^2 \frac{\partial u}{\partial t} = 0, \quad b^2 = \omega^2 / D^*, \end{aligned} \quad (7-13)$$

$$\left(\frac{\partial u}{\partial x} + \epsilon (c_2^0 + u) \right)_{x=\pm 1} = 0, \quad u(t=0) = -c_2^0, \quad \text{and}$$

$$u(x, z, t) = \sum_{n=0}^{\infty} \lambda^n u_n(x, z, t). \quad (7-14)$$

Combining Eqs.(7-13 and 14) and noting that the summation variable is a dummy variable, we obtain

$$\begin{aligned} & \frac{\partial^2 u_0}{\partial x^2} + \epsilon \frac{\partial u_0}{\partial x} + \theta x (1-x^2) \frac{\partial u_0}{\partial z} + \omega^2 \frac{\partial^2 u_0}{\partial z^2} - 2K\omega^2 \frac{\partial u_0}{\partial z} + (K\omega)^2 c_2^0 - \theta K x (1-x^2) c_2^0 \\ & - b^2 \frac{\partial u_0}{\partial t} = 0, \end{aligned} \quad (7-15)$$

$$\left(\frac{\partial u_0}{\partial x} + \epsilon (c_2^0 + u_0) \right)_{x=\pm 1} = 0; \quad u_0(t=0) = -c_2^0.$$

For $n \geq 0$ the general form of the perturbation equations is

$$\begin{aligned} & \frac{\partial^2 u}{\partial x^2} n + \epsilon \frac{\partial u}{\partial x} n + \theta x(1-x^2) \frac{\partial u}{\partial z} n + \omega^2 \frac{\partial^2 u}{\partial z^2} n - 2K\omega^2 \frac{\partial u}{\partial z} n + (K\omega)^2 u_{n-1} - \theta Kx(1-x^2) u_{n-1} \\ & - b^2 \frac{\partial u}{\partial t} n = 0, \end{aligned} \quad (7-16)$$

$$\left(\frac{\partial u}{\partial x} n + \epsilon u_n \right)_{x=\pm 1} = 0, \quad u_n(t=0) = 0.$$

To solve Eq.(7-15), we note that one of the terms, that due to convection, is a function of x only. We assume

$$u_0(x, z, t) = W_0(x, t) + \phi_0(x, z, t). \quad (7-17)$$

Then

$$\frac{\partial^2 W_0}{\partial x^2} + \epsilon \frac{\partial W_0}{\partial x} - \theta Kx(1-x^2) c_2^0 - b^2 \frac{\partial W_0}{\partial t} = 0, \quad (7-18)$$

$$\left(\frac{\partial W_0}{\partial x} + \epsilon (c_2^0 + W_0) \right)_{x=\pm 1} = 0; \quad W_0(t=0) = -c_2^0,$$

and

$$\begin{aligned} & \frac{\partial^2 \phi_0}{\partial x^2} + \epsilon \frac{\partial \phi_0}{\partial x} + \theta x(1-x^2) \frac{\partial \phi_0}{\partial z} + \omega^2 \frac{\partial^2 \phi_0}{\partial z^2} - 2K\omega^2 \frac{\partial \phi_0}{\partial z} + (K\omega)^2 c_2^0 - b^2 \frac{\partial \phi_0}{\partial t} = 0, \\ & \left(\frac{\partial \phi_0}{\partial x} + \epsilon \phi_0 \right)_{x=\pm 1} = 0, \quad \phi_0(t=0) = 0. \end{aligned} \quad (7-19)$$

Since the boundary condition for Eq.(7-18) requires that $\partial W_0/\partial t$ and $\partial W_0/\partial x$ are order of ϵ , we omit terms of second order in ϵ and find

$$\frac{\partial^2 W_0}{\partial x^2} - \theta Kx(1-x^2) c_2^0 - b^2 \frac{\partial W_0}{\partial t} = 0 \quad (7-20)$$

with

$$\frac{\partial W_0}{\partial t} + \epsilon c_2^0 = 0 \text{ at } x = -1, 1, \quad W_0(x, 0) = -c_2^0. \quad (7-21)$$

Eq.(7-20) is a second order linear inhomogenous partial differential equation whose solution (Boyce and DiPrima [1977]) is

$$W_0(x, t) = c_2^0 \sum_{n=1}^{\infty} \frac{1 - (-1)^n}{(n\pi)^2} \left[4\epsilon e^{-(n\pi/2b)^2 t} - \frac{32\theta K}{(n\pi)^2} \left(1 - \frac{12}{(n\pi)^2} \right) \left(1 - e^{-(n\pi/2b)^2 t} \right) \right. \\ \left. x \cos[n\pi(x+1)/2] + \epsilon c_2^0 x - c_2^0 \right]. \quad (7 - 22)$$

As time goes to infinity, Eq.(7-22) becomes

$$W_0(x, t) = c_2^0 \sum_{n=1}^{\infty} \frac{[1 - (-1)^n] 32\theta K}{(n\pi)^4} \left(1 - \frac{12}{(n\pi)^2} \right) \cos[n\pi(x+1)/2] \\ + \epsilon c_2^0 x - c_2^0. \quad (7 - 23)$$

Now

$$c_2^0 \sum_{n=1}^{\infty} \frac{[1 - (-1)^n] 32\theta K}{(n\pi)^4} \left(1 - \frac{12}{(n\pi)^2} \right) \cos[n\pi(x+1)/2] \\ - c_2^0 K \theta (x^3/6 - x^5/20 - x/4). \quad (7 - 24)$$

This identity may be verified by expanding the right hand side of Eq.(7-24) in terms of $\cos[n\pi(x+1)/2]$ for x from -1 to 1. Applying this identity we rewrite Eq.(7-23) as

$$W_0(x) = -c_2^0 K \theta (x^3/6 - x^5/20 - x/4) + \epsilon c_2^0 x - c_2^0. \quad (7 - 25)$$

If, as we expect, from chapter 6, $K\theta = 21\epsilon/4$, then

$$W_0(x) = -\frac{c_2^0}{80} \epsilon \left(25x - 70x^3 + 21x^5 \right) - c_2^0 . \quad (7-26)$$

Now we turn to Eq.(7-19). First we ignore the $(\omega K)^2$ term in this equation. Then

$$\begin{aligned} \frac{\partial^2 \phi_0}{\partial x^2} + \epsilon \frac{\partial \phi_0}{\partial x} + \theta x(1-x^2) \frac{\partial \phi_0}{\partial z} + \omega^2 \frac{\partial^2 \phi_0}{\partial z^2} - 2K\omega^2 \frac{\partial \phi_0}{\partial z} - b^2 \frac{\partial \phi_0}{\partial t} &= 0 , \\ \left(\frac{\partial \phi_0}{\partial x} + \epsilon \phi_0 \right)_{x=\pm 1} &= 0, \quad \phi_0(t=0) = 0 , \\ j_2^H(x, z, t) &= 0, \quad z=0, L . \end{aligned} \quad (7-27)$$

If we first integrate Eq.(7-27) for x from -1 to 1 and then use the boundary condition for x , Eq.(7-27) becomes

$$\omega^2 \int_{-1}^1 \frac{\partial^2 \phi_0}{\partial z^2} dx - \int_{-1}^1 2K\omega^2 \frac{\partial \phi_0}{\partial z} dx + \int_{-1}^1 f(x) \frac{\partial \phi_0}{\partial z} dx - b^2 \int_{-1}^1 \frac{\partial \phi_0}{\partial t} dx = 0 , \quad (7-28)$$

with $f(x) = \theta x(1-x^2)$ and

$$\begin{aligned} \int_{-1}^1 f(x) \frac{\partial \phi_0}{\partial z} dx &= \frac{\partial \phi_0}{\partial z} F(x) \Big|_{x=-1}^1 - \int_{-1}^1 F(x) \frac{\partial^2 \phi_0}{\partial x \partial z} dx , \\ F(x) &= \int f(x) dx . \end{aligned} \quad (7-29)$$

To derive an expression for $\frac{\partial^2 \phi_0}{\partial x \partial z}$, we integrate indefinitely the first equation of Eqs.(7-27) with respect to x then differentiate with respect to z . Thus

$$\frac{\partial^2 \phi_0}{\partial x \partial z} - \epsilon \frac{\partial \phi_0}{\partial z} - \omega^2 \int \frac{\partial^3 \phi_0}{\partial z^3} dx + \int 2K\omega^2 \frac{\partial^2 \phi_0}{\partial z^2} dx - \int f(x) \frac{\partial^2 \phi_0}{\partial z^2} dx + b^2 \int \frac{\partial^2 \phi_0}{\partial z \partial t} dx$$

Now substituting this expression into Eqs.(7-29) and rearranging to

give $\int_{-1}^1 f(x) \frac{\partial \phi_0}{\partial z} dx$, we use this integral to

eliminate $\int_{-1}^1 f(x) \frac{\partial \phi_0}{\partial z} dx$ in Eqs.(7-28). This leads to

$$\begin{aligned} & \omega^2 \int_{-1}^1 \frac{\partial^2 \phi_0}{\partial z^2} dx - \int_{-1}^1 2K\omega^2 \frac{\partial \phi_0}{\partial z} dx + \frac{\partial \phi_0}{\partial z} F(x) \Big|_{x=-1}^{x=+1} + \epsilon \int_{-1}^1 F(x) \frac{\partial \phi_0}{\partial z} dx \\ & + \int_{-1}^1 F(x) \left(\int_{-1}^1 F(x) \frac{\partial^2 \phi_0}{\partial z^2} dx \right) dx - 2K\omega^2 \int_{-1}^1 F(x) \left(\int_{-1}^1 \frac{\partial^2 \phi_0}{\partial z^2} dx \right) dx + \omega^2 \int_{-1}^1 F(x) \left(\int_{-1}^1 \frac{\partial^3 \phi_0}{\partial z^3} dx \right) dx \\ & - b^2 \int_{-1}^1 F(x) \left(\int_{-1}^1 \frac{\partial^2 \phi_0}{\partial z \partial t} dx \right) dx - b^2 \int_{-1}^1 \frac{\partial \phi_0}{\partial t} dx = 0 . \end{aligned} \quad (7-30)$$

In order to simplify Eq.(7-30), we assume that for the zeroth order approximation, ϕ_0 is independent of x . This is effectively true for TGTD of the liquid mixture because the concentration gradient along the z direction due to fluid convection along the same direction is much larger than the concentration gradient due to the temperature gradient along the x direction. Making use of this assumption, we have the following very simple equations

$$\left(2\omega^2 + E \right) \frac{\partial^2 \phi_0}{\partial z^2} + \left(-4K\omega^2 + H \right) \frac{\partial \phi_0}{\partial z} - 2b^2 \frac{\partial \phi_0}{\partial t} = 0 , \quad (7-31)$$

and

$$H = \int_{-1}^1 \epsilon F(x) dx, \quad E = \int_{-1}^1 F^2(x) dx. \quad (7-32)$$

To derive Eq.(7-31), we have applied the odd and even function properties of $f(x)$ and $F(x)$ respectively. The two constants H and E are easily evaluated:

$$F(x) = \theta(x^2/2 - x^4/4 - 1/4); \quad H = -8\epsilon\theta/30; \quad E = 16\theta^2/315. \quad (7-33)$$

By Eqs.(6-13), $\theta \approx 0.1m$, $\epsilon \approx 5 \times 10^{-3}$, $a \approx 10^{-3}m$, and $K = 21\epsilon/(4\theta) = 0.25m^{-1}$. Then $E \approx 5 \times 10^{-4}m^2$ and $\bar{H} \approx 1.3 \times 10^{-4}m$. Thus $E \gg 2\omega^2 = a^2/2 = 5 \times 10^{-7}m^2$ and $\bar{H} \gg 4K\omega^2 = a^2K \approx 2.5 \times 10^{-7}m$. Neglecting $2\omega^2$ and $4K\omega^2$, Eq.(7-31) becomes

$$\frac{\partial^2 \phi_0}{\partial z^2} - (\bar{H}/E) \frac{\partial \phi_0}{\partial z} - (2b^2/E) \frac{\partial \phi_0}{\partial \tau} = 0, \quad \bar{H} = H. \quad (7-34)$$

Now $\bar{H}/E = 21\epsilon/(4\theta)$. From Eqs.(6-25 and 27) $21\epsilon/(4\theta) = K$. Thus $\bar{H}/E = K$. We have thus obtained from the time-dependent equation the K factor, which is very important in TGTD (Tyrrell [1961], Horne and Bearman [1967]). Although the general approaches are quite different, the factor K appears independently in both the steady state and the time-dependent solutions for TGTD. This result supports the validity of the assumptions made earlier in this section.

To solve Eq.(7-34), the boundary condition in the z direction must be known. For a column closed at both ends the flux along the column at both top and bottom must vanish, and from this condition we must be able to derive a proper boundary condition for the z component. The flux along the z direction for TGTD can be written as (ch. 2)

$$j_z = v_z(x)c_2 - D^* \frac{\partial c_2}{\partial z} . \quad (7-35)$$

By the second of Eqs.(7-4), j_z vanishes at the boundary, so

$$v_z(x)c_2 - D^* \frac{\partial c_2}{\partial z} = 0 , \text{ at } z=0, L . \quad (7-36)$$

Since c_2 is the sum of $R(x,t)$ and $Y(x,z,t)$ by Eq.(7-5), we have

$$\frac{\partial Y}{\partial z} - v(x)Y/D^* + v(x)R(x,t)/D^* , \text{ at } z=0, L, \quad (7-37)$$

where we drop the subscript. Keeping in mind that starting from Eq.(7-37) all the following mathematical manipulations are true only at $z=0$ and L , we then combine Eq.(7-11) with Eq.(7-37) to obtain

$$\frac{\partial u}{\partial z} - K(c_2^0 + u) - v(x)(c_2^0 + u)/D^* + v(x)R(x,t)e^{K(z-L/2)z}/D^* . \quad (7-38)$$

At this point, we introduce a perturbation device. With the help of Eq.(7-14), in orders of λ^n Eq.(7-38) becomes

$$\frac{\partial u_0}{\partial z} - K(c_2^0 + u_0) - v(x)(c_2^0 + u_0)/D^* + v(x)R(x,t)e^{K(z-L/2)z}/D^* , \quad (7-39)$$

$$\frac{\partial u_n}{\partial z} = [v(x)/D^* + K]u_n , \quad n \geq 1 . \quad (7-40)$$

The zeroth order equation can be rewritten in terms of $W_0(x,t)$ and

$$\phi_0(x,z,t)$$

$$D^* \frac{\partial \phi_0}{\partial z} = [v(x) + D^* K] [c_2^0 + W_0(x, t) + \phi_0(x, z, t)] + e^{K(z-L/2)} R(x, t) v(x), \quad (7-41)$$

where we used Eqs.(7-17). Eq.(7-41) cannot be used as it stands, because both W_0 and R are time dependent. However the relaxation times of W_0 and R are typically of order $(a^2/\pi^2 D^*)$. Taking $a \approx 0.1 \text{ cm}$, $D^* \approx 10^{-5} \text{ cm}^2/\text{sec}$. for $n=1$, the relaxation time is about 100 seconds. Thus the exponential factor $e^{-(n\pi)^2 D^* t/a^2}$ is very small after about 8 minutes. The relaxation time along the column height is a few hours or longer (Naokata and Kimie [1984]). By comparing these two relaxation times, we see that the steady state concentration in the x direction is reached when the vertical concentration gradient is still insignificant. On the other hand, the horizontal concentration gradient is very small compared to the vertical gradient and we therefore take only steady state parts for $W_0(x, t)$ and $R(x, t)$. This introduces no significant error but simplifies our vertical boundary condition tremendously. Hence Eq.(7-41) becomes

$$D^* \frac{\partial \phi_0}{\partial z} = [v(x) + D^* K] [\tilde{W}_0(x) + \phi_0(x, z, t)] + e^{K(z-L/2)} R_s(x) v(x), \quad (7-42)$$

where $\tilde{W}_0(x) = W_{0s} + c_2^0$, and both W_{0s} and R_s are steady state concentrations.

The following treatment for boundary conditions is the same as before for differential equation ϕ_0 . We first integrate Eq.(7-42) for x from -1

to 1 and note that $v(x)/D^* = 4f(x)/a^2$, $f(x) = \theta x(1-x^2)$. After some computations we end up with

$$E \frac{\partial \phi_0}{\partial z} - \bar{H} \phi_0 + \int_{-1}^1 f(x) \bar{W}_0(x) dx + e^{K(z-L/2)} \int_{-1}^1 f(x) R_s(x) dx, \quad (7-43)$$

where $\bar{H}$ and E are defined by Eqs.(7-33). The two integrals are evaluated easily.

$$\begin{aligned} \int_{-1}^1 f(x) \bar{W}_0(x) dx &= \int_{-1}^1 f(x) [W_0(x) + c_2^0] - 2\epsilon c_2^0 \theta / 80 \int_{-1}^1 (x-x^3) \left(25x - 70x^3 + 21x^5 \right) dx = 0 \\ \int_{-1}^1 f(x) R_s dx &= \frac{2\epsilon c_2^0}{e^\epsilon - e^{-\epsilon}} \theta \int_{-1}^1 x(1-x^2) e^{-\epsilon x} dx \approx -\frac{4\epsilon \theta c_2^0}{15}. \end{aligned} \quad (7-44)$$

To evaluate these two integrals, we used Eqs.(7-10 and 26), expanded $e^{-\epsilon x}$ and neglected terms of order ϵ^2 in deriving the second integral. Finally,

$$\frac{\partial \phi_0}{\partial z} - K \phi_0 - \frac{4\epsilon \theta c_2^0}{15E} e^{K(z-L/2)}, \quad z=0, L. \quad (7-45)$$

Because by Eqs.(7-34) $\epsilon \theta = 30\bar{H}/8$, then

$$\frac{\partial \phi_0}{\partial z} - K \left[\phi_0 - c_2^0 e^{K(z-L/2)} \right], \quad z=0, L. \quad (7-46)$$

Eq.(7-46) is the boundary condition subject to differential equation (7-34). Having Eq.(7-46) in hand, we can solve Eqs.(7-34) without difficulties. The equations to be solved are

$$\frac{\partial^2 \phi_0}{\partial z^2} - (\bar{H}/E) \frac{\partial \phi_0}{\partial z} - (2b^2/E) \frac{\partial \phi_0}{\partial t} = 0 ,$$

$$\frac{\partial \phi_0}{\partial z} = K \left[\phi_0 - c_2^0 e^{K(z-L/2)} \right] , \quad z=0, L , \quad (7-47)$$

$$\phi_0(z, t=0) = 0 .$$

We first let $\phi_0(z, t) = \bar{\phi}(z, t) - Kc_2^0 z e^{K(z-L/2)}$. Then in terms of $\bar{\phi}$

$$\frac{\partial^2 \bar{\phi}}{\partial z^2} - K \frac{\partial \bar{\phi}}{\partial z} - 2b^2/E \frac{\partial \bar{\phi}}{\partial t} = 0 ,$$

$$\frac{\partial \bar{\phi}}{\partial z} = K \bar{\phi} , \quad z=0, L , \quad (7-48)$$

$$\bar{\phi}(z, t=0) = Kz c_2^0 e^{K(z-L/2)} ,$$

where we have neglected terms of order K^2 in the first of Eqs.(7-48).

The method of solving Eqs.(7-48) can be found in any partial differential equations text book. The solution is

$$\bar{\phi} = B_0 \bar{\phi}_0(z) + \sum_{n=1}^{\infty} B_n \bar{\phi}_n T_n(t) , \quad B_0 = \left[\frac{KL}{1 - e^{-KL}} - 1 \right] c_2^0 ,$$

$$B_n = \frac{-2K \left(\frac{n\pi}{L} \right)^2 \left[1 - (-1)^n e^{KL/2} \right]}{\left[(K/2)^2 + (n\pi/L)^2 \right]^2} , \quad T_n(t) = \exp \left[\frac{-E}{2b} \left[(K/2)^2 + (n\pi/L)^2 \right] t \right] ,$$

$$\bar{\phi}_0 = e^{K(z-L/2)} ,$$

$$\bar{\phi}_n = \left[\cos(n\pi z/L) + \frac{KL}{(2n\pi)} \sin(n\pi z/L) \right] e^{K(z-L/2)/2} \quad (7-49)$$

Thus the solution for Eq.(7-47) is

$$\phi_0(z, t) = B_0 \bar{\phi}_0(z) + \sum_{n=1}^{\infty} B_n \bar{\phi}_n T_n(t) - K z c_2^0 e^{K(z-L/2)} . \quad (7-50)$$

C. DISCUSSIONS OF THE TIME DEPENDENT SOLUTION

In this section we discuss some of the results derived in this chapter. It is clear that we have solved the problem of the concentration distribution as a function of space and time to zeroth order. This has not been done before. Now it is possible to predict the concentration at any point any time in the column while the experiment is in progress.

For convenience in discussing our solution, we combine Eqs. (7-5, 11 and 17) and write

$$c_2(x, z, t) = e^{K(L/2-z)} [c_2^0 + W_0(x, t) + \phi_0(z, t)] + R(x, t) ,$$

$$W_0(x, t) = c_2^0 \sum_{n=1}^{\infty} \frac{1 - (-1)^n}{(n\pi)^2} \left[4\epsilon e^{-(n\pi/2b)^2 t} - \frac{32\theta K}{(n\pi)^2} \left(1 - \frac{12}{(n\pi)^2} \right) \left(1 - e^{-(n\pi/a)^2 t} \right) \right]$$

$$+ x \cos[n\pi(x+1)/2] + \epsilon c_2^0 x - c_2^0 ,$$

$$\phi_0(z, t) = c_2^0 \left(\frac{KL}{1 - e^{-KL}} - 1 \right) e^{K(z-L/2)} + c_2^0 \sum_{n=1}^{\infty} \frac{-2K \left(\frac{n\pi}{L} \right)^2}{L \left(\frac{n\pi}{L} \right)^2} \frac{[1 - (-1)^n e^{KL/2}]}{[(K/2)^2 + (n\pi/L)^2]^2}$$

$$\times \left[\cos(n\pi z/L) + \frac{KL}{2n\pi} \sin(n\pi z/L) \right] e^{K(z-L/2)/2}$$

$$\times \exp \left[-\frac{t}{\tau} \left((KL/2)^2 + (n\pi)^2 \right) \right] - K z c_2^0 e^{K(z-L/2)} ,$$

$$R(x, t) = \frac{2\epsilon c_2^0}{e^\epsilon - e^{-\epsilon}} e^{-\epsilon x} - 4\epsilon c_2^0 e^{-\epsilon x} \sum_{n=1}^{\infty} \frac{(n\pi)^2 [1 - (-1)^n e^\epsilon]}{[\epsilon^2 + (n\pi)^2]^2} \\
\times \left[\cos[(x+1)n\pi/2] - \frac{\epsilon}{n\pi} \sin[(x+1)n\pi/2] \right] \exp\left[-\frac{[(n\pi)^2 + \epsilon^2] D^* t}{a^2}\right], \\
\tau = 2b^2 L^2 / E = \frac{362880 D^*}{a^6} \left(\frac{\eta L}{\Delta T \rho_0 \alpha g} \right)^2, \quad (7-51)$$

where K , ϵ and σ^* all have been defined before.

The solution is the sum of three terms. $\phi_0(z, t)$ is a function of column height and time only, while $R(x, t)$ is a function of column width and time only. We call $\phi_0(z, t)$ the pure convection contribution to TGT. $\phi_0(z, t)$ does not directly depend on the temperature gradient. Instead, the temperature gradient affects only the progress towards steady state concentration distribution along the column height because the relaxation time is inversely proportional to $(\Delta T)^2$. A higher temperature gradient leads to faster convection and a higher velocity reduces the time required to reach steady state. When steady state is attained ϕ_0 is independent of ΔT . In general, from the definition of τ , large ΔT , thermal expansivity α , density ρ , gravitational force g (if the experiment is performed on a planet with large g) and small viscosity η will lead to a small relaxation time. Since α , η , D^* and ρ_0 are almost constant and do not change much during the course of the experiment for small ΔT , the dimensions a and L , the annular gap width and column height, are very important in setting τ . Usually the column height can vary from a few centimeters up to about half an meter. Experimentally

Naokata and Kimie [1984] have verified the strong dependence of τ on L . A longer column requires a longer time to reach steady state, but will lead to a higher concentration difference along the column. When steady state is established one has the largest separation of solute from solvent along the column. This can be seen from our numerical calculations (Figs. 7-1, 2, and 3)). Up to now in this discussion we have been using Eqs. (7-51) for the relaxation time. The real relaxation time is $\tau/[(KL/2)^2 + (n\pi)^2]$. $(KL)^2$ is usually very small compared with π^2 unless L is over 10 meters, which is unlikely. We therefore ignore this term and use only $\tau' = \tau/\pi^2$ hereafter.

The most important factor which affects the τ' is a^6 , the annular spacing of the column. A small change in a will change τ' very significantly. To obtain a higher concentration gradient, one prefers a narrower annular spacing, but the time required to reach steady state increases dramatically with smaller a . It is interesting to note that when the annular spacing approaches zero there is no thermogravitational thermal diffusion because convection of the fluid will not occur.

To finish the discussion, we compare the steady state with that obtained in chapter 6. At steady state the functions $\phi_0(z)$, $W_0(z, x)$ and $R(x, t)$ take the following forms

$$\phi_0(z) = \left(\frac{KL}{1 - e^{-KL}} - 1 - Kz \right) c_2^0, \quad R(x) = \frac{2\epsilon c_2^0}{e^{\epsilon} - e^{-\epsilon}} e^{-\epsilon x}$$

$$W_0(z, x) = -\frac{\epsilon c_2^0}{80} [x(25 - 70x^2 + 21x^3)] e^{K(L/2 - z)}. \quad (7 - 52)$$

$$\text{With } c_2(x, z) = \phi_0(z) + \bar{W}_0(z, x) + R(x), \quad (7 - 53)$$

$$c_2(x, z) = c_2^0 + c_2^0 K \left(\frac{L}{2} - z \right) - \frac{\epsilon c_2^0}{80} [x(25 - 70x^2 + 21x^3)] \{ 1 + K(\frac{L}{2} - z) \}$$

$$-c_2^0 \left(1 - \frac{\epsilon}{80} x (25 - 70x^2 + 21x^3) \right) \left(1 + K \left(\frac{L}{2} - z \right) \right). \quad (7-54)$$

Here we have expanded all exponential terms up to first order for K and ϵ . This result is the same as Eq.(6-31). Although the general approaches of chapter 6 and 7 are very different, the steady state results are the same for the zeroth order solution. This validates the assumptions made in dealing with the time dependent solution.

Figures(7-1, 2, and 3) display the concentration distribution. These curves are calculated from Eq.(7-51).

D. WORKING EQUATIONS

The measurements of solute concentration at the two ends of the TGT column can be made at either steady state or transient state (Gaeta, Perna, Scala, and Bellucci [1982], and Naokata and Kimie [1984]). The advantage of steady state measurements is that the concentration gradient has reached its extreme values at both ends, so it is easy to measure with a relatively small error. The disadvantage is that it is very time consuming to reach steady state. Because of this, one also measures the concentration change at early times. In order to use our theory to account for the experimental results at early times, some further work is needed.

Because experimentally one monitors the average concentration change at the column ends, it is necessary to convert our concentration distribution equation by averaging along the annular dimension. Mathematically, we evaluate the integral

$$\langle c_2(z, t) \rangle = \frac{\int_{r_1}^{r_2} r c_2(r, z, t) dr}{\int_{r_1}^{r_2} r dr} \quad (7-55)$$

With x as variable, Eq.(7-55) is

$$\langle c_2(z, t) \rangle = \frac{\int_{-1}^1 r c_2(x, z, t) e^{2\delta x} dx}{\int_{-1}^1 e^{2\delta x} dx} \quad (7-56)$$

where we have used Eqs.(4-20). The next step is to substitute $c_2(x, z, t)$ given by Eqs.(7-51) into Eq.(7-56) to evaluate the integral. We omit the lengthy details of calculations and simply write down the result.

$$\begin{aligned} \frac{\langle c_2(z, t) \rangle}{c_2^0} = & A \left[\sum_{n=1,3,5,\dots}^{\infty} B_n(z) \left(1 - e^{-\lambda_n^2 t} \right) + C + \sum_{n=1}^{\infty} E_n e^{-\lambda_n^2 t} \right] + \left(\frac{KL}{1 - e^{-KL}} - 1 - Kz \right) \\ & + e^{K(L/2 - z)/2} \sum_{n=1}^{\infty} G_n(z) e^{-t/\tau'(n)}, \end{aligned} \quad (7-57)$$

with

$$B_n(z) = 64\epsilon\delta \frac{\left[1 - (-1)^n e^{4\delta} \right] \left[1 - \frac{42}{(n\pi)^2} \left(\frac{12}{(n\pi)^2} - 1 \right) \right]}{(n\pi)^2 \left[(4\delta)^2 + (n\pi)^2 \right]} e^{K(L/2 - z)/2}, \quad A = 2\delta / (e^{4\delta} - 1),$$

$$G_n(z) = \frac{8KL(2n\pi)^2 \left[(-1)^n e^{KL/2} - 1 \right]}{\left[(KL)^2 + (2n\pi)^2 \right]} \left[\cos(n\pi z/L) + \frac{KL}{2n\pi} \sin(n\pi z/L) \right],$$

$$C = \frac{2 \left(e^{4\delta - 2\epsilon} - 1 \right) \epsilon}{\left(1 - e^{-2\epsilon} \right) (2\delta - \epsilon)} , \quad \tau'_n = \frac{362880 D^*}{a^6} \left(\frac{\eta L}{\Delta T \rho_0 \alpha g} \right)^2 (\pi n)^{-2} ,$$

$$\lambda_n^2 = \left(\frac{(n\pi)^2}{a^2} \right) D^* , \quad E_n = -32\epsilon\delta\pi^2 - \frac{\left[1 - (-1)^n e^\epsilon \right] \left[(-1)^n e^{4\delta - \epsilon} - 1 \right]}{\left(\frac{\epsilon^2}{\pi^2} + (n\pi)^2 \right)^2 \left((4\delta - \epsilon)^2 + (n\pi)^2 \right)} . \quad (7 - 58)$$

Now we define a new function

$$\Delta \langle c_2 \rangle = c_2(0, t) - c_2(L, t) \quad (7 - 59)$$

Thus $\Delta \langle c_2 \rangle$ represents the concentration difference between the bottom and top of the column. Substituting Eqs.(7-52) back into Eq.(7-57), then letting $z=0$ and L respectively, Eq.(7-59) becomes

$$\begin{aligned} \frac{\Delta \langle c_2 \rangle}{c_2^0} = & KL \left[1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{e^{-t/\tau'_n}}{(2n+1)^2} \right] \\ & + \frac{2A\delta\epsilon}{15} (1 + e^{4\delta}) \sinh(KL/2) \left(1 - e^{-\lambda_0^2 t} \right) , \end{aligned} \quad (7 - 60)$$

where λ_0^2 is the first term of $\lambda_n^2 = (2n+1)^2 \pi^2 D^* / a^2$. The reason for just

taking the $n=0$ term is that $e^{-\lambda_n^2 t}$ is nearly zero for $n \geq 1$ when $t \geq 60$ seconds. To derive Eq.(7-60) we have used relation

$$\sum_{n=1}^{\infty} \frac{1 - \frac{42}{(n\pi)^2} \left[\frac{12}{(n\pi)^2} - 1 \right]}{\pi^4 (2n+1)^4} = \frac{1}{960} . \quad (7 - 61)$$

We also have ignored terms such as $(KL)^2$, $(4\delta)^2$, in comparison with $(n\pi)^2$ term, and have expanded terms like $e^{2\epsilon}$ and $e^{4\delta}$. Eq.(7-60) reduces to zero at time zero.

As time goes to infinity, we have the maximum for $\Delta\langle c_2 \rangle$, which is

$$\frac{\Delta\langle c_2 \rangle}{c_2^0} = KL + \frac{2A\delta\epsilon}{15} (1 + e^{4\delta}) \sinh(KL/2)$$

$$\approx \frac{504\sigma^* \eta D^* L}{a^4 \rho_0 \alpha g} \left[1 + \frac{\Delta T \sigma^*}{30\delta} \right] \quad (7-62)$$

Eq.(7-62) is the working equation for steady state evaluation of the Soret coefficient. $\Delta\langle c_0 \rangle$ is experimentally measured. By solving Eq.(7-62) for σ^* one obtains the Soret coefficient.

Eq.(7-60) is the working equation before steady state, and can be used at any time during the experiment. To avoid the series, it is desirable to derive a simple equation which can be applied to a certain

time period. To do this we must evaluate $\sum_{n=0}^{\infty} \frac{e^{-t/\tau'_n}}{(2n+1)^2}$. We redefine this

term as

$$f(\mu) = \sum_{n=0}^{\infty} \frac{e^{-\mu(2n+1)^2}}{(2n+1)^2}, \quad \mu = \left[\frac{362880D^*}{a^6\pi^2} \left(\frac{\eta L}{\Delta T \rho_0 \alpha g} \right)^2 \right]^{-1} t, \quad (7-63)$$

then for small μ

$$\frac{df(\mu)}{d\mu} = - \sum_{n=1}^{\infty} e^{-\mu(2n+1)^2} \approx - \int_0^{\infty} e^{-\mu(2n+1)^2} dn \quad (7-64)$$

The integral is tabulated (Gradshteyn and Ryzhik [1980]), and Eq.(7-64) becomes

$$\frac{df(\mu)}{d\mu} = -(\pi/\mu)^{1/2} \frac{[1 - \text{erf}(\sqrt{\mu})]}{4} \quad (7-65)$$

or $f(\mu) = (\pi\mu)^{1/2} \text{erf}(\sqrt{\mu}) + 1/(2e^{-\mu}) - (\pi\mu)^{1/2}/2 + C$; where erf stands for error function and the constant is evaluated at $\mu=0$. Thus

$$f(\mu) = \frac{(\pi\mu)^{1/2} \text{erf}(\sqrt{\mu})}{2} + \frac{e^{-\mu}}{2} - \frac{(\pi\mu)^{1/2}}{2} + \frac{\pi^2}{8} - \frac{1}{2} \quad (7-66)$$

By expanding Eq.(7-66) in powers of μ and retaining only the first two terms, we derive

$$f(\mu) \approx \pi^2/8 - \frac{(\pi\mu)^{1/2}}{2} \approx \sum_{n=0}^{\infty} \frac{e^{-\mu(2n+1)^2}}{(2n+1)^2} \quad (7-67)$$

The accuracy of Eq.(7-67) depends on how small μ is. Table 7-1 gives a comparison between the function $f(\mu)$ and the infinite summation. As we can see from the table, for about 1% error, μ can be as big as 0.7. Taking μ be 0.5, Eq.(7-67) will be a very good approximation. Because

$$\mu = \frac{t\pi^2 a^6 (\Delta T \rho_0 \alpha g)^2}{362880 D^* (\eta L)^2}, \quad (7-68)$$

if $\mu \approx 0.5$, $t \approx 3$ to 7 hours, depending on the values of L , a and ΔT . With the constraints, the time dependent working equation for a column without reservoirs is

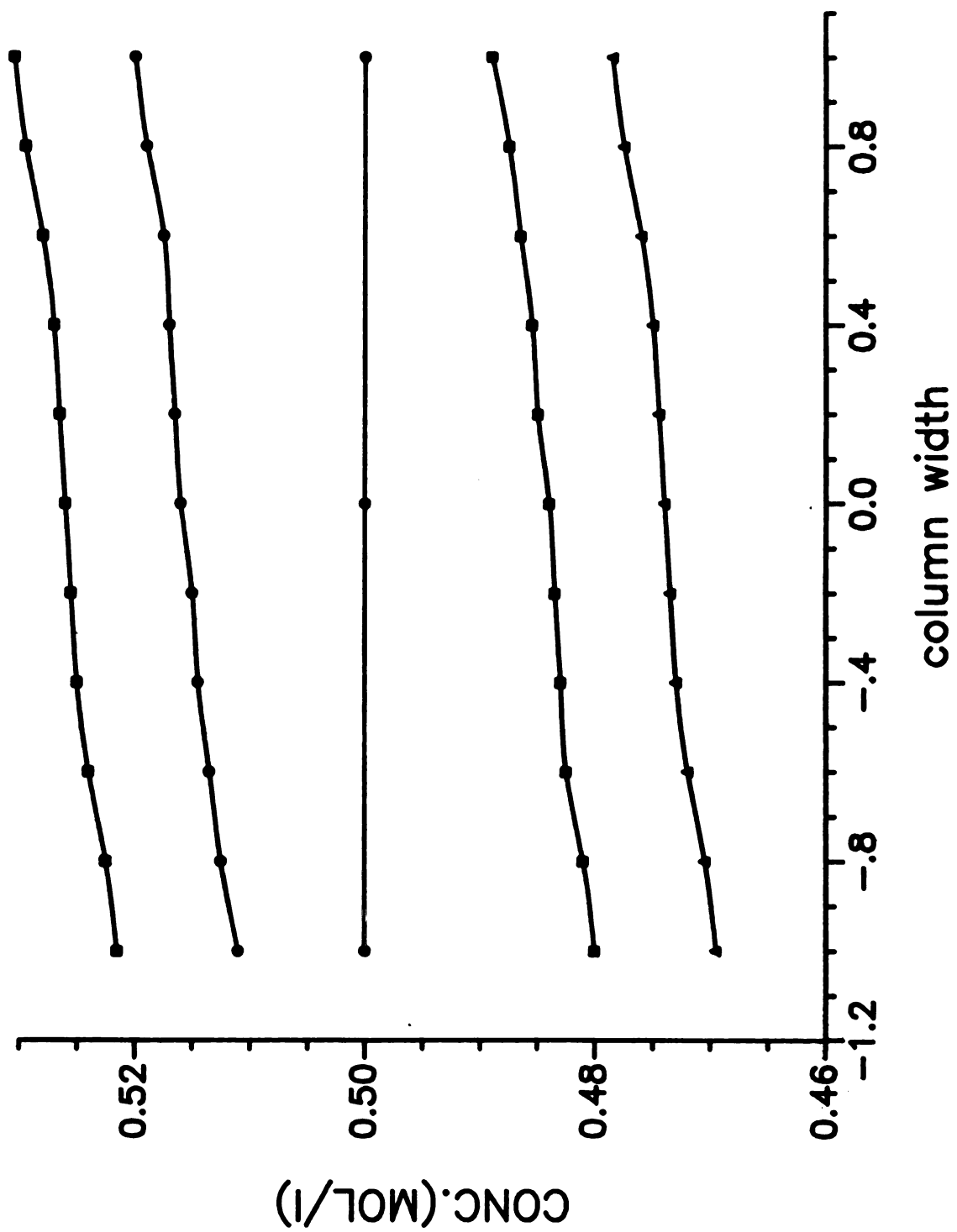
$$\frac{\Delta \langle c_2 \rangle}{c_2^0} = \frac{4KL/\mu}{\pi^{3/2}} + \frac{2\delta\epsilon}{15} \sinh(KL/2) \left(1 - e^{-\lambda_0^2 t} \right) . \quad (7 - 69)$$

We also give two additional working equations, which can be used for measurements at either the top or the bottom,

$$\begin{aligned} \frac{\langle c_2(0, t) \rangle - c_2^0}{c_2^0} &= \frac{2KL/\mu}{\pi^{3/2}} + \delta\epsilon \left(\frac{e^{-KL}}{15} + \frac{2}{3\pi^2} \right) \left(1 - e^{-\lambda_0^2 t} \right) , \\ \frac{\langle c_2(0, t) \rangle - c_2^0}{c_2^0} &= -\frac{2KL/\mu}{\pi^{3/2}} - \delta\epsilon \left(\frac{e^{-KL}}{15} + \frac{2}{3\pi^2} \right) \left(1 - e^{-\lambda_0^2 t} \right) . \end{aligned} \quad (7 - 70)$$

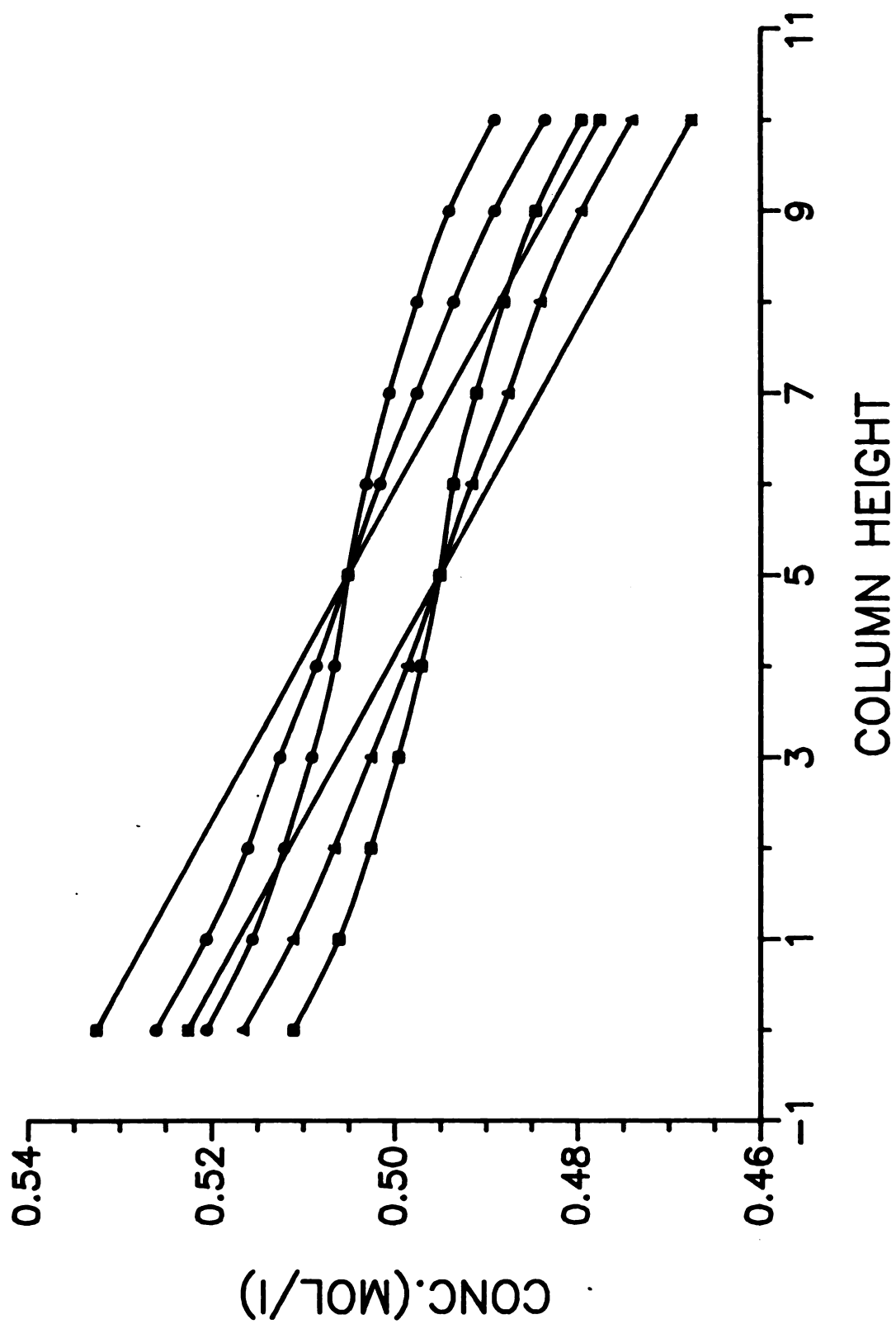
Figure(7-1)

Concentration distribution as a function of column width x at a given time t and column height z . For $c_2^0 = 0.5 \text{ mol./dm}^3$, $\Delta T = 10\text{K}$, column height $L = 10\text{cm}$. From top to bottom, line 1 represents the concentration distribution at $t = 1$ hour, $z = 0$ (bottom of the column); line 2, $t = 0.2$ hour, $z = 0$; line 3, $t = 0$, z ; line 4, $t = 0.2$ hour, $z = 10\text{cm}$ (top of the column); line 5, $t = 1$ hour, $z = 10\text{cm}$. Note that the TGTD steady state concentration distribution as a function of column width for any z is not linear because of convection along the column. At $t = 1.0$ hour, the distribution is almost steady state for $L = 10\text{cm}$. However, for PTD, the steady state concentration distribution is linear (Bierlein [1955], Horne and Anderson [1970]).



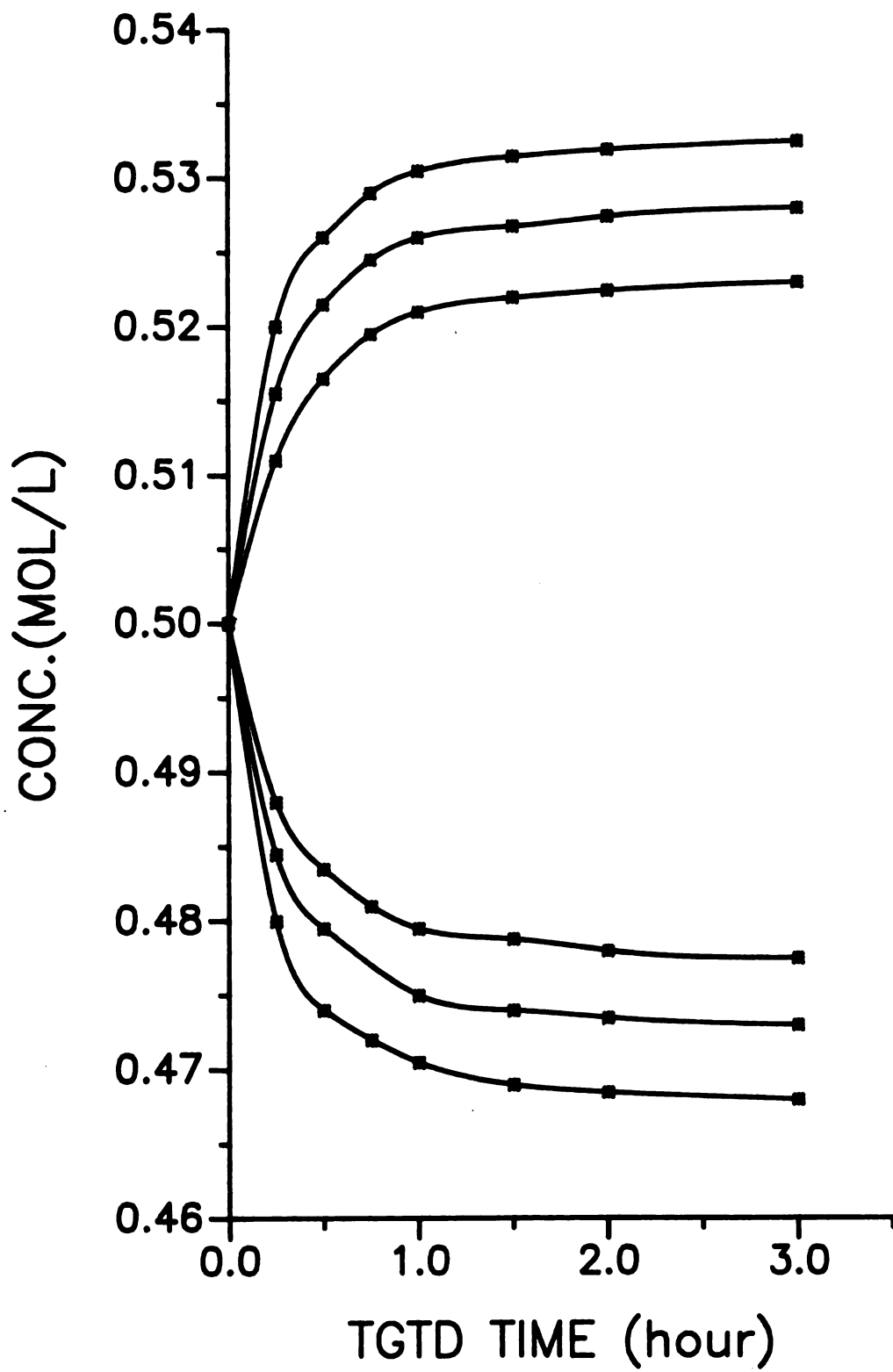
Figure(7-2)

Concentration distributions as functions of column height at a given x and t . Parameters are as in Fig.(7-1). Upper group curves ,from top to bottom, represent the concentration distribution at $x=1$ (at cold wall) and $t=\infty$, 0.5 and 0.25 hours respectively. Lower group curves from top to bottom, are at $x=-1$ (at hot wall) and $t=\infty$, 0.5, and 0.25 hours respectively.



Figure(7-3)

Concentration distributions as function of time t at a given x and z . Parameters are as in Fig.(7-1 and 2). Upper group curves:(at the bottom of the column, $z=0$), from top to bottom, $x=1$, 0 and -1 . Lower group curves:(at the top of the column, $z=10\text{cm}$), from top to bottom, $x=1$, 0, and -1 .



Figure(7-4)

Average concentration distributions at the top and bottom of the column as function of time t for a given column height L . Here, parameters as in Fig.(7-1) and Eq.(7-57) are used for the plots. Upper group curves are from top to bottom, at $L=50\text{cm}$, 30cm , and 10cm , and at $z=0$. Lower group curves, from top to bottom, $L=10\text{cm}$, 30cm , and 50cm and at $z=L$.

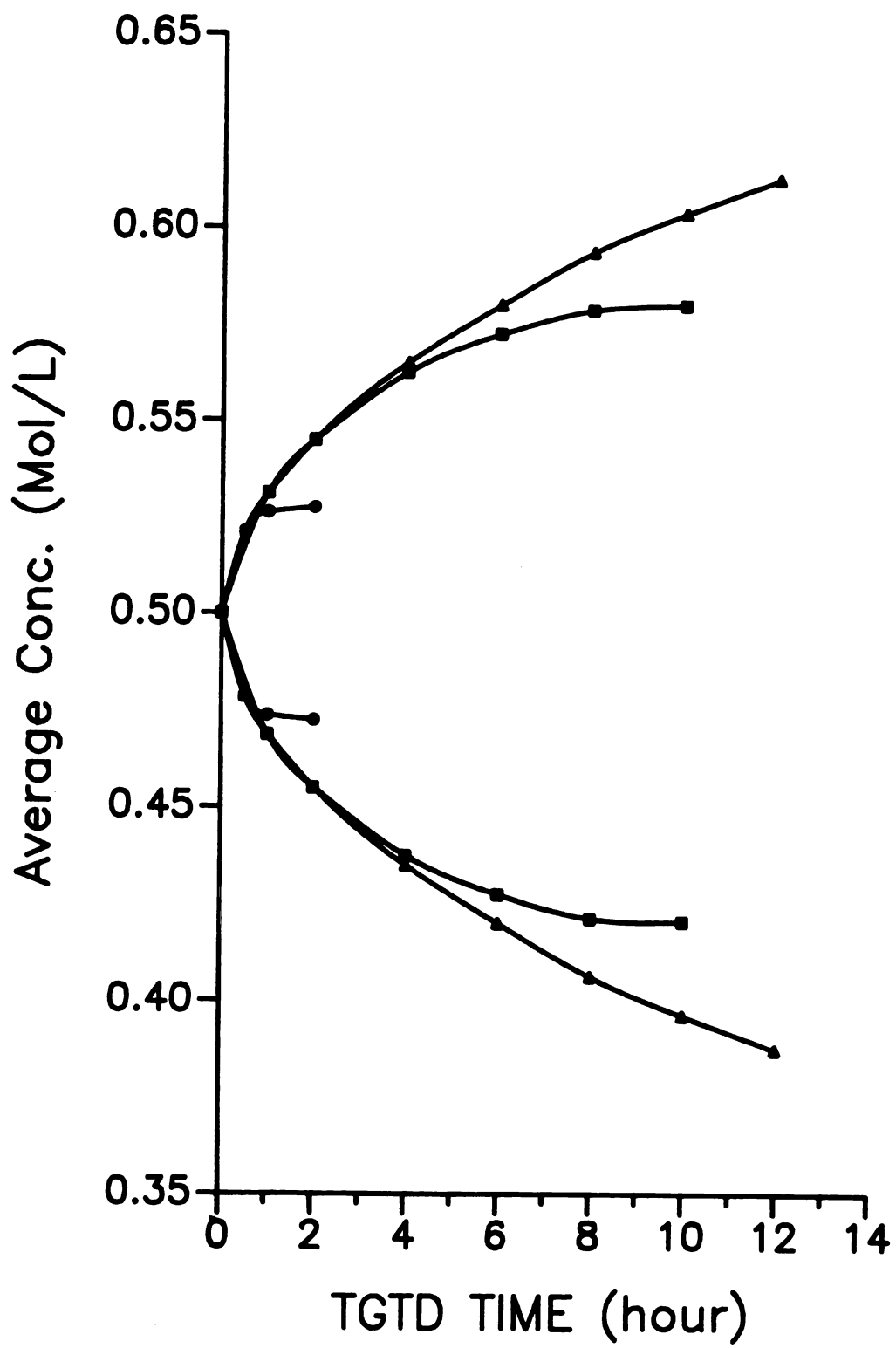


Table 7-1

Numerical comparison between the infinite summation and its asymptotic form for a given μ .

μ	$\sum_{n=0}^{\infty} \frac{e^{-\mu(2n+1)^2}}{(2n+1)^2}$	$\frac{\pi^2}{8} - \frac{(\pi\mu)^{1/2}}{2}$
0.00	$\pi^2/8$	$\pi^2/8$
.01	1.14507785	1.14507758
.1	.953450989	.953451000
.5	.6078	.60704

We have summed up to 500 terms in evaluating this infinite summation.

CHAPTER 8

THEORY OF RESERVOIRS

A. GENERAL REMARKS

In chapter 7, we discussed the time-dependent theory of a column with both ends closed. However, for the experimental purpose of evaluating Soret coefficients, the column with both ends closed is not the most useful. This is because the annular gap is usually very small and it is not easy to measure the concentration difference between the two ends, except at steady state. Many of the experimental studies of Soret coefficients have used a TGTD column with reservoirs connected to both ends of the column. The volumes of the reservoirs vary from about 15 up to 500cm³, and the two reservoirs may have equal or different volumes (de Groot [1945], Prigogine, de Brouckere, and Amand [1950], Horne and Bearman [1962], Beyerlein and Bearman [1964], Gaeta, Perna, Scala, & Bellucci [1982], Naokata and Kimie [1984]).

In general the temperature gradient is applied only to the column,

not to the reservoirs. Initially, the column and the reservoirs are filled with solution, with the concentration distribution uniform for the whole system. After the temperature gradient is applied to the column, solute will, in general, migrate downward and solvent upward. After a while, the lower reservoir becomes more concentrated than the solution in the column, and inside the reservoir, isothermal diffusion begins. Similarly, isothermal diffusion occurs inside the upper reservoir because the solute concentration is smaller at the entrance to the upper reservoir than it is within the reservoir. At steady state, the reservoir concentrations are the same as the concentrations at the entrances to the reservoirs. Thus the difference in reservoir concentration at steady state is the same as the difference in concentration between the two ends of the column. Because the volume of the reservoirs is much larger than that of the column, it is easier to monitor the concentration change in the reservoirs than in the column. That is why most experiments have utilized reservoirs.

Two kinds of apparatus have been used. One is the cylindrical type which we deal with in this work, while the other is a rectangular thermogravitational cell, combining two flat vertical plates, one heated and the other cooled (de Groot [1946], Tyrell [1961]). Traditionally, the theory of a time-dependent TGTD column with two reservoirs has been based on a theory developed for gaseous mixtures by Furry, Jones, and Onsager (1939), and Furry and Jones (1946). An approximate time dependent TGTD theory for dilute binary solutions was developed by de Groot (1946). The main assumption made in all previous approaches is that material reaching the upper or lower reservoir is almost instantaneously distributed uniformly throughout the reservoir. This assumption was first presented by Furry, Jones, and Onsager for the

treatment of TGTD in gases. It is nearly true for gases, because gas molecules diffuse much faster than liquid molecules. The diffusion constant is of order $0.1\text{cm}^2/\text{sec}$ for gases, but for liquid mixtures is of order $10^{-5}\text{cm}^2/\text{sec}$. Thus, for gases, molecules reaching the reservoirs can diffuse rapidly into them and they are rapidly distributed uniformly throughout the reservoirs. For liquid mixtures, the diffusion process is very slow. The working equation (Tyrell [1961]) for the concentration distribution in a TGTD apparatus with two equal reservoirs at short time based on the above assumption is

$$\left(\frac{c_B}{c_T} - 1\right) \approx \frac{\bar{\rho} \alpha g b a^3 (\Delta T)^2}{360 \eta V} s t, \quad (8-1)$$

where s is the experimental Soret coefficient, V the volume of reservoir, b is the width of the plate, and the other coefficients have their usual meanings. Thus if one could measure the solute concentrations c_B and c_T in the bottom and top reservoirs at a given time and given initial concentration, one will be able to evaluate s through Eq.(8-1). As we can see from Eq.(8-1) if $c_B/c_T > 1$, (for $T_M > 4^\circ\text{C}$), then s is positive and if $c_B/c_T < 1$, then s is negative. Clearly, if solute indeed concentrates in the lower reservoir then the Soret coefficient is positive. Soret coefficients determined by pure thermal diffusion experiments are positive and of order of 10^{-3}K . Recently, Gaeta and coworkers (1982) reported from their TGTD experiments that in certain concentration regions the ratio $c_B/c_T < 1$, and then s becomes negative for NaCl and KCl binary aqueous solutions. That is, in those concentration regions, the solute is enriched in the upper reservoir

rather than in the lower one. To explain this unusual experimental result, they suggest order-disorder transitions between solvent and solute which involve sharp changes in solvation. Later, however, Naokata and coworkers [1984] could not reproduce the unusual concentration dependence of Soret coefficient in their TGTD column. Gaeta et al. used a rectangular TGTD cell. Earlier, Prigogine et al. [1950] reported similar results from a rectangular TGTD cell.

In this work, the reservoir geometry is cylindrical, not rectangular. Experimentally, it is much easier to attain precise geometry and precise temperature control in a cylindrical apparatus.

B. DIFFERENTIAL EQUATION OF DIFFUSION

The fundamental differential equation of diffusion in an isotropic isothermal medium is, by Eq.(2-76),

$$\frac{\partial c_2}{\partial t} = D^* \nabla^2 c_2 \quad (8-2)$$

where c_2 is the solute concentration and D^* the modified diffusion coefficient. We neglect the convection velocity term $\mathbf{v} \cdot \nabla c_2$ in writing Eq.(8-2) because the reservoirs are assumed isothermal and convection will not occur. In cylindrical coordinates, Eq.(8-2) is

$$\frac{\partial c_2}{\partial t} = \frac{D^*}{r} \left\{ \frac{\partial}{\partial r} \left(r \frac{\partial c_2}{\partial r} \right) + \frac{1}{r} \frac{\partial^2 c_2}{\partial \phi^2} + r \frac{\partial^2 c_2}{\partial z^2} \right\}. \quad (8-3)$$

Assuming $\partial c_2 / \partial \phi = 0$, we have

$$\frac{\partial c_2}{\partial t} - \frac{D}{r} \left\{ \frac{\partial}{\partial r} \left(r \frac{\partial c_2}{\partial r} \right) + r \frac{\partial^2 c_2}{\partial z^2} \right\}. \quad (8-4)$$

To solve Eq.(8-4), boundary and initial conditions must be known. The initial condition is that at the time of starting the experiment, c_2 in the reservoirs is c_2^0 , the initial concentration. One end of the reservoir is closed and the other end is connected to the column. The boundary conditions for the closed end and for the outer wall reflect the fact that nothing will diffuse through the reservoir walls. The situation is very complicated for the end connected to the column because the concentration at the junction between column and reservoir is a function of space and time. If, however, the annular spacing of the column is much much less than that of the reservoir, and the concentration variation along r from r_1 to r_2 is very small in the column, we can replace $c_2(r, t)$ by its average concentration $\langle c_2(t) \rangle$. We write for the boundary conditions at the lower junction

$$c_2(r_2, z=0, t) = \langle c_2(t) \rangle = g(t), \quad r_1 \leq r \leq r_2, \quad (8-5)$$

where $g(t)$ is the average concentration at the bottom end of the column. For the diffusion process in the bottom reservoir, the differential equation and boundary conditions are

$$\frac{\partial c_2}{\partial t} - \frac{D}{r} \left\{ \frac{\partial}{\partial r} \left(r \frac{\partial c_2}{\partial r} \right) + r \frac{\partial^2 c_2}{\partial z^2} \right\}, \quad r_2 < r < r_3, \quad h < z < 0, \quad t > 0,$$

$$c_2(r_2, t, z=0) = g(t), \quad \left. \frac{\partial c_2}{\partial r} \right|_{r_3} = \left. \frac{\partial c_2}{\partial z} \right|_h = 0, \quad t > 0,$$

$$c_2(t=0) = c_2^0 \quad (8-6)$$

Eqs.(8-6) tell us that there is a point concentration source at the upper entrance to the bottom reservoir. Note that if the source term $g(t)$ is just c_2^0 , the solution of Eqs.(8-6) will be just $c_2 = c_2^0$. If $g(t) > c_2^0$, then solute will diffuse into the reservoir, while if $g(t) < c_2^0$, solute will diffuse out of the reservoir.

C. SOLUTION OF DIFFERENTIAL EQUATIONS

We first let

$$c_2 = U + c_2^0 \quad (8-7)$$

Then

$$\frac{\partial U}{\partial t} - \frac{D}{r} \left\{ \frac{\partial}{\partial r} \left(r \frac{\partial U}{\partial r} \right) + r \frac{\partial^2 U}{\partial z^2} \right\}, \quad r_2 < r < r_3, \quad h < z < 0 \quad t > 0,$$

$$U(r_2, t, z=0) = \bar{g}(t), \quad \left. \frac{\partial U}{\partial r} \right|_{r_3} = \left. \frac{\partial U}{\partial z} \right|_h = 0, \quad t > 0,$$

$$U(t=0) = 0, \quad \bar{g}(t) = g(t) - c_2^0 \quad (8-8)$$

Eqs.(8-8) can be solved if the solution of the following partial differential equation can be obtained

$$\frac{\partial W}{\partial t} - \frac{D}{r} \left\{ \frac{\partial}{\partial r} \left(r \frac{\partial W}{\partial r} \right) + r \frac{\partial^2 W}{\partial z^2} \right\}, \quad r_2 < r < r_3, \quad t > 0,$$

$$W(r_2, z=0) = 1, \quad \left. \frac{\partial W}{\partial r} \right|_{r_3} = \left. \frac{\partial W}{\partial z} \right|_h = 0, \quad t > 0,$$

$$W(t=0) = 0, \quad (8-9)$$

then (Carslaw and Jaeger [1959])

$$U(r, z, t) = \int_0^t \bar{g}(\lambda) \frac{\partial W}{\partial t}(t-\lambda) d\lambda. \quad (8-10)$$

If we suppose a form of solution for $W(r, z, t)$

$$W(r, z, t) = R(r, t) V(z, t), \quad (8-11)$$

Eqs.(8-9) become

$$\frac{\partial V}{\partial t} - D \frac{\partial^2 V}{\partial z^2}, \quad V(0, t) = 1, \quad \left. \frac{\partial V}{\partial z} \right|_h = 0, \quad t > 0,$$

$$V(t=0, z) = 0, \quad (8-12)$$

$$\frac{\partial R}{\partial t} - \frac{D}{r} \left\{ \frac{\partial}{\partial r} \left(r \frac{\partial R}{\partial r} \right) \right\}, \quad r_2 < r < r_3, \quad t > 0,$$

$$R(r_2) = 1, \quad \left. \frac{\partial R}{\partial r} \right|_{r_3} = 0, \quad t > 0,$$

$$R(t=0) = 0. \quad (8-13)$$

To derive Eqs.(8-12 and 13), we have assumed that $R(r=r_2, t) = V(z=0, t) = 1$,

$t > 0$, which means that at the origin, both functions equal unity, the same as unit concentration c_2^0 . This assumption is reliable if we take a look at the second equation of Eqs.(8-9). Physically, it tells us that at the origin, or at $r=r_2$, $z=0$, there is a constant concentration source of unity for $t > 0$, and at $t=0$ the concentration in the reservoir is initially zero. Solute does not flow out at r_3 and $z=h$. At the origin, the solute concentration will be unity along any direction, or the diffusion from the z direction is independent of the r direction, Thus the solution for W can be written as the form of the products of V and R .

The solution for V has two forms. Using a Laplace transformation, we have

$$V(z, t) = \sum_{m=0}^{\infty} (-1)^m \operatorname{erfc} \left[\frac{2h(m+1) - z}{2\sqrt{(D^* t)}} \right] + \sum_{m=0}^{\infty} (-1)^m \operatorname{erf} \left[\frac{2hm - z}{2\sqrt{(D^* t)}} \right], \quad (8 - 14)$$

where erf represents the error function with argument $\left[\frac{2hm - z}{2\sqrt{(D^* t)}} \right]$ and the

complementary error function is defined by $\operatorname{erfc}(x) = 1 - \operatorname{erf}(x)$. An alternative form can be derived by the method of separation of variables,

$$V(z, t) = 1 - \frac{4}{\pi} \sum_{m=0}^{\infty} \frac{\sin \left[\frac{(2m+1)}{2h} \pi z \right]}{(2m+1)^2} \exp \left(-\frac{(2m+1)^2 \pi^2 D^* t}{4h^2} \right). \quad (8 - 15)$$

The solution for $R(r, t)$ is

$$R=1+\pi \sum_{n=0}^{\infty} a(\alpha_n) \phi_0(\alpha_n r) e^{-\alpha_n^2 D^* t}, \quad a(\alpha_n) = \frac{J_1^2(\alpha_n r_3)}{J_0^2(\alpha_n r_2) - J_1^2(\alpha_n r_3)}, \quad (8-16)$$

with

$$\phi_0(\alpha_n r) = J_0(\alpha_n r) Y_0(\alpha_n r_2) - J_0(\alpha_n r_2) Y_0(\alpha_n r) \quad (8-17)$$

α_n satisfies

$$\phi_1(\alpha r_3) = J_1(\alpha r_3) Y_0(\alpha r_2) - J_0(\alpha r_2) Y_1(\alpha r_3) = 0. \quad (8-18)$$

For the details of solving these equations see Appendix A.

The solution for W is, by Eqs.(8-11,15 and 16), now

$$W = \left[1 + \pi \sum_{n=0}^{\infty} a(\alpha_n) \phi_0(\alpha_n r) e^{-\alpha_n^2 D^* t} \right] \left[1 - \frac{4}{\pi} \sum_{m=0}^{\infty} \Omega_m(z) e^{-d_m^2 D^* t} \right], \quad (8-19)$$

with

$$\frac{\sin \left[\frac{(2m+1)}{2h} \pi z \right]}{(2m+1)^2} = \Omega_m(z), \quad \frac{(2m+1)^2 \pi^2}{4h^2} = d_m^2. \quad (8-20)$$

The solution of Eqs.(8-6) is given by combining Eqs.(8-7,10 and 19)

$$\begin{aligned} & \frac{c_2}{c_0^2} - 1 + \int_0^t \bar{g}(\lambda) \frac{\partial}{\partial t} \left\{ \left[1 + \pi \sum_{n=0}^{\infty} a(\alpha_n) \phi_0(\alpha_n r) e^{-\alpha_n^2 D^* (t-\lambda)} \right] \right. \\ & \quad \left. \times \left[1 - \frac{4}{\pi} \sum_{m=0}^{\infty} \Omega_m(z) e^{-d_m^2 D^* (t-\lambda)} \right] \right\} d\lambda. \end{aligned} \quad (8-21)$$

D. DISCUSSION OF THE SOURCE FUNCTION

To obtain an exact solution for Eq.(8-21), an actual form for the source function $g(\lambda)$ must be known. From chapter 7, the average concentration distribution function as a function of time at the two ends of the column can be written approximately as

$$\langle c_2 \rangle_T = c_2^0 - \gamma(1 - e^{-\theta^2 D^* t}) c_2^0, \quad \langle c_2 \rangle_B = c_2^0 + \gamma(1 - e^{-\theta^2 D^* t}) c_2^0, \quad (8 - 22)$$

where

$$\gamma = KL/2, \quad \theta^2 = \frac{a^6 \pi^2}{362880 (D^*)^2} \left(\frac{\Delta T \rho_0 \alpha g}{\eta L} \right)^2. \quad (8 - 23)$$

Experimentally, it has been observed (Naokata and Kimie, [1984]) that the average concentration change in time at the column ends (for a column with reservoirs) has the same form as Eq.(8-22), but γ and θ are essentially adjustable parameters to the experimentalists.

Now we make the following assumptions for source functions at the two column ends.

$$g_B(t) = c_2^0 + \gamma c_2^0 (1 - e^{-\theta^2 D^* t}), \quad g_T(t) = c_2^0 - \gamma c_2^0 (1 - e^{-\theta^2 D^* t}), \quad (8 - 24)$$

and for short times the above equations reduce to

$$g_B(t) \approx c_2^0 (1 + \gamma \theta^2 D^* t), \quad g_T(t) \approx c_2^0 (1 - \gamma \theta^2 D^* t). \quad (8 - 25)$$

E. CONCENTRATION DISTRIBUTION IN THE RESERVOIR WITH EXPONENTIAL AND CONSTANT SOURCE FUNCTIONS

Substituting Eqs.(8-24) into Eq.(8-21) and making use of the last equation of Eqs.(8-8), the general solution is found for the concentration in the bottom reservoir. The detailed mathematical manipulations are presented in Appendix B.

$$\begin{aligned}
\frac{c_2^B}{c_2^0} = 1 + \gamma & \left[-\pi \sum_{n=0}^{\infty} \frac{\alpha_n^2 a(\alpha_n) \phi_0(\alpha_n r)}{\alpha_n^2 - \theta^2} \left(e^{-\alpha_n^2 D^* t} - e^{-\theta^2 D t} \right) + \frac{4}{\pi} \sum_{m=0}^{\infty} \frac{d_m^2 \Omega_m(z)}{d_m^2 - \theta^2} \times \right. \\
& \left. \left(e^{-d_m^2 D^* t} - e^{-\theta^2 D^* t} \right) + 4 \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{a(\alpha_n) \phi_0(\alpha_n r) \Omega_m(z) E_{mn}^2}{E_{mn}^2 - \theta^2} \left(e^{-E_{mn}^2 D^* t} - e^{-\theta^2 D^* t} \right) \right. \\
& + 4 \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} a(\alpha_n) \phi_0(\alpha_n r) \Omega_m(z) \left(1 - e^{-E_{mn}^2 D^* t} \right) + \frac{4}{\pi} \sum_{m=0}^{\infty} \Omega_m(z) \left(1 - e^{-d_m^2 D^* t} \right) \\
& \left. - \pi \sum_{n=0}^{\infty} a(\alpha_n) \phi_0(\alpha_n r) \left(1 - e^{-\alpha_n^2 D^* t} \right) \right], \quad (8-26)
\end{aligned}$$

where $E_{mn}^2 = \alpha_n^2 + d_m^2$.

Putting a minus sign in front of γ for Eq.(8-26), we obtain the concentration in the top reservoir. Note that at $t=0$, Eq.(8-26) is simply unity and as t approaches infinity, we get

$$\begin{aligned}
\frac{c_2^B}{c_2^0} = 1 + \gamma & \left[4 \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} a(\alpha_n) \phi_0(\alpha_n r) \Omega_m(z) + \frac{4}{\pi} \sum_{m=0}^{\infty} \Omega_m(z) \right. \\
& \left. - \pi \sum_{n=0}^{\infty} a(\alpha_n) \phi_0(\alpha_n r) \right]. \quad (8-27)
\end{aligned}$$

Using the relations (Appendix B)

$$\pi \sum_{n=0}^{\infty} a(\alpha_n) \phi_0(\alpha_n r) = -1, \quad \frac{4}{\pi} \sum_{m=0}^{\infty} \Omega_m(z) = 1, \quad (8-28)$$

we get from Eq.(8-27)

$$\frac{c_2^B}{c_2^0} = 1 + \gamma. \quad (8-29)$$

Therefore, when a steady state is established, the concentrations in the reservoirs will be equal to the concentrations at the two ends of the column. If we solve Eqs.(8-6) for steady state, we end up with the same result. This is also the previous result since upon averaging Eq.(7-54) and taking $z=0$, it is just Eq.(8-29).

Now we need to evaluate the average concentration change with time in the reservoirs. The average concentration is

$$\langle c_2^B(t) \rangle = \frac{1}{V_R} \int_0^{2\pi} \int_0^h \int_{r_2}^{r_3} r c_2^B(r, z, t) d\omega dr dz, \quad (8-30)$$

where V_R is the volume of reservoir. Making use of Eq.(8-26) as well as the integrals in the Appendices A and B we have

$$\begin{aligned} \frac{\langle c_2^B(t) \rangle}{c_2^0} = 1 + \frac{2\pi\gamma}{V_R} & \left[2h \sum_{n=0}^{\infty} \frac{a(\alpha_n)}{\alpha_n^2 - \theta^2} \left(e^{-\alpha_n^2 D^* t} - e^{-\theta^2 D^* t} \right) + \frac{r_3^2 - r_2^2}{h} \sum_{m=0}^{\infty} \frac{1}{d_m^2 - \theta^2} \times \right. \\ & \left. \left(e^{-d_m^2 D^* t} - e^{-\theta^2 D^* t} \right) + \frac{4}{h} \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{a(\alpha_n) E_{mn}^2}{\alpha_n^2 d_m^2 (E_{mn}^2 - \theta^2)} \left(e^{-\theta^2 D^* t} - e^{-E_{mn}^2 D^* t} \right) \right] \end{aligned}$$

$$\begin{aligned}
& + \frac{4}{h} \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{a(\alpha_n)}{d_m^2 \alpha_n^2} \left(e^{-E_{mn}^2 D^* t} - 1 \right) + \frac{r_3^2 - r_2^2}{h} \sum_{m=0}^{\infty} \frac{1}{d_m^2} \left(1 - e^{-d_m^2 D^* t} \right) \\
& + 2h \sum_{n=0}^{\infty} \frac{a(\alpha_n)}{\alpha_n^2} \left(1 - e^{-\alpha_n^2 D^* t} \right) \Bigg]. \quad (8-31)
\end{aligned}$$

At this stage, we have solved the reservoir problem. We have found the concentration distribution in the reservoir as a function of space and time as well as the average concentration change in time in the reservoir. However, Eq.(8-31) is too complicated to apply for practical purposes. We want particularly to know what will happen during the experimental time interval shortly after the beginning of the experiment.

Before answering that question, it is interesting to examine Eq.(8-31) for a special case. If θ^2 is much smaller than d_m^2 and α_n^2 , then $\alpha_n^2 - \theta^2 \approx \alpha_n^2$ and $d_m^2 - \theta^2 \approx d_m^2$. In other words, if the rate of flow into the reservoir determines the rate of the process and the solute diffusing into the reservoir will spread throughout the whole reservoir immediately, then Eq.(8-31) reduces to

$$\begin{aligned}
\frac{\langle c_2^B(t) \rangle}{c_2^0} = & 1 + \frac{2\pi\gamma}{V_R} \left[\frac{4}{h} \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{a(\alpha_n)}{d_m^2 \alpha_n^2} - \frac{r_3^2 - r_2^2}{h} \sum_{m=0}^{\infty} \frac{1}{d_m^2} - 2h \sum_{n=0}^{\infty} \frac{a(\alpha_n)}{\alpha_n^2} \right] \times \\
& \left(e^{-\theta^2 D^* t} - 1 \right). \quad (8-32)
\end{aligned}$$

Using the equations in Appendix B

$$\sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{a(\alpha_n)}{d_m^2 \alpha_n^2} = \frac{h^2}{8} (r_3^2 - r_2^2), \quad \sum_{m=0}^{\infty} \frac{1}{d_m^2} = \frac{h^2}{2},$$

$$\sum_{n=0}^{\infty} \frac{a(\alpha_n)}{\alpha_n^2} = \frac{1}{4} (r_3^2 - r_2^2), \quad (8-33)$$

to eliminate infinite sums in Eq.(8-32) we get simply

$$\frac{\langle c_2^B(t) \rangle}{c_2^0} = 1 + \gamma \left(1 - e^{-\theta^2 D^* t} \right). \quad (8-34)$$

This is just the same as Eq.(8-22). If $\theta^2 \rightarrow 0$, then the concentration is just the initial concentration in the reservoir. This case corresponds to the zero time situation.

On the other hand we rewrite Eq.(8-31) as

$$\begin{aligned} \frac{\langle c_2^B(t) \rangle}{c_2^0} = & 1 + \frac{2\pi\gamma}{V_R} \left[\frac{h}{2} (r_3^2 - r_2^2) - \frac{4}{h} \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{a(\alpha_n) \theta^2}{\alpha_n^2 d_m^2 (E_{mn}^2 - \theta^2)} e^{-E_{mn}^2 D^* t} \right. \\ & + \frac{r_3^2 - r_2^2}{h} \sum_{m=0}^{\infty} \frac{\theta^2}{d_m^2 (d_m^2 - \theta^2)} e^{-d_m^2 D^* t} + 2h \sum_{n=0}^{\infty} \frac{\theta^2 a(\alpha_n)}{\alpha_n^2 (\alpha_n^2 - \theta^2)} e^{-\alpha_n^2 D^* t} \\ & + \frac{4}{h} \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{a(\alpha_n) E_{mn}^2}{\alpha_n^2 d_m^2 (E_{mn}^2 - \theta^2)} e^{-\theta^2 D^* t} - \frac{r_3^2 - r_2^2}{h} \sum_{m=0}^{\infty} \frac{1}{d_m^2 - \theta^2} e^{-\theta^2 D^* t} \\ & \left. - 2h \sum_{n=0}^{\infty} \frac{a(\alpha_n)}{\alpha_n^2 - \theta^2} e^{-\theta^2 D^* t} \right]. \quad (8-35) \end{aligned}$$

To write down Eq.(8-35), we have rearranged Eq.(8-33) and used Eqs.(8-33). As $\theta^2 \rightarrow \infty$, Eq.(8-35) becomes,

$$\frac{c_2^B(t)}{c_2^0} = 1 + \frac{2\pi\gamma}{V_R} \left[\frac{h}{2}(r_3^2 - r_2^2) + \frac{4}{h} \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{a(\alpha_n)}{\alpha_n^2 d_m^2} e^{-E_{mn}^2 D^* t} - \frac{r_3^2 - r_2^2}{h} \sum_{m=0}^{\infty} \frac{1}{d_m^2} e^{-d_m^2 D^* t} - 2h \sum_{n=0}^{\infty} \frac{a(\alpha_n)}{\alpha_n^2} e^{-\alpha_n^2 D^* t} \right]. \quad (8-36)$$

This case corresponds to the constant source concentration since Eq.(8-36) could have been derived if we replace $\bar{g}(\lambda)$ in Eq(8-21) by the constant γ , and it tells us that if the source function is a constant, the rate of diffusion is only dependent on the reservoir's dimensions.

F. CONCENTRATION DISTRIBUTION IN THE RESERVOIR WITH A LINEAR SOURCE FUNCTION

If the source function is linear in time, we substitute Eqs.(8-25) into Eq.(8-21) and make use of the last equation of Eqs.(8-8) to derive

$$\frac{c_2^B}{c_2^0} = 1 + \gamma \theta^2 \left[D^* t + \pi \sum_{n=0}^{\infty} \frac{a(\alpha_n) \phi_0(\alpha_n r)}{\alpha_n^2} \left(1 - e^{-\alpha_n^2 D^* t} \right) - \frac{4}{\pi} \sum_{m=0}^{\infty} \frac{\Omega_m(z)}{d_m^2} \left(1 - e^{-d_m^2 D^* t} \right) - 4 \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{a(\alpha_n) \phi_0(\alpha_n r) \Omega_m(z)}{E_{mn}^2} \left(1 - e^{-E_{mn}^2 D^* t} \right) \right]. \quad (8-37)$$

Applying Eq.(8-30), we have for the average concentration change in time in the bottom reservoir

$$\begin{aligned} \frac{\langle c_2^B \rangle}{c_2^0} = & 1 + \gamma \theta^2 \left[D^* t - \frac{4\pi\hbar}{V_R} \sum_{n=0}^{\infty} \frac{a(\alpha_n)}{\alpha_n^4} \left(1 - e^{-\alpha_n^2 D^* t} \right) - \frac{2\pi(r_3^2 - r_2^2)}{\hbar V_R} \sum_{m=0}^{\infty} \frac{1}{d_m^4} \left(1 - e^{-d_m^2 D^* t} \right) \right. \\ & \left. + \frac{8\pi}{\hbar V_R} \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{a(\alpha_n)}{(d_m \alpha_n E_{mn})^2} \left(1 - e^{-E_{mn}^2 D^* t} \right) \right]. \quad (8-38) \end{aligned}$$

Obviously, there is no steady state solution for a source function linear in time. However, since we are more interested in early time, we assume that the time is short enough that we can expand all exponential times in Eq.(8-38). On the other hand we notice that all summations in Eq.(8-38) converge very fast. At early time, the average concentration change will be almost linear. This is because the terms

$$1 - e^{-E_{nm}^2 D^* t}, \quad 1 - e^{-\alpha_n^2 D^* t}, \quad \text{and} \quad 1 - e^{-d_m^2 D^* t}$$

will all be linear for small time intervals and these infinite sums converge after only a few terms. Although the main feature of Eq.(8-38) is that $\langle c_2 \rangle$ is almost linear in time, it is not easy to make a satisfactory simplification for this

equation because the term $\sum_{n=0}^{\infty} \frac{a(\alpha_n)}{\alpha_n^4}$ cannot be written in a closed form

(we can show that

if α_n^k for $k=2,3,\dots$, the sum $\sum_{n=0}^{\infty} \frac{a(\alpha_n)}{\alpha_n^k}$ has a closed form only for $k=2$,

and for $k>2$ there are no closed mathematical expressions). Here $a(\alpha_n)$

and α_n are given by Eqs.(8-16 and 17).). If θ^2 is known, Eq.(8-38)

should be used to evaluate the Soret coefficient. We still want a more simplified equation, and as an approximation, we take only one term for all sums and expand the exponential terms. (The exact way of simplifying Eq.(8-38) is to work out the asymptotic forms for terms such as

$$\sum_{n=0}^{\infty} \frac{a(\alpha_n)}{\alpha_n^k} \text{ and}$$

$$\sum_{n=0}^{\infty} \frac{a(\alpha_n)}{\alpha_n^k} e^{-\alpha_n^2 D^* t} . \text{ This approach is fraught with mathematical}$$

difficulties.) Thus we have

$$\begin{aligned} \sum_{n=0}^{\infty} \frac{a(\alpha_n)}{\alpha_n^4} \left(1 - e^{-\alpha_n^2 D^* t}\right) &\approx a(\alpha_0) (D^* t / \alpha_0^2), & \sum_{m=0}^{\infty} \frac{1}{d_m^4} \left(1 - e^{-d_m^2 D^* t}\right) &\approx D^* t / d_0^2 \\ \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{a(\alpha_n)}{(d_m \alpha_n E_{mn})^2} \left(1 - e^{-E_{mn}^2 D^* t}\right) &\approx \frac{a(\alpha_0) D^* t}{\alpha_0^2 d_0^2} . \end{aligned} \quad (8-39)$$

Substituting these equations into Eq.(8-38) and rearranging, we obtain a very approximate linear equation

$$\begin{aligned} \frac{\langle c^B(t) \rangle}{c_2^0} &= 1 + \left[1 - \left(\frac{8}{\pi^2} + \frac{4a(\alpha_0)(\pi^2 - 8)}{\alpha_0^2 \pi^2 (r_3^2 - r_2^2)} \right) \right] \gamma \theta^2 D^* t . \\ &= 1 + \left(1 - \frac{8}{\pi^2} \right) \left[1 - \frac{4a(\alpha_0)}{\alpha_0^2 (r_3^2 - r_2^2)} \right] \gamma \theta^2 D^* t , \end{aligned} \quad (8-40)$$

where we used the relation $V_R = \pi h(r_3^2 - r_2^2)$.

The average concentration change in the upper reservoir is given by putting a minus sign in front of γ for Eq.(8-40), which is

$$\frac{\langle c^T(t) \rangle}{c_2^0} = 1 - \left[1 - \left(\frac{8}{\pi^2} + \frac{4a(\alpha_0)(\pi^2 - 8)}{\alpha_0^2 \pi^2 (r_3^2 - r_2^2)} \right) \right] \gamma \theta^2 D^* t.$$

$$= 1 - \left(1 - \frac{8}{\pi^2} \right) \left[1 - \frac{4a(\alpha_0)}{\alpha_0^2 (r_3^2 - r_2^2)} \right] \gamma \theta^2 D^* t \quad (8 - 41)$$

The error caused by Eq.(8-40 and 41) will be dependent on the relaxation time; the smaller the time, the better the Eqs.(8-40 and 41). This can be seen by the following arguments. First we write

$$\sum_{m=0}^{\infty} \frac{1}{d_m^4} \left(1 - e^{-d_m^2 D^* t} \right) = \frac{16h^4}{\pi^4} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^4} (1 - e^{-B(2m+1)^2}), \quad (8 - 42)$$

where

$$B = \left(\frac{\pi}{2h} \right)^2 D^* t. \quad (8 - 43)$$

Then, we put

$$\sum_{m=0}^{\infty} \frac{1}{(2m+1)^4} (1 - e^{-B(2m+1)^2}) \approx B. \quad (8 - 44)$$

Table(8-1) shows the numerical comparison between B and Eq.(8-42). For $B \leq 0.2$, the relative error due to Eq.(8-44) is about 3% and the error is about 9% for $B \leq 0.3$. We assume $B \leq 0.2$, then

$$t \leq \frac{0.8h^2}{\pi^2 D^*}. \quad (8 - 45)$$

This tells us that if Eq.(8-44) is used to replace the infinite sum, and the error due to this approximation is expected to be less than 3%, then

t must satisfy Eq.(8-45). For $h=2\text{cm}$, Eq.(8-45) gives $t \leq 9$ hours.

Table 8-1

B	0.0	0.1	0.2	0.3
$\sum_{m=0}^{\infty} \frac{1}{(2m+1)^4} (1 - e^{-B(2m+1)^2})$	0.0	0.1046	0.194	0.271

The situation for $\sum_{n=0}^{\infty} \frac{a(\alpha_n)}{\alpha_n^4} \left(1 - e^{-\alpha_n^2 D^* t}\right)$ is, however, much more

complicated, for only the smallest (the first) roots are tabulated for $r_3/r_2 > 1$ (Bogert [1951]). We are unable to give a comparison like Table 3, but we know that α_n increases very rapidly as n increases. The asymptotic forms of α_n and $a(\alpha_n)$ are given by α'_n and $a(\alpha'_n)$

$$\alpha'_n \approx \frac{(2n+1)\pi}{2(r_3 - r_2)}, \quad a(\alpha'_n) \approx \frac{r_2 [1 - \sin(2\alpha'_n r_3)]}{r_3 [1 + \sin(2\alpha'_n r_2)] - r_2 [1 + \sin(2\alpha'_n r_3)]} \quad (8 - 46)$$

This relation is valid only for large n . In table 4 we give a comparison between the first roots calculated by Eq.(8-18) and Eqs.(8-46) for a given ratio of r_3/r_2 . $a(\alpha'_0)$ and $a(\alpha'_0)$ are calculated by the second equation of Eqs.(8-46).

The table suggests that α_n increases as n increases. We therefore assume

$$\sum_{n=0}^{\infty} \frac{a(\alpha_n)}{\alpha_n^4} \left(1 - e^{-\alpha_n^2 D^* t}\right) \approx \frac{a(\alpha_0)}{\alpha_0^4} \left(1 - e^{-\alpha_0^2 D^* t}\right) + \sum_{n=1}^{\infty} \frac{a(\alpha'_n)}{(\alpha'_n)^4} \left(1 - e^{-(\alpha'_n)^2 D^* t}\right)$$

$$\approx a(\alpha_0) D^* t / \alpha_0^2 \quad (8 - 47)$$

$$\alpha_0^2 D^* t \leq A \quad (8 - 48)$$

For error less than 3% for above equation, $A \leq 0.2$.

Table 8-2

r_3/r_2	1.01	1.10	1.20	1.50	2.00	3.00	5.00
α_0	$\frac{156.8}{r_2}$	$\frac{15.41}{r_2}$	$\frac{7.57}{r_2}$	$\frac{2.90}{r_2}$	$\frac{1.36}{r_2}$	$\frac{0.63}{r_2}$	$\frac{0.28}{r_2}$
α'_0	$\frac{157.1}{r_2}$	$\frac{15.71}{r_2}$	$\frac{7.85}{r_2}$	$\frac{3.14}{r_2}$	$\frac{1.57}{r_2}$	$\frac{0.79}{r_2}$	$\frac{0.39}{r_2}$
$a(\alpha_0)$	----	16.08	5.82	1.42	1.54	0.68	0.44
$a(\alpha'_0)$	100	10.0	5.00	2.00	1.00	0.33	0.207
α'_0	$\frac{471.2}{r_2}$	$\frac{47.1}{r_2}$	$\frac{33.6}{r_2}$	$\frac{9.42}{r_2}$	$\frac{4.71}{r_2}$	$\frac{2.36}{r_2}$	$\frac{1.18}{r_2}$

If we require that the relaxation time along the z direction is the same as along r, then from Eq.(8-48) and Eq.(8-43) (taking the equal sign), the height of reservoir is related to r by

$$h^2 = \frac{\pi^2}{4\alpha_0^2} \left(\frac{A}{B} \right). \quad (8-49)$$

Thus Eq.(8-49) must be used for proper design of the reservoirs, and the constants A and B are determined by Eq.(8-47) and Eq.(8-44). If α_n is given by Eq.(8-46) and $r_3 - r_2 = h$, then by Eq.(8-48 and 43), $A=B$ and Eq.(8-49) is an identity.

Now we combine Eqs.(8-40 and 41) to derive

$$\frac{\langle c_2^B \rangle}{\langle c_2^T \rangle} - 1 = \frac{2\bar{\gamma}D^*\theta^2t}{1 - \bar{\gamma}D^*\theta^2t}, \quad (8-50)$$

$$\bar{\gamma} = \gamma \left[1 - \left(\frac{8}{\pi^2} + \frac{4a(\alpha_0)(\pi^2 - 8)}{\alpha_0^2 \pi^2 (r_3^2 - r_2^2)} \right) \right] = \gamma \left(1 - \frac{8}{\pi^2} \right) \left[1 - \frac{4a(\alpha_0)}{\alpha_0^2 (r_3^2 - r_2^2)} \right] \gamma \theta^2 D^* t$$

If $\bar{\gamma}D^*\theta^2t$ is much less than 1, (true for $t \leq 5$ hours) this leads to

$$\frac{\langle c_2^B \rangle}{\langle c_2^T \rangle} - 1 = \frac{2\bar{\gamma}D^*\theta^2t}{1 - \bar{\gamma}D^*\theta^2t} \approx 2\bar{\gamma}D^*\theta^2t \quad (8-51)$$

Eq.(8-51) is our working equation for calculating the Soret coefficient from a TGT D experiment at an early time period. The time length is controlled by the dimensions of the reservoir. Eq.(8-49) gives the

relation between h and r and A and B are determined properly from the accuracy requirement of the approximation of Eqs.(8-44 and 47).

Now we replace θ^2 by Eqs.(8-23) to give a practical form of the working equation

$$\frac{\langle c_2^B \rangle}{\langle c_2^T \rangle} - 1 = \frac{[a\pi(\Delta T)]^2}{6!} \left(\frac{\rho_0 \alpha g}{\eta L} \right) \left[1 - \left(\frac{8}{\pi^2} + \frac{4a(\alpha_0)(\pi^2 - 8)}{\alpha_0^2 \pi^2 (r_3^2 - r_2^2)} \right) \right] \sigma^* t \quad (8-52)$$

Eq.(8-52) is to be compared with Eq.(8-1). Using Gaeta and coworker's data (1982), $V_R = 15 \text{ cm}^3$, $a = 0.045$, $b = 8 \text{ cm}$, $L = 4.8 \text{ cm}$ and $\Delta T = 16^\circ \text{C}$, we calculate the numerical coefficients for these two equations. We take $V_R = \pi h(r_3^2 - r_2^2) = 15 \text{ cm}^3$ and assume $r_3^2/r_2^2 = 2$, then use Eq.(8-49) to evaluate h (we have taken $A=B=0.2$). We get $h = 1.155 \text{ cm}$, $r_2 = 1.174 \text{ cm}$, $r_3 = 2.34$ and $a(\alpha_0)$ as well as α_0 is from table 4. Substituting these values into Eq.(8-52) and Eq.(8-1) we find

$$\frac{\langle c_2^B \rangle}{\langle c_2^T \rangle} - 1 \approx 5.4 \times 10^{-5} \left(\frac{\rho_0 \alpha g}{\eta} \right) \sigma^* t, \quad \sigma^* = c_1 \bar{V}_1 s - \alpha \quad (8-53)$$

$$\frac{\langle c_2^B \rangle}{\langle c_2^T \rangle} - 1 \approx 3.5 \times 10^{-5} \left(\frac{\rho_0 \alpha g}{\eta} \right) s t, \quad (8-54)$$

Because s and σ^* are of the order of 10^{-3} , we expect Eqs.(8-53 and 54) are also the same order; then Eq.(8-52) and Eq.(8-1) are qualitatively equal. A better result is derived if we remember

$$\frac{1}{1-x} = 1+x+x^2+x^3+\dots; \quad (8-55)$$

then a better approximation for Eq.(8-50) is

$$\frac{\langle c_2^B \rangle}{\langle c_2^T \rangle} - 1 = \frac{2\bar{\gamma}D^*\theta^2t}{1-\bar{\gamma}D^*\theta^2t} \approx 2\bar{\gamma}D^*\theta^2t(1+\bar{\gamma}D^*\theta^2t), \quad (8-56)$$

where the $\bar{\gamma}D^*\theta^2t$ is given by Eqs.(8-23). Eq.(8-56) is a second order algebraic equation for σ^* . By solving it we will have two values for σ^* , and only a meaningful root will be applicable to evaluate s from the last equation of Eqs.(8-53).

As we pointed out the working equation Eq.(8-52) is only an approximation, but we do think it will be applicable at least qualitatively under the requisite experimental conditions. Furthermore, justification of usage of θ^2 from Eq.(8-23) must be done experimentally.

G. SUMMARY AND DISCUSSION

In this chapter we developed the theory of TGTD column with two equal volume reservoirs. The theory is based on diffusion. The practical differential equation for the diffusion process in the reservoirs is established using this model. The equation is solved to obtain the concentration distribution in the reservoirs as a function of space and time. The solution is dependent on the choices of the boundary concentration distribution, i.e the source function. Several special cases were discussed, and corresponding equations were developed.

We were particularly interested in deriving a working equation applicable at an early stage of the experiment and from which the thermal diffusion coefficients or Soret coefficients could be estimated. The result is given in section F. For certain restrictions of reservoir dimensions as well as time, we do obtain a working equation to estimate the Soret coefficients if the average concentrations in both top and bottom reservoirs are measured. Because at present we do not know the asymptotic expansions such as

$$\sum_{n=0}^{\infty} \frac{a(\alpha_n)}{\alpha_n^4} \left(1 - e^{-\alpha_n^2 D^* t} \right), \quad \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{a(\alpha_n)}{(d_m \alpha_n E_{mn})^2} \left(1 - e^{-E_{mn}^2 D^* t} \right), \quad (8 - 57)$$

the accuracy of the working equation given in section F is uncertain. If possible Eq.(8-38) should be used. However, at present, only the smallest roots are given for different ratios of r_3/r_2 . The difficulty of computing the roots of Eq.(8-18) hinders usage of Eq.(8-38). We are unable to find the asymptotic roots for Eq.(8-18) because the arguments cannot be made large enough to do so. We hope this difficulty will be solved later.

Another important aspect of TGTD with reservoirs is that although the general form of exponential decay type source function is confirmed experimentally (Naokata and Kimie [1984]) and used in our problem, the actual form of relaxation time for such exponential decay is not yet established. The source function relaxation time used to derive our working equation was borrowed from the theory of TGTD without reservoirs. Our linear source function came from the direct expansion of the exponential term as time t is small. This "short-time" scale depends

upon the dimensions of the column, and the temperature gradient as well as the physical properties of the solution, as can be seen from Eqs.(8-23). Usually, this "short-time" is about a few hours for a typical column and ΔT . Time dependent TGTD is a very sophisticated problem even without reservoirs. For TGTD with reservoirs, we used our diffusion model so that the problem can be attacked, and find a very approximate working equation to estimate Soret coefficients.

There is a marked discrepancy between the working equation derived by us and the one used before. However we see from our numerical calculation that the two working equations are of the same order, which means that a cylindrical type TGTD column gives about the same separation of solute from solvent with a rectangular cell type TGTD column. However, the biggest difference between our equation and the one used before is that Eq.(8-52) is made of two terms with opposite signs. This can be seen by rewriting Eq.(8-52)

$$\frac{\langle c_2^B \rangle}{\langle c_2^T \rangle} - 1 - \frac{[a(\Delta T)]^2}{6!} \left(\frac{\rho_0 \alpha g}{\eta L} \right) (\pi^2 - 8) \left[1 - \frac{4a(\alpha_0)}{\alpha_0^2(r_3^2 - r_2^2)} \right] \sigma^* \tau. \quad (8 - 58)$$

Because all terms outside the square bracket are positive, the sign change depends on the two terms in the bracket. If the second term in

the bracket is larger than 1, then $\frac{\langle c_2^B \rangle}{\langle c_2^T \rangle}$ is less than 1, the

concentration in the bottom reservoir is less than that in the top reservoir, thus instead of migrating to the bottom reservoir, solute moves against the temperature gradient up to top reservoir. This is true

if the reservoir is very small. Using table 4 we found that if $r_3/r_2 < 1.2$

then the square bracket term is negative, and $\langle c_2^B \rangle$ is less than $\langle c_2^T \rangle$.

But if $r_3/r_2 > 1.2$, then solute concentrated in the bottom reservoir as it usually does (We remind the readers here that we did find by calculating the concentration distributions in the column without reservoirs at very early time period that when column length is over 20 cm, the solution is a little bit more concentrated at upper section of the column.). Therefore, in order to ensure that the solution is more concentrated in the bottom reservoir, one has to design one's reservoir carefully, and our equation provides a useful qualitative criteria for that purpose.

The disadvantage of the old working equation is that if $\frac{\langle c_2^B \rangle}{\langle c_2^T \rangle}$ is less

than 1, one obtains a negative Soret coefficient or thermal diffusion coefficient from the old equation. Then to explain such an unusual situation of electrolyte solutions at low concentrations (about 5×10^{-3} to 1.3×10^{-1} mol) and an average temperature of around 30°C , the authors (Gaeta et al. [1982]) claimed that there must be a phase transition under the conditions described above. But from our working equation, it is apparent that the possibility that a negative sign occurs for Eq.(8-58) is due to the improper choices of the dimensions of the reservoirs such that $r_3^2 - r_2^2$ is too small. In other words, for small reservoirs, it is possible to make a conversion of direction of regular TGT during the early time of experiment. Because we did not work out the TGT theory for a rectangular cell, we are unable to apply our working equation to recalculate Gaeta et al.'s experimental results. If larger reservoirs had been used in their experiments, negative Soret

coefficients would probably not have occurred. Our conclusion implies that it is unlikely that there is any kind of phase transition in dilute electrolyte solution. The conversion of TGT D is more likely due to improper design of the apparatus. We also mention here that Naokata and Kimie [1984] were unable to reproduce the results of Gaeta et al. From our point of view this is because they used relatively larger and cylindrical geometry reservoirs. Moreover the pure thermal diffusion experiments of Petit, Renner, and Lin (1984) yielded only positive Soret coefficients.

Since the Japanese workers reported explicitly the detailed time course of their results (through curves), it is should be possible to obtain σ^* from their paper as long as the dimensions of reservoirs are given. It is not possible to recalculate the Italian results to obtain reliable σ^* since the Italians report only their calculated results, not their experimental results.

CHAPTER 9

SUGGESTIONS FOR FUTURE WORK

We have already seen from previous chapters that the complexity of time-dependent TGTG prevents us from solving the problem exactly. Only the zeroth or for some cases at most the first order solutions are obtained, and nothing can be done for the solutions with order higher than 1. However, we still have had a clear and deep look at the time-dependent TGTG problem and have established a solid foundation for any further research on the problem. Whenever possible, a numerical solution should be done to check the accuracy of the perturbation solutions. For the steady state, we have found an accurate result, but more research is required for the transient state, particularly for the transient state with two reservoirs.

The situation for the transient state with reservoirs is extremely complicated due to the uncertain boundary conditions at the column ends. We thus hope to reformulate a proper mathematical form for matter flux at the interfaces between the column and reservoirs either empirically or theoretically, so that one can derive the corresponding boundary conditions in the transient state. At the interfaces where the

temperature gradient vanishes, the formulation of matter flux at interfaces is not easy, and even if it could be done, the boundary conditions would be too complicated to hold out much hope of solving the concentration equation.

In chapter 8, we found the concentration distribution in the reservoirs based on diffusion models, but we still do not know the concentration distribution in the column. The average matter flux has following form:

$$j_z^* = Kc_2^0 D^* (L - 2z) (1 - e^{-\lambda^2 t}) \text{ at } z = 0, L, \quad (9 - 1)$$

where $Kc_2^0 D^* (L - 2z)$ is the steady state flux of the column without reservoirs. Note that $j_z^* (z=0) = -j_z^* (L)$, which is to say that the flux is antisymmetric at the two ends. When a final steady state is reached, the concentrations in the top or bottom reservoirs are the concentrations at the respective ends of the column. The only disturbance in the reservoir comes from the interfaces where concentration gradients are built up due to TGTG in the column. We expect that the factor λ^2 will be a very complicated quantity dependent on the dimensions of reservoirs as well on the properties of electrolyte solutions. One possibility is that

$$\lambda^2 = C(L, a) \frac{\rho \beta (\Delta T)^2 D^* \sigma^*}{\eta} V_R, \quad (9 - 2)$$

where $C(L, a)$ is a constant which depends on the dimensions of the column

and V_R is the volume of the reservoirs, (Tyrrell [1962]), Naokata and Kimie [1984]). On the other hand, the zeroth order average flux in the column is from chapter 7,

$$j_z = \frac{8D^*e^{-KL}}{a^2} \left(H\bar{\phi}_0 - E \frac{\partial \bar{\phi}_0}{\partial z} \right). \quad (9-3)$$

On the boundaries, or at the interfaces, these two fluxes must be the same, thus at $z = 0, L$,

$$j_z^* - Kc_2^0(L-2z)(1-e^{-\lambda^2 t}) - \frac{8D^*e^{-KL}}{a^2} \left(H\bar{\phi}_0 - E \frac{\partial \bar{\phi}_0}{\partial z} \right) = j_z. \quad (9-4)$$

An alternative way of looking at this problem is that the net flux in the column is

$$j_N = j_z - j_z^*, \quad (9-5)$$

where the additional term is due to the reservoir effect. After subtracting this effect we have the modified flux j_N , which is still zero. Combining Eq. (7-48) with (9-4), we have the following differential equation with proper boundary and initial conditions.

$$\frac{\partial^2 \bar{\phi}_0}{\partial z^2} - k \frac{\partial \bar{\phi}_0}{\partial z} - \frac{2b^2}{E} \frac{\partial \bar{\phi}_0}{\partial t} = 0,$$

$$\frac{\partial \bar{\phi}_0}{\partial z} = K\bar{\phi}_0 - \frac{a^2}{8D^*E} Kc_2^0 (1 - e^{-\bar{\lambda}^2 DV_T t}) e^{LK} \Big|_{z=0},$$

$$\frac{\partial \bar{\phi}_0}{\partial z} = K\bar{\phi}_0 + \frac{a^2}{8D^*E} Kc_2^0 (1 - e^{-\bar{\lambda}^2 DV_T t}) e^{LK} \Big|_{z=L},$$

$$\bar{\phi}_0 = KZC_2^0 e^{KL}, \text{ at } t=0, \bar{\lambda}^2 = C(L, a) \frac{\rho\beta(\Delta T)^2 \sigma^*}{\eta}, \quad (9-6)$$

where V_T and V_B are respectively the volume of top and bottom reservoirs. The above equation reduces to Eq. (7-48) as V_R approaches to zero. Solution of Eqs.(9-6) will be not easy because of time dependent boundary conditions and the actual form of λ^2 must be given. It is hoped that this can be done to get the concentration distribution in the TGTD column with two reservoirs.

In chapter 8, the concentration distribution in the reservoir is given, and a simple transient working equation is derived to estimate the Soret coefficients. Because of the difficulty of evaluating the higher roots of Eq. (8-18), the first term is used to accomplish the transient working equation. Numerical work is needed to give some higher order roots for Eq. (8-18), thus a more accurate working equation could be given by counting more terms of the infinite summations. From the point of view of mathematics, the best way is to work out the asymptotic forms of following sums such as

$$\sum_{n=1}^{\infty} \frac{a(\alpha_n)}{\alpha_n^2} e^{-\alpha_n^2 Dt}, \quad \sum_{n=1}^{\infty} \frac{a(\alpha_n)}{(\alpha^2 - \theta^2)} e^{-\alpha_n^2 Dt}.$$

A P P E N D I X A

SOLUTION OF PARTIAL DIFFERENTIAL EQUATION (8 - 13)

$$\frac{\partial R}{\partial t} = \frac{D}{r} \frac{\partial}{\partial r} \left(r \frac{\partial R}{\partial r} \right) , \quad R(r=r_2)=1, \quad \left. \frac{\partial R}{\partial r} \right|_{r=r_3} = 0$$

$$R(t=0)=0 \quad . \quad (A - 1)$$

If

$$R(r, t) = \Phi(r, t) + V(r) , \quad (A - 2)$$

then Eqs.(A-1) becomes

$$\frac{\partial \Phi}{\partial t} = \frac{D}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \Phi}{\partial r} \right) , \quad \Phi(r=r_2)=0, \quad \left. \frac{\partial \Phi}{\partial r} \right|_{r=r_3} = 0$$

$$\Phi(t=0) = -V(r) , \quad (A - 3)$$

and

$$\frac{d}{dr} \left(r \frac{dV}{dr} \right) = 0, \quad V(r_2)=1, \quad \left. \frac{dV}{dr} \right|_{r_3} = 0 \quad . \quad (A - 4)$$

The solution of Eqs.(A-4) is

$$V(r)=1 \quad (A - 5)$$

We solve Eqs.(A-1) by the method of separation of variables. Writing

$$\Phi(r,t)=T(t)\phi(r), \quad (A - 6)$$

we have

$$\frac{d}{dr}\left(r\frac{d\phi}{dr}\right)+\alpha^2\phi=0, \quad \phi(r_2)=1, \quad \left.\frac{d\phi}{dr}\right|_{r_3}=0, \quad (A - 7)$$

and

$$\frac{dT}{dt}=-\alpha^2DT, \quad (A - 8)$$

with α^2 an arbitrary separation constant. The solution of Eq.(A-8) is

$$T(t)=ae^{-\alpha^2Dt}, \quad (A - 9)$$

where a is an integration constant. To solve Eqs.(A-7), we make the independent variable transform

$$r=\beta x. \quad (A - 10)$$

This gives, by Eqs.(A-7 and 10),

$$\frac{d^2\phi}{dx^2}+\frac{1}{x}\frac{d\phi}{dx}+(\alpha\beta)^2\phi=0. \quad (A - 11)$$

If $\alpha\beta=1$, then

$$r=x/\alpha \quad (A - 12)$$

Eq.(A-11) is a standard form of Bessel's differential equation of the zeroth order if Eq.(A-12) is satisfied. One of the the solution is

$$\phi_0(r) = AJ_0(\alpha r) + BY_0(\alpha r), \quad B = -\frac{J_0(\alpha r_2)}{Y_0(\alpha r_2)}A, \\ \phi'_0(\alpha r_3) - J'_0(\alpha r_3)Y_0(\alpha r_2) - J_0(\alpha r_2)Y'_0(\alpha r_3) = 0, \quad (A - 13)$$

or

$$\phi_1(\alpha r_3) - J_1(\alpha r_3)Y_0(\alpha r_2) - J_0(\alpha r_2)Y_1(\alpha r_3) = 0, \quad (A - 14)$$

where we have made use of Eqs.(A-7), and J_0 , J_1 , Y_0 , Y_1 , J'_0 , Y'_0 are respectively the zeroth and first order Bessel's function of the first and second kind and their derivatives. Furthermore, the constant α must be the root of the second of Eq.(A-13) or of Eq.(A-14). Because there are infinitely many positive nondegenerate roots (Bogert,[1951]), we rewrite the first of Eqs.(A-13)

$$\phi_0(\alpha_n r) = A_n^* \left[J_0(\alpha_n r)Y_0(\alpha_n r_2) - J_0(\alpha_n r_2)Y_0(\alpha_n r) \right] \\ n=1, 2, 3, \dots, \quad A_n^* = A/Y_0(\alpha_n r_2) = A_n, \quad (A - 15)$$

where α_n satisfies Eq.(A-14). The general solution of Eqs.(A-7) is the infinite sum of Eqs.(A-15)

$$\phi = \sum_{n=1}^{\infty} A_n \phi_0(\alpha_n r). \quad (A - 16)$$

Now, combining Eqs.(A-3,4,5,6,9, and 16), we have

$$\Phi(r, t) = \sum_{n=1}^{\infty} A_n \phi_0(\alpha_n r) e^{-\alpha_n^2 D t}$$

$$\phi_0(\alpha_n r) = J_0(\alpha_n r) Y_0(\alpha_n r_2) - J_0(\alpha_n r_2) Y_0(\alpha_n r) . \quad (A - 17)$$

$$\Phi(r, t=0) = \sum_{n=1}^{\infty} A_n \phi_0(\alpha_n r) = 1, \quad (A - 18)$$

where we have redefined $\phi_0(\alpha_n r)$ and A_n is a new constant.

For Eq.(A-18) to be true, we must expand the constant 1 in terms of $\phi_0(\alpha_n r)$, and A_n must be the nth coefficient of the expansion. To this end we must compute the required integrals since they do not appear in the literature. Assuming the two differential equations

$$r^2 \frac{d^2 \phi_0(\alpha_n r)}{dr^2} + r \frac{d\phi_0(\alpha_n r)}{dr} + \alpha_n^2 r^2 \phi_0(\alpha_n r) = 0, \quad (A - 19)$$

$$r^2 \frac{d^2 \phi_0(\alpha_m r)}{dr^2} + r \frac{d\phi_0(\alpha_m r)}{dr} + \alpha_m^2 r^2 \phi_0(\alpha_m r) = 0, \quad (A - 20)$$

$$n=1, 2, \dots, \quad m=1, 2, \dots,$$

where α_n and α_m are any two roots of Eq.(A-14), we multiply Eq.(A-19) by $\phi_0(\alpha_m r)$, and Eq.(A-20) by $\phi_0(\alpha_n r)$, then subtract Eq.(A-20) from Eq.(A-19), and finally integrate the result from r_2 to r_3 to obtain

$$(\alpha_n^2 - \alpha_m^2) \int_{r_2}^{r_3} r \phi_0(\alpha_n r) \phi_0(\alpha_m r) dr$$

$$= r \left[\alpha_m \phi_0(\alpha_n r) \phi_0'(\alpha_m r) - \alpha_n \phi_0(\alpha_m r) \phi_0'(\alpha_n r) \right]_{r_2}^{r_3} . \quad (A - 21)$$

Here, ϕ'_0 is the derivative with respect to the argument $\alpha_n r$ or $\alpha_m r$, not just r . For $m \neq n$, Eq.(A-21) reduces to

$$(\alpha_n^2 - \alpha_m^2) \int_{r_2}^{r_3} r \phi_0(\alpha_n r) \phi_0(\alpha_m r) dr \\ - r_3 \left[\alpha_m \phi_0(\alpha_n r_3) \phi'_0(\alpha_m r_3) \right] - r_2 \left[-\alpha_n \phi_0(\alpha_m r_2) \phi'_0(\alpha'_n r_2) \right], \quad (A - 22)$$

where we have applied Eqs.(A-13,14 and 17). Because $\phi_0(\alpha_m r_2)$ and $\phi'_0(\alpha_m r_3)$ are also zero by Eqs.(A-13,14 and 17), we have

$$\int_{r_2}^{r_3} r \phi_0(\alpha_n r) \phi_0(\alpha_m r) dr = 0, \quad \text{for } \alpha_m \neq \alpha_n. \quad (A - 23)$$

For $\alpha_m = \alpha_n$, the situation is complicated and we give only an outline of the proof. We rewrite Eq.(A-21) as

$$\int_{r_2}^{r_3} r \phi_0(\alpha_n r) \phi_0(\alpha_m r) dr \\ = \frac{r}{\alpha_n^2 - \alpha_m^2} \left[\alpha_m \phi_0(\alpha_n r) \phi'_0(\alpha_m r) - \alpha_n \phi_0(\alpha_m r) \phi'_0(\alpha'_n r) \right]_{r_2}^{r_3}. \quad (A - 24)$$

When $\alpha_n \rightarrow \alpha_m$ the right hand side of Eq.(A-24) requires application of

L'Hospital's rule, which yields after some manipulations,

$$\int_{r_2}^{r_3} r \phi_0^2(\alpha_n r) dr$$

$$= \frac{r_3^2}{2} \left[\left(\phi_0'(\alpha_n r_3) \right)^2 + \phi_0^2(\alpha_n r_3) \right] - \frac{r_2^2}{2} \left[\left(\phi_0'(\alpha_n r_2) \right)^2 + \phi_0^2(\alpha_n r_2) \right]. \quad (\text{A} - 25)$$

To obtain Eq.(A-25), we have used Eqs.(A-13,14 and 17 and 19), the Wronskian (Abramowitz and Stegun [1970])

$$W[J_\nu(z), Y_\nu(z)] = J_{\nu+1}(z)Y_\nu(z) - J_\nu(z)Y_{\nu+1}(z) = -\frac{2}{\pi z}, \quad (\text{A} - 26)$$

and the identities

$$J_{\nu+1}(z) = \frac{\nu}{z} J_\nu(z) - J_\nu'(z), \quad Y_{\nu+1}(z) = \frac{\nu}{z} Y_\nu(z) - Y_\nu'(z). \quad (\text{A} - 27)$$

Then

$$\phi_0'(\alpha_n r_3) = -\phi_1(\alpha_n r_3) = 0, \quad \phi_0'(\alpha_n r_2) = -\phi_1(\alpha_n r_2) = -\frac{2}{\pi \alpha_n r_2}. \quad (\text{A} - 28)$$

Using these relations, we finally derive from Eqs.(A-25 and 23)

$$\int_{r_2}^{r_3} r \phi_0(\alpha_n r) \phi_0(\alpha_m r) dr = \begin{cases} \frac{2}{(\pi \alpha_n)^2} \left[\frac{J_0^2(\alpha_n r_2)}{J_1^2(\alpha_n r_2)} - 1 \right], & n=m \\ 0, & n \neq m \end{cases} \quad (\text{A} - 29)$$

Eq.(A-29) is very important, and we will repeatedly apply it.

Having obtained Eq.(A-29), we now expand Eq.(A-18). Because $r \phi_0(\alpha_n r)$ forms a complete set of orthogonal functions with different α_n , we multiply Eq.(A-18) by $r \phi_0(\alpha_m r)$ and then integrate from r_2 to r_3 to give

$$A_n = \frac{\int_{r_2}^{r_3} r \phi_0(\alpha_n r) dr}{\int_{r_2}^{r_3} r \phi_0^2(\alpha_n r) dr} = \frac{(\pi \alpha_n)^2}{2} \left[\frac{J_0^2(\alpha_n r_2)}{J_1^2(\alpha_n r_2)} - 1 \right]^{-1} \int_{r_2}^{r_3} r \phi_0(\alpha_n r) dr. \quad (A - 30)$$

In order to evaluate the integral in Eq.(A-30), we derive a general form for this type of integral.

$$\int r^{\mu+1} \phi_0(\alpha_n r) dr = \frac{1}{\alpha_n^{\mu+2}} \int z^{\mu+1} \phi_0(z) dz, \quad z = \alpha_n r \quad (A - 31)$$

with μ a constant. The following two relations are needed for evaluating Eq.(A-31) (Tranter, [1968]),

$$\begin{aligned} \int z^{\mu+1} J_\nu(z) dz &= z^{\mu+1} J_{\nu+1}(z) + (\mu - \nu) z^\mu J_\nu(z) - (\mu^2 - \nu^2) \int z^{\mu+1} J_\nu(z) dz \\ \int z^{\mu+1} Y_\nu(z) dz &= z^{\mu+1} Y_{\nu+1}(z) + (\mu - \nu) z^\mu Y_\nu(z) \\ &\quad - (\mu^2 - \nu^2) \int z^{\mu+1} Y_\nu(z) dz \end{aligned} \quad (A - 32)$$

We substitute Eqs.(A-32) into Eq.(A-31) and use Eqs.(A-17) to derive

$$\begin{aligned} \int r^{\mu+1} \phi_0(\alpha_n r) dr &= \alpha_n^{-(\mu+2)} \left[z^{\mu+1} \phi_1(z) + \mu z^{\mu+1} \phi_0(z) \right. \\ &\quad \left. - \mu^2 \int z^{\mu-1} \phi_0(z) dz \right]. \end{aligned} \quad (A - 33)$$

We note that Eq.(A-33) is exactly the same as Eqs.(A-32) in form with $\nu=0$, and ϕ_ν is replaced by either J_ν or Y_ν . We immediately derive from

Eq.(A-33) for $\mu=0$

$$\int_{r_2}^{r_3} r \phi_0(\alpha_n r) dr = -\frac{2}{\pi \alpha_n^2} , \quad (A - 34)$$

where Eqs.(A-14 and 26) are used. The integral in Eq.(A-30) now is eliminated by Eq.(A-34), and A_n is then,

$$A_n / \pi = \frac{J_1^2(\alpha_n r_3)}{J_0^2(\alpha_n r_2) - J_1^2(\alpha_n r_3)} . \quad (A - 35)$$

The solution of Eqs.(A-1) is, by Eqs.(A-2,5,9,17 and 34),

$$R-1+\pi \sum_{n=1}^{\infty} a(\alpha_n) \phi_0(\alpha_n r) e^{-\alpha_n^2 D t} , \quad a(\alpha_n) = \frac{J_1^2(\alpha_n r_3)}{J_0^2(\alpha_n r_2) - J_1^2(\alpha_n r_3)} . \quad (A - 36)$$

A P P E N D I X B

SOLUTION OF PARTIAL DIFFERENTIAL EQUATION (8-6)

The solution of Eqs.(8-6) is obtained by differentiating the square bracket product in Eq.(8-21),

$$\begin{aligned}
 & \frac{c_0^B}{c_0^2} - 1 - \pi D \sum_{n=1}^{\infty} \alpha_n^2 a(\alpha_n) \phi_0(\alpha_n r) \int_0^t e^{\alpha_n^2 D(\lambda-t)} g(\lambda) d\lambda \\
 & + 4D \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} a(\alpha_n) \phi_0(\alpha_n r) \Omega_m(z) E_{mn}^2 \int_0^t e^{E_{mm}^2 D(\lambda-t)} g(\lambda) d\lambda \\
 & + \frac{4}{\pi} D \sum_{m=1}^{\infty} d_m^2 \Omega_m(z) \int_0^t e^{d_m^2 D(\lambda-t)} g(\lambda) d\lambda, \quad E_{nm}^2 = \alpha_n^2 + d_m^2. \quad (B-1)
 \end{aligned}$$

$$g(\lambda) = -\gamma(1 - e^{-\theta^2 D \lambda})$$

For the $g(\lambda)$ given, Eq.(B-1) becomes

$$\begin{aligned}
& \frac{c_0^B}{c_2^2} - 1 + \gamma \left[-\pi \sum_{n=1}^{\infty} \frac{\alpha_n^2 a(\alpha_n) \phi_0(\alpha_n r)}{\alpha_n^2 - \theta^2} \left(e^{-\alpha_n^2 D t} - e^{-\theta^2 D t} \right) + \frac{4}{\pi} \sum_{n=1}^{\infty} \frac{d_m^2 \Omega_{mn}(z)}{d_m^2 - \theta^2} \times \right. \\
& \left. \left(e^{-\frac{d_m^2 D t}{\theta^2}} - e^{-\theta^2 D t} \right) + 4 \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \frac{a(\alpha_n) \phi_0(\alpha_n r) \Omega_m(z) E_{mn}^2}{E_{mn}^2 - \theta^2} \left(e^{-E_{mn}^2 D t} - e^{-\theta^2 D t} \right) \right. \\
& \left. + 4 \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} a(\alpha_n) \phi_0(\alpha_n r) \Omega_m(z) \left(1 - e^{-E_{mn}^2 D t} \right) + \frac{4}{\pi} \sum_{m=1}^{\infty} \Omega_m(z) \left(1 - e^{-\frac{d_m^2 D t}{\theta^2}} \right) \right. \\
& \left. - \pi \sum_{n=1}^{\infty} a(\alpha_n) \phi_0(\alpha_n r) \left(1 - e^{-\alpha_n^2 D t} \right) \right]. \quad (B-2)
\end{aligned}$$

Eq.(B-2) contains many infinite sums, and is difficult to apply in practice. We are able to perform some of the sums. Consider first the summation

$$Y(z) = \sum_{n=1}^{\infty} \frac{d_m^2 \Omega_{mn}(z)}{d_m^2 - \theta^2}. \quad (B-3)$$

Using Eqs.(8-20) to eliminate $\Omega_m(z)$ and d_m^2 , we derive

$$Y(z) = \sum_{n=0}^{\infty} \frac{(2m+1) \sin[(2m+1)x]}{(2m+1)^2 - \zeta^2}, \quad x = \frac{\pi z}{2h}, \quad \zeta^2 = \frac{\theta^2 (2h)^2}{\pi^2}. \quad (B-4)$$

To sum Eqs.(B-4), we use the two relations (Gradshteyn and Ryzhik, [1980])

$$\sum_{n=1}^{\infty} \frac{k(-1)^k \sin(kx)}{k^2 - \zeta^2} = \frac{\pi \sin[\zeta(2m\pi - x)]}{2 \sin(\zeta\pi)}, \quad (\text{B} - 5)$$

$$\sum_{n=1}^{\infty} \frac{k \sin(kx)}{k^2 - \zeta^2} = \frac{\pi \sin[\zeta(2m+1)\pi\zeta - x\zeta]}{2 \sin(\zeta\pi)}. \quad (\text{B} - 6)$$

If we subtract Eq.(B-6) from Eq.(B-5), then

$$\sum_{n=0}^{\infty} \frac{(2k+1) \sin[(2k+1)x]}{(2k+1)^2 - \zeta^2} = \frac{\pi}{4 \sin(\zeta\pi)} \left\{ \sin[(2m+1)\pi\zeta - x\zeta] - \sin[\zeta(2m\pi - x)] \right\},$$

$$0 < x < \pi, \quad m=0, \pm 1, \pm 2, \dots \quad (\text{B} - 7)$$

Taking $m=0$, Eqs.(B-7) reduce to

$$\sum_{n=0}^{\infty} \frac{(2k+1) \sin[(2k+1)x]}{(2k+1)^2 - \zeta^2} = \frac{\pi}{4 \sin(\zeta\pi)} \left\{ \sin[(\pi - x)\zeta] - \sin(\zeta x) \right\}, \quad (\text{B} - 8)$$

and comparing Eq.(B-8) with Eqs.(B-3 and 4), we obtain

$$\sum_{n=1}^{\infty} \frac{d_m^2 \Omega_{mn}(z)}{d_m^2 - \theta^2} = \frac{\pi}{4} \left\{ \frac{\sin[(2h-z)\theta] - \sin(\theta z)}{\sin(2h\theta)} \right\}. \quad (\text{B} - 9)$$

Integrating both sides of Eq.(B-9) from 0 to h for z , we obtain

$$\sum_{m=1}^{\infty} \frac{1}{d_m^2 - \theta^2} = \frac{\pi}{4\theta} \operatorname{tg}(h\theta). \quad (\text{B} - 10)$$

It is also possible to perform the infinite sum

$$X(r) = \pi \sum_{n=1}^{\infty} \frac{\alpha_n^2 a(\alpha_n) \phi_0(\alpha_n r)}{\alpha_n^2 - \theta^2} . \quad (B - 11)$$

To evaluate this summation, we define

$$\begin{aligned} D_0(\theta r) &= J_0(\theta r) Y_0(\theta r_3) - J_0(\theta r_3) Y_0(\theta r) \\ \phi_0(\theta r) &= J_0(\theta r) Y_0(\theta r_2) - J_0(\theta r_2) Y_0(\theta r) \\ \phi_1(\theta r) &= J_1(\theta r) Y_0(\theta r_2) - J_0(\theta r_2) Y_1(\theta r) . \end{aligned} \quad (B - 12)$$

The following relationships are satisfied,

$$D_1(\theta r) = -D'_0(\theta r), \quad D_0(\theta r_2) = -\phi(\theta r_3), \quad \phi_1(\theta r) = -\phi'_0(\theta r). \quad (B - 13)$$

The trick here is to expand $\phi_0(\theta r)$ in terms of orthogonal functions

$\phi_0(\alpha_n r)$. We write

$$\phi_0(\theta r) = \sum C_n \phi_0(\alpha_n r) . \quad (B - 14)$$

Then

$$C_n = \frac{\int_{r_2}^{r_3} r \phi_0(\alpha_n r) \phi_0(\theta r) dr}{\int_{r_2}^{r_3} r \phi_0^2(\alpha_n r) dr} , \quad (B - 15)$$

and because (Luke, [1962])

$$\int_{r_2}^{r_3} r \phi_0(\alpha_n r) \phi_0(\theta r) dr = - \frac{r_3 \theta \phi_0(\alpha_n r_3) \phi_1(\theta r_3)}{\alpha_n^2 - \theta^2}, \quad (\text{B} - 16)$$

we obtain

$$C_n = - \frac{r_3 \theta \phi_0(\alpha_n r_3) \phi_1(\theta r_3)}{\alpha_n^2 - \theta^2} (\pi \alpha_n)^2 a(\alpha_n), \quad (\text{B} - 17)$$

where we have used Eq.(A-29). By Eq.(B-14),

$$\sum \frac{\theta \phi_0(\alpha_n r_3) \phi_1(\alpha_n r)}{\alpha_n^2 - \theta^2} (\pi \alpha_n)^2 a(\alpha_n) = - \frac{2 \phi_0(\theta r)}{r_3 \theta \phi_1(\theta r_3)}. \quad (\text{B} - 18)$$

The next step is to expand $D_0(\theta r)$ in terms of $\phi_0(\alpha_n r)$,

$$D_0(\theta r) = \sum B_n \phi_0(\alpha_n r). \quad (\text{B} - 19)$$

As before, we obtain for B_n

$$B_n = - \frac{(\pi \alpha_n)^2 a(\alpha_n)}{2\pi(\alpha_n^2 - \theta^2)} \left[r_3 \theta \phi_0(\alpha_n r_3) D_1(\theta r_3) + r_2 \alpha_n \phi_1(\alpha_n r_2) D_0(\theta r) \right]. \quad (\text{B} - 20)$$

Combining Eqs.(B-20,19 and 18), we finally obtain for Eq(B-11)

$$\sum_{n=1}^{\infty} \frac{\alpha_n^2 a(\alpha_n) \phi_0(\alpha_n r)}{\alpha_n^2 - \theta^2} = \frac{\phi_0(\theta r) D_1(\theta r_3) - D_0(\theta r) \phi_1(\theta r_3)}{D_0(\theta r_2) \phi_1(\theta r_3)},$$

$$r_2 < r < r_3. \quad (\text{B} - 21)$$

As $\theta \rightarrow 0$, we can show that the limiting form of Eq.(B-21) is

$$\pi \sum_{n=1}^{\infty} a(\alpha_n) \phi_0(\alpha_n r) = -1, \quad (\text{B} - 22)$$

and Eq.(B-22) is just Eq.(A-18), the initial condition of the partial differential equation(A-3).

If we multiply both sides of Eq.(B-22) by r , then integrate from r_2 to r_3 , the result is

$$\sum_{n=1}^{\infty} \frac{a(\alpha_n)}{\alpha_n^2 - \theta^2} = -\frac{r_2}{2\theta} \left[\frac{\phi_1(\theta r_3) D_1(\theta r_2) - \frac{4}{\pi^2 r_2 r_3 \theta^2}}{D_0(\theta r_2) \phi_1(\theta r_3)} \right], \quad (\text{B} - 23)$$

where we have used Eqs.(A-26,31,32, 33, and 34). At $\theta=0$, Eq.(B-23) reduces to a very simple form. To show this, we rewrite Eq.(B-23)

$$\sum_{n=1}^{\infty} \frac{a(\alpha_n)}{\alpha_n^2 - \theta^2} = -\frac{r_2}{\theta^3} \left[\frac{\phi_1(\theta r_3) D_1(\theta r_2) \theta^2 - \frac{4}{\pi^2 r_3 r_2}}{2 D_0(\theta r_2) \phi_1(\theta r_3)} \right]. \quad (\text{B} - 24)$$

Then

$$\begin{aligned} \sum_{n=1}^{\infty} \frac{a(\alpha_n)}{\alpha_n^2} &= \lim_{\theta \rightarrow 0} -\frac{r_2}{\theta^3} \left[\frac{r_3 \theta \phi_0(\theta r_3) D_1(\theta r_2) + \theta r_2 \phi_1(\theta r_3) D_0(\theta r_2)}{4 \theta D_0(\theta r_2) \phi_1(\theta r_3)} \right] \\ &= -(r_3^2 - r_2^2)/4. \end{aligned} \quad (\text{B} - 25)$$

To get the last line of Eq.(B-25), we have successively employed L'Hospital's rule. A simpler way to show this is to multiply Eq.(B-22) by r , then integrate from r_2 to r_3 to lead to Eq.(B-25).

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