THERMAL DIFFUSION IN LAMINAR FLOW

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by

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PREFACE

The work described in this dissertation was carried out in the Department of Chemical Engineering in the University of Cambridge between October 1961 and December 1964. Except where specifically acknowledged in the text, it is the original and independent work of the author. Neither the present dissertation nor any part thereof has previously been submitted at any other University.

It is a pleasure to record my gratitude to Dr. J.C.R. Turner, my supervisor, for the guidance and encouragement he has given throughout the course of my research at Cambridge, and to Dr. J.N. Agar for many stimulating discussions over the same period. Thanks are also due to the workshop staff for their assistance in the construction of the apparatus, in particular to Mr. E.C. Doggett who made the diffusion cell.

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SUMMARY

Equations are developed describing the attainment of Soret equilibrium of two component systems in laminar duct flow. The resulting diffusion equation is solved in a simplified form valid for small temperature intervals by a suitable finite difference approximation. Consideration of the errors involved lead to an upper limit on the temperature interval for the validity of the final solution.

An apparatus is designed and built in which an initially uniform solution flows in a laminar fashion between two horizontal plates across which a temperature difference is maintained. At the end of the duct so constructed, the solution is split into two fractions by a horizontal knife-edge. These two fractions, corresponding to the top and bottom halves of the duct, are collected and analysed. The separation for a given solution at the end of a duct of finite length depends on the flowrate and is given by the theoretical treatment.

The flow cell is calibrated with 0.05m aqueous cadmium sulphate which is chosen for its known thermal diffusion properties and the fact that it can be conveniently analysed by a conductimetric technique. Agreement with theoretical predictions is found to be excellent over the entire approach to the steady state. Con-
Cvection effects, which are the main source of error in the conventional pure Soret effect cell, are shown to be negligible.

Application to organic mixtures and the use of Rayleigh interferometry in their analysis is discussed in relation to the system carbon tetrachloride-cyclohexane. Soret coefficients and heats of transport are determined as functions of composition over the entire range. Comparison with recent results in a thermogravitational column confirm the view that such columns cannot be used to obtain reliable quantitative data.
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CHAPTER 1

INTRODUCTION

When a temperature gradient is applied in a solution a separation of components usually occurs. The phenomenon is called thermal diffusion. The concentration gradient which is gradually set up gives rise in turn to ordinary diffusion and a tendency to remix. After some time a steady state is established in which the material fluxes are reduced to zero and the concentration gradient becomes time-invariant. In the case of liquids, this separation is termed the Soret Effect. The resulting steady state is not an equilibrium state according to the thermodynamic sense because it is dependent on the heat flux to sustain it.

In a two component system, the Soret coefficient $\sigma$ is defined in terms of the concentration gradient existing in the steady state, that is the maximum possible separation,

$$- \sigma \frac{dT}{dy} = \left( \frac{d\ln m}{dy} \right)_\infty,$$

... (1.1)

where $y$ is the space coordinate in the direction of diffusion, $\sigma$ refers to component 1 (in Chapter 2 it will be denoted by $\sigma_{12}$, $\sigma_{12} = - \sigma_{21}$). The negative sign is a convention which makes $\sigma$ positive when the solute (component 1) diffuses to the cold wall. Its magnitude is about $10^{-3}$ deg.$^{-1}$
The Soret coefficient is not a fundamental quantity but is a convenient variable for use in the flux equation. It is however related to the heat of transport \( q^* \) which is a fundamental property specific to each solution. For a non-ionised solute, the molar heat of transport is given by

\[
q^*_m = RT^2 (1 + \frac{\partial \ln \alpha}{\partial \ln m}) \sigma, \quad \ldots (1.2)
\]

where \( \alpha \) is the activity coefficient on the molality scale. For a simple salt dissociating into \( \nu_1 \) ions of type 1 and \( \nu_2 \) ions of type 2,

\[
q^* = \nu_1 q^*_1 + \nu_2 q^*_2 = (\nu_1 + \nu_2) RT^2 (1 + \frac{\partial \ln \alpha^*}{\partial \ln m^*}) \sigma, \quad \ldots (1.3)
\]

where \( q^*_1 \) and \( q^*_2 \) are the heats of transport of the cation and anion and \( \alpha^* \) is the mean ionic activity coefficient.

Theories of the Soret effect are complex and attempts to predict the heat of transport have usually failed either on account of a grossly oversimplified model or through inability to evaluate the final result numerically. These theories have been discussed at length in a number of recent reviews.\(^{(1-4)}\) They will not be considered further except to point out the relation of the most recent developments with existing experimental results.

The field of organic mixtures, in which there are least experimental measurements and in which many of the existing ones are hopelessly inaccurate, is the field where most theoretical
progress can be made because here it is possible to use simplifications which most nearly correspond to the behaviour of real systems. For example, resulting from the recent attempts made by the Kirkwood school to develop a unified theory of transport processes in liquids, Bearman, Kirkwood and Fixman\(^{(5)}\) have been able to give an approximate result for the heat of transport in the special case of regular solutions of spherically symmetrical particles. Such a result is immediately amenable to an experimental test. On the other hand, it is not possible to apply this theory directly to ionic solutions for which there would be ample experimental results for verification. Helfand and Kirkwood\(^{(6)}\) have produced a modified theory giving expressions for the heat of transport in ionic solutions but it is impossible to evaluate them numerically. Much the same difficulty has been experienced by Agar,\(^{(4)}\) who recently developed Eastman's continuum model\(^{(7)}\) for ionic solutions. He obtained an expression for the concentration dependence of the heat of transport in dilute aqueous solutions which is similar in form to that of Helfand and Kirkwood but which still contains terms which are inaccessible to observation.

It can be seen that there is a need for accurate measurements of the Soret effect in certain organic systems whose properties are chosen to conform as nearly as possible to the simplifications made in the theories. The present work is concerned with developing an apparatus for this purpose. The principle of the lam-
inar flow cell will be introduced following a discussion of the
more conventional type of pure Soret cell.

In laboratory investigations, the emphasis lies in the
accuracy with which the Soret coefficient can be determined rather
than on the separation which can be achieved. The best design of
cell is one in which convectional disturbances are, as nearly as
possible, eliminated. For this reason a vertical temperature
gradient is applied and the liquid is heated from above. The tem-
perature difference is kept down to 10 degrees C. so that mean
values may be used for the physical parameters concerned; in par-
ticular, the measured $\sigma$ can be assumed to correspond to the mean
cell temperature. In experiments of this kind, the characteristic
time, or the time taken to approach the steady state, is propor-
tional to the square of the cell height. It is important, there-fore, to keep this height as small as possible to avoid an incon-
veniently long experiment.

Some measure of success has been obtained in cells in
which the concentration changes are followed 'in situ' by optical
(8-17) or conductimetric (18-24) methods. Of these, references
(15-17) are concerned with organic systems and the remainder with
aqueous solutions. To ensure adequate sensitivity of measurement
these cells are about 1 cm. high, requiring about 3-10 hours,
depending on the diffusion coefficient, to approach the steady
state. They are constructed to contain the solution between two
horizontal conducting plates with side walls which are supposed to be non-conductors. Their cross-sectional geometry and the nature of the side walls depend on the method of measurement. To distinguish them from the flow cell they will be referred to as "static-type" cells.

Now it would appear from equation (1.1) that \( \sigma \) could be obtained from a single steady state observation of the time-invariant concentration gradient. It is found in practice, though, that such a measurement always leads to a low value of \( \sigma \) because local convection currents cause a certain amount of remixing and the steady state is never accurately attained. Even though in most solutions the heavier component concentrates at the cold wall, thereby increasing the density at the bottom of the cell and tending to stabilize the system, small local horizontal temperature gradients still give rise to a limited amount of convection. If the cell is mounted with the end plates horizontal and the temperatures are steady, then such horizontal gradients can only be caused by;

(i) Variable physical properties: variations due to temperature dependence of the thermal conductivity will be different in the liquid and the side walls, causing the isothermals to be bent near the walls.

(ii) Non-uniform walls: bolts which do not go right through the walls, filling holes in the walls, end gaskets to seal the cell, the central tapping electrode in the conductimetric method, etc., all tend to bend the isothermals
near the walls.

For unsteady temperatures heat flow will always occur through the walls unless their thermal conductivity is identical with that of the liquid. Inaccuracies due to convection can be reduced either by observing the initial separation, which is independent of such disturbances but which is difficult to measure or, better, by following the entire approach to the steady state and interpreting the results in terms of a solution of the phenomenological equations describing the time-dependence of the process.

In 1956 Thomaes\(^{(25)}\) described a flow cell in which a solution of initially uniform concentration flows in a laminar fashion through a narrow duct across which a temperature gradient is maintained. At the end of the duct the solution is divided into two fractions about the centre-line and the concentration difference between these two streams is measured externally. One immediate advantage is that the cell height can be reduced to a fraction of a mm., cutting the time required to attain the steady state by a factor of at least one hundred. Another advantage results from the conclusion above, that horizontal temperature gradients are basically wall effects; for these should be insignificant in a flat sandwich-shaped cell like the flow cell. Recently Turner\(^{(26)}\) backed by the preliminary work of two tripos projects at the University of Cambridge,\(^{(27,28)}\) built a similar cell and demonstrated that separations of the right order were obtained with 0.05m solutions of CdSO\(_4\) and NaOH. It seemed that good results could be
obtained with an improved cell design.

An alternative to the above methods based on pure Soret diffusion is the thermogravitational, or Clusius-Dickel column. Here the solution is contained between vertical surfaces maintained at different temperatures and spaced a small distance apart. Thermal diffusion occurs in a horizontal direction while natural convection induces bulk flow vertically near the walls. Solution enriched in one component near the hot surface ascends to a reservoir attached to the top of the apparatus while solution depleted in the same component descends down the cold wall to be collected in a lower reservoir. A steady state is ultimately set up in which the final concentration difference can be made much larger than in the pure Soret cell. In contrast to the pure Soret cell, the applied temperature difference determines the rate of attainment of the steady state and has practically no effect on the separation. Instead, the latter is critically dependent on the wall spacing (an inverse 4th power dependence). While useful as a method of separation, the thermogravitational column has produced very little in the way of reliable quantitative results. Solution of the phenomenological equations are more difficult than in the simple cell. Much of the confusion surrounding experimental observations results in a failure of the theory(3,29,30) to include the composition dependence of density, known as the "forgotten effect". In a recent paper, Horne and Bearman(31) have solved the steady state equation including explicitly the forgotten effect. Their treatment is based on a
cylindrical column for which they present some results for the carbon tetrachloride - cyclohexane system to support their claim that the thermogravitational column can be used for accurate analysis of the Soret effect.

The above discussion is not intended to exhaust the methods used to investigate thermal diffusion in liquids; for this, reference must be made to the reviews mentioned earlier, but it is included as background to a discussion in Chapter 5 of the relative merits of the flow and static-type cells and to a criticism in Chapter 6 of Horne and Bearman's results and conclusions regarding the thermogravitational column. The remaining part of this thesis is concerned with the phenomenological theory of the flow cell and the development of such a cell for use with organic systems.
CHAPTER 2

PHENOMENOLOGICAL THEORY OF THE LAMINAR FLOW CELL

The differential equation governing the change in concentration in the flow cell is derived and solved in a simplified form, valid for small temperature intervals, by a suitable finite difference approximation. The measured separation, namely the difference between the mean concentration in the upper and lower halves of the duct, follows from this solution.

2.1 Introduction

Thomaes, in his original interpretation of the flow cell,\(^{(25)}\) used a perturbation technique in which he assumed the solution for uniform velocity (that for the static cell with \(t = \frac{x}{u}\)) and added a perturbation term to account for the actual parabolic distribution. His results are incorrect because the perturbation term is not always small. The present treatment is similar to Turner's\(^{(26)}\) but the finite difference approximation is improved. The errors are more fully discussed in Chapter 4.

The treatment given here is restricted to two components without natural convection. Volume changes in the solution are taken into account. The solution flows in a duct between two parallel flat plates, distance \(2a\) apart, across which a temperature
difference $\Delta T$ is maintained. The surface temperature of each of these plates is assumed to be uniform, the upper one being hotter than the lower one. That the cell is sufficiently wide for the flow to be independent of the side walls is shown by Han's data: \[ \text{(32)} \]

he finds that for our aspect ratio \( \frac{2a}{b} = 0.006 \), \( \frac{u_{\text{max}}}{u} \) differs by less than \( \frac{1}{2} \% \) from its value for flow between two infinite plates. The problem is therefore one of two dimensions (Figure 1). We shall suppose that the heat flux is everywhere perpendicular to the direction of flow. This assumption, which is always introduced in solutions for the conventional equidimensional static-type cell, is clearly more satisfactory for a flat sandwich-type cell because here lateral heat loss through the side walls is not significant.

A one dimensional approximation is also used for the diffusion vector, the component along the duct being ignored in comparison with the convection term. Although the diffusion velocity becomes significant at the walls where the velocity approaches zero, its effect on the mean concentration in each half of the duct is unimportant. Neglect of this term restricts the treatment to liquids. All entry effects are neglected. Thus we assume that the fully developed velocity and temperature distributions are set up immediately upon entry to the duct. Since the thermal diffusivity is always much greater than the mass diffusity \( \left( \frac{K}{\rho} \right) \) is about 100 in dilute aqueous solutions and 60 in organic systems), the temperature distribution will be attained very much more quickly than the concentration gradient. The velocity entry length depends
on the flowrate but the largest encountered in our experiments only amounted to about 0.3% of the length of the duct.

2.2 Flux Equation and Frame of Reference

Most phenomenological treatments of the Soret effect, which are not concerned exclusively with dilute solutions, take for their premise a flux equation based on mole fractions.\textsuperscript{(15,29,33)} In this way they seek to avoid complications arising from the concentration dependence on temperature. Although in Bierlein's work,\textsuperscript{(33)} which is most generally used for the analysis of experimental results on pure Soret cells, allowance has been made for the temperature dependence of the molar density, the effect of the volume changes on the thermal diffusion is still not clear. Another objection arises from a discussion about the relevant frame of reference. The basic equation for a two component solution is usually taken as

\[
J_i^N = -c_i \left[ \frac{\partial N_i}{\partial y} + \sigma_{ij} N_i N_j \frac{\partial T}{\partial y} \right], \quad \ldots (2.1)
\]

which derives from a mole fixed reference plane defined by

\[
J_1^N + J_2^N = 0. \quad \ldots (2.2)
\]

The corresponding definition of the Soret coefficient arises from the steady state \(J_i^N = 0\), whence

\[
-\sigma_{ij} \frac{\partial T}{\partial y} = \frac{1}{N_1 N_2} \frac{\partial N_i}{\partial y} = \frac{\partial}{\partial y} (\ln n). \quad \ldots (2.3)
\]
Now, unless the spatial coordinate \( y \) is transformed according to Hartley and Crank\(^{(34)} \), equation (2.1) must be solved with the continuity equation,

\[
\frac{\partial J_1^a}{\partial y} = -\frac{\partial c_1}{\partial t}, \tag{2.4}
\]

where \( J_1^a \) is the flux of component 1 with respect to an 'apparatus-fixed' frame of reference. Bierlein and previous workers seem to have ignored this distinction of reference frame and have combined equations (2.1) and (2.4) by assuming, without justification, the equality of \( J_1^N \) and \( J_1^a \). This is not generally true. In fact their flux equation (2.1) was originally derived for gaseous systems\(^{(35)} \).

Agar\(^{(36)} \) has recently introduced a solution suitable for liquid systems, with \( c \) as a measure of concentration, in which the fluxes are based on a 'zero-volume flow' (or Fick) frame of reference defined by

\[
J_1^{Fv} V_1 + J_2^{Fv} V_2 = 0. \tag{2.5}
\]

He shows that, under conditions normally associated with pure Soret effect cells, the 'Fick' frame can be satisfactorily approximated by the 'apparatus-fixed' frame, and therefore that no unjustified assumptions need be made in the combination of the flux and continuity equations.

According to Agar, the basic equation for the thermal diffusion flux is
\[ J_1^F = -D \left[ \frac{\partial \phi}{\partial y} + (\phi_2 \sigma_{12} + \alpha)c_1 \frac{\partial T}{\partial y} \right], \quad \ldots \ (2.6) \]

where \( \phi_2 \) is the volume fraction \( \phi_2 V_2 \) of component 2 (the solvent in dilute solutions) and \( D \) is the diffusion coefficient associated with the usual form of Fick's law for isothermal systems,

\[ J_1^F = -D \frac{\partial c_1}{\partial y}. \quad \ldots \ (2.7) \]

The definition of \( \sigma_{12} \) derives again from the condition \( J_1^F = 0 \); with the Gibbs-Duhem equation for non-isothermal systems, we find

\[ -\sigma_{12} \frac{\partial T}{\partial y} = \frac{\partial}{\partial y} \ln(\frac{c_1}{c_2}) = \frac{\partial}{\partial y} (\ln m). \quad \ldots \ (2.8) \]

We see that this is identical with Bierlein's definition for all concentrations; it is the approach to the steady state which differs in the two treatments. As already mentioned, the sign convention makes the Soret coefficient positive when component 1 concentrates at the cold wall. We also notice that the thermal diffusion term in (2.6), as in (2.1), is symmetrical with respect to the concentration of both components. The use of \( c \) as a measure of concentration necessitates the inclusion of an expansion term, \( \alpha c_1 \frac{\partial T}{\partial y} \), which has nothing to do with thermal diffusion but which will modify the separation achieved.

The above discussion shows that Agar's flux equation (2.6) has a more sound basis for application to Soret diffusion than the more generally accepted equation (2.1). For this reason it will be used in the present work.
It is convenient to note here the simplifications made by Agar to the flux equation. A modified Soret coefficient is introduced, defined by

$$s_{12} = \frac{\tau}{2} \sigma_{12}.$$  \hspace{1cm} (2.9)

In contrast to the symmetry of $\sigma_{12}$, $s_{12} \neq -s_{21}$. In dilute solutions (of component 1 in 2) $s_{12}$ is indistinguishable from $\sigma_{12}$. A further simplification consists in making the substitution

$$c_1 = c_\alpha + \bar{c}h,$$  \hspace{1cm} (2.10)

where $c_\alpha$ and $\bar{c}$ are defined by

$$d c_\alpha = -c_\alpha \alpha dT.$$  \hspace{1cm} (2.11)

and, for the flow cell,

$$\frac{3}{2} \int_{-a}^{a} c_1 (1 - \frac{v^2}{a^2}) \, dy = \frac{3}{2} \int_{-a}^{a} c_\alpha (1 - \frac{v^2}{a^2}) \, dy = 2a\bar{c}.$$  \hspace{1cm} (2.12)

Here $\bar{c}$ is the mean concentration, $c_\alpha$ is the concentration in a non-isothermal solution of uniform molality, and hence $h$ is a measure of the change in concentration relative to a solution of uniform molality. It follows from these definitions that

$$\int_{-a}^{a} h(1 - \frac{v^2}{a^2}) \, dy = 0.$$  \hspace{1cm} (2.13)
The flux equation (2.6) now becomes

\[ J_{1y}^F = -\delta D \left[ \frac{\partial h}{\partial y} + (s+\alpha)h \frac{\partial T}{\partial y} + s \frac{\alpha}{\sigma} \frac{\partial T}{\partial y} \right], \quad ... (2.14) \]

where the subscripts have been dropped from \( s_{12} \). This will be regarded as our basic equation for the thermal diffusion flux. Apart from some very small effects due to volume changes consequent on concentration changes, it is exact. Although the introduction of \( h \) may appear to be an unnecessary complication, it does in fact simplify the problem with the advantage that at all stages in the calculation the effect of expansion is both understood and accounted for.

### 2.3 Thermal Diffusion in Laminar Flow

Combining the components of the flux vector,

\[ J_{1y}^F = -\delta D \left[ \frac{\partial h}{\partial y} + (s+\alpha)h \frac{\partial T}{\partial y} + s \frac{\alpha}{\sigma} \frac{\partial T}{\partial y} \right], \quad ... (2.15) \]

and

\[ J_{1x}^F = u c_4, \quad ... (2.16) \]

with the continuity equation,

\[ \nabla \cdot J_{1y}^F = 0 \quad ... (2.17) \]

and introducing the dimensionless variables,

\[ X = \frac{Dx}{4a_2u} \quad ... (2.18) \]

and

\[ Y = \frac{Y}{a}, \quad ... (2.19) \]
we obtain
\[
\frac{\partial^2 h}{\partial Y^2} + \frac{\partial}{\partial Y} \left[ (s+\alpha)h \frac{\partial T}{\partial Y} \right] + s \frac{\partial}{\partial Y} \frac{\partial^2 T}{\partial Y^2} = \frac{3}{8} \left( 1-Y^2 \right) \frac{\partial h}{\partial X}, \ldots (2.20)
\]

where u has been written in terms of a parabolic velocity profile.

Equation (2.20) describes the cell operating in a time-invariant state, \( \frac{\partial c_1}{\partial t} = 0 \). The transformed variable X assumes a role equivalent to the dimensionless time introduced in the solution for the static cell. Practically, X is varied for a given solution by changing the flow rate through the cell. The right-hand side of (2.20) follows from the condition \( \frac{\partial T}{\partial t} = 0 \), whence \( \frac{\partial c_1}{\partial X} = 0 \) and \( \frac{\partial c_1}{\partial X} = 0 \).

We seek a solution for small \( \Delta T \). In typical experiments h is initially zero and never exceeds the steady state value; hence h and its derivatives are of order \( \Delta T \). Since the temperature gradient is also of order \( \Delta T \), the term \( \frac{\partial}{\partial Y} \left[ (s+\alpha)h \frac{\partial T}{\partial Y} \right] \) is of order \( \Delta T \) and is therefore small compared with the dominant terms in (2.20). We further notice that \( \frac{\partial s}{\partial X} = 1+ \) terms of order \( \Delta T \).

Now, in the above development, appropriate mean values have been assumed for D and s. These are the values at the mean cell temperature \( T_0 \). In any solution in which the temperature dependence of D and s is ignored, the errors must in general be of order \( \Delta T \).

Consequently there is little justification for retaining any terms above the first order in \( \Delta T \). Ignoring, then, all terms of order \( \Delta T \) and above, equation (2.20) becomes
\[
\frac{\partial^2 h}{\partial y^2} + s \frac{\partial^2 T}{\partial y^2} = \frac{3}{8} (1-y^2) \frac{\partial h}{\partial x} .
\] ...

(2.21)

Since there is no mass flux at the walls, the boundary conditions are \( J^F_{1Y} = 0 \) at \( Y = \pm 1 \). To the above approximation these become

\[
\frac{\partial h}{\partial y} = -s \frac{\partial T}{\partial y} , \quad \text{at } Y = \pm 1 .
\]

... (2.22)

Under steady temperatures, \( \frac{\partial T}{\partial y} = \frac{1}{\beta \Delta T} \) for all \( X \), so (2.21) and (2.22) become

\[
\frac{\partial^2 h}{\partial y^2} - \frac{3}{8} (1-y^2) \frac{\partial h}{\partial x} = 0 ,
\]

... (2.23)

bounded by

\[
\frac{\partial h}{\partial y} = -\frac{1}{2} \beta \Delta T , \quad \text{at } Y = \pm 1 , \quad \text{all } X .
\]

... (2.24)

The solution is initially of uniform molality, so we must finally specify

\[
h = 0 , \quad \text{at } X = 0 , \quad \text{all } Y .
\]

... (2.25)

The form of equation (2.23) is well known since it also describes the temperature distribution in laminar duct flow. This problem, which is analogous to the classic Graetz problem for pipe flow, (37) has been considered by many workers of whom Brown, (38) among the recent ones, may be quoted for his extensive bibliography. The case usually considered is the effect of a step-change in temperature at the point \( X = 0 \) in the duct on the subsequent temperature profile subject either to constant wall temperatures or constant wall heat flux. It is immediately apparent that these
boundary conditions are not appropriate to our case.

2.4 The Steady State

It follows, by putting $J_Y^F = 0$, that in the steady state $(X \to \infty)$

$$\left( \frac{\partial h}{\partial Y} + s \frac{\partial T}{\partial Y} \right)_{\infty} = 0. \quad \ldots \ (2.26)$$

Integrating with condition (2.13), we find

$$h_{\infty}(Y) = -\frac{\frac{1}{2} s \Delta Y}{6} \quad \text{to terms of } O(\Delta T) \quad \ldots \ (2.27)$$

which is identical with the steady state in the static-type cell.

Practically, it will be remembered, we require the mean concentration for each half-width of the duct at a uniform temperature which is conveniently taken as the mean cell temperature $T_0$. Let these concentrations be $\bar{c}'$ and $\bar{c}''$ for the top and bottom half of the cell respectively; the subscripts referring to component 1 have been dropped. In general, volume changes occurring on removal of the temperature gradient will only affect terms of order $(\Delta T)^2$ and above. For the simple treatment considering only terms of order $(\Delta T)$ it is therefore immaterial whether the solution is "cooled" to $T_0$ before or after the separation at the blade. From the definition of $h$, equation (2.10), the concentration after the temperature gradient has been removed is seen to be $\bar{c}(1+h)$. Integrating from $Y=0$ to $Y=1$, with the velocity profile as weighting factor, we derive
Similarly for the bottom half of the duct,

\[ \tilde{c}^* = \tilde{c}(1+ \frac{3}{16} s\Delta T) + O(\Delta T)^2. \]  ... (2.29)

The separation, conveniently expressed as a fraction of the duct inlet concentration \( c_0 \) (equal to \( \tilde{c} \)), is given by

\[ \left( \frac{\tilde{c}^* - \tilde{c}'}{c_0} \right)_\infty = \frac{3}{8} s\Delta T + O(\Delta T)^2. \]  ... (2.30)

In fact it will be shown in a more complete treatment of the steady state (Chapter 4), including the expansion effects and the viscosity variation, that all terms of order \( (\Delta T)^2 \) cancel out leaving only trivial terms of order \( (\Delta T)^3 \). Calculations resulting from this treatment set an upper limit on the temperature difference of 20 degrees C. to ensure the validity of (2.30).

### 2.5 Time Dependent Solution

It is convenient to consider the concentration as the sum of a transient term, which tends to zero as \( X \to \infty \), and a steady state term,

\[ h(X,Y) = \frac{1}{2} s\Delta T \psi(X,Y) + h_\infty(Y). \]  ... (2.31)

The introduction of the factor \( \frac{1}{2} s\Delta T \) makes the transient term \( \psi \) independent of the unknown parameter \( s \) and renders the calculation general. Utilizing (2.31), equations (2.23-25) become
\[ \frac{\partial^2 \psi}{\partial Y^2} - \frac{3}{8} (1 - Y^2) \frac{\partial \psi}{\partial X} = 0, \quad \ldots \quad (2.32) \]

bounded by

\[ \frac{\partial \psi}{\partial Y} = 0, \quad Y = \pm 1, \quad 0 \leq X \leq \infty \quad \ldots \quad (2.33) \]

with the initial condition

\[ \psi = Y, \quad X = 0, \quad -1 \leq Y \leq 1. \quad \ldots \quad (2.34) \]

The new variable has the advantage that it makes the boundary conditions (2.33) homogeneous. From (2.33) and (2.34), we see that \( \psi \) is an odd function of \( Y \) about the duct axis \( Y = 0 \).

2.6 Finite Difference Approximation

Since \( \psi \) is antisymmetric about the duct axis, it is only necessary to consider the domain bounded by \( 0 \leq Y \leq 1 \) and \( 0 \leq X \leq \infty \). Let \( \Delta X \) and \( \Delta Y \) be increments of the variables \( X \) and \( Y \), where \( \Delta Y = \frac{1}{J} \), \( J \) being an integer. The set of points in the \( X,Y \) plane given by \( X = n\Delta X, \, Y = (j-1)\Delta Y \), where \( n = 0,1,2, \ldots \), and \( j = 1,2, \ldots, J+1 \), defines the grid (see over), whose mesh size is determined by \( \Delta X \) and \( \Delta Y \).

The approximation \( \psi(n\Delta X, j\Delta Y) \) is denoted by \( \psi_{n,j} \).

Because equation (2.32) is parabolic, the usefulness of an explicit difference approximation is limited by the stability

\[ \ldots \]

\[ \text{It is more convenient, as far as the computer programme is concerned, to dimension the } Y \text{ axis from } 1 \text{ to } J+1 \text{ rather than from } 0 \text{ to } J. \]
An implicit system, on the other hand, involves no such criterion and is therefore preferable. Introducing a six-point space difference (the Crank-Nicholson scheme),

\[
\left( \frac{\partial^2 \psi}{\partial y^2} \right)_{n,j} = \frac{\psi_{n+1,j+1} - 2\psi_{n,j+1} + \psi_{n+1,j-1} + (\psi_{n,j+1} - 2\psi_{n,j} + \psi_{n,j-1})}{2(\Delta Y)^2}
\]

\[\ldots + O(\Delta Y)^2, \quad \ldots \quad (2.35)\]

with an explicit "time" difference,

\[
\left( \frac{\partial \psi}{\partial x} \right)_{n,j} = \frac{\psi_{n+1,j} - \psi_{n,j}}{\Delta X} + O(\Delta X), \quad \ldots \quad (2.36)
\]
into (2.32), we have the following difference approximation to our differential equation,

\[ \psi_{n+1,j+1} - 2\psi_{n+1,j} + \psi_{n+1,j-1} \]

\[ = -\psi_{n,j+1} + 2\psi_{n,j} \left[ 1 - \frac{3(\Delta Y)^2(1-Y_j^2)}{8\Delta X} \right] - \psi_{n,j-1}, \quad \ldots \quad (2.37) \]

where the truncation errors, obtained from the remainder in a Taylor's series expansion of \( \psi_{n+1,j} \) etc. about \( \psi_{n,j} \), have been dropped. The central boundary condition is simply \( \psi_1 = 0 \). At the wall, a backward difference formula for \( \frac{\partial \psi}{\partial Y}_{n,j+1} \) with the same truncation error as in (2.35) is employed, so the condition becomes

\[ \psi_{n+1,J+1} - \frac{h}{3} \psi_{n+1,J} + \frac{1}{3} \psi_{n+1,J-1} = 0. \quad \ldots \quad (2.38) \]

For a discussion concerning the stability and convergence of the approximation (2.37) reference should be made to a standard text, e.g. Richtmyer. Suffice it to say here that the system is stable (i.e. that the errors inherent in the difference equation do not grow exponentially, but damp out) and that stability is a necessary and sufficient condition for convergence (meaning that the solution of the difference equation approaches the exact solution of the differential equation (2.32) in the limit, \( \Delta X, \Delta Y \rightarrow 0 \), as the mesh is refined). In practice it is only necessary to reduce the mesh size until satisfactory convergence is obtained.
Equation (2.37), together with the boundary conditions, leads to a set of \( J+1 \) linear algebraic equations involving the unknown \( \psi \)'s in line \( n+1 \) in terms of known values in the previous line, \( n \). Dropping the subscripts \( n, n+1 \), we have for line \( n+1 \),

\[
\begin{align*}
\psi_1 &= 0 \\
\psi_{j-1} + a_j \psi_j + \psi_{j+1} &= d_j \quad 2 \leq j \leq J, \quad \ldots (2.39) \\
\frac{1}{3} \psi_{j-1} - \frac{4}{3} \psi_j + \psi_{j+1} &= 0
\end{align*}
\]

where \( a_j \) and \( d_j \) are known scalars,

\[
\begin{align*}
a_j &= -2 \left[ 1 + \frac{3(\Delta Y)^2(1-Y^2_j)}{8\Delta X} \right] \\
d_j &= -\psi_{n,j+1} + 2\psi_{n,j} \left[ 1 - \frac{3(\Delta Y)^2(1-Y^2_j)}{8\Delta X} \right] - \psi_{n,j-1} \\
\end{align*}
\]

... (2.40)

By eliminating \( \psi_1 \) and \( \psi_{J+1} \), the left-hand side of (2.39) reduces to a tridiagonal matrix,

\[
\begin{align*}
a_2 \psi_2 + \psi_3 &= d_2 \\
\psi_{J-1} + a_J \psi_J + \psi_{J+1} &= d_J \quad 3 \leq j \leq J-1, \\
\frac{2}{3} \psi_{J-1} + \left( a_J + \frac{4}{3} \right) \psi_J &= d_J
\end{align*}
\]

... (2.41)

which is conveniently written in matrix notation as \( A \psi = d \), or
It is clearly inefficient to invert the $A$ matrix and then use the inverse matrix to obtain the solution for each "time" step in turn, because the inverse matrix itself is a dense array. A great saving in multiplication is achieved by retaining the form of (2.42) and using a form of Gaussian elimination for each step.

Following such an elimination procedure ascribed to Thomas, \(^{(40,41)}\) which is specific to tridiagonal matrices, we make the substitutions,

$$
q_2 = \frac{1}{a_2} \\
q_j = \frac{1}{(a_j - a_{j-1})} \quad 3 \leq j \leq J-1, \\
q_J = \frac{1}{\left[(a_J + \frac{b}{J}) - \frac{2}{J} a_{J-1}\right]} \\
g_2 = d_2 q_2 \\
g_j = (a_j - g_{j-1}) q_j \quad 3 \leq j \leq J-1, \\
g_J = (a_J - \frac{2}{J} g_{J-1}) q_J
$$

These transform the set of equations (2.41) into,

$$
\psi_J = \varepsilon_J \\
\psi_j = g_j - a_j \psi_{j+1} \quad 2 \leq j \leq J-1
$$

\[(2.44)\]
The purpose of the substitution is immediately apparent. The parameters \( q \) and \( g \) are calculated in order of increasing \( j \), then (2.44) is used to calculate the \( \psi \) in order of decreasing \( j \), i.e. \( \psi_j, \psi_{j-1}, \ldots, \psi_3, \psi_2 \). To complete the row we have \( \psi_1 = 0 \) and the explicit relation
\[
\psi_{j+1} = \frac{1}{2} \psi_j - \frac{1}{2} \psi_{j-1},
\]
amely the boundary conditions.

The numerical solution is now obtained by a marching process beginning with the initial condition, equation (2.34), for the line \( n = 0 \). Successive lines are calculated for increasing values of \( X \). The complete calculation has been programmed in Fortran language for an I.B.M. 1620 digital computer.

The duct was divided into 100 space increments \( (\Delta Y = .01) \) and the "time" increments \( \Delta X \) were then refined to give satisfactory convergence. As the steady state is approached the changes in concentration become small and, for a given accuracy, the increments \( \Delta X \) can be increased to save computing time. By starting with \( \Delta X = .00001 \) and increasing gradually to \( \Delta X = .0005 \), a suitable solution was obtained. The calculation was continued as far as \( X = .5 \).

The concentration profiles follow from the relation
\[
h = \frac{1}{2} s \Delta T (\psi - Y).
\]
In Figure 2 they are plotted over the top half of the duct for various values of \( X \). The profiles over the bottom half are antisymmetrical with respect to the top half and are therefore not shown. Recalling that we are only considering terms of order \( (\Delta T) \), we see that \( h \) is equivalent to \( (c - c_0)/c_0 \).
As in the steady state, the separation at the end of the
duct is obtained by integrating across each half-width. In order to
make the calculation general, the Soret coefficient is eliminated
by comparing the separation at each value of \( X \) with that at the
steady state. Following this, we introduce a separation factor \( F \),
defined by

\[
F(X) = \frac{(\Delta \bar{d})X}{(\Delta \bar{d})_{\infty}} = \frac{\bar{d} - \bar{d}'}{\frac{\Delta}{\delta}} \mathcal{S}_0 \Delta T, \quad \ldots (2.45)
\]

whose relation with \( h \) is readily shown to be

\[
F(X) = \frac{8}{s \Delta T} \int_{-1}^{1} h(1-Y^2) \, dY + o(\Delta T). \quad \ldots (2.46)
\]

To calculate \( F \) from the computed data we define \( \bar{\Psi} = \int_{-1}^{1} \psi(1-Y^2) \, dY \); then, to the usual degree of accuracy, \( F = 1 - 4 \bar{\Psi} \). The function \( \bar{\Psi} \)
is conveniently calculated from the computed data by numerical inte-
gration. A five point integration formula is included in the Fortran
programme for this purpose. The test of satisfactory convergence
was applied to the \( F \) curve, since it is the only form of the solution
with practical significance. The calculation was found to have
converged everywhere to at least three significant figures. \( F \) is
shown as a function of \( X \) in Figure 3 and in Appendix I a table
is provided to aid the experimental analysis.

We have solved the equations using \( c \) as a measure of
concentration. The $F$ curve represents the separation $\Delta c$ as a fraction of the steady state value $\Delta c_\infty$. It must be pointed out that this curve is not identical, except in the steady state, with that representing $\Delta N$ as a fraction of $\Delta N_\infty$.

2.7 The Initial Slope

The initial rate of change of $F$ is of interest. By writing the continuity equation (2.17) in the form

$$\frac{\partial J}{\partial Y} = -\frac{3}{8} \frac{\partial D}{\partial a} (1-Y^2) \frac{\partial h}{\partial X}, \quad \ldots (2.47)$$

we see from (2.46) that the rate of change of $F$ (with respect to $X$) is proportional to the flux at $Y=0$:

$$\frac{dF}{dX} = \frac{8}{aS \Delta T} \int_{-1}^{0} h(1-Y^2) dY = -\frac{64}{3S \Delta S \Delta T} J(0). \quad \ldots (2.48)$$

But for $X \to 0$, both $h$ and $\frac{\partial h}{\partial Y}$ are zero at $Y=0$, so from (2.15),

$$J(0) = -\frac{a}{2} \frac{S \Delta S \Delta T}{a} \quad \ldots (2.49)$$

and hence,

$$\left(\frac{dF}{dX}\right)_{X \to 0} = \frac{32}{3}. \quad \ldots (2.50)$$

The initial slope is drawn in Figure 3.
2.8 Variational Calculation of the Lower Eigenvalues

The function $F(X)$ can be represented analytically in the form,

$$F(X) = 1 - \sum_{n=1}^{\infty} A_n R_n \exp\left(-\frac{8}{3} \lambda_n^2 X\right) \quad \ldots (2.51)$$

where the exponential terms in the summation decrease very quickly in magnitude as $n$ increases for all but small $X$. The solution for large $X$, where only the first term in the series is important, can be found using a variational technique without excessive computation, and will in fact be adequate for the range in which most of the experimental results occur. Such a calculation is not justified merely to check the difference approximation, but the form of (2.51) has other advantages. It will be shown in Chapter 6 how the first term approximation assists in the calibration and provides a method for estimating $D$ from experimental results in cases where the diffusion coefficient is not available; a procedure which is necessary if $s$ is to be found accurately. Furthermore, an exactly similar calculation allows the effect of the temperature dependence of viscosity to be estimated for large $X$ (the experimental region) without having to work through from $X = 0$ as in the difference method. For these reasons the treatment is developed here in full. The numerical calculations are fewer then might be expected.

The calculus of variations is well established for solving problems in the theory of elasticity and has, more recently, been
used for the solution of heat transfer problems in duct flow. Sparrow and Siegel\(^{(42)}\) have shown how the technique lends itself, with relative ease of computation, to the calculation of the first few eigenvalues in Sturm-Liouville problems. The method will be developed here for our particular case. For detailed information on the mathematical fundamentals, reference should be made to Hilderbrand\(^{(43)}\) or some other standard text.

On separating the variables in equation (2.32), we obtain

\[
\psi = \sum_{n=1}^{\infty} C_n R_n(Y) \exp\left(-\frac{y}{2} \lambda_n^2 x\right), \quad \ldots (2.52)
\]

where the eigenfunctions are the solutions of

\[
\frac{d^2 R_n}{dY^2} + \lambda_n^2 (1-Y^2) R_n = 0, \quad \ldots (2.53)
\]

with boundary conditions

\[
R_n(0) = 0, \quad \frac{d}{dY} R_n(1) = 0. \quad \ldots (2.54)
\]

The problem is to determine the eigenvalues \(\lambda_n^2\) and the eigenfunctions \(R_n(Y)\) of equation (2.53). We require a good approximation to \(\lambda_1\) and a rough estimate of \(\lambda_2\) to determine the range over which the single term approximation is valid. To formulate the corresponding variational problem, first multiply both sides of (2.53) by a variation \(\delta R\) and then integrate the result over \((0,1)\) to obtain
\[ \int_0^1 \frac{d^2 R_n}{dY^2} \, \delta R \, dY + \int_0^1 \lambda_n^2 (1-Y^2) R_n \, \delta R \, dY = 0. \quad \ldots (2.55) \]

The second integrand is the variation of \( \frac{1}{2} \lambda_n^2 (1-Y^2) R_n^2 \). If the first integral is transformed by integration by parts, it takes the form,\(^*\)

\[ \left[ \frac{dR_n}{dY} \delta R \right]_0^1 - \int_0^1 \frac{dR_n}{dY} \, \delta \left( \frac{dR_n}{dY} \right) \, dY. \]

If the end condition \((2.54)\) is imposed, the integrated term vanishes, since \( \delta R(0)=0 \), and equation \((2.55)\) transforms into

\[ \delta \int_0^1 \left[ \lambda_n^2 (1-Y^2) R_n^2 - \left( \frac{dR_n}{dY} \right)^2 \right] \, dY = 0, \quad \ldots (2.56) \]

where the factors \( \frac{1}{2} \) have been dropped.

It follows that the problem of determining the eigenfunctions of \((2.53)\), subject to \((2.54)\), is equivalent to determining functions satisfying \((2.54)\) which render the integral in \((2.56)\) stationary. The variational problem in the form of \((2.56)\) is particularly well suited to numerical procedures for obtaining an approximate solution to equation \((2.53)\). One such technique, known

\(^*\)If \( Y \) is an independent variable (and hence \( \delta Y \equiv 0 \)) the operators \( \delta \) and \( d/dY \) are commutative.
as the Ritz method, consists essentially of assuming that the desired solution \( R_n(Y) \) can be approximated by a linear combination of \( m \) suitably chosen functions, each of which satisfies the boundary conditions (2.54). For the case of the \( n^{th} \) eigenfunction, we have

\[ R_n = A_{n1}R_{n1} + A_{n2}R_{n2} + \ldots + A_{nm}R_{nm}, \quad \ldots (2.57) \]

where the A's are constants determined so that (2.56) is satisfied. For eigenvalues higher than the first there are additional conditions for the A's to satisfy, namely that the eigenfunctions be orthogonal with respect to the weighting function \((1-Y^2)\),

\[ \int_0^1 (1-Y^2)R_nR_m \, dY = 0, \quad m = n-1, n-2, \ldots, 1. \quad \ldots (2.58) \]

A modification of the Ritz method, suitable for computation, consists in obtaining a sequence of approximations in which the first assumption is merely \( A_{n1}R_{n1} \), the second is \( A_{n1}R_{n1} + A_{n2}R_{n2} \) and so on, the \( m^{th} \) assumption being equation (2.57). The relevant A's are determined at each stage of the process as indicated above. By comparing successive approximations, the calculation can be continued until the required degree of accuracy is obtained.

An obvious set of functions which satisfy (2.54) are

\[ \sin(2k-1)\frac{\pi}{2}Y, \quad k = 1, 2, 3, \ldots \]

We shall find that only three terms are required and shall restrict
the argument to the series,
\[
R_1(Y) = A_{11}\sin\frac{\pi}{2}Y + A_{12}\sin\frac{3\pi}{2}Y + A_{13}\sin\frac{5\pi}{2}Y, \quad \ldots (2.59)
\]

then the result of replacing \( R_1 \) by its approximation in (2.56) is
\[
\delta \int_0^1 \left[ \lambda^2(1-Y^2)(A_{11}\sin\frac{\pi}{2}Y + A_{12}\sin\frac{3\pi}{2}Y + A_{13}\sin\frac{5\pi}{2}Y)^2 \right. \\
- \frac{\pi^2}{4} (A_{11}\cos\frac{\pi}{2}Y + 3A_{12}\cos\frac{3\pi}{2}Y + 5A_{13}\cos\frac{5\pi}{2}Y)^2 \left. \right] dY = 0.
\]

\[
\ldots (2.60)
\]

Carrying out the integrations, making use of the orthogonality of
the harmonics, there results
\[
\delta \left[ \left\{ \frac{1}{2} - \lambda^2 \left( \frac{1}{3} - \frac{1}{\pi^2} \right) \right\} A_{11}^2 + \left[ \frac{9\pi^2}{8} - \lambda^2 \left( \frac{1}{3} - \frac{1}{9\pi^2} \right) \right] A_{12}^2 + \left[ \frac{25\pi^2}{8} - \lambda^2 \left( \frac{1}{3} - \frac{1}{25\pi^2} \right) \right] A_{13}^2 \\
- \frac{5}{2\pi^2 \lambda^2} A_{11} A_{12} - \frac{17}{8\pi^2} A_{12} A_{13} + \frac{13}{18\pi^2} A_{13} A_{11} \right] = 0.
\]

\[
\ldots (2.61)
\]

Noting that the A's are the quantities to be varied, equation (2.61)
is written as
Since the variations in the $\delta A$'s are arbitrary, their coefficients must vanish giving a set of linear homogeneous equations for $A_{11}$, $A_{12}$ and $A_{13}$. The condition for a non-trivial solution is

\[
\begin{bmatrix}
\frac{\pi^2}{4} - 2\lambda \left(\frac{1}{3} - \frac{1}{n^2}\right) \\
- \frac{5}{2n^2} \lambda^2 \\
\frac{13}{18n^2} \lambda^2
\end{bmatrix}
- \begin{bmatrix}
\frac{9\pi^2}{4} - 2\lambda \left(\frac{1}{3} - \frac{1}{9n^2}\right) \\
\frac{25\pi^2}{4} - 2\lambda \left(\frac{1}{3} - \frac{1}{25n^2}\right) \\
- \frac{17}{8n^2} \lambda^2
\end{bmatrix}
\begin{bmatrix}
A_{11} \\
A_{12} \\
A_{13}
\end{bmatrix}
= 0.
\]

\[\gamma_{263}\]

resulting in a cubic equation for $\lambda^2$. The three roots to this equation are the third, second and first approximations to the first three eigenvalues in ascending order. Using a superscript
to denote the order of the approximation, the roots would be $\lambda_1^{(3)}$, $\lambda_2^{(2)}$ and $\lambda_3^{(1)}$. Lower order approximations are obtained by considering fewer terms in (2.59). The result is

$$\lambda_1^{(1)} = 2.30, \quad \lambda_2^{(2)} = 2.2639, \quad \lambda_3^{(3)} = 2.2632,$$

$$\lambda_2^{(1)} = 6.7, \quad \lambda_2^{(2)} = 6.30,$$

the third eigenvalue being of no interest to us.

To obtain the corresponding approximations to the eigenfunctions, we require to evaluate the coefficients $A_{11}$ etc. Only two independent relations between these coefficients can be obtained by setting the coefficients of the $6A$'s to zero in (2.62). A third equation must be found from an arbitrarily imposed condition. We put $R_n(1) = 1$. This is allowable since $C_n$ is determined from the initial condition and is independent of the new condition. Now, from (2.52) and the relation between $F$ and $\bar{W}$, the separation is of the form

$$F(X) = 1 - 4 \sum_{\lambda_n}^\infty C_n \exp\left(-\frac{8}{3} \lambda_n^2 X \right) \int_0^1 R_n(1-Y^2) dY, \quad \cdots (2.64)$$

from which we see that the integral $\bar{F}_n = \int_0^1 R_n(1-Y^2) dY$ plays an important part. The approximations to this quantity are calculated to be
\[ R_1^{(1)} = 0.342, \quad R_1^{(2)} = 0.391, \quad R_1^{(3)} = 0.392, \]
\[ R_2^{(1)} = -0.07, \quad R_2^{(2)} = -0.11. \]

After calculating the coefficients \( c_1 \) and \( c_2 \) from the initial condition (2.34) using the orthogonality of the eigenfunctions in the standard manner, we arrive at the desired expression,

\[ F(X) = 1 - 1.045\exp(-13.66X), \quad x \geq 0.03. \quad \ldots \; (2.65) \]

The range is not critical and represents the region over which the second exponential term, approximated by \( 0.026\exp(-89X) \), is less than 1% of \( F(X) \). Agreement with the computed difference approximation is excellent:

<table>
<thead>
<tr>
<th>( X )</th>
<th>( F(X) ) Eqn(2.65)</th>
<th>Second expn. term</th>
<th>( F(X) ) diff. approx.</th>
</tr>
</thead>
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<td>.030</td>
<td>.306</td>
<td>+.002</td>
<td>.308</td>
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</tbody>
</table>
CHAPTER 3

DESCRIPTION OF APPARATUS

To follow the description of the cell, reference may be made to the design drawing (Figure 4) and to photographs taken before and after its assembly (Figures 5 and 6). The constructed cell follows the design drawing except for two minor points noted below. Accompanying an account of the apparatus are a flow diagram (Figure 7) and photographs showing a general and a close-up view of the rig (Figures 8 and 9).

3.1 The Cell

The duct consists of two \( \frac{1}{2} \) in. copper plates bolted together and separated by a gasket. This gasket is a single piece of \( \frac{1}{16} \) in. thick P.T.F.E. encircling the duct, the surfaces of which are strips raised above the flanges so that the depth, after bolting the plates together, is about 0.3 mm. The width of the duct is 5.0 cm. while the length is nominally 15 cm. Both the duct surfaces and the flanges are ground flat to a tolerance of \( \pm 0.0005 \) in.

The inlet to the duct is a \( \frac{5}{32} \) in. i.d. stainless steel tube leading through the top copper plate (the hot side) into a vertical slit which opens out to the width of the duct. This tube is inclined slightly to the horizontal to avoid trapping air in the entrance section. The end of the duct is flared out to acc-
ommomote a stainless steel blade* which separates the flow into two halves. The blade, or knife-edge, is wedge-shaped and is held in position by a \( \frac{1}{16} \) in. thick tail fitting between the copper plates in a similar manner to the gasket. It rests on raised shoulders, one on each side, which provide \( \frac{3}{64} \) in. gaps above and below the blade through which the top and bottom fractions pass on their way out of the cell. The blade is machined so that its sharp edge rests horizontally across the duct and, as nearly as possible, bisects it. The shoulders, which are slightly wider than the duct so that the knife-edge stretches across its full width, are machined to be a push-fit into both copper plates.

Behind the knife-edge are slots cut into the copper at the same angle as the sides of the blade. These slots are constricted to meet \( \frac{3}{32} \) in. i.d. stainless steel tubes through which the effluent streams pass from the cell. Sitting flush to the back of the blade and right across the width of the slot, are \( \frac{3}{32} \) in. thick strips of P.T.F.E.\(^\text{N}\) through each of which are drilled 36 uniformly spaced .028 in. diameter holes. The purpose of these is to provide sufficient resistance to flow to ensure a uniform

---

*Originally, as shown on Figure 4, a P.T.F.E. blade was used. The large coefficient of expansion of P.T.F.E. relative to copper caused the blade to become S-shaped when the temperature gradient was applied, the result being that the separations obtained were low.

\(^\text{N}\)The sintered bronze strips, indicated in the design drawing, were found to have too high a resistance to flow.
liquid take-off across the width of the duct: it has, it will be remembered, already been assumed that the flow is independent of the duct width.

Water from thermostat tanks, pumped through reservoirs attached to the copper plates, provides the required temperature difference across the cell. The reservoirs are 1 in. high and made from brass strips screwed into place on the copper plates. They are hard-soldered to render them leakproof. Situated at the end of each reservoir at 30 degree angles to the horizontal are $\frac{1}{2}$ in. copper pipes.

Three $\frac{1}{8}$ in. diameter holes are drilled through one side of each of the copper plates. They are drilled to reach the centre-line of the duct and at an angle calculated to bring them within a few thousandths of an inch of the duct surface. Because, however, it is impossible to drill a hole this length and diameter in copper without the drill wandering from true, the thermocouples finished further from the duct surface than originally planned. In fact for the hot plate they are as much as 0.2 inch out. Their exact positions were determined from measurements made on the cell before assembly and are given at the end of this chapter together with other cell dimensions. There are, then, three pairs of thermocouples spaced along the length of the duct recording the temperature difference and mean temperature at these positions.

The completed cell, as described above, is nickel plated
to avoid corrosion. No plating penetrated the thermocouple holes because of their small diameter. The cell is mounted horizontally above the thermostat tanks.

3.2 **Attainment of Constant Temperature Difference**

Since the separation is directly proportional to $\Delta T$, then for 1% overall accuracy it is required not only to measure $\Delta T$ to 1% but to keep it constant at all points along the duct to the same degree of accuracy, that is 0.1 degree for a 10 degree C. temperature difference. With simple counter-current flow, as implied by the design drawing, it was impossible to achieve this even with a flowrate as high as 20 litres min$^{-1}$. Baffles attached to the reservoir covers or packing with various materials, the best of which were copper raschig rings, improved matters but not enough. A system was resorted to in which controlled jets of thermostated water were allowed to impinge in different places directly on to the copper plates. Such a set-up was employed in both reservoirs; the arrangement in the top one can be seen in Figure 9. Six $\frac{1}{8}$ in. gas needle valves are soldered in a vertical position along a distributor plate which forms the cover of the reservoir. In this way the amount of water issuing from each of six $\frac{1}{16}$ in. holes, evenly spaced along the centre-line on the underside of the distributor, is individually controlled. With a similar distributor on the bottom reservoir, the amount of heat transferred at different places along the duct can be controlled so that the temp-
erature difference measured by each of the three pairs of thermocouples is identical. Though of less importance, it is also possible to keep the mean temperature constant along the entire length of the cell.

3.3 The Flow System

Solution from a 5 litre aspirator bottle, situated above the cell, passes through a glass sinter before entering the cell. The two effluent streams are cooled to a uniform temperature by a heat exchanger, single-pass with 4 in. long \( \frac{3}{8} \) in. i.d. stainless steel tubes on the solution side, through which water is pumped from a small thermostat kept approximately at ambient temperature. The separated fractions are collected in two "burettes" fixed in a vertical position in front of the cell. They are 90 cm. lengths of 1.4 cm. i.d. precision bore tubing joined at the bottom by a length of P.V.C. tubing to a mercury reservoir. By lowering the reservoir, the mercury levels in the burettes fall so that equal quantities of solution are drawn from above and below the blade and stored in the burettes. By raising the mercury after a run the products can be expelled through the sampling tubes and analysed at leisure. All glass tubing between the cell and burettes is capillary and the "dead-volume" at the top of the burettes is as small as is practicable. The mercury reservoir, or hoist, is attached to a vertical screw thread driven by a \( \frac{1}{16} \) h.p. synchronous motor. A Köpp Variator (a continuously variable gear box with
a ratio from \( \frac{1}{3} \) to 3) and a secondary gear box (to select the required range for the variator) provide a range of total flowrate from 2 to 200 cm\(^3\) min\(^{-1}\). Corresponding Reynolds numbers based on the duct dimensions are 1.5 and 150, which are well inside the laminar regime. A counter on the variator facilitates selection of the desired flowrate. The hoist structure is separate from the main rig so that it is unaffected by vibrations from the latter. Wooden rules behind the burettes enable the rate of fall of the mercury menisci to be timed.

Consider the start of a run when the mercury is at the top of the burettes, the taps in the lines from the aspirator bottle are open and the hydrostatic pressure on the burette side balances the mercury in the reservoir. If now the reservoir begins to descend at a constant speed, the mercury in the burettes will not immediately assume its terminal speed (which incidentally is not the same as the speed of the hoist) but accelerates slowly to it. The time taken to reach the terminal speed depends on the resistance to flow, largely made up of the sintered glass disk at the inlet and the P.T.F.E. filters at the back of the blade. Although the total resistance has been kept as low as possible, the initial acceleration is significant for the faster runs when the mercury may have reached the bottom of the burettes before the terminal speed has been effectively attained. This problem is surmounted by allowing the hoist to drop a predetermined distance from the position of hydrostatic equilibrium before
the taps at the top of the burettes are opened. The terminal speed can, as it were, be anticipated and the mercury accelerates to it almost immediately. There is, however, one more problem concerned with flow resistance. After the terminal speed has been attained, the mercury levels in the burettes will only be the same if the resistance to flow in both the lines is identical. This, of course, will not be exactly so and, in consequence, a valve must be inserted in the line with the lower resistance. Basically, the valve used consists of two concentric cones and is adjusted by screwing the central one, or the plunger, into the outside one. The seal is a P.T.F.E. "O"-ring round the plunger. The valve is never required to stop the flow completely, though in fact it is machined well enough to do so. It is fitted between the heat exchanger and the burettes in the line carrying the top fraction.

All metal-glass connections are P.T.F.E. tubing, while everywhere else ball and socket ground glass joints are used. The latter conveniently allow the burette assembly to be removed for cleaning. No grease is employed anywhere. The taps, the detailed function of which will become clear when the experimental procedure is discussed, are all lubricated with a film of P.T.F.E. applied by spraying the surface with an aerosol suspension.

3.4 The Thermostats and Temperature Control

The thermostats are two tanks of approximately 50 litres capacity nominally kept at 20 and 30 degrees C. Control is by
means of Electro Methods adjustable contact thermometers. Each regulator is placed in the grid circuit of a triode valve, the anode current of which operates a Sunvic hot-wire relay. In this way the relatively large current which is necessary to operate the relay does not pass through the regulator, sparking at the mercury surface is reduced and the life of the regulator is increased. Furthermore, frequent adjustment is unnecessary. The circuit is shown in Figure 10.

Both tanks are equipped with 300 Watt tubular heaters and water cooling coils. The cold tank has an additional cooling coil supplied by a small refrigerator installed to cope with the summer laboratory temperatures. Two Stuart Turner size 10 rotary pumps mounted above each tank are used for stirring, while size 12 pumps circulate water from each thermostat through the cell reservoirs.

It might be thought, with 300 Watt heaters as the means of temperature control, that oscillations in the cell temperature might result. This is not so. The heat flux through the cell is sufficiently high to require large capacity heaters and any local oscillations in the thermostats are damped out before the duct surface is reached. In fact it was found possible to keep the thermocouple readings constant to 0.1 mv (.025 deg.C) during a run.

3.5 Thermocouples

Six \( \frac{1}{8} \) in. diameter copper-constantan thermocouples fit in the side of the copper end plates. Glycerol is used to ensure
good thermal contact.

Because of the vertical temperature gradient in the copper plates, there exists a temperature difference of about 0.1 degree C. across each drilled hole. The thermocouples are required to measure the mean temperature at the end of the hole. However, though they are a good fit, their junction inevitably makes better thermal contact in one particular place than in any other. In consequence, rotation of the thermocouples leads to a change in the observed temperature. For example, thermocouples made by soldering a constantan wire to the end of a cylindrical sheath of copper, through which the wire passes, gave on rotation in each hole a variation of 5 mv (0.125 deg.C.) in the presence of the temperature gradient. The extremes correspond to an effective contact of the junction with the top and bottom of the hole. Such variations are reduced by making the sheath out of, and surrounding the junction with, a bad thermal conductor.

The best results were obtained with thermocouples consisting essentially of 32 S.W.G. copper and constantan wires fused together and Araldite-ed to the end of twin bore silica tubes. Rotation of these gave only a 2 mv variation.

The thermocouples are connected to a common cold junction. They were calibrated with an N.P.L. standard mercury-in-glass thermometer graduated in hundredths of a degree. The set were so nearly identical that one calibration curve sufficed for them all, the
error in this being no greater than the uncertainty in their position.

3.6 Cell Dimensions

The following dimensions were determined before the cell was assembled,

- Width of duct (ruler) = 5.00 cm.
- Length of duct (ruler) = 15.50 cm.
- Height of duct surface above flange (depth gauge) = 0.0250 ± 0.003 in. (same for both plates)
- Thickness of gasket (micrometer) = 0.063 ± 0.001 in.

The duct width after assembly, as calculated from the last two measurements, would be 0.013 in. This, of course, assumes that the P.T.F.E. was not compressed when the bolts were tightened, but it will be at least as good an estimate as obtained with a feeler gauge round the outside of the assembled cell, the latter being uncertain because the electro-plating piles up on the corners.

The location and distances of the thermocouple holes from the duct surface were determined by measuring their depth and angle. The vertical distances, in inches, of the thermocouple junctions from the duct surface are given in the following table,
<table>
<thead>
<tr>
<th>Location of Thermocouple</th>
<th>Hot Plate</th>
<th>Cold Plate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Entrance end</td>
<td>.221</td>
<td>.135</td>
</tr>
<tr>
<td>Middle</td>
<td>.209</td>
<td>.146</td>
</tr>
<tr>
<td>Exit end</td>
<td>.189</td>
<td>.141</td>
</tr>
</tbody>
</table>

All the holes were found to be within .04 in. horizontally from the centre.

Because of the distance of the thermocouples from the surface, the temperature difference across the duct will be slightly smaller than the measured difference. The correction will depend on the thermal conductivity of the liquid being used.
CHAPTER 4

THE MATHEMATICAL MODEL RECONSIDERED

The approximations involved in the mathematical model and those subsequently introduced in simplifying the resulting differential equation are reconsidered. An estimate is given of the temperature interval below which the previous solution may be considered correct.

4.1 Introduction

The phenomenological theory described in Chapter 2 is based on a simplified mathematical model which differs in several respects from the true physical situation in the apparatus just described.

A solution has been presented in which the physical parameters have been assumed constant and appropriate mean values used. In principle, as Agar points out in his solution for the static cell\(^{(36)}\), this is not true and \(D, s, \alpha, \sigma\) and \(\frac{dT}{dy}\) may all be functions of \(c\) and \(T\). For the flow cell, variations in viscosity \(\mu\) must also be taken into account. The separation around the knife-edge must be considered in more detail, particularly with reference to the volume changes which occur when the solutions are cooled to a uniform temperature. It is convenient to do this for the steady state where we do not have to resort to numerical analysis. At the other end
of the cell we must examine the entry effects, for neither the velocity profile nor the temperature distribution are set up immediately upon entry to the duct.

Besides the above points, which can all be given a quantitative treatment, there are many irregularities and deviations arising from practical difficulties and constructional uncertainties in the apparatus. Some of these can only give rise to speculation and their neglect is only justified by the successful operation of the cell, while others, such as the uncertainty of the effective duct dimensions, necessitate the calibration of the cell using a system of known thermal diffusion properties. Points such as these are discussed in Chapter 6.

4.2 Variable Physical Parameters

Since the change in concentration during Soret diffusion is small, the concentration dependence of the relevant physical parameters can be ignored in comparison with their temperature dependence. D and s have a rather large dependence on T and, therefore, are certainly not independent of Y. As an example, consider an aqueous salt solution with a mean temperature of 25 degrees C. and a temperature difference of 10 degrees C.; D will change by about 25% of its mean value and s by about $1 \times 10^{-3} \text{deg}^{-1}$ which is of the same order as its absolute value and may even cause s to change sign. In organic mixtures these variations are usually
smaller, though not markedly so. Although it is clear that the constant parameter solution will give correct results if $\Delta T$ is sufficiently small, it is far from obvious that the solution is satisfactory for $\Delta T=10$ deg.C. With this in mind, Agar\(^{(45)}\) concerned solely with the pure Soret cell, obtained a more accurate solution of the equivalent differential equation (equation (2.20) with the right-hand side replaced by $\frac{\partial h}{\partial t}$). Including the temperature dependence of $D, \alpha, c_a$ and $\frac{\partial T}{\partial y}$, he shows how the equation may be transformed to a linear differential equation in which the coefficients are constant to a higher degree of approximation than in the original equation. After solving the new equation and inserting numerical values describing the variations of the parameters for the case of aqueous solutions, Agar concludes that the errors arising from the use of mean values are entirely trivial, being of order $(\Delta T)^3$, if the quantity concerned is ultimately determined by measurements made at points situated symmetrically above and below the central plane. We could indeed formulate a similar equation for the flow cell, including the unsymmetrical velocity profile due to viscosity variations across the duct, which could be solved by numerical techniques similar to those already employed. Firstly, however, it would be less satisfactory because all numerical values would have to be substituted before the equation was solved, and secondly, the existence of practical problems such as the necessity for calibrating the cell do not justify a more accurate solution.

It is proposed to adopt Agar's conclusion and to assume that it
applies equally well to the flow cell. It remains, then, only to justify the use of a mean viscosity in the time-dependent solution, but first we shall reconsider the steady state.

4.3 The Steady State Reconsidered in Detail

The separation around the blade is considered in more detail than before, particularly with reference to the volume changes which occur after it. Variation of \( s, c \) and \( \frac{\partial T}{\partial Y} \) will be taken into account and all terms of order \( (\Delta T)^2 \) will be retained. It will be shown that all terms of order \( (\Delta T)^2 \) cancel out, leaving only trivial terms of order \( (\Delta T)^3 \) in the expression for the separation. The third order terms are too cumbersome to carry through the calculation here, but an estimate of their magnitude will be given at the end.

Equation (2.15) with \( J_{1Y}^P = 0 \) becomes

\[
\frac{dh}{dY} + \left[ (s+a)h + s \frac{\partial a}{\partial Y} \right] \frac{dT}{dY} = 0. \quad \ldots (4.1)
\]

Allowing for the variation of parameters is straightforward in the steady state.

The temperature dependence of the Soret coefficient is expressed in the form,

\[
s = s_0 + (T-T_0)s'_0 + \frac{1}{2}(T-T_0)^2s''_0, \quad \ldots (4.2)
\]

where \( s_0, s'_0 \) and \( s''_0 \) are the coefficient and its derivatives referred
to \( Y = 0 \). No extra temperature dependence results from using \( s_0 \) in place of \( s'_0 \); it is easily shown that the derivatives \( s'_0 \) and \( s'_o \) are the same order of magnitude. In dilute aqueous solutions at 25 degrees C, \( s'_0 = 1 \times 10^{-4} \text{deg}^{-2} \) for most uni-univalent salts.\(^{(10,19,46)}\)

Results for organic systems are not so reliable and show a large variation between different systems. For example, Saxton and Drickamer's data\(^{(47,48)}\) with a stirred diaphragm cell give a variation between \( 0.2 \times 10^{-4} \) and \( 1.4 \times 10^{-4} \text{deg}^{-2} \) in \( s'_0 \) over a range of systems, while the more reliable data of Bierlein, Finch and Bowers\(^{(17)}\) for benzene-n-heptane in a pure Soret cell give much lower values, varying over the composition range from \( 0.02 \times 10^{-4} \) to \( 0.08 \times 10^{-4} \text{deg}^{-2} \). The only information concerning \( s''_0 \) is based on Longsworth's data for aqueous KCl,\(^{(10)}\) from which \( s''_0 = -7 \times 10^{-7} \text{deg}^{-3} \).

For pure water at 25 degrees C, the coefficient of expansion, \( \alpha = 2.27 \times 10^{-4} \text{deg}^{-1} \), is usually small compared with \( s'_0 \), but for organic systems the two parameters are of the same order; for example, \( \alpha = 1.25 \times 10^{-3} \text{deg}^{-1} \) for CCl\(_4\) at the same temperature. Variation of \( \alpha \) with temperature is always insignificant compared with \( s'_0 \).

By expanding the thermal conductivity \( k \) about \( Y = 0 \), the temperature gradient can be shown to be

\[
\frac{dT}{dy} = \frac{1}{2} \kappa \Delta T (1 - \frac{1}{2} \kappa \Delta T Y),
\]

where \( \kappa = \left( \frac{d\ln k}{dT} \right)_0 \). The results of Challoner and Powell\(^{(49)}\) give
K = 2.46 \times 10^{-3} \text{deg}^{-1} \text{ for pure water and } K = -1.48 \times 10^{-3} \text{deg}^{-1} \text{ for CCl}_4 \\
\text{at 25 degrees C. Lateral heat flow and convection have been ignored. Although in a 1 cm. high cell there is a limited amount of convection which gives rise to a greater variation than implied by (4.3), results from our cell indicate that it is convection free.}

The velocity profile is irrelevant to the value of $h_\infty$ but, nevertheless, it affects the separation at the blade. We must therefore also consider the variation in viscosity. This we do by writing the profile in the form,

\[ u = \frac{3}{2} \bar{u} (1-Y^2)(1+\beta_1 \Delta T Y + \beta_2 (\Delta T)^2 (1-5Y^2)), \]  

(4.4)

where $\beta_1 = -\frac{1}{6}(\frac{d \ln \mu}{dT})_0$ and $\beta_2 = -\frac{\frac{d^2(1/\mu)}{dT^2}}{140}$. For pure water at 25 degrees C., $\beta_1 = 4.0 \times 10^{-3} \text{deg}^{-1}$ and $\beta_2 = -8.7 \times 10^{-7} \text{deg}^{-2}$, but for organic solvents the coefficients are lower; thus in CCl$_4$, $\beta_1 = 1.9 \times 10^{-3} \text{deg}^{-1}$ at the same temperature.

Finally, $\frac{d\alpha}{dY}$ is expanded as a function of $Y$ by solving equation (2.11) with the condition $\int_{-1}^{1} \frac{d\alpha}{\bar{u}} \, dY = 2 \bar{c}$:

\[ \frac{d\alpha}{dY} = 1 - \frac{1}{2} \alpha \Delta T Y - \frac{1}{40} \alpha (\Delta T)^2 \left[ (\alpha + K)(1-5Y^2) - 4 \beta_1 \right] + O(\Delta T)^3. \]  

(4.5)

Returning now to the steady state equation (4.1), using (4.2-5) and integrating with the condition $\int_{-1}^{1} \frac{h \, dY}{\bar{u}} = 0$, we obtain the solution,
\[
\begin{align*}
\begin{split}
    h_\infty(Y) &= -\frac{1}{2} s_o \Delta T Y - \frac{1}{40} (\Delta T)^2 \left[ \left( s_o^2 + s_o K + 2 s_o \alpha - s_o' \right) (1 - 5Y^2) - 4s_o \beta_1 \right] \\
        &\quad + O(\Delta T)^3,
\end{split}
\end{align*}
\]

Reintroducing \( c \), equation (2.10), we find the concentration profile in the duct to be

\[
\begin{align*}
  c_{\Delta T} &= \bar{c} \left\{ 1 - \frac{1}{2} (s_o + \alpha) \Delta T Y - \frac{1}{40} \left[ (s_o + \alpha)^2 + K(s_o + \alpha) - s_o' \right] (1 - 5Y^2) - 4\beta_1 (s_o + \alpha) \right\} (\Delta T)^2 \\
  &\quad + O(\Delta T)^3,
\end{align*}
\]

where the subscript \( \Delta T \) indicates the presence of the temperature gradient.

At the end of the duct the solution is divided into two streams around a knife-edge which is centred on the axis \( Y = 0 \). Equal volumes are collected in burettes which are conveniently, though not necessarily, considered to be at the mean cell temperature \( T_0 \). However, because the temperatures of the half streams in the cell are different, a larger volume flowrate occurs above the blade than below it; the result being, since the flow is laminar, to displace the effective position of the blade downwards a small distance \( \delta \) (see page 70). From a conservation of mass, \( \delta \) is found to be \( \frac{1}{6} \Delta T \left( \alpha - 2\beta_1 \right) + O(\Delta T)^3 \). As before, the mean concentrations of the two streams at \( T_0 \) are \( \bar{c}' \) and \( \bar{c}'' \) for the top and bottom halves of the cell respectively. The mean velocity is unaffected by the presence of the temperature distribution if the latter is
considered to be symmetrical with respect to the centre of the cell. By integrating $c_{\Delta T}$ over the top half of the duct between $Y=-\delta$ and 1 with the velocity profile as weighting factor, we find that the molar flowrate of solute above the blade is $\overline{u}b\bar{c}(1-\frac{3}{16}s_0\Delta T)+O(\Delta T)^3$, where $b$ is the breadth of the cell. Similarly for the flowrate below the blade, we have $\overline{u}b\bar{c}(1+\frac{3}{16}s_0\Delta T)+O(\Delta T)^3$. With an overall mass balance to relate $\bar{u}$ with the velocity in the burettes, we finally obtain

$$\left(\frac{\bar{c}^*}{c_0}\right)_{\infty} = \frac{3}{8}s_0\Delta T + O(\Delta T)^3. \quad \ldots (4.8)$$

Calculation of the third order term is tedious and involves many terms. The dominant ones are those containing $s_0$ and its derivatives, although in aqueous solutions $\beta_1$ is also significant. The result can best be expressed as the error $\Delta s_0$ in the Soret coefficient when determined from the first order approximation, regarding the third order solution as correct. As an example consider three cases, $s_0=0$, $5\times10^{-3}$, and $10\times10^{-3}\text{deg}^{-1}$. Using the physical properties of dilute aqueous solutions, with $\Delta T=10\text{ deg C}$, $10^3\Delta s_0$ is found to be $-0.0004$, $+0.0005$ and $+0.001\text{ deg}^{-1}$ respectively.

Such calculations can be used to fix an upper limit on $\Delta T$ for the validity of the first order equation (in the steady state). If we specify a tolerable error of, say, $|\Delta s_0|\leq 0.005\times10\text{ deg}^{-1}$, then we arrive at the conditions

\begin{align*}
(i) \quad & \Delta T \leq 20\text{ deg C} \\
(ii) \quad & |s_0| \leq 10^{-2}\text{deg}^{-1}
\end{align*}
None of these is critical; in many cases even larger temperature differences may be used without loss of accuracy. Clearly, then, the only significant errors will be experimental.

In theory the heat exchanger is dispensible and the effluent streams can be allowed to enter the burette at the temperature they leave the cell. "Cooling" takes place down the length of the burette until room temperature is attained at the mercury surface; thus the temperature, particularly the hot side, is a function of burette height and time. By considering carefully the conservation of mass in this system, it can be shown that, if the burettes are cooled to a uniform temperature after the run but before the concentrations are compared, equation (4.8) is still valid. In practice the heat exchanger is retained because, with both burettes at room temperature, the effect of local draughts is the same on either side and the separation remains unaffected.

4.4 Viscosity Variations and the Time Dependent Solution

Retaining the unsymmetrical terms, the relation between $F(X)$ and $h$, equation (2.46) can be rewritten to a higher degree of accuracy. Thus, writing $\Delta \kappa = \alpha + \chi h$, expanding $\alpha$ according to (4.5) and integrating with the skew velocity profile (4.4), it can be shown that,
\[
F(X) = \frac{4}{s \Delta T} \left( \int_{-\delta}^{1} - \int_{-1}^{-\delta} \right) h(1-Y^2)(1+\beta \Delta TY) \, dY + O(\Delta T)^2 \quad \ldots \quad (4.9)
\]

where \( \delta \) is the same as before. Since \( F \) is zero order in \( \Delta T \), the second order term corresponds to the \((\Delta T)^3\) error in the separation. From the definition of \( \psi \), equation (2.31), and the steady state solution, we have \( h = \frac{1}{2} s \Delta T (\psi - \psi) + O(\Delta T)^2 \). The second order terms in \( h \) cancel out in the following integration in the same way as in the integration of (4.7). Substitution in (4.9) gives, on simplification,

\[
F(X) = 1 - 2 \left( \int_{-\delta}^{1} - \int_{-1}^{-\delta} \right) \psi(1-Y^2)(1+\beta \Delta TY) \, dY + O(\Delta T)^2 \quad \ldots \quad (4.10)
\]

Experimentally we are interested in the solution for "large" \( X \), so to investigate the errors under these conditions we employ the variational technique already described. We shall refer to the previous solution with the simple parabolic velocity profile as the unperturbed problem. The perturbed problem reduces to finding the eigenvalues and eigenfunctions of the equation,

\[
\frac{d^2 R_n}{dY^2} + \lambda_n^2(1-Y^2)(1+\beta \Delta TY)R_n = 0, \quad \ldots \quad (4.11)
\]

(c.f. equation (2.53)). Because the perturbed calculation is not symmetrical about \( Y = 0 \), we must consider the complete domain \(-1 \leq Y \leq 1\) with boundary conditions,
\[
\frac{d}{dY} R_n(\pm 1) = 0. \quad \ldots (4.12)
\]

If the same series as before, \( \sum \sin(2k-1) \frac{\pi}{2} Y \), is used as an approximation to \( R_n \) (it satisfies (4.12)) and substituted in the variational integral,

\[
\delta \int_{-1}^{1} \left[ \lambda_n^2 (1-Y^2)(1+\beta_1 Y) R_n^2 - \left( \frac{dR_n}{dY} \right)^2 \right] dY = 0, \quad \ldots (4.13)
\]

then, because \( \int_{-1}^{1} Y (1-Y^2) \left[ \sum \sin(2k-1) \frac{\pi}{2} Y \right]^2 dY = 0 \), the perturbation term containing \( \beta_1 \) disappears and the problem is reduced to the unperturbed case, since for the remaining integrals in (4.13), \( \int_{-1}^{1} = 2 \int_{0}^{1} \). The second order perturbation involving \( \beta_2 \) does not disappear but its effect is insignificant. The eigenvalues and eigenfunctions are therefore unchanged. For similar reasons the coefficients \( C_n \) are also identical with the previous set.

Now we return to (4.10) and substitute the series solution for \( \psi \), equation (2.52). Using the fact that \( R_n(1-Y^2) \) is an odd function about \( Y = 0 \) and concerning ourselves solely with the first exponential term, the expression reduces to

\[
F(X) = 1 - 4C_1 \exp\left( -\frac{8}{3} \lambda_1^2 X \right) \int_{-1}^{1} R_1(1-Y^2) \, dY + O(\Delta T)^2 \ldots (4.14)
\]

Comparing this with the unperturbed equation (2.64) and using the
previous notation, we notice, on writing \( \int_{-\delta}^{\delta} R_1(1-Y^2) dY = \bar{R}_1 + R_1^{(\delta)} \), that the error \( R_1^{(\delta)} = \int_{-\delta}^{\delta} R_1(1-Y^2) dY \) is second order in \( (\Delta T) \). Of course, there are other second order terms in (4.14) containing \( \beta_1 \) in combination with other parameters, but these all derive from \( a_\alpha \) and \( h_{\infty} \) and have, as such, been accounted for in the previous section. The relevant error for the present discussion is \( R_1^{(\delta)} \). In calculating it we are only concerned with the viscosity effect; accordingly we put \( a = 0 \), whence \( \delta = -\frac{1}{4} \beta_1 \Delta T \). Substituting \( \beta_1 \Delta T = 4 \times 10^{-2} \), we find that the ratio \( R_1^{(\delta)}/\bar{R}_1 \) is only \( 9 \times 10^{-5} \).

4.5 Entry Effects: Temperature Distribution

So far we have assumed that both the steady state temperature and velocity distribution are set up immediately upon entry to the duct. Because this is not strictly true we must estimate the effect of finite entry lengths on the separation obtained.

It is not possible to predict accurately the temperature across the inlet of the duct. Although the solution enters through the hot plate, some of it has already been in contact with the cold plate before the duct entrance. Since, however, the entry length is small, we only require to find the approximate magnitude of the effect. This we can do most simply by taking the special case of the solution entering the duct with a uniform temperature equal to the mean of the two plates; under these circumstances the temperature gradient is symmetrical about the X-axis and, in particular, the gradients at the boundaries are equal.
It has been shown previously that for unsteady temperatures the concentration changes are given by equation (2.21),

$$\frac{\partial^2 h}{\partial Y^2} + s \frac{\partial^2 T}{\partial Y^2} = \frac{3}{8} (1-Y^2) \frac{\partial h}{\partial X}.$$ ... (4.15)

The temperature distribution is governed by the heat conduction equation corresponding to (2.23),

$$\frac{\partial^2 T}{\partial Y^2} - \frac{3}{8} (1-Y^2) \frac{\partial T}{\partial X} = 0,$$ ... (4.16)

where \( X' = \frac{Kx}{4a^2 \bar{u}} = \frac{K}{D} X \). Equation (4.16) can be solved by simple adjustment of the boundary conditions in the original problem. By eliminating the term \( \frac{\partial^2 T}{\partial Y^2} \) from (4.15) and (4.16) and introducing the new variable

$$g = h - \frac{8D}{K-D} (T-T_o),$$ ... (4.17)

there results an equation similar in form to the original one,

$$\frac{\partial^2 g}{\partial Y^2} - \frac{3}{8} (1-Y^2) \frac{\partial g}{\partial X} = 0,$$ ... (4.18)

with the following conditions,

$$\frac{\partial g}{\partial Y} = - \frac{sK}{K-D} \frac{\partial T}{\partial Y}, \quad Y = \pm 1, \quad 0 \leq X \leq \infty,$$ ... (4.19)

$$g = 0, \quad X = 0, \quad -1 \leq Y \leq 1.$$ ... (4.20)

The boundary plates of the duct are brought to a steady temperature before the beginning of a run, so for the upper and lower plates we have,
\[ T_\pm = T_o \pm \frac{1}{2} \Delta T, \]  \hspace{1cm} \ldots (4.21) 

which is independent of \( X \). The temperature gradient is an even function of \( Y \) tending to a steady value \( \frac{\partial T}{\partial Y} = \frac{1}{2} \Delta T \), which corresponds to the final temperature distribution, \( T_\infty = T_o + \frac{1}{2} \Delta T Y \).

The variation of temperature at the boundaries can be written
\[ \left( \frac{\partial T}{\partial Y} \right)_{\pm 1} = \frac{1}{2} \Delta T \left[ 1 + X(X) \right], \]  \hspace{1cm} \ldots (4.22) 

where \( \chi \to \infty \) as \( X \to 0 \) and \( \chi \to 0 \) as \( X \to \infty \). \( \chi \) is found by solving equation (4.16) subject to the boundary conditions (4.21). Now we have a problem which differs from the solution previously obtained, in which \( \frac{\partial T}{\partial Y} \) was constant and equal to \( \frac{1}{2} \Delta T \), in so much as its boundary conditions are initially variable and tend to those of the previous solution only as \( X \to \infty \). The method of superposition of integrals can be used to give the solution of (4.18) in terms of the previous solution. Agar (36) developed this calculation to estimate the "warming-up" correction in his static cell. Using the fact that the steady temperature is attained very much more quickly than the Soret equilibrium and that, in practice, we are only interested in values of \( X \) greater than the entry length, he showed that the effect was governed by a correction \( X^* \) to the \( X \)-coordinate, given by
\[ X^* = \frac{D}{K} \int_0^\infty X(X) \, dX, \]  \hspace{1cm} \ldots (4.23)
where \( x^* \) can be thought of as a gained length. Evaluating \( X(X) \) by modifying the boundary conditions of the original programme as indicated, one obtains \( x^* = 0.050 \frac{D}{K} \), where \( \frac{D}{K} \) ranges from 0.010 in dilute aqueous solutions to about 0.015 in organic solutions. The reason that \( x^* \) is positive, i.e. that there is an effective increase in the duct length, is that the temperature gradient at the boundaries is infinite when \( X=0 \), thereby inducing greater initial separation than had previously been assumed. However it is seen that \( x^* \) should never be greater than 0.0007 and therefore it may safely be ignored.

4.6 Velocity Distribution

For the velocity distribution we may consider that the profile is uniform at the entrance to the duct changing gradually from a flat "turbulent-shaped" profile to fully developed laminar flow further downstream. There is no correspondingly simple analytical technique to that used above by which this entry length may be determined but there is much published information available concerned with the velocity in the entrance region in ducts of various shapes.

Consider a solution for rectangular ducts due to Han.\(^{32}\)

The entrance length \( L_e \), which he defines as the length where the centre-line velocity is 99\% of the fully developed velocity, is

\[
1.0 \times 10^{-2}D_e Re \text{ for a duct of zero aspect ratio. } D_e \text{ is the hydraulic diameter (4a in our case). The largest value of } L_e \text{ encountered}
\]
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in our experiments is $5 \times 10^{-2}$ cm, or about 0.3% of the duct length. Clearly, the effect of such a short entrance region on the solution of the diffusion equation is negligible, even for fast diffusing substances. However, since the factor determining the importance of the entry length is $\frac{D}{\nu}$, we see that if the temperature were raised ($D$ increases and $\nu$ decreases) it would be necessary to determine at least the order of magnitude of the correction to the separation. The flow cell may in future be run at different temperatures, so we shall consider an extreme case.

Han gives his velocity profiles as a function of a dimensionless length down the duct $\frac{X}{\text{Re}}$, which we can denote by $X_H$. Thus we have $X = \frac{4D}{\nu} X_H$. If we choose $D = 7.5 \times 10^{-5}$ cm$^2$ sec$^{-1}$ and $\nu = 3.0 \times 10^{-3}$ cm$^2$ sec$^{-1}$ (which case might be encountered if the temperature were raised to 50 degrees C.) then we should have $X = 0.1 X_H$.

Using this we can include Han's velocity profiles in the entry region of the finite difference solution and a comparison of the predicted separation can be made with the original solution in which a laminar profile was assumed throughout. Since the effect is small and only an order of magnitude answer is required, much time can be saved by increasing the mesh size in the programme. The original programme was also run through with the larger mesh size before the comparison was made. We can conveniently express the result (to ± 25%) in the same way as with the temperature entry length, namely a correction to the $X$-axis. The result is $X^* = -0.0002$. That $X^*$ is negative, i.e. the effective length of the duct is decreased,
is because the velocity near the walls, where the initial separation takes place, is greater in the entrance region than that in fully-developed laminar flow. Even under the most adverse conditions likely to be met, then, the correction is negligible; and furthermore it is in the opposite sense to the temperature entry effect.
CHAPTER 5

EXPERIMENTAL PROCEDURE

Essentially a run consists of drawing a solution at a constant rate through the diffusion cell, across which a known temperature difference exists, and collecting it in two fractions corresponding to the top and bottom halves of the duct. In practice, though, there are many points to attend to before conditions are correct for a run and it is these with which this chapter is concerned. Analysis of the products depends on the system under investigation, thus aqueous solutions were analysed conductimetrically and organic mixtures optically. Details of these techniques are given in Chapters 6 and 7.

Before a run the temperatures recorded by the thermocouples were adjusted so that the temperature difference along the duct varied by less than 0.1 degree C. and the mean temperature lay between 24.95 and 25.05 degrees C. Variation in mean temperature along the duct was rarely greater than for the temperature difference.

With the mercury at the top of the burettes and the variator set for the required flowrate, trial runs were performed to determine the valve setting and the initial drop of the mercury reservoir to anticipate the terminal speed in the burettes. Once the correct valve setting was obtained it was only necessary to measure
the rate of fall in one burette. The initial drop was determined by trial and error. Using a 0.01 second stopwatch, the initial rate of fall was measured over several 2 cm. sections and compared with the terminal speed. With practice, it became easy to judge the necessary distance. Both the points just mentioned were only important for the fast runs. Thus the valve was used in the fully open position for all runs where the flowrate was less than 20 cm.$^3$/min.$^{-1}$. Similarly, there was no correction for the initial acceleration when the flowrate was less than 15 cm.$^3$/min.$^{-1}$ and only for much faster runs did it become important (e.g. for $Q = 100$ cm.$^3$/min.$^{-1}$ the initial drop was about 6 cm.). When there was no correction the runs were started from the position of hydrostatic equilibrium. For faster runs still ($Q > 40$ cm.$^3$/min.$^{-1}$), the temperatures recorded by the thermocouple pair nearest the duct entrance became significantly dependent on the flowrate. When this arose, final adjustment to the temperature difference had to be made during the trial runs. After each trial run the solution was returned directly to the aspirator bottle by raising the mercury reservoir.

Though the seal round the cell is liquid proof, it is still possible for air to be drawn into the duct; if, for instance, the cell is allowed to cool with the taps at either end closed. As a precaution the cell was flushed out at this stage to remove any air which may be present. By lowering the mercury reservoir about one foot and then opening the taps above the burettes it was found that small pockets of trapped air were removed.
Again with the mercury at the top of the burettes, a preliminary run was performed under the correct conditions for the final run. Its purpose was to ensure that the lines between the cell and the burettes were filled with solution of the correct concentration, for otherwise the first few ccs. drawn into the burettes may be of quite a different concentration. It is not possible, of course, to avoid collecting the solution remaining in the cell before a run. Since, however, its separation corresponds to the steady state and its volume was always about 1% of the total volume collected, a simple correction could be made for it (see the results in Chapter 6).

Having returned the mercury once again to the top of the burettes, shaken the aspirator to ensure a uniform feed concentration and checked the thermocouple readings, the final run was commenced. During it, the initial acceleration was checked with the 0.01 second stop-watch and the overall rate of fall measured with a 0.1 second stop-watch. The temperatures were read at frequent intervals. After collecting a total of about 200 ccs., the run was stopped by closing the taps above the burettes.

Instead of having a uniform composition, the concentration of the solutions remaining in the burettes after a run varied with their height. It seems that the concentration profile across the duct at the blade still exists, at least partially, when the solution enters the burettes. The resulting gravitational circulation
gives rise to a vertical concentration gradient. In order that this should happen, the flow everywhere between the separating blade and the burettes must be laminar and in such a regime that the radial diffusion is negligible. The characteristic time for radial diffusion in laminar pipe flow, that is the time taken for the radial concentration gradient to die down to \( \frac{1}{e} \) of its initial value, is given by Taylor \(^{(50)}\) as \( a^2/15D \), where 'a' is the pipe radius.

In the flow through the P.T.F.E. filter and the \( \frac{1}{8} \) in. diameter heat exchange and capillary tubing the characteristic times are 8 seconds and 160 seconds, while the times spent in each during the slowest run (\( Q = 2 \text{ cm}^3\text{ min}^{-1} \)) were 1 second and 25 seconds respectively. Therefore, as expected, radial diffusion has little dispersing effect on the concentration gradient. In each of these sections the Reynolds number was well within the laminar range, though sharp corners may have given rise to local eddies causing a certain amount of mixing as the flowrate was increased; the side containing the valve was always more thoroughly mixed. Before measuring the separation, it is clearly best to mix up the contents of each burette. This was done by wrapping a heating tape round the bottom few inches of the liquid columns and heating until the convection currents had eliminated the concentration gradients.

To measure the separation, the contents of the burettes were compared directly with each other. Several samples, spaced evenly along the length of the burettes, were analysed after each run. After some runs, the product streams were compared directly
with the feed to check that no contamination had occurred in the passage through the cell.
with the feed to check that no contamination had occurred in the passage through the cell.
CHAPTER 6

CALIBRATION OF THE CELL

Calibration runs and the use of the cell with aqueous solutions are described. The behaviour of the cell is compared with the predictions of the phenomenological theory and agreement is found to be excellent. Convection effects, which are considered to be the main source of error in the static cell, are shown to be negligible.

6.1 Necessity for Calibration

Calibration is essential for two reasons. Firstly, and in the true sense of the word, to determine the cell constant \( \frac{Lb}{2a} \), which is required to fix the scale of the \( X \)-coordinate and secondly, as a check on the steady state and the satisfactory operation of the cell.

If we aim at an overall accuracy of 1%, then \( X \) must be known to the same order, for although the separation is relatively insensitive to the \( X \)-coordinate near the steady state, it is directly proportional to it in the initial stages. It is evident from the tolerances in the cell dimensions that their use to estimate the duct width can give \( 2a \) to no better than 10%. The uncertainty is mainly due to variations in the gasket thickness. There is also
some doubt about the duct length due to the end effects, particularly where it is flared-out around the blade. For these reasons \( \frac{Lb}{2a} \) was obtained by a calibration in which a series of runs was performed with a solution whose Soret coefficient and diffusion coefficient were accurately known. In this way a mean value was found which is characteristic of the diffusion process for which the cell was designed.

A check on the steady state separation is a guide to the correct housing of the blade. However carefully it has been machined and assembled, it might neither be in the centre of the duct nor be horizontal. The centering is unimportant as long as the knife-edge is not far out. Since the flow is laminar and the solution is drawn round the blade so that the flowrates either side of it are fixed, a slight vertical misplacement of it must be compensated by a bending of the streamlines near the knife-edge, leaving the

![Diagram](image)

<table>
<thead>
<tr>
<th>Y=1</th>
<th>non-horizontal blade</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \delta )</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Y=-1</td>
<td>vertically-misplaced blade</td>
</tr>
</tbody>
</table>

separation unaffected. A non-horizontal or skewed blade, on the other hand, will reduce the observed separation. In the solution collected above the blade there will be a quantity of liquid A
(see sketch) which has, in general, a lower concentration than the quantity $B$ which should have been collected. As an example of the error involved, $\delta$ must be as high as $0.18$ to lower the steady state separation by $2\%$. Because the blade is housed in the widened section of the duct, the skewness is unlikely to be as large as this. It was noted in Chapter 2 that in the initial stages of the separation the concentration changes occurred only at the walls. Hence, for low $X$, skewness of the blade will have no effect.

6.2 The Calibration System: Cadmium Sulphate

The cell was calibrated with a $0.05\text{m}$ solution of $\text{CdSO}_4$ at $25$ degrees C. Reasons for this choice were as follows:

(i) Good agreement exists among present literature values for the Soret coefficient, $\sigma = 7.25 \times 10^{-3}$ deg.$^{-1}$ ($11,19,21,24$). The maximum error is considered to be $2\%$, if anything on the low side due to convection.

(ii) The diffusion coefficient is known; $D = 0.60 \times 10^{-5}$ cm$^2$ sec.$^{-1}$ ($11$)

(iii) $\sigma$ is large, giving rise to a separation of approximately $2\frac{1}{2}\%$ in the steady state.

(iv) Cadmium sulphate has a large stabilizing effect on convection due to the large $\sigma$ and a high density. Agar

---

*While concerned with aqueous solutions $\sigma$ will be used instead of $s$. The two Soret coefficients are identical in dilute solutions.*
and Turner(19) in their experiments with the static cell found it to be most stable of the salts they investigated.

(v) The separation is conveniently and accurately analysed by a conductimetric technique.

A series of runs was performed at flowrates covering the entire approach to the steady state. The solution was made up from A.R. cadmium sulphate in de-aerated conductivity water (specific conductance $1 \times 10^{-6} \text{ cm}^{-1} \text{ ohm}^{-1}$). Before each run the solution in the aspirator was heated to about 35 degrees C. to remove air which had been absorbed in storage and which might be desorbed inside the cell during the run. In all the runs the temperature difference was nominally 10 degrees C. and the mean temperature 25 degrees C.

Corrections to the observed temperature difference allowing for the distance of the thermocouples from the surfaces of the duct were calculated assuming a 10 degree difference either side of a composite block consisting of two $\frac{1}{2}$ in. copper plates separated by 0.013 in. of water. From the known positions of the thermocouples, corrections averaged for the top and bottom plates were found to be 0.25 and 0.20 degrees C. respectively.

6.3 Conductivity Measurements

Conductance cells of the Jones and Bollinger type suitable for high conductivity solutions (see for example reference
(51), p.565) were used to analyse the effluent streams. Two such cells, filled directly from the burettes, made up the ratio arms of a transformer bridge. Details of the bridge together with the power pack, amplifier and detector are given in reference (52). A frequency of 1 Kc/sec. was used. The conductance cells, which gave a resistance of the order of 1500 ohms with 0.05m cadmium sulphate, were immersed in an oil thermostat maintained at 25 degrees C. and controlled to ± .01 degree.

Knowing the ratio of the cell constants, direct comparison of the resistance of two samples gives the ratio of their specific conductances. For small concentration differences, changes in specific conductance at constant temperature are given by

\[
\frac{d\kappa}{\kappa} = \frac{dc}{c} \left(1 + \frac{d\ln A}{d\ln c}\right). \quad \ldots (6.1)
\]

If the equivalent conductance were independent of concentration, the term in brackets would be unity and the specific conductance would be directly proportional to concentration. Though this is not the case, it can be shown that its assumption leads to an apparent Soret coefficient defined by

\[
\sigma_{\text{app}} = \sigma_{\text{true}} \left(1 + \frac{d\ln A}{d\ln c}\right). \quad \ldots (6.2)
\]

The arithmetic involved is therefore reduced by working in terms of apparent concentration changes; thus we have

\[
\left(\frac{c''}{c'}\right)_{\text{app}} = \frac{\kappa''}{\kappa'}, \quad \ldots (6.3)
\]
from which the separation in the form $\frac{\Delta \rho}{\rho_0 \text{app}}$ is easily calculated.

Five samples were analysed from the burettes for each run. Before and after sampling, the ratio of cell constants was checked by filling each conductance cell with feed solution. In all the calibration runs variation of cell constant ratio during analysis was much less than 1% of the measured separation. The full sensitivity of the bridge, 2 parts in $10^6$, could not be used with conductance cells owing to their slightly irregular behaviour (small but random changes in cell constant appear to be a characteristic of these cells) and the absence of better temperature control.

Due to the analysis, however, reproducibility in samples taken after each run correspond to an uncertainty in $\frac{\Delta \rho}{\rho_0}$ of $\pm 4 \times 10^{-5}$, a figure which is less than 1% of the separation in even the fastest run.

In a few of the runs comparisons were made directly between the feed and each of the products. The conclusion in each case was that no contamination of the solution occurred in its passage through the cell. The slight discrepancies found between the feed and the mean of the product concentrations were assumed to be due to variations in the feed itself. Similar variations (about 0.01% of the mean concentration) were detected by Turner. (26)

6.4 Results and their Interpretation

In treating the results we shall assume that both $\frac{Lb}{2a}$ and $\sigma$ are unknown. The Soret coefficient can be determined from
the approach to the steady state by a method analogous to that used for the static cell.\(^{(20)}\) By showing that this approach follows the theoretical prediction, we shall be demonstrating that the separation obtained with an infinitely slow flowrate is, in fact, the steady state. Since any disturbance or imperfection in the cell necessarily reduces the separation, attainment of the steady state would indicate that the blade had been correctly positioned. The conductance measurements give \(\frac{\Delta \delta}{c_0}\) as a function of the flowrate \(Q\) (Table 6.1). The following iterative procedure\(^*\) is a method for determining both \(\frac{L_b}{2a}\) and \(\sigma\) from the results:

(i) **Guess** \(\frac{L_b}{2a}\). Dimensions measured before assembly (Chapter 3) would indicate a cell constant of 2350 cm. This provides a first approximation to \(X\) for each flowrate.

(ii) **Plot** \(\frac{\Delta \delta}{c_0}\) \(\text{expt}\) against \(F(X)_{th}\). Here \(F(X)_{th}\) is the theoretical separation corresponding to the \(X\) values fixed in (i). From equation \((2.45)\) it is seen that this should be a straight line with a slope \(\frac{3}{8} \sigma \Delta T\). If it is not, then \(\frac{L_b}{2a}\) is wrong. The best procedure in this case is to estimate \(\frac{\Delta \delta}{c_0}\) from the graph, then;

(iii) **Noting** that \((2.65)\) can be written

\[
\log (1-F) = \log 1.045 - 13.66 \left(\frac{L_b}{2a}\right) \frac{1}{Q},
\]

\(\text{*To avoid confusion with other subscripts, the 'app' associated with } \sigma \text{ and } \sigma \text{ is omitted.}\)
plot \( \log (1-F)_{\text{expt}} \) against \( \frac{1}{c} \). Here \( F_{\text{expt}} = \frac{(\Delta \theta)}{c_0^{\text{expt}}} / (\Delta \theta)_{\text{co}} \).

Since \( D \) is known, the slope gives \( \frac{Lb}{2a} \). This plot is relatively insensitive to the original choice of \( \frac{Lb}{2a} \) and should give the cell constant correctly at the first attempt.

(iv) Replot (ii) with the new cell constant. If it is a straight line, \( c \) is calculated from the slope.

Graphs for the last two stages are given in Figures 11 and 12. In the log plot the straight line is drawn through the points for the higher flowrates, since for the lower ones \( (1-F) \to 0 \) producing a large error in the logarithm. The point corresponding to the lowest flowrate is fixed on the line by the iterative process. The deduced cell constant is 2130 cm. with a probable error of ±20 cm. The separations plotted in Figure 12 (see also Table 6.2) have been corrected to allow for the fact that 1% of the solution collected in each run is in the steady state, namely that solution which occupied the cell before the run. The correction consisted in multiplying the observed separation by the factor \( F/(0.01 + 0.99F) \).

Only in the faster runs is its effect noticeable. The results have been reduced to a mean temperature difference to eliminate unreal scatter. Figure 12 is a straight line confirming that the approach to the steady state is as predicted. If the blade were skewed, for instance, one would expect the separation to fall off as \( F(X) \to 1 \). Since \( \frac{(\Delta \theta)}{c_0^{\text{app}}} \) has been employed throughout, the slope of the linearized separation gives the apparent Soret coefficient. The conductance factor is 0.779. Equation (6.2) then gives
## TABLE 6.1

**Calibration with 0.05m CdSO₄ : Experimental Results**

Mean temperature = 25.0 degrees C.

<table>
<thead>
<tr>
<th>Run</th>
<th>(Q) (cm³ min⁻¹)</th>
<th>(\Delta T) (degree C)</th>
<th>(\frac{\Delta T}{\omega_o}^{app} \times 10^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>2.17</td>
<td>10.54</td>
<td>22.46</td>
</tr>
<tr>
<td>A2</td>
<td>3.04</td>
<td>10.42</td>
<td>21.53</td>
</tr>
<tr>
<td>A3</td>
<td>3.60</td>
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</tr>
<tr>
<td>A4</td>
<td>4.50</td>
<td>10.36</td>
<td>19.80</td>
</tr>
<tr>
<td>A5</td>
<td>5.90</td>
<td>10.36</td>
<td>18.19</td>
</tr>
<tr>
<td>A6</td>
<td>7.45</td>
<td>10.43</td>
<td>16.67</td>
</tr>
<tr>
<td>A7</td>
<td>8.87</td>
<td>10.47</td>
<td>15.33</td>
</tr>
<tr>
<td>A8</td>
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<td>10.43</td>
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</tr>
<tr>
<td>A9</td>
<td>14.47</td>
<td>10.43</td>
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</tr>
<tr>
<td>A10</td>
<td>21.8</td>
<td>10.43</td>
<td>8.19</td>
</tr>
<tr>
<td>A11</td>
<td>42.8</td>
<td>10.43</td>
<td>4.56</td>
</tr>
</tbody>
</table>

Separations quoted in this table are uncorrected.
TABLE 6.2

Calibration with 0.05m CdSO₄ 4: Calculated Results

$\Delta T_{\text{mean}} = 10.43$ degrees C.

$\frac{L_b}{2a} = 2130$ cm.

<table>
<thead>
<tr>
<th>Run</th>
<th>$X$</th>
<th>$F(X)_{\text{th}}$</th>
<th>$\left(\frac{\Delta \sigma}{\sigma_0}\right)_{\text{app}} \times 10^3$</th>
<th>$F(X)_{\text{expt}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>.353</td>
<td>.992</td>
<td>22.24</td>
<td>.992</td>
</tr>
<tr>
<td>A2</td>
<td>.254</td>
<td>.967</td>
<td>21.55</td>
<td>.962</td>
</tr>
<tr>
<td>A3</td>
<td>.213</td>
<td>.943</td>
<td>20.93</td>
<td>.934</td>
</tr>
<tr>
<td>A4</td>
<td>.170</td>
<td>.897</td>
<td>19.92</td>
<td>.889</td>
</tr>
<tr>
<td>A5</td>
<td>.130</td>
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<td>.816</td>
</tr>
<tr>
<td>A6</td>
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<td>.493</td>
</tr>
<tr>
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<td>.359</td>
</tr>
<tr>
<td>A11</td>
<td>.0180</td>
<td>.191</td>
<td>4.38</td>
<td>.195</td>
</tr>
</tbody>
</table>

Separations quoted in this table have been corrected allowing for 1% of the solution at the steady state and are referred to a mean temperature difference for the purpose of Figure 12.
\[ \sigma_{\text{true}} = 7.36 \times 10^{-3} \, \text{deg}^{-1}, \] a value which is 1.5\% higher than the literature one.

The heat of transport \( q^* \) derived from our Soret coefficient and an activity factor, \( \frac{3\ln S_m}{3\ln m} = -0.485, (54) \) is 1340 cal mole\(^{-1}\).

There are many other points which could be raised, such as the possibility of local eddies having a mixing effect in the cell. Their absence will be presumed proven by the satisfactory operation of the cell.

One important factor has so far been assumed to contain no error, namely the temperature difference. The correction applied for the position of the thermocouples is 0.45 degrees C, nearly 5\% of the observed value. Error here will affect the steady state separation and, as such, may be indistinguishable from any skewness in the blade. It is considered, however, that this error will not be greater than 1\%.

We are now in a position to compare the experimental results of the calibration with the theoretical curve, see Figure 13. The agreement is excellent. It will be remembered that the only adjustment made in the calibration was to the X-axis. It seems that the desired overall accuracy of 1\% has been achieved.

The iterative procedure described, in which both \( \frac{Lb}{2a} \) and \( \sigma \) are derived from the results, is of more general use than previously indicated. In many systems it is required to find the
Soret coefficient when accurate diffusion data are unavailable; then the procedure is the same, but with D unknown instead of the cell constant.

6.5 Stability of Cell: Lithium Iodide

So far in this Chapter almost no mention has been made of convection, although in the Introductory Chapter it was pointed out that the resultant remixing was the chief source of error in static cell results. The cadmium sulphate system was in fact chosen for its convection stability so that other defects could be detected, which might have existed in the cell and which would otherwise have been obscured.

In experiments in which the liquid is heated from above, convection currents arise solely from small horizontal temperature gradients, the causes of which were outlined in Chapter 1. Agar and Turner[19] were able to correlate the amount of convection in their cell by means of two Rayleigh numbers, \( R_T = \frac{g \alpha \Delta T \omega^3}{\nu K} \) and \( R_C = \frac{g \alpha \Delta T \omega^3 \left( \frac{3}{\gamma} \right)}{\nu D} \), which measure the stabilizing effect of the temperature and concentration gradients respectively. Because \( K \gg D \), the concentration gradients have the more important stabilizing influence. The correlation relates the stabilizing tendency of different salts in a given cell and although the amount of convection depends very much on the design of the cell, the use of the correlation is to predict the relative stability among different systems. Agar and Turner's conclusions are unaffected by the pre-
sence of forced convection. In their original cell convection effects were serious and the Soret coefficient had to be estimated from the initial slope $\sigma_{in}$, rather than the steady state $\sigma_{st}$, because of the remixing which occurred in the latter. As already mentioned the most stable solution they investigated was 0.05m CdSO₄, for which $\sigma_{st}$ was only 1% lower than $\sigma_{in}$. Their least stable, on the other hand, was 0.01m LiI where $\sigma_{st}$ was 63% lower than $\sigma_{in}$, remixing being apparent soon after the commencement of the experiment. Such an extreme exists because $\sigma$ is negative and the solute diffuses to the hot wall of the cell, thereby reducing the stable density gradient set up by the temperature difference. In our notation, their separation curve for lithium iodide would be represented by the following sketch:

![Diagram of separation curve](https://via.placeholder.com/150)

Although Snowden and Turner greatly improved the design of the static or equidimensional cell, as far as convection hazards were
concerned, and obtained more accurate values of $\sigma$ by analysing the approach to the steady state, salts which diffused to the hot plate could still only be analysed by the initial slope and invariably gave a low result.

As intimated in the Introduction a sandwich-shape like the flow cell should be less prone to convection currents than the static cell. If it is horizontal then all non-vertical temperature gradients are wall effects and all wall effects should be negligible in this kind of cell. It is also likely that the small duct width makes any cellular motion unstable.$^{(55)}$

In the light of the above discussion the best test of stability in the flow cell would be the 0.01m lithium iodide system. Direct comparison with the shortcomings of the static cell is then possible. A.R. standard lithium iodide was not available but there was no trace of iodide apparent in the sample used. No attempt was made to purify it further since the point of the exercise was to verify the stability of the cell rather than to determine the Soret coefficient of lithium iodide. The solution, after standardization against silver nitrate, was found to be 0.0095m. Results of four runs are plotted in Figure 14 (see also Table 6.3). All the runs lie on a straight line through the origin (within the limits of accuracy expected for such a small separation), verifying that the approach to the steady state is as predicted by a theory in which convection has been assumed absent.
### TABLE 6.3

**Stability test with 0.01m LiI : Results**

Exact concentration = 0.0095m  
Mean temperature = 25.0 degrees C.

<table>
<thead>
<tr>
<th>Run</th>
<th>Q (cm³ min⁻¹)</th>
<th>ΔT (deg.C)</th>
<th>-($\Delta\Sigma_o$) x 10³</th>
<th>X</th>
<th>F(X)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>4.43</td>
<td>10.49</td>
<td>6.04</td>
<td>.378</td>
<td>.994</td>
</tr>
<tr>
<td>B2</td>
<td>4.44</td>
<td>10.43</td>
<td>6.06</td>
<td>.377</td>
<td>.994</td>
</tr>
<tr>
<td>B3</td>
<td>13.2</td>
<td>10.43</td>
<td>4.83</td>
<td>.127</td>
<td>.816</td>
</tr>
<tr>
<td>B4</td>
<td>21.0</td>
<td>10.42</td>
<td>3.99</td>
<td>.0797</td>
<td>.648</td>
</tr>
</tbody>
</table>

Separations quoted in this table have been corrected allowing for 1% of the solution at the steady state. In Figure 14 the separations are referred to a mean temperature difference.
Using conductance and activity factors as given in reference (52), the Soret coefficient $\sigma$ and heat of transport $Q^*$ for 0.01m LiI at 25.0 degrees C. are $-1.62 \times 10^{-3}$ deg$^{-1}$ and -548 cal mole$^{-1}$ respectively. Conventional ionic heats of transport of univalent ions in 0.01m. solution based on the results of Snowdon and Turner at this temperature (these are smoothed values of $Q^*$ based on the additivity of ionic heats of transport in dilute solutions) predict $Q^* = -513$ cal mole$^{-1}$ for lithium iodide; the direct measurement of $\sigma$ being disregarded by these authors as low. Agar and Turner's original results which were mostly obtained from measurements on the initial slope are all slightly higher than those of Snowdon and Turner. They obtain, again from smoothed ionic heats of transport, a value $Q^* = -566$ cal mole$^{-1}$. Our result, lying between these two, cannot be completely discredited on grounds of possible impurity because any such impurity would probably have a positive Soret coefficient and reduce the magnitude of the observed separation, thus increasing the discrepancy with the more generally accepted values of Snowdon and Turner. Deviations from additivity due to electrophoretic terms are unlikely in 1:1 electrolytes at such low concentrations. It seems, then, that Snowdon and Turner's results may be slightly low.

6.6 Conclusion

It has been shown that the flow cell operates as predicted by the phenomenological theory and that a result obtained by fol-
Following the approach to the steady state should give the Soret coefficient to within 1% of the correct value. The unknown cell dimensions have been determined by calibration so that any system, for which there exists a sensitive enough method of analysis, can be investigated. In particular, the use of organic systems in the cell, the original object of the project, can be examined (Chapter 7).

One previously unmentioned point has been raised, that is the effect of gasket creep on the duct width in the absence of a metallic spacer. Providing the cell is not disassembled and the bolts round the outside are not adjusted the width must remain unchanged; creep of the gasket can only reduce the breadth of the duct and this will clearly be a negligible effect.
Application of the flow cell to organic solutions is demonstrated with the system carbon tetrachloride-cyclohexane. Calibration and use of a Rayleigh interferometer for analysing the separations is discussed. Soret coefficients and heats of transport are determined as functions of composition over the entire range and the results are compared with existing values. This comparison leads to a discussion concerning the use of thermogravitational columns for quantitative work.

7.1 Choice of System

After considering several techniques of analysis, Rayleigh interferometry was adjudged to be the most useful. With a suitable choice of cell length, it can be adapted to most binary organic solutions. For its satisfactory demonstration a system is required with a large enough refractive index difference between the pure components to afford accurate analysis and, as before, known diffusion coefficients and a separation which is both large and stable. Of the many systems which fulfil these conditions at 25 degrees C., carbon tetrachloride-cyclohexane has the additional advantage that Horne and Bearman\(^{(31)}\) have recently investigated it in a thermogravitational column using the same method of analysis. Comparison
of results from the flow cell with those of Horne and Bearman will provide useful information concerning the use of the thermogravimetric column as an analytical tool in the determination of Soret coefficients.

7.2 Interferometric Analysis.

Analysis was carried out with a Hilger and Watts M154 Rayleigh interference refractometer. Its use enabled the burette samples to be compared directly in terms of their refractive index difference. White light from a primary source is collimated and passed through adjacent vertical slits forming two narrow parallel beams. If the primary slit is narrow enough, its image viewed in the focal plane of a telescope placed in the path of the parallel beams consists of an interference pattern. An optical cell (Figure 15) containing two liquid compartments is positioned between the collimator and telescope so that the upper half of each beam passes through the liquid but the lower half does not. If the cell contains mixtures of different refractive index then the optical path lengths of the beams passing through it differ so that the interference pattern is out of phase with a reference pattern formed by the light passing beneath the chambers. The instrument is operated by turning a micrometer drum which rotates a glass compensating plate in the path of one of the upper beams. When the interference patterns have been aligned the optical path lengths are equivalent. The drum reading \( y \) is related to the angle through which the compen-
sating plate has been moved to affect alignment and, as such, depends on the difference in refractive index of the samples in the cell.

The drum and an attached vernier scale divide the range of the interferometer into 2000 divisions. To avoid backlash errors in the micrometer screw, each reading was approached from above the alignment position and taken to a dead-stop (i.e. without overshoot). Each y recorded was the average of ten readings, the standard deviation usually being less than 0.2. With a 1 cm. cell this corresponds to a refractive index difference of $9 \times 10^{-7}$. Steady state separations observed correspond to refractive index differences varying from $1.3 \times 10^{-4}$ in 10% mixtures to $4.2 \times 10^{-4}$ in the middle of the composition range. Use of a 1 cm. cell therefore provides adequate sensitivity to observe the approach to the steady state even near the ends of the composition range.

The need for an extensive calibration in which y is regarded as a function of the mean composition as well as composition difference has been pointed out by Horne and Bearman. Empirical equations similar to theirs will be discussed in Section 7.4. Their treatment also allows for the discontinuities which are characteristic of the relation of the drum reading y with composition difference. As the latter is increased from zero, there comes a point where the first order fringe becomes indistinguishable from the zeroth order one, resulting in an ambiguity in y. With a further increase in composition difference the first order fringe assumes
the form that the zeroth order one had and is therefore mistaken for it when alignment is made with the reference set. The result is a discontinuity in the calibration curve. Over the range of the instrument several such discontinuities occur. Their positions, relevant to the range in which the interferometer will be used, must be determined prior to the analysis of each system studied.

Evaporation losses would give rise to a small but steady drift in y persisting after all other effects had died out. If bad, the fringes would appear bent at the top due to cooling of the surface. To avoid such losses a cover incorporating a mercury seal is fitted over the cell. P.T.F.E. plugs, shaped as shown in Figure 15, were machined to be a push-fit into the tops of the liquid compartments. Round the outside of the cell is a nylon ring. The plugs and ring are designed to leave $\frac{1}{16}$ in. wide grooves around the top of the cell which, when filled with mercury, provide the means of sealing each compartment. The exit lines from the burettes were fitted with stainless steel syringe needles. After a run the sealed cell was filled directly from the needles which passed through $\frac{1}{16}$ in. diameter holes tapped in the centre of each plug. Each cell chamber was filled so that the liquid meniscus settled just below the P.T.F.E. plug. The filling holes are countersunk so that nylon bolts screwed into them may be similarly sealed with mercury. A water jacket bolted to the refractometer base is designed to surround the cell completely except for its transmitting faces. Water at 25.0 degrees C, controlled to 0.01 degrees, is pumped from a
thermostat tank through the jacket and its detachable lid.

It was found necessary to wait one hour, after positioning the cell in the water jacket, before taking readings. Calculations show that the vapour space above the liquid is not large enough to alter the liquid composition significantly, indeed, for carbon tetrachloride - cyclohexane the relative volatility is nearly unity. Between readings the cell was rinsed several times with A.R. grade acetone using tissues to wipe the outer optical surfaces. Overnight the cell was always immersed in glass cleaning solution.

7.3 Gravimetric Preparation of Standard Solutions

Solutions were prepared gravimetrically in special weighing flasks similar in principle to those designed for volatile liquids by Wood and Brusie(56) and more recently used by Horne and Bearman.(31) The flasks (Figure 16) consisted of two chambers, each of approximately 100ml capacity, connected near the top by a U-tube. With mercury in the U-tube, the two sides were sealed so that none of the first component escaped on addition of the second. Both components were mixed in the closed flask after weighing. The flasks were designed to allow 50ml of the solution to be mixed efficiently by tipping backwards and forwards between the two chambers without wetting the stoppers.

A tare flask, almost identical with the weighing flask, was used during all the weighings to reduce the surface effects. In
calculating the true masses of the weighed components, corrections were made for air displaced by the liquids and the vapour in the weighing flasks. Because of the large vapour volume in these flasks, allowance must also be made for the fact that the mass fraction in the liquid will differ slightly from the overall composition determined by the weighings. The above corrections were considered in full by Horne and Bearman (p.2359) and will not be rediscussed here.

The standard solutions were stored in special 50 ml. volumetric flasks fitted round their stoppers with mercury seals. In these flasks the vapour volume was reduced to a minimum. The most reproducible method of transference from weighing to storage flask was found to be by syringe.

Horne and Bearman estimate the uncertainty in the mass fraction of their standard solutions to be less than $1 \times 10^{-5}$. Our experience shows this to be optimistic. Besides the obvious and unaccounted-for transfer loss, there always exists a small leakage of vapour through the stoppers of the flasks during weighing. Although preliminary experiments were used to estimate such losses and some allowance was therefore made for them, they still remain uncertain. If, for instance, the ambient temperature increases after component 1 has been weighed, the increase in pressure inside that chamber could easily double the leakage through the stopper. These, and considerations such as the accuracy of the balance and consistancy of the weights, lead us to estimate an error of
\[ \pm 2 \times 10^{-5} \text{ in the calculated mass fraction.} \]

7.4 Calibration of Interferometer.

By defining a modified drum reading which is proportional to the change in refractive index \( \Delta n \) and expressing a suitable dependence of \( \Delta n \) on composition difference including the variation with mean composition, Horne and Bearman derive the following empirical relationship,

\[ (y-y_0) \left[ 1-A(y+y_0) \right] - x\delta = \frac{L}{\lambda} \Delta \phi_1 \left( k_0 + k_1 \bar{\phi}_1 + k_2 \bar{\phi}_2 \right), \quad \ldots \quad (7.1) \]

in which \( y_0 \) is the drum reading when the optical path lengths are identical, \( A \) is an instrumental constant (approximately \( 2 \times 10^{-5} \)), \( x \) is the number of discontinuities between \( y \) and \( y_0 \), \( \delta \) is the interference spacing in terms of drum reading (we found \( \delta = 13.0 \)), \( L \) is the liquid path length, \( \lambda \) is the wavelength of the light, \( \Delta \phi_1 \) is the volume fraction difference and \( \bar{\phi}_1 \) the mean volume fraction of the liquids in the two chambers and, finally, \( k_0 \), \( k_1 \) and \( k_2 \) are constants. Compositions are expressed in terms of volume fraction because refractive indices of mixtures are more nearly additive in volume fraction than any other composition variable.

Horne and Bearman point out that small variations occurring in \( y_0 \) reduced the effectiveness of (7.1) as a calibration equation. They found, however, that the variations can be eliminated by making each comparison with the cell in two different positions. One edge of the cell is marked to distinguish between the chambers and two
readings are taken, first with the mark on the left of the observer \( y_L \) and then, by turning the cell round, with the mark on the right \( y_R \). The difference between the two zero readings \( (y_{oL} - y_{oR}) \) was observed to remain constant providing they were both measured at the same temperature. With this procedure, equation (7.1) is rewritten in the form

\[
Y = \Delta y_1 \left( k_o^\ast + k_1^\ast \hat{y}_1 + k_2^\ast \hat{y}_2 \right) - a^\ast, \quad \ldots \quad (7.2)
\]

where the interferometrically observed quantity \( Y \) is given by

\[
Y = (y_L - y_R) \left[ 1 - A(y_L + y_R) \right] - x\delta, \quad \ldots \quad (7.3)
\]

and the quantity \( (y_{oL} - y_{oR}) \) has been included in the constant \( a^\ast \). Here \( x \) is the number of discontinuities between \( y_L \) and \( y_R \) and the constants \( k_o^\ast, k_1^\ast \) and \( k_2^\ast \) are the products of \( 2(L\delta/\lambda) \) with, respectively, \( k_o, k_1 \) and \( k_2 \). Equations (7.2) and (7.3) were used by Horne and Bearman in their calibration.

It is a matter of conjecture as to the correct place at which to introduce the discontinuity term \( x\delta \) in the original argument. Horne and Bearman defined their modified drum reading so that it was a discontinuous function. Had they included \( x\delta \) in its definition, rather than introducing it later, (7.3) could be rewritten as

\[
Y = (y_L - y_R - x\delta) \left[ 1 - A(y_L + y_R) \right].
\]

Since the overall change in \( y_o \), and hence in \( (y_L + y_R) \), during our
experiments was less than 2, variations of the term in square brackets are negligible and it can be assumed constant. Including it in the other constants, \( k_0^*, k_1^*, k_2^* \) and \( a^* \), the combined calibration equation can be written

\[
Y = (y_L - y_R - x^3) = \Delta \psi_1 (k_0^* + k_1^* \beta_1 + k_2^* \beta_1^2) - a^*. \tag{7.4}
\]

We shall adopt this equation. Its justification finally lies in the proof that it satisfactorily correlates the behaviour of the interferometric quantity \( Y \). The brief outline leading to (7.2) and (7.3) has been included as background to the discussion of our results with those of Horne and Bearman.

Preliminary experiments showed that there were only two discontinuities in the range of composition differences encountered. Both of these occurred near the end of that range, corresponding approximately to the drum readings 872 and 963. Because there were only two, allowance for them became a simple matter. Throughout our experiments \( y_0 \) remained within ±1 of 910.

To obtain a reliable calibration, composition differences of the same order as the expected separations were employed. The variable \( Y \) was determined for 33 pairs of solutions over the entire range of compositions. Partial molar volumes for the system were calculated from the data of Wood and Gray\(^{(57)}\) and used to calculate volume fractions in terms of mass fractions. A 5th order polynomial fitted the calculated values with negligible error,
\[ \phi' = 0.5029w_1 + 0.1391w_1^2 + 0.4802w_1^3 - 0.448w_1^4 + 0.3226w_1^5 \ldots (7.5) \]

The four constants in (7.4) were determined by a multiple least squares regression to be, \( k_0^{*} = 14.45 \times 10^3 \), \( k_1^{*} = 2.977 \times 10^3 \), \( k_2^{*} = 0.976 \times 10^{-3} \) and \( a^{*} = 3.0 \) with a standard deviation in Y of 0.7. Deviations for each composition were random, so the error may be considered to lie in the sampling and not in the calibration formula.

7.5 Results: Carbon tetrachloride - cyclohexane

A series of runs was conducted at 25.0 degrees C. and the separations measured, by the interferometric technique just described, for five different compositions over the range of the carbon tetrachloride - cyclohexane system. In volume (and mole) fractions of carbon tetrachloride, these compositions approximated to 0.1, 0.3, 0.5, 0.7 and 0.9. The mean, or feed, composition was determined using an Abbé refractometer. Readings on this could be made reproducibly to \( 1 \times 10^{-4} \) in refractive index, corresponding to about a 0.3% change in composition in our system. After the refractometer reading had been checked with a glass test piece of known refractive index, it was calibrated in volume fractions over the composition range with the gravimetrically prepared solutions remaining from the interferometer calibration.

Corrections to the observed temperature difference across the flow cell are, in general, less important with organic solutions
because of their lower thermal conductivities. In the case of carbon tetrachloride - cyclohexane, assuming an average thermal conductivity, the corrections for the top and bottom plates were found to be 0.07 and 0.05 degrees C, respectively.

Because of the greater time required for analysis with organic solutions, only three sample pairs were examined for each run. Convective mixing in the burettes was generally less efficient than with aqueous solutions, giving rise to a variation in $Y$ of about $\pm 0.3$ in the samples analysed.

Blackening of a mercury surface by cyclohexane which had been in contact with certain metals was pointed out by Horne and Bearman. They ascribed it to the catalytic production of small quantities of cyclohexylhydroperoxide in their apparatus. A similar surface reaction with the mercury was observed in our burettes. The fact that no contamination of mercury occurred in the weighing bottles supports the theory that the impurity is produced in the cell. To show that its presence was unimportant, we compared interferometrically the feed with the product compositions. The conclusions were the same as for aqueous solutions, namely that the slight discrepancies, again about 0.01% of the mean composition, were due to variations in the feed itself and in any case were too small to worry about. The only effect, then, arising from the production of cyclohexylhydroperoxide is the inconvenience of a dirty mercury surface in the burettes. The resulting drag of the meniscus was never allowed to become serious, in fact the complete
burette assembly was cleaned out twice during the carbon tetra-
chloride - cyclohexane runs.

Preliminary tests revealed little dissolved air in the
solutions so it was considered unnecessary to take any precautions
against it. However, it soon became apparent that air was getting
into the cell by another means. The relatively high expansion co-
efficient of most organic solvents, compared with that of water,
increases the chance of drawing air into the duct while the cell is
being cooled, particularly if the taps either side of it are closed.
As the air accumulates, much of it collects near the P.T.F.E. filters
eventually blocking small sections of them and effectively skewing
the separation around the blade. When this happens, reproduc-
ibility is lost and the results become scattered. Air trapped in
this manner can be removed by exhaustive flushing, but it is better
to prevent its intake by allowing the cell to cool before the taps
are closed.

The carbon tetrachloride was British Drug House's A. R.
grade with a refractive index $n_D^{25} = 1.4608$ (c.f. literature value =
1.4607). Two samples of cyclohexane were used. The first, B.D.H.
spectroscopic grade, had a refractive index $n_D^{25} = 1.4258$ (c.f.
literature value = 1.4263) and was used in the calibration and for
theruns at the carbon tetrachloride end of the composition range.
The second, of which we only had about 2 litres, was a specially
distilled sample by courtesy of the British Petroleum Company at
Sunbury-on-Thames, for which $n_D^{25} = 1.4263$. The pure B.P. sample was used for all runs on solutions containing 50 mole \% or more cyclohexane (i.e. runs C7 - C16).

It might be thought, in the absence of sufficient quantity of pure cyclohexane* and in the interests of consistancy, that it would be better to carry out the entire set of experiments with the B.D.H. cyclohexane; small amounts of impurity usually have little effect on the resultant thermal diffusion. But, on testing this assumption by performing a run with B.D.H. cyclohexane, the interferometric separation was observed to be nearly one fifth of that for a solution containing 10 \% of carbon tetrachloride. Preliminary conclusions from chromatographic and infrared analyses indicate about 1\% of total impurity most likely to be unsaturated hydrocarbons such as 2:2- and 2:4-dimethylpentane with a very small trace of benzene. With a concentration as low as this, the impurity's Soret coefficient would have to be at least $10^{-2}$ deg$^{-1}$ to account for the separation.

After realizing the seriousness of the impurity, we repeated the runs at the cyclohexane end of the diagram ($\mathcal{L}_1 = 0.1$, 0.3 and 0.5) with the B.P. sample which, in contrast to the B.D.H. solvent, showed no detectable separation when run through the appar-

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*If more time had been available all cyclohexane would have been purified by rectification at the start. To obtain the purity of the B.P. sample by this method is, however, a lengthy process.
atus. Surprisingly, though, no difference was apparent between the results with the different solvents at \( \bar{y}_1 = 0.1 \). It appears, therefore, that the impurity only becomes significant when the solution is almost entirely cyclohexane. If this is the case, it is safe to assume that the runs at the carbon tetrachloride end of the composition range (\( \bar{y}_1 = 0.7 \) and 0.9), using B.D.H. cyclohexane, remain unaffected.

The validity of the calibration for solutions containing B.P. cyclohexane must be considered. In the mean composition, for instance, it is important to be correct near the pure components, where the quantity \( \bar{y}_1 \bar{y}_2 \) (see equation (7.7)) changes rapidly.

The refractive index–composition curve associated with the Abbe refractometer can easily be emended by applying a correction at the cyclohexane end which decreases linearly to zero for pure carbon tetrachloride. Similar considerations applied to the interferometer calibration lead to errors in \( Y \) which are only a fraction of its observed standard deviation, so there is little point in attempting a correction.

Writing the theoretical separation in the form

\[
\Delta \bar{o}_1 = \frac{3}{8} \bar{\sigma}_1 \Delta T \, F(X), \quad \ldots \quad (7.6)
\]

where \( \bar{o}_1 = o_0 \), and assuming \( \Delta \bar{o}_1 = \Delta \bar{\nu}_1 / \bar{\nu}_1 \), we obtain from the definitions of \( \bar{s}, \bar{\nu}_1 \) and \( \bar{\nu}_2 \),

\[
\Delta \bar{\nu}_1 = \frac{3}{8} \bar{\sigma} \bar{\nu}_1 \bar{\nu}_2 \Delta T \, F(X). \quad \ldots \quad (7.7)
\]
In other words, by retaining the volume fraction as the composition variable, we can calculate the Soret coefficient \( \sigma \) directly. The assumption relating the composition differences \( \Delta \xi_1 \) and \( \Delta \eta_1 \) is based on the constancy of the partial molar volume \( \bar{V}_1 \) over the small change in composition. In fact for carbon tetrachloride - cyclohexane mixtures \( \bar{V}_1 \) changes by less than 0.7% over the entire range of compositions, so (7.7) is clearly valid.

Results for the five compositions are listed in Table 7.1. The Soret coefficients are determined from the slope of linearized separations in which \( \Delta \xi_1 / \xi_1 \bar{V}_2 \) is plotted against \( F(X) \). For convenience of presentation the separations for each composition are corrected to a common temperature difference to enable all the results to be compared on one graph (Figure 17). Data for this plot are given in Table 7.2. Diffusion coefficients required to calculate \( X \) were interpolated from the data of Hammond and Stokes \( ^{(58)} \).

The majority of runs were conducted close to the steady state. In the case of the equi-molar mixture, a relatively fast run (C10) was carried out as a test of the diffusion data. The fact that this run lies on a straight line through the other points and the origin confirms the validity of the diffusion coefficient (it also, of course, corroborates the calibration in Chapter 6).

In mole fraction units, equation (1.2) for the heat of transport becomes

\[
Q_1^\pi = RT^2 N_2 \left( 1 + \frac{\partial \ln f_1^1}{\partial \ln N_4^1} \right) \sigma. \quad \ldots (7.8)
\]
### TABLE 7.1

**Carbon tetrachloride - cyclohexane: Experimental Results**

Mean temperature = 25.0 degrees C.

<table>
<thead>
<tr>
<th>Run</th>
<th>$\bar{J}_1$</th>
<th>$D \times 10^5$ (cm$^2$ sec$^{-1}$)</th>
<th>$Q$ (cm$^3$ min$^{-1}$)</th>
<th>$\Delta T$ (deg.C)</th>
<th>$\gamma$</th>
<th>$\Delta J_1 \times 10^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>0.089</td>
<td>1.474</td>
<td>3.97</td>
<td>10.98</td>
<td>33.4</td>
<td>2.07</td>
</tr>
<tr>
<td>C2</td>
<td>0.302</td>
<td>1.439</td>
<td>4.03</td>
<td>10.89</td>
<td>82.8</td>
<td>5.20</td>
</tr>
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<td>0.493</td>
<td>1.399</td>
<td>4.08</td>
<td>10.93</td>
<td>98.2</td>
<td>6.07</td>
</tr>
<tr>
<td>C4</td>
<td>0.705</td>
<td>1.348</td>
<td>4.13</td>
<td>10.79</td>
<td>81.3</td>
<td>4.88</td>
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<td>C5</td>
<td>0.897</td>
<td>1.298</td>
<td>4.17</td>
<td>10.81</td>
<td>37.9</td>
<td>2.14</td>
</tr>
<tr>
<td>C6</td>
<td>0.897</td>
<td>1.298</td>
<td>4.17</td>
<td>10.81</td>
<td>37.9</td>
<td>2.14</td>
</tr>
<tr>
<td>C7</td>
<td>0.897</td>
<td>1.298</td>
<td>4.17</td>
<td>10.81</td>
<td>37.9</td>
<td>2.14</td>
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<td>C8</td>
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<td>1.298</td>
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Separations quoted in this table are uncorrected. The diffusion data are from reference (58).
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\( \Delta T_{\text{mean}} = 10.90 \) degrees C., \( \frac{Lb}{2a} = 2130 \text{ cm.} \)

Separations quoted in this table have been corrected allowing for 1% of the solution being at the steady state and are referred to a mean temperature difference for the purpose of Figure 17.
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Component 1 $\equiv$ CCl$_4$.  

TABLE 7.3  

Soret Coefficient and Heat of Transport for carbon tetrachloride - cyclohexane at 25.0 degrees C.
The activity factor is derived from the vapour pressure data of Scatchard, Wood and Mochel\(^{59}\) for carbon tetrachloride - cyclohexane at 40 degrees C. To correct the data to 25 degrees C, 
\[ \frac{\partial}{\partial T} \left( \frac{3 \ln f_1}{3 \ln N_1} \right) \]
is estimated from Adcock and McGlashan's measurements\(^{60}\) of the heats of mixing of the same system. Derived values of the Soret coefficient and heats of transport are compiled in Table 7.3 as functions of the mole fraction of carbon tetrachloride. The Soret coefficient is plotted over the composition range in Figure 18. Results of previous investigators are included on this graph and will be discussed in the next section. For the heat of transport, since \( Q^*_1 \to 0 \) as \( N_2 \to 0 \), we concern ourselves with the variation of \( Q^*_1/N_2 \) (Figure 19).

There seems little point in attempting to estimate the combined uncertainty in the derived values of \( \sigma \) by detailed consideration of the error involved at each step in the process. As concluded by Horne and Bearman after such an analysis, the observed deviations in the final result would be greater than the calculated ones. No doubt the reason for this is that a significant and unaccountable error occurs in the transference of the solutions. For the observed error, we calculate that the standard deviation of the points in Figure 17 corresponds to an uncertainty of \( \pm 0.6\% \) in the slopes which shows a reproducibility of \( \pm 0.04 \times 10^{-3} \) deg\(^{-1}\) in the Soret coefficient.
7.6 Thermogravitational Columns and Comparison with Previous Work

Results of previous investigators of the carbon tetrachloride - cyclohexane system are shown in Figure 18. The following discussion is concerned mainly with the conclusions of Horne and Bearman (31) in so far as they relate to the use of the thermogravitational column for obtaining quantitative thermal diffusion data. In their first paper, they present a solution for the steady state in a cylindrical column which accounts quantitatively for the forgotten effect. Though the analysis is involved, there is no reason to suspect their final expression for the vertical composition gradient or the claim that their treatment removes the objections and short-comings of the previous solutions. In a second paper, they attempt an experimental verification of their equations using the carbon tetrachloride - cyclohexane system in a column with end reservoirs. The system is appropriate on account of its large forgotten effect, for it is here that the previous solutions failed. The thermal diffusion factor \(a(=\sigma T)\) is derived from the steady state composition difference between the top reservoir (assumed to be perfectly mixed) and the feed. Horne and Bearman's deduction that there is satisfactory agreement between experiment and theory is based on a comparison with the results obtained by Thomas (15) in a static cell. Agreement in fact only exists in the cyclohexane half of the diagram and even then no account has been taken of the fact that Thomas' results were probably subject to convection errors. Our results, while agreeing near the pure components, do not show
the minimum near the centre of the composition range characteristic of Horne and Bearman's values.

End effects probably contribute to the error in Horne and Bearman's experiments. While they have considered the possibility of small vertical components in the temperature gradient near the reservoirs and have shown their effect to be negligible, they have not commented on the assumption of perfect mixing in the reservoirs. Since the gap width is small compared with the diameter of the reservoir, one would expect intuitively some of the liquid entering from the hot wall to find its way down the cold wall before it became mixed into the bulk fluid in the reservoir. The consequence would be to shorten the effective height of the column, thereby decreasing the separation and reducing the observed thermal diffusion factor.

It is of interest, though probably of no consequence, that the discrepancy between the results of the flow cell and those of the thermogravitational column are of the same order as the forgotten effect over the entire range, being most significant for equi-molar mixtures and unimportant in dilute solutions. The forgotten effect in thermogravitational columns arises from the composition dependence of density. If there exists a density difference between the pure components, then their lateral separation will influence the density gradient resulting from the temperature difference. In the case of carbon tetrachloride - cyclohexane
diffusion of the heavier component towards the cold wall increases this density gradient thereby reinforcing convection and enhancing the resultant separation. The fact that Horne and Bearman's results differ from ours by the magnitude of the forgotten effect, however, cannot explain the discrepancy since there can be no corresponding effect in the flow cell.

The importance of the time-dependent solution in thermal diffusion investigations and its use in assessing the reliability of the results has already been emphasized. In static-type cells, for example, the best results were obtained by following the approach to the steady state. Again, in the flow cell the complete absence of convection was shown by demonstrating agreement with the predicted time-dependence. Without examining the approach to the steady state, it cannot be ascertained whether the observed time-invariant condition coincides with the theoretically predicted steady state. It is here that the chief criticism of Horne and Bearman's work lies. All their deductions are from steady state observations. Furthermore, they remark that their best theoretical prediction of the time required to reach the steady state was as much as 50% in error. Though this may in part be due to assumptions made in their time-dependent solution, it is felt that a satisfactory time-dependence of a thermogravitational column must be established before the steady state values are considered reliable.
Besides Thomaes' results, which have been briefly mentioned, there is only one other investigation covering the range of compositions in the carbon tetrachloride - cyclohexane system and that is the work of Tichacek et al. in a stirred diaphragm cell (61) (See again Figure 18). These cells, in which the temperature gradient is applied across a porous frit and the resulting concentration changes observed in stirred reservoirs either side of it, are designed primarily to eliminate convection errors. Their failure arises from unsuccessful attempts to determine the effective temperature difference across the diaphragm. Measured temperature differences are always high, though by an amount which depends very much on the particular diaphragm used. If, however, this is the only serious error in Tichacek's work, then the uncertainty affects all his points alike and there is a valid comparison with our data as far as the composition dependence of the Soret coefficient is concerned. This comparison will be little affected by the fact that Tichacek's data are at 40 degrees C.
CHAPTER 8

CONCLUSION

The value of the laminar flow cell as a method of investigating the Soret effect has been adequately demonstrated with both aqueous solutions and organic mixtures. Because of its apparent freedom from convective remixing it is believed to be one of the most precise means available for measuring Soret coefficients. The fact that the separation is measured externally, allowing the use of any convenient analytical technique, makes the flow cell more versatile than the static cell.

Results with the system carbon tetrachloride - cyclohexane have thrown doubt on the recent conclusions of Horne and Bearman concerning the use of thermogravitational columns in quantitative work. It appears that such columns, particularly those fitted with end reservoirs, cannot be used to obtain reliable thermal diffusion data. There is, however, still the possibility that columns without reservoirs may provide results which will conform satisfactorily with theoretical predictions, though here, of course, analytical difficulties in following the separation present a major problem. Some work along these lines is just being started under the supervision of Dr. Agar.

The future of the flow cell has already been outlined in
Chapter 1. Work on organic systems will be continued with a view to testing the statistical mechanical theory of transport processes and its predictions concerning the heat of transport in binary organic mixtures.
APPENDIX I

Values of the Separation Function $F(X)$

The following is a table compiled from the computed difference approximation described in Chapter 2. It lists the separation function, defined by equation $(2.45)$, as a function of $X$. 
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APPENDIX II

Soret Coefficients of Dilute Aqueous Electrolytes at 10 degrees C.

Results are given for a brief series of runs at 10 degrees C. with M/100 aqueous electrolytes in a conductimetric static cell. The work was carried out during March 1962 in the Department of Physical Chemistry by kind permission of Dr. J.N. Agar, using the experimental set-up left by Price — see reference (24). The scope is not very extensive because the experiments were primarily designed to occupy the period during which the flow cell was being built. It is for this reason that they are relegated to an appendix.

The calculated results are as follows:

Concentration in all cases = 0.0100m
Mean temperature = 9.4 ± 0.1 degrees C.
Nominal temperature difference = 10 degrees C.

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<tr>
<td>HCl</td>
<td>2.16</td>
<td>7.89</td>
<td>2397</td>
</tr>
<tr>
<td>NaF</td>
<td>0.997</td>
<td>3.04</td>
<td>921</td>
</tr>
<tr>
<td>KCl</td>
<td>1.284</td>
<td>-0.64</td>
<td>-194</td>
</tr>
<tr>
<td>BaCl_2</td>
<td>0.820</td>
<td>3.00</td>
<td>1240</td>
</tr>
</tbody>
</table>
Values of D underlined are estimated from the experimental observations because reliable literature data are unavailable. The Soret coefficient of KCl is calculated from the initial slope since the de-mixing process is unstable and rapid convection occurs.
NOMENCLATURE

D  Isothermal diffusion coefficient (cm$^2$ sec$^{-1}$).
F  Separation factor, equation (2.45).
J$_i$ Flux density of component $i$ (moles cm$^{-2}$ sec$^{-1}$).
K  Thermal diffusivity (cm$^2$ sec$^{-1}$).
L  Duct length (cm).
N$_i$ Mole fraction of component $i$.
Q  Total volumetric flowrate through duct (cm$^3$ sec$^{-1}$ or cm$^3$ min$^{-1}$)
Q$^*$ Heat of transport (cal mole$^{-1}$).
R  Gas constant (cal mole$^{-1}$ deg$^{-1}$).
R$_n$ $n^{th}$ eigenfunction.
Re  Reynolds number.
T  Temperature (deg); $\Delta T$ represents the temperature difference across the duct.
V$_i$ Partial molar volume of component $i$ (cm$^3$ mole$^{-1}$).
X  Dimensionless x-coordinate equal to $Dx/4a^2u$ (Figure 1)
Y  Dimensionless y-coordinate equal to $y/a$ (Figure 1). Interferometrically observed variable (Chapter 7).

a  Duct half-depth (half-width) (cm), (Figure 1).
b  Duct breadth (cm).
\( c \)  
Molar density (moles cm\(^{-3}\)) - only used as such in equation (2.1).

\( c_i \)  
Concentration of component \( i \) (moles cm\(^{-3}\)).

\( c_0 \)  
Concentration of component 1 at the inlet, \( c_0 = \bar{c} \).

\( c_\alpha \)  
Concentration of component 1 in a non-isothermal solution of uniform molality, equation (2.11).

\( \bar{c} \)  
Mean concentration of component 1; \( \bar{c}' \) and \( \bar{c}'' \) refer to the top and bottom streams respectively; \( \Delta \bar{c} = \bar{c}'' - \bar{c}' \).

\( f_i \)  
Activity coefficient of component \( i \) on the mole fraction scale.

\( g \)  
Defined by equation (4.17).

\( h \)  
Acceleration due to gravity (cm sec\(^{-2}\)).

\( k \)  
Defined by equation (2.10).

\( k \)  
Thermal conductivity of solution (cal cm\(^{-1}\) sec\(^{-1}\) deg\(^{-1}\)).

\( m \)  
Molality of component 1 - solute (mole kg\(^{-1}\)).

\( n_D \)  
Refractive index on the Sodium-D line at 25 degrees C.

\( s_{12} \)  
Modified Soret coefficient of component 1, equal to \( 2 s_{12} \) (deg\(^{-1}\)); \( s' \) and \( s'' \) refer to its first and second temperature derivatives.

\( t \)  
Time (sec).

\( u \)  
Velocity along the x-coordinate (cm sec\(^{-1}\)); \( u_{\text{max}} \) is the maximum or centre-line velocity; \( \bar{u} \) is the mean velocity of flow.

\( w_i \)  
Mass fraction of component \( i \).

\( x \)  
Space coordinate along the duct length - Figure 1 (cm).

\( y \)  
Space coordinate across the duct - Figure 1 (cm).

Interferometric drum reading (Chapter 7).
\( \alpha \) Thermal expansion coefficient of solution (deg\(^{-1}\)).

\( \beta_1, \beta_2 \) Viscosity coefficients, equation (4.4).

\( \gamma \) Activity coefficient on the molality scale; \( \gamma_+ \) is the mean ionic activity coefficient.

\( \delta \) Variational operator (Chapter 2).

Effective displacement of blade from centre-line \( Y = 0 \) (Chapter 4).

Interfringe spacing (Chapter 7).

\( \kappa \) Specific conductance of solution (ohm\(^{-1}\) cm\(^{-1}\)); \( \kappa^t \) and \( \kappa^b \) refer to the top and bottom fractions.

\( \lambda \) Wavelength of light source.

\( \lambda_n \) \( n \)th eigenvalue.

\( \Lambda \) Equivalent conductance of solution (ohm\(^{-1}\) cm\(^2\)).

\( \mu \) Viscosity of solution (gm cm\(^{-1}\) sec\(^{-1}\)).

\( \nu_i \) Number of ions of type \( i \) formed on dissociation of one molecule of electrolyte.

\( \rho \) Density of solution (gm cm\(^{-3}\)).

\( \sigma_1, \sigma_{12} \) Soret coefficient of component 1 (deg\(^{-1}\)), equation (1.1).

\( \varphi_i \) Volume fraction of component \( i \), equal to \( c_i V_i \).

\( \chi \) Defined by equation (4.22).

\( \psi \) Defined by equation (2.31).

\( \infty \) Subscript referring to the steady state.
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LIST OF FIGURES

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2. Concentration Profiles at Various $X$.
3. The Theoretical Separation.
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13. The Experimental Separation.
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\[ y = a, \quad y = 1 \]
\[ y = 0, \quad y = 0 \]
\[ y = -a, \quad y = -1 \]

HOT PLATE, \( T_2 = T_1 + \Delta T \)

COLD PLATE, \( T_1 \)

**FIG 1** THE DUCT MODEL
FIG 2 CONCENTRATION PROFILES AT VARIOUS X
\[ F(X) = 1 - 1.045 \exp(-13.66X), \quad X \geq 0.03 \]

\[ X = \frac{Dx}{4ad} \]

**FIG 3**  **THE THEORETICAL SEPARATION**
**THERMAL DIFFUSION CELL FOR LIQUIDS**

**FIG 4**
FIG. 5 THE CELL BEFORE ASSEMBLY
Feed sample

Solution from aspirator bottle

"O" gauge sintered glass disk

Laminar flow cell

Heat exchanger

Valve

Product samples

Burettes

Mercury reservoir

P.V.C. tubing

FIG 7 FLOW DIAGRAM
Thermostat heater

R is 2.500 ohms and reduces the anode current to that specified for the relay.

EL33 is a pentode used as a triode by strapping the screens to the anode.

FIG 10 TEMPERATURE CONTROL CIRCUIT
FIG 11
LOG PLOT TO DETERMINE THE CELL CONSTANT

3 + log(1-F)

\[ \text{intercept} = \log 1.045 \]

O - 0.05m CdSO₄

from the slope, \( \frac{Lb}{2a} = 2.130 \text{ cm.} \)
FIG 12
LINEARIZED PLOT OF SEPARATION

All points corrected to
$\Delta T = 10.43 \text{ deg}$

$\sigma_{app} = 5.73 \times 10^{-3} \text{ deg}^{-1}$
FIG 13  THE EXPERIMENTAL SEPARATION

The theoretical curve shown

$0 - 0.05 \text{m CdSO}_4$

$X = \frac{D L b}{2 a Q}$
All points corrected to

\[ \Delta T = 10.44 \text{ deg} \]

\[ \sigma_{\text{app}} = -1.55 \times 10^{-3} \text{ deg}^{-1} \]

**FIG 14** STABILITY IN INVERTED CONCENTRATION GRADIENT
Mercury sc als
P.T.F.E. plugs with filling holes closed by nylon screws
Nylon ring around cell
Solution
Fused silica
Reference fringes formed from light passing through the cell end plates only.

FIG 15  CROSS SECTION OF OPTICAL CELL WITH MERCURY SEAL

FIG 16  WEIGHING BOTTLE FOR VOLATILE MIXTURES
Mean temperature = 25.0 deg C.

All points referred to $\Delta T = 10.90$ deg C.

FIG 17  LINEARIZED SEPARATIONS
CARBON TETRACHLORIDE-CYCLOHEXANE
FIG 18 Soret COEFFICIENT
CARBON TETRACHLORIDE - CYCLOHEXANE
FIG 19  HEAT OF TRANSPORT

CARBON TETRACHLORIDE - CYCLOHEXANE