A THEORETICAL STUDY OF MASS TRANSFER FROM AN INTERNALLY CIRCULATING LIQUID DROP

by

Alan Stanley Brignell

A thesis presented for the
Degree of Doctor of Philosophy of
the University of London.

Department of Chemical Engineering
and Chemical Technology,
Imperial College,
London.

September 1970

Abstract

This thesis is a description of the theory of the extraction of a solute from a spherical liquid drop which is moving at terminal velocity through another fluid. Free convective effects are ignored and the flow field is assumed to be known.

In Chapter 1 the problem is specified in detail.

In Chapter 2 previously published work that is relevant to the present work is described.

In Chapter 3 the qualitative aspects of the problem are considered and the wakes and boundary layers described.

In Chapter 4 the quantitative aspects of the mass transfer inside the drop are described.

In Chapter 5 the quantitative aspects of the mass transfer in the boundary layers are described.

In Chapter 6 the rate of mass transfer from the drop is calculated.

In Chapter 7 the experimental evidence relating to the theory is discussed and the results of the theory summarized.

Acknowledgements

This thesis is prepared under the supervision of Dr. A.R.H. Cornish whom I wish to thank for his help and advice.

Many of the ideas in this thesis have been suggested to me by Dr. D.W. Moore, both in his published work and in private discussion, and I wish to thank him for this.

I am also grateful to the Science Research Council who provided me with a Research Studentship during the course of this work.

CONTENTS

NOTATION

This notation list contains only symbols that are not defined on every occasion that they are used.

a	radius of drop
A	parameter in boundary layer solution. See page 98
B	parameter in boundary layer solution. See page 98
C	order of magnitude of overall concentration in drop
C'	order of magnitude of local concentration
c'	concentration, equal to mass of solute dissolved per unit volume of solution
c	normalised concentration. See page 17
c_1	value of c inside drop
c_o	value of c outside drop
$\bar{c}$	average value of c on a stream surface. See page 68
$\bar{c}_{k,j}$	value of $\bar{c}$ when $m = (k-1)\delta m$ and $i = (j-1)\delta i$
c^*	deviation of c from $\bar{c}$
$\bar{c}'$	derivative of $\bar{c}$ with respect to m
$\bar{c}_a$	first approximation to $\bar{c}$
$\bar{c}_b$	defined by $\bar{c} = \bar{c}_a + Pe^{-\frac{1}{2}}.\bar{c}_b$
D	coefficient of diffusion
D_1	coefficient of diffusion inside drop
D_o	coefficient of diffusion outside drop

E	equilibrium constant. Defined on page 16
F	– $\dfrac{16\ E\sqrt{D_1 X_e}\ p_b(\infty)}{E\sqrt{D_1} + \sqrt{D_o}}$
h	boundary layer thickness
H	$\oint h_m h_q h_\lambda \, dq$
h_m, h_q, h_λ	non-dimensionalised scale factors for m, q, λ co-ordinate system. Defined in Appendix Two.
i	$t \dfrac{D_1}{a^2}$ non-dimensionalised time
J	$\oint \dfrac{h_q h_\lambda}{h_m} \, dq$
J'	derivative of J with respect to m
J_k	value of J when $m = (k-1)\delta m$
j subscript	= 0 or 1 to indicate outside or inside of drop, respectively. Also used in discussion on numerical calculation to indicate the j^{th} mesh point
K_o	$= E\ c_o$
K_1	$= c_1 - A\ Y - B$
m	$= 4\ p^2\ (1 - p^2)\sin^2\theta$
n_a	$= \dfrac{E\sqrt{D_1} - \sqrt{D_o}}{E\sqrt{D_1} + \sqrt{D_o}}$
n_b	$= \dfrac{2\ E\sqrt{D_1}\ A\ \sqrt{X_e}}{E\sqrt{D_1} + \sqrt{D_o}}$

n_c	$= \dfrac{\sqrt{D_o}B}{E\sqrt{D_1} + \sqrt{D_o}}$
Pe	$\dfrac{v_o a}{D}$ Peclet number
Pe_o	Peclet number outside drop
Pe_1	Peclet number inside drop
p	non-dimensionalised distance from drop's centre $a\,p = r$
$p(z)$	$= Q(Y)$
$p_b(z)$, $p_c(z)$	defined by $p(z) = n_b\,p_b(z) + n_c\,p_c(z)$
$\overline{Q}(Y)$	concentration profile in internal boundary layer for small values of X
$Q(Y)$	$= \overline{Q}(Y) - A\,Y - B$
$Q^*(Y)$	$= \overline{Q}(Y) - A\,Y$
q	$= \dfrac{p^4 \cos^4\theta}{2p^2 - 1}$ co-ordinate orthogonal to m and λ
Re	$= \dfrac{Ua}{\nu}$ Reynolds number
r	distance from drop's centre of mass
R	$= p - \dfrac{1}{\sqrt{2}}$
s	axial component of cylindrical co-ordinate system with origin at front stagnation point: $s = a - r\cos\theta$
Sc	$= \dfrac{\nu}{D}$ Schmidt number

t	time
T	order of magnitude of t
U	speed of fluid flow at infinity
u	$= p^2$
u_1, u_2	the two zeroes of $u(1-u) - \frac{1}{4}m$, $u_1 \geqslant u_2$
v	fluid speed
$\underline{v}$	velocity field
v_m	component of $\underline{v}$ in direction of increasing m
v_q	component of $\underline{v}$ in direction of increasing q
v_r	radial component of $\underline{v}$
v_θ	component of $\underline{v}$ in direction of increasing θ
v_o	fluid speed at meeting of drop's surface and equatorial plane
w	radial component of cylindrical co-ordinate system
X	$= -\cos\theta + \frac{\cos^3\theta}{3} + \frac{2}{3}$
X_e	value of X at the rear stagnation point: $X_e = \frac{4}{3}$
Y	$= y^* \sin^2\theta$
y^*	$= y \, Pe_j^{\frac{1}{2}}$
y	$= \frac{r - a}{a}$ non-dimensionalised distance from drop's surface
z	$= \frac{-Y}{2\sqrt{X_e}}$
z'	$= \frac{-Y'}{2\sqrt{X_e}}$

δi	step length in time direction for numerical calculation
δm	step length in m direction for numerical calculation
Δ	$\Delta^2 = (1-2p^2)^2\sin^2\theta + (1-p^2)^2\cos^2\theta$
ϕ	$= \pi - \theta$
λ	co-ordinate such that λ = constant are planes through the axis of symmetry
ν	kinematic viscosity
π	ratio of circle's circumference to its diameter
ψ	stream function such that: $v_r = \frac{1}{r^2 \sin\theta}\frac{\partial\psi}{\partial\theta}$, $v_\theta = \frac{-1}{r\sin\theta}\frac{\partial\psi}{\partial r}$
θ	angular co-ordinate, measured from upstream direction
∇	vector differential operator, equal to $\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}$ where x,y,z are Cartesian co-ordinates.
∇^2	differential operator, equal to $\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ where x,y,z are Cartesian co-ordinates
erfc	integral operator: $\text{erfc } z = \frac{2}{\sqrt{\pi}}\int_z^\infty \exp(-x^2)\, dx$
ierfc	integral operator: $\text{ierfc } z = \int_z^\infty \text{erfc}(x)\, dx$
exp	exponential function

** equivalence relation: a ** b means a is of the same order of magnitude as b

The word "interior" refers to everything enclosed by the drop's surface, except the internal boundary layer-wake system.

CHAPTER 1

A statement of the problem

1. Introduction

The purpose of this thesis is to examine the forced convective transfer of a solute from a steadily falling liquid drop. This work is intended to form a first stage in the understanding of this type of system. The situations discussed will be idealised and will have little or no immediate application to industrial processes; this simplification is necessary because the complexity of the problem and the studies made of it so far are such as to require an investigation of the basic processes, before a more comprehensive theory can be evolved.

The situation under consideration is that of a liquid drop moving at constant velocity through a second fluid (the two liquids being immiscible) whilst a solute that is initially at higher concentration inside the liquid drop than outside, transfers from the inside to the outside by a diffusion process. The drop's interior is assumed to be steadily circulating without turbulence, and free convection is assumed to be unimportant. Furthermore it is assumed that the Peclet number of the diffusion process is large -

in the sense that the rate of mass transfer by convection in either solvent is much greater than the rate of mass transfer associated with the diffusion of solute molecules through the solvent. It is also assumed, at least in the sections dealing with the quantitative aspects of the process, that the drop is spherical and that the motion takes place either at high Reynolds number or at low Reynolds number (these regimes will be made more precise later).

The principal effect that the thesis will consider is that of the internal circulation, and it is with this in mind that these assumptions have been formulated. It is possible - in fact relatively easy - to form drops which have little or no internal motion, but these cases will not be considered here. This implies that there is no variation in surface tension along the surface of the drop - such a variation might arise if, for example, a surface active material were present.

For the purpose of considering these assumptions in greater detail it is convenient to divide them into two groups - firstly, those assumptions that relate to diffusion, and secondly, those assumptions that relate to the fluid motion.

2. Diffusion assumptions

It is assumed that the diffusion of a solute in a solvent may be described by the equation:

$$\frac{\partial c'}{\partial t} = -\underline{v}.\nabla c' + D\nabla^2 c' \quad \ldots \quad (1)$$

where c' is the concentration of the solute, defined by

c' = mass of solute dissolved per unit volume of solution,

t is the time,

$\underline{v}$ is the velocity of the fluid,

and D, which is the diffusion coefficient, is a quantity which describes the rate of diffusion of the solute molecules through the solvent. D is assumed to be constant, in the sense that it does not depend on any of the variables in the equation. It is, however, dependent on the chemical constitution of the solution.

D is defined by:

rate of mass transfer through a surface by diffusion per unit area

$$= - D\int \frac{\partial c'}{\partial n}\, dS$$

where $\frac{\partial c'}{\partial n}$ is the gradient of concentration in the direction of the mass transfer and normal to the surface,

dS is an element of the surface,

and the integration is taken over the surface.

Equation (1), which will be referred to as the diffusion equation, gives a valid description of the transfer process, provided that the concentration is sufficiently small. In other words, this investigation is restricted to systems in which the solution is always uniformly sufficiently dilute. This assumption is a realistic one and does not excessively restrict the application of the theory.

It will also be necessary to postulate a relationship between the concentrations on either side of an interface separating two liquids. This interface is a three-dimensional region but in this discussion it will be treated as though it were a surface, which is reasonable since its thickness is very small compared with the magnitudes of the other distances involved in the problem. It is assumed that if a solution A of concentration γ_1 is separated by an interface from a solution B of concentration γ_2 , then the relationship between γ_1 and γ_2 is given by:

$$\gamma_1 = E\gamma_2 ,$$

where the equilibrium constant E is a parameter dependent upon the chemical nature of the solutions but not on their concentrations. If the two solutions were in equilibrium this is of course the relationship that would hold. The assumption that it holds if they are not in equilibrium is realistic provided, once again, that they are sufficiently dilute.

A final assumption concerning the interface is that it cannot contain any solute. Thus the flux of solute into one side of any part of the interface must equal the flux of solute out of the other side of the same part.

It is convenient to normalise the concentration so that it has value one inside the drop initially, and value zero outside the drop initially. The normalised variables that will be used here are:

$$c_1 = \frac{c' - Ec_0^i}{c_1^i - Ec_0^i} \quad \text{inside the drop}$$

and

$$c_0 = \frac{c' - c_0^i}{c_1^i - Ec_0^i} \quad \text{outside the drop}$$

where the superscript i indicates an initial value, the subscript 0 indicates the region outside the drop, and the subscript 1 indicates the region inside the drop.

The relationship connecting the concentrations on either side of an interface is preserved by this normalisation, and c satisfies the same equation as c', namely the diffusion equation (1)

An important assumption deals with the comparative effectiveness of convection and molecular diffusion when considered as mass transfer processes. A solute moves in one of two ways - either it is carried along by the motion of the solvent, which is convection; or it moves through the solvent in such a way as to reduce the concentration gradients, which is molecular diffusion. In most physically realistic situations this latter process is much slower than the former.

The two effects may be compared by considering the terms that represent them in the diffusion equation (1). There the rate of change of concentration $\frac{\partial c'}{\partial t}$ is related to two quantities: $-\underline{v}.\nabla c'$, which represents the convection, and $D\nabla^2 c'$ which represents the molecular diffusion.

Consider, for example, a one-dimensional variation in concentration. Then it is clear that ∇c will have the order of magnitude of $\frac{C'}{a}$ where a is some characteristic length and C' is a characteristic concentration; and $\nabla^2 c$ will have the order of magnitude of $\frac{C'}{a^2}$.
Thus the ratio:

$$\frac{\text{rate of change of concentration due to convection}}{\text{rate of change of concentration due to molecular diffusion}}$$

is equal (in order of magnitude) to $\frac{Ua}{D}$,
where U is a characteristic speed of the motion.

This fraction $\frac{Ua}{D}$ is called the Peclet number and will be denoted by Pe. In many systems it is much greater than one. Typical orders of magnitude of the parameters U, a, and D would be 10^{-2}m/s, 10^{-3}m, and 10^{-9} m^2/s respectively. Thus a typical value for the Peclet number would be 10^4.

In Chapter 5, for reasons of algebraic simplicity, the Peclet number will be re-defined, but this re-definition will involve merely a multiplicative constant of order one, and for the present order of magnitude calculations this distinction is of no importance.

This investigation will use the principles of boundary layer theory and consequently will be restricted to cases where the Peclet number is much greater than one - there is no point at this stage in expressing more exactly the range of Peclet number for which the theory is valid: the effects of different values of the Peclet number will become apparent at later stages in the discussion.

It is also assumed that only forced convection is important - that is the variations in density that occur are sufficiently small not to affect the fluid motion. And it is assumed that the flux of solute is always sufficiently small for it not to contribute significantly to the fluid velocity. An important, and well-known, result of these assumptions is that the motion is independent of the diffusion (although the diffusion remains dependent on the fluid motion). This is to be expected since the only parameters dependent on the fluid's properties to enter into the Navier-Stokes equations (which determine the fluid motion) are density and viscosity. Clearly if these parameters do not vary and if the boundary conditions are fixed the flow will be independent of the nature of the fluid. The assumption that these parameters only vary by a small amount is really implicit in the assumption that the concentration is uniformly small. This assumption has already been made in order to ensure the validity of the diffusion equation (1), so that no new type of restriction is being introduced, although there may of course be a quantitative difference in the permissible magnitude of the concentration.

Finally, it should be mentioned that throughout this discussion it will be assumed that the diffusion coefficients D_o and D_1 ~~of~~ in the two solvents are of the same order of magnitude. This restriction is not essential and may be removed without affecting the following analysis, provided that care is taken to distinguish between the outer and inner Peclet numbers, which would then be of different orders of magnitude (but, of course, both would still have to be of order greater than one). The basic characteristics of the transfer process would be unchanged, so this complication has been avoided here.

3. Flow assumptions

Because the flow does not depend on the diffusion it is possible to discuss the flow field before proceeding with the investigation of the mass transfer. It is not the purpose of this thesis to derive the flow in and around a liquid drop. Instead two analytic solutions for flows of this type will be assumed to be valid approximations to reality, one at low Reynolds number, the other at high Reynolds number, but both for spherical drops only, and both for steady state flows.

The term "Reynolds number" as used here is intended more as an indication of the relative importance of inertial and viscous forces in the flow rather than as an exact quantity. Strictly speaking there should be two Reynolds numbers - one for the interior flow and the other for the exterior flow - but implicit in this discussion is the assumption that both are of the same order of magnitude, so no clarity is gained by distinguishing between the two fluids in this matter. The expression "high Reynolds number" should therefore be taken to mean that the inertial effects predominate over the viscous effects everywhere in the flow, and the expression "low Reynolds number" means that the viscous effects predominate. For the sake of numerical exactness, however, the Reynolds numbers will be defined by

$$Re_j = \frac{Ua}{\nu_j}$$

where U is the speed of the fluid at infinity relative to the drop,

a is the radius of the drop,

ν is the kinematic viscosity of the fluid,

and the subscript j is zero in the drop exterior, and one in the drop interior.

In the interests of algebraic simplicity the centre of mass of the drop is assumed to be stationary whilst the fluid at infinity is in motion. In the case of ~~uniform~~ steady motion this situation is dynamically equivalent to the more usual situation of a drop falling through a fluid which is at rest at infinity.

For the low Reynolds number case (Re<<1) it is assumed that the flow corresponds to that described by Hadamard (1), and Rybczynski (2). That is the flow inside the drop is given by the stream function

$$\psi_1 = \frac{U}{a^2} \frac{(a^2r^2 - r^4)}{4(K + 1)} \sin^2\theta ,$$

where K is the ratio $\frac{\mu_1}{\mu_o} = \frac{\text{viscosity of internal fluid}}{\text{viscosity of external fluid}}$

whilst the flow outside is given by

$$\psi_o = -\frac{U}{4}\left(2r^2 - \frac{3K+2}{K+1}ar + \frac{K}{K+1}\frac{a^3}{r}\right)\sin^2\theta$$

Here r and θ are co-ordinates in a spherical polar co-ordinate system. r is the distance from the origin (the centre of mass of the drop) and θ is the angle between the radius drawn from the origin to the given point and the axis of symmetry. $\theta = 0$ corresponds to the upstream direction. The third co-ordinate λ does not enter into these equations because of the axial symmetry. This symmetry will be assumed throughout the discussion.

For the same reason as that given by Proudman and Pearson (8) in their discussion on flow around a solid sphere at low Reynolds number - namely that the inertial terms in the equation of motion are not uniformly negligible compared to the viscous term - this solution will not be valid at large distances (of the order of $\frac{a}{Re}$) from the drop, but, since such large distances will not be encountered, this qualification is not of practical importance. In any case the velocity field given by this solution is a uniformly valid approximation - it is only when derivatives of the velocity are required that inaccuracies may occur.

Speeds of drops or bubbles measured in experiments (e.g. Haberman and Morton (3)) agree well with the predictions of Hadamard and Rybczynski's theory, although it does seem that sufficiently small drops always deviate from the predicted value. This may well be due to nothing more than lack of internal circulation caused, in the manner described by Frumkin and Levich (4), by traces of surface active material being present, rather than to any actual inaccuracy in the theory. But even if this speculation is not correct the theory provides a good explanation of the motion of some liquid drops.

At higher Reynolds numbers ($Re \gg 1$) the flow may be approximated by Hill's spherical vortex (5) together with the potential flow around a sphere. Harper and Moore (6) have shown that this approximation is uniformly valid, the only discrepancies being small perturbations of order $URe^{-\frac{1}{2}}$ (or less) from this first approximation except near stagnation points where the order is $URe^{-1/3}$. They also demonstrate that there is reasonable agreement between the results of their theory and experimental work.

The fact that the perturbations are of order $URe^{-\frac{1}{2}}$ enables the expression "high Reynolds number" to be made more precise. These stream functions will be valid approximations to the flow when the Reynolds number is sufficiently large for terms of order $Re^{-\frac{1}{2}}$ to be negligible (to the required degree of accuracy) compared with terms of order one. Thus, neglecting terms of order $Re^{-\frac{1}{2}}$ the flow inside the drop at high Reynolds number is described by:

$$\psi_1 = \frac{3}{4}\frac{U}{a^2}(a^2r^2 - r^4)\sin^2\theta$$

and the flow outside is described by

$$\psi_o = -\frac{1}{2} Ur^2 \left(1 - \frac{a^3}{r^3}\right) \sin^2\theta$$

It is important to realise that the two stream functions for the internal flows are merely constant multiples of one another. The shapes of the stream surfaces are therefore identical in the two cases. This not only simplifies the calculations but means that the transfer processes are virtually identical since, as will become apparent later, the diffusion is affected mainly by the shape of the stream surfaces and not by the actual speed of the motion.

The flow pattern in the low Reynolds number case is illustrated in Figure 1. In the case of high Reynolds number there is a similar flow pattern outside the drop, and an identical flow pattern inside the drop. In both cases the flow is axi-symmetrical, and also symmetrical about the drop's equatorial plane. There are stagnation points at the drop's front and rear poles, and a circle of stagnation points at $r = \frac{1}{\sqrt{2}}$, $\theta = \frac{\pi}{2}$. This circle will in future be referred to as the stagnation ring.

The problem of determining an analytic expression for the flow at high Reynolds number in and around a non-spherical drop does not seem to have been solved. Corresponding to Hill's vortex in the spherical case there is a

Hill's spheroidal vortex which solves the problem for a spheroidal drop in inviscid flow. However the fortunate coincidence that simplifies the problem in the spherical case - namely that the tangential velocity of the inviscid flow is continuous at the interface - does not recur in the spheroidal problem. It seems likely, therefore, that a boundary layer is formed which significantly affects the flow so that Hill's spheroidal vortex, although it may be a valid approximation throughout much of the flow field, may not be a uniformly valid approximation. A solution of the transfer problem for the spheroidal case would be of debateable value if the solution were dependent on an uncertain expression for the flow field and so this problem will not be dealt with here.

For a different reason the diffusion problem for a non-spherical drop at low Reynolds number will not be considered. By using Proudman and Pearson's method Taylor and Acrivos (7) were able to establish an expression for the shape of a drop at small Reynolds number in the form of a perturbation expansion, together with a similar expression for the flow. Because these expressions are merely perturbation expansions - that is expansions in terms of the perturbation parameters, which are asymptotically valid as the parameters tend to zero - they do not represent significant changes to the spherical case. That is to say, the principal effects remain those of the spherical case, and to a first approximation the results are not altered. This does not mean that these results are of no use, but no significant new effects will be introduced by considering this modified flow pattern. In a discussion like the present one that is concerned principally with investigating the basic processes rather than the details, the inclusion of these non-spherical effects would add greatly to the algebraic complexity of the solution without contributing a corresponding increase in understanding.

4. Analogy with vorticity transport problem

Frequently there is at least a superficial resemblance between fluid flow and a mass transfer process in a fluid, with the Peclet number having a similar relationship to the diffusion as the Reynolds number has to the flow. Thus, whereas vorticity boundary layers and wakes may form in high Reynolds number flow so concentration boundary layers and wakes may form in high Peclet number transfer processes. This analogy between vorticity and concentration is sometimes of value because it may be that a solution is known for a flow but is not known in the equivalent diffusion process. This is the case with the problem that is the subject of this thesis.

In this case the equivalent flow situation is the flow in and around a liquid drop which is moving through another liquid at high Reynolds number. This flow has been studied by Harper and Moore (6) and, as was mentioned in the previous section, they found that the flow was perturbed by a small amount from Hill's spherical vortex and a system of vorticity boundary layers and wakes was formed. Clearly one might hope that a similar system of concentration boundary layers and wakes would occur in the problem of mass transfer from a liquid drop and, as will be demonstrated in a later chapter, this does in fact happen. Unfortunately the analogy is not as complete as one might have hoped, so that the detailed calculations in Harper and Moore's work cannot be used to solve the diffusion problem. In the flow case vorticity is generated at the surface of the drop. In the mass transfer case there are no sources of solute. The mass transfer situation is therefore intrinsically time dependent, the vorticity transfer is not.

Of course this difference affects other aspects of the situation and the final result is that the two situations are not as similar as might have been expected.

This does not, however, alter the fact that the boundary layer - wake systems are very similar so that the flow solution provides an excellent guide to the solution of the diffusion problem.

CHAPTER 2

Survey of Previous Work

A large number of papers have been published on various aspects of mass transfer from drops, ranging from models for the mechanisms involved to experimental measurements. This section does not, however, provide a detailed historical survey of the research, nor even an account of these published results, but is a discussion of the comparatively few published papers that have considered the same subject as this thesis (that is extraction of solute from a liquid drop) in a similar theoretical manner and used mathematical analysis to obtain a solution. A more comprehensive account of the work done in the field of transfer from bubbles and drops may be found in review papers by Calderbank (19) and by Brounshtein, Zheleznyak, and Fishbein (20).

Before moving on to these theories, however, one paper that deals with an attempt to solve the mass transfer problem by numerical means should be mentioned. This is the paper by Johns and Beckman (9). By assuming that the flow pattern is given by Hadamard's solution and by approximating the diffusion equation by a finite difference equation, they are able to obtain solutions for a range of Peclet number from 0 to 80, in the case when all the resistance to diffusion is inside the drop. They provide concentration profiles which demonstrate that the flow near the axis of the drop profoundly affects the concentration in this region by convecting fluid at low concentration from the rear of the drop - this is one of the few papers to emphasize that this effect occurs. One of the major purposes of this present thesis is to demonstrate that this axial convection has an important effect on the mass transfer.

The other papers to be described here deal with the problem by a mathematical analysis approach. Three of these theories - two by Levich, Krylov, and Vorotilin (10, 11) and one by Ruckenstein (12) - consider that the behaviour of the boundary layer determines the mass transfer, and consequently they attempt to solve the boundary layer equations. The first of the papers by Levich et al., and the paper by Ruckenstein both use essentially the same method - an approximation, valid in the concentration boundary layers, to the diffusion equation is found. The resulting problem has three independent variables (one in time, two in space - axial symmetry having been assumed) and one of them is reduced to the status of a parameter either by a Laplace transformation (Levich) or by a transformation of variables (Ruckenstein). This leaves a two-variable problem which can be reduced to the one-dimensional heat equation and hence solved. Both approaches use Hadamard's flow in the low Reynolds number case and arrive at equivalent solutions. Ruckenstein also considers the high Reynolds number case, for which he uses Hill's spherical vortex.

The second paper by Levich _et_ _al_. (11) is restricted to the consideration of an interval of time in which the boundary layer is assumed to be in a steady state. The resulting equation is solved by the "Poincare-Lighthill-Kuo method" which involves expanding the dependent variable and one of the independent variables in the form of perturbation expansions in terms of a parameter. The remaining independent variable (again axial symmetry is assumed) is then expanded in such a way that the solutions obtained do not contain singularities that would lead to non-convergence. The solution obtained is of greater accuracy than that in the first paper (10) and the first order terms of the two solutions are in agreement.

All three papers assume that the solute concentration in the drop's core (that is away from the boundary layer) is unchanged throughout the process - an assumption which, as Levich points out in (10), is not inconsistent with the assumption that diffusion occurs because the relaxation time of the boundary layer (that is the time taken for the concentration in the boundary layer to fall by roughly its initial order of magnitude) is much shorter than the time taken for the concentration in the drop core to be similarly affected. It is therefore a reasonable assumption to ignore the change in the core's concentration, although this restricts the validity of the solutions to the initial stages of the diffusion process.

A second point requiring emphasis is that all these solutions are obtained by assuming that the concentration inside the drop in the region near the front stagnation point is at all times equal to the initial concentration in the drop. In other words it is assumed that the internal boundary layer is, near the front stagnation point, constantly being fed with fresh solute. This assumption is likely to be valid only in a very brief period when the diffusion process has just commenced and it will become invalid when fluid from the boundary layer in the region of the rear stagnation point is swept up the axis of the drop by the drop's internal convection and carried to the region of the front stagnation point, and thence into the boundary layer. This fluid will be lacking in solute, since during its original passage through the boundary layer some of the solute will have diffused into the drop's exterior, and, as will be demonstrated in Chapter 3, this lack is not overcome during the passage of the fluid up the axis of the drop. If this is so, then the paper by Ruckenstein (12) and one of the papers by Levich _et_ _al_.(10) can be applicable only to a period of time shorter than the time that is required for fluid to be convected up the drop's axis, whilst the second paper by Levich _et_ _al_. (11) can have no region of application at all, since, as the authors point out, the assumption of a steady state requires that the time be greater than the period of circulation of the drop, whilst the assumption of constant concentration in the interior near the front stagnation point requires that the time be less than the period of circulation of the drop. (Of course, these times are not meant to be exact, but merely indications of the order of magnitude of the times for which the theories may be valid.) This question of the time required for the boundary layer to attain a "steady state" will be examined in more detail in Chapter 3, where it will be shown that there is reason to suspect that Ruckenstein's result for the high Reynolds number case is not valid.

The approach favoured in these papers contrasts with that used by Kronig and Brink (13). Instead of assuming that the behaviour of the boundary layer is the governing factor in determining the mass transfer Kronig and Brink assumed that the diffusion process in the interior of the drop was of paramount importance. The problem that they consider is that of mass transfer when all the resistance to diffusion is inside the drop. By assuming that the concentration at any point inside the drop is a function only of the stream function (an assumption which can be justified for diffusion at high Peclet number, except in a thin region near the drop's surface, which is ignored by Kronig and Brink) they are able to reduce the problem to one in two independent variables - one in time and one in space. The resulting differential equation is then solved by separation of variables, the Rayleigh-Ritz method being used to solve one of the equations because its complexity prohibits an analytic solution.

It is not clear whether Kronig and Brink were aware of the importance of convection along the axis of the drop but the co-ordinate system used is such as to give the central axis the same co-ordinate value as the drop's surface. Consequently the condition on the concentration that is imposed at the drop's surface is automatically imposed also at the drop's axis and this has the effect of implying the presence of an internal wake of zero concentration. It is also worth noting that instead of applying a boundary condition at the drop's stagnation ring, Kronig and Brink make the assumption that the concentration at a given time may be approximated by a quadratic function of the stream function. An assumption of this type - namely that a polynomial approximation is possible - is usual in the Raleigh-Ritz method.

This paper by Kronig and Brink is probably the best known theoretical treatment of the problem and several attempts have been made to obtain experimental verification of their results. These will be discussed further in the final chapter of this thesis (Chapter 7).

The results given in Kronig and Brink's original paper have been extended by finding higher eigenvalues and functions. This work was done by L. van den Brandeler and the results are given in a paper by Heertjes, Holve, and Talsma (14).

CHAPTER 3

The boundary layer and wake system

The purpose of this chapter is to discuss in qualitative terms the process of extraction of a solute from a liquid drop falling through another liquid.

1. Initial conditions

One of the more important distinctions to be made is that between the initial period, in which the drop is accelerating or decelerating and the motion is unsteady, and the ensuing period in which the drop is moving with a steady terminal velocity. In the latter period the drop motion is well understood (at least for a spherical drop in the extremes of high and low Reynolds number) and it is this period that this discussion will mainly consider. Some comment on the initial period is, however, necessary, if for no other reason than to ensure that the initial conditions for extraction from the drop are physically reasonable.

Discussions on diffusion from falling bodies sometimes begin by assuming that the body is moving at terminal velocity through a liquid when the diffusion process starts.

Obviously this picture does not correspond exactly to reality for, no matter how short the time that the body takes to assume its terminal velocity, the diffusion process will already have produced some movement of solute into the bulk fluid. But if this time is sufficiently small it is clear that the penetration distance will also be small and, in this case, the description given above may suffice to give an understanding of the subsequent events. It is therefore useful to estimate the distance that the solute will penetrate whilst the drop is attaining its terminal velocity.

The flow will be governed by the Navier-Stokes equation of motion, which is:

$$\frac{\partial \underline{v}}{\partial t} + \underline{v}.\nabla\underline{v} = -\frac{1}{\rho}\nabla p + \nu\nabla^2\underline{v}$$

where ρ is the fluid density,

p is the pressure,

and ν is the kinematic viscosity.

In the case of a drop moving at small Reynolds number (i.e. much less than one) the inertial terms in the equation of motion may be neglected, leaving:

$$\frac{\partial \underline{v}}{\partial t} = -\frac{1}{\rho}p + \nu\nabla^2\underline{v}$$

So that, taking U to be a characteristic speed (the terminal velocity), a a characteristic length of the motion (the body's radius), and T to be the time taken to attain the terminal velocity

$$\frac{U}{T} \quad ** \quad \nu\frac{U}{a^2}$$

and therefore

$$T \quad ** \quad \frac{a^2}{\nu}$$

Here and elsewhere in this thesis the symbol ** is used to indicate that the quantities on each side of it are of the same order of magnitude. To the degree of accuracy required in this type of calculation the derivatives may be estimated by considering the order of magnitude of the variation in the dependent variable as the independent variable changes. Thus the derivative $\frac{\partial u}{\partial t}$ is approximated by $\frac{U}{T}$, and the derivative $\frac{\partial^2 u}{\partial x^2}$ by $\frac{U}{a^2}$.

The diffusion process is described by:

$$\frac{\partial c}{\partial t} + \underline{v}.\nabla c = D\nabla^2 c$$

so that the effect of molecular diffusion (as opposed to convection, which does not aid the penetration but merely carries the solute approximately parallel to the drop's surface) is described in order of magnitude terms by:

$$\frac{C'}{T'} \quad ** \quad \frac{DC'}{d^2}$$

where C' represents the change in concentration in time T' .

Thus in time T the diffusion effect should penetrate a distance d , given by

$$d \ast\ast \sqrt{DT} = \sqrt{\frac{Da^2}{\nu}} = a.Sc^{-\frac{1}{2}}$$

where Sc is the Schmidt number, defined by

$$Sc = \frac{\nu}{D} .$$

Thus the effects occurring during the initial period when the drop has not attained its terminal velocity will be negligible provided that only distances from the body's surface greater than $a.Sc^{-\frac{1}{2}}$ are considered.

In fact much of the future discussion will be concerned with concentration boundary layers whose thicknesses are of the order $a.Pe^{-\frac{1}{2}}$. These will be substantially unaffected provided that

$$a.Pe^{-\frac{1}{2}} \gg a.Sc^{-\frac{1}{2}} .$$

But this is equivalent to

$$Re \ll 1 ,$$

which is always true for the low Reynolds number regime. These boundary layers will not therefore be significantly affected in the initial period.

For high Reynolds number the result of this type of estimate is not so encouraging. In this case the ~~inertial~~ diffusion of vorticity into the interior determines the length of the initial period ~~terms in the equation of motion dominate~~, so that

$$T \quad ** \quad \frac{a^2}{\nu}$$

The time taken for the drop to reach terminal velocity is therefore of the order of $\frac{a^2}{\nu}$. In this time the diffusion effect will penetrate a distance d, given by:

$$d \quad ** \quad \left(D\frac{a^2}{\nu}\right)^{\frac{1}{2}} = a.Sc^{-\frac{1}{2}}$$

and this is much larger than ~~the same order as~~ the thickness of the boundary layer but much smaller than a

The drop interior away from the boundary layer will not therefore be directly affected, but the effects of the initial period will be significant in the boundary layer. For this reason Ruckenstein (12) may be mistaken when, in his description of the time dependent boundary layer round a drop, he uses the condition of no penetration as an initial condition for the high Reynolds number problem.

2. The Boundary Layers

Whatever the value of the Reynolds number, concentration boundary layers will form both on the inside and on the outside of the surface of the drop. These layers represent the regions in which the molecular diffusion has an effect on the concentration comparable to that of the convection.

The interface is a surface at which there is a sudden change in the properties of the fluid - in particular there is a sudden change in the diffusion coefficient, and this affects the concentration field. The direct effect does not penetrate a large distance from the interface: as a parcel of fluid moves it is in contact with the interface for only a short time of order T, say, and in this time the parcel can only be affected to a depth h, say. This depth can be determined by considering the rate of change of concentration due to molecular diffusion as given by the diffusion equation. In order of magnitude terms:

$$\frac{C'}{T} \;**\; \frac{DC'}{h^2}$$

However, the speed of a particle moving down the surface of the drop is of the order of the characteristic speed of the fluid U, and the length of the drop's surface is of the order of the drop's radius a, so that such a particle is in contact with the surface of the drop for a time of order $\frac{a}{U}$, and in that time the effect can only penetrate a distance h where

$$h \;**\; \left(D\frac{a}{U}\right)^{\frac{1}{2}} = a.Pe^{-\frac{1}{2}} .$$

This, then, is the thickness of the boundary layers. Since the Peclet number is very large the layers are clearly very thin.

This applies to both the internal and the external boundary layer. Just as there are two Reynolds numbers so there are two Peclet numbers - one for the external fluid, and one for the internal fluid - but for the purpose of this order of magnitude calculation there is no point in distinguishing between them.

3. Wakes

The fluid in these concentration boundary layers will participate in the general motion round the drop. When it reaches the neighbourhood of the rear stagnation point the fluid outside the drop turns away from the drop surface to form a wake. Similarly, the fluid in the inside boundary layer turns away from the drop surface and forms an "internal wake". The fluid in this wake moves up the central axis of the drop until, in the neighbourhood of the front stagnation point, it merges back into the inside boundary layer. This system of boundary layers and wakes is pictured in Figure 2. It should be emphasized that the words "boundary layer" and "wake" as used here refer to properties of the concentration field, and not to properties of the flow (although, in the high Reynolds number case, there will also be vorticity boundary layers and their associated wakes).

It is possible to estimate the thickness of these concentration wakes by considering the flow, at least in the two cases of high Reynolds number and low Reynolds number when the flow is known. In either case, as was explained in Chapter 1 the stream function inside the drop is of the form

$$\psi_1 = \frac{v_o\ r^2}{2\ a^2}\left(1 - \frac{r^2}{a^2}\right) \sin^2\theta \qquad . . . (2)$$

where v_o is the flow speed on the drop's surface, at the equator. The boundary layer has been shown to be of thickness $a.Pe^{-\frac{1}{2}}$ and, on substituting $a(1 - Pe^{-\frac{1}{2}})$ for r in the equation for the stream function (2), it is clear that the stream surface that bounds the boundary layer is given by

$$\psi_1 \ ** \ v_o a^2\ Pe^{-\frac{1}{2}}$$

Substituting this value for ψ_1 in the equation for the stream function and changing to a cylindrical polar co-ordinate system, with w as the radial co-ordinate (measured from the drop's axis) and s the axial co-ordinate (measured from the rear stagnation point towards the drop's centre), results in:

$$v_o\ a^2\ Pe^{-\frac{1}{2}} \ ** \ \frac{v_o}{2}\ w^2\ \left(1 - \frac{w^2 + (a - s)^2}{a^2}\right)$$

Solving this for w gives the distance of the stream surface from the axis. When s is of the order of a the smaller solution for w is given by:

$$w \quad ** \quad a.Pe^{-\frac{1}{4}}$$

Thus the stream surface that bounds the boundary layer is at a distance $a.Pe^{-\frac{1}{4}}$ from the drop's axis at its closest approach.

But the internal wake is formed of the fluid that has flowed from the boundary layer and it will therefore be bounded by the same stream surface as bounded the boundary layer. It has just been shown that this stream surface is at a distance $a.Pe^{-\frac{1}{4}}$ from the drop's axis. Consequently the internal wake has thickness $a.Pe^{-\frac{1}{4}}$.

A similar calculation demonstrates that the external wake also has thickness $a.Pe^{-\frac{1}{4}}$.

The two wakes, therefore are much thicker than the two boundary layers.

To summarize: boundary layers of thickness $a.Pe^{-\frac{1}{2}}$ are formed on both the inside and the outside surface of the drop. In the region of the rear stagnation point these merge into an internal and external wake respectively. Both these wakes are of thickness $a.Pe^{-\frac{1}{4}}$. The internal wake lies along the central axis of the drop and rejoins the internal boundary layer in the region of the front stagnation point.

4. Relative diffusion rates

The relative thicknesses of the wakes and boundary layers is of importance in obtaining a qualitative understanding of the diffusion process because their effect is to determine the relative rates of the mass transfer from one stream surface to another in the different regions.

Consider a flow system which has two regions A and B . Suppose that the fluid flows from A into B and that as it moves from one region to the other the stream surfaces move further apart - in other words any two stream surfaces are separated by a greater distance in region B than separates the same stream surfaces in region A . Suppose also there is a variation, from one stream surface to another, in the concentration of some solute, and that the flow is sufficiently fast for a fluid particle to be carried through the system in such a short time that molecular diffusion is not able to greatly change its concentration (i.e. the Peclet number is large). Now, because the stream surfaces have different concentrations a diffusion process will occur in region A . As the fluid flows from A into B the stream surfaces approximately maintain their original concentrations (because of the high Peclet number) but they move further apart, causing the concentration gradient to fall. Since the rate of the diffusion process falls when the gradient falls it follows that the rate of diffusion from one stream surface to another is smaller in B than it is in A .

The essential point here is that in regions in which the stream surfaces are relatively close together diffusion between the stream surfaces is much faster than in regions where the stream surfaces are relatively far apart. Now this situation is exactly that met when the fluid in the boundary layer moves into either of the two wakes. In the boundary layer the change in concentration from its internal value to its external value takes place over a distance of order $a.Pe^{-\frac{1}{2}}$, whereas in the wakes the concentration change takes place over a distance $a.Pe^{-\frac{1}{4}}$, which is an order of magnitude larger (provided that the Peclet number is sufficiently large) so that the wakes are a much less effective system for mass transfer. This has an important consequence when the case of the internal wake is considered. The thinness of the boundary layer enables the fluid in it to significantly alter its concentration in its passage round the inside of the drop's surface, and it would be expected that, since the wake is so much thicker, fluid in the wake could travel a similar distance without its concentration being significantly changed. Now, because the distance along the drop's axis is of the same order of magnitude as the semi-circumference of the drop this means that when the internal wake flows along the central axis and back into the inside boundary layer in the region of the front stagnation point its concentration is relatively unaltered. Thus the concentration of a particle which is part of the boundary layer-wake system is the same when it reaches the region of the front stagnation point as it was when it left the region of the rear stagnation point in spite of having moved along the central axis of the drop in the internal wake.

In other words if the concentration in the region of the rear stagnation point is given as a function of the stream function then the concentration in the region of the front stagnation point will, to a first approximation, be the same function of the stream function.

It is clear that some attention should be paid to the length of time that the particle spends in the internal wake system, for if a fluid particle spends a relatively long time in a region in which the stream surfaces are far apart its concentration may alter by an amount comparable with that of a particle which has spent a relatively short time in a region where the stream surfaces are relatively close together. This is of particular importance in the boundary layer-wake system because the thinness of the regions involved means that flow very close to the stagnation points must be considered, and it is therefore necessary to eliminate the possibility that fluid lingers in the wake for sufficient time for diffusion from one stream surface to another to significantly alter the concentration profile.

The time for a particle to make the journey through the internal wake may be estimated by considering the stream function. Using the cylindrical polar co-ordinate system that was introduced earlier in this chapter (namely, with w as radial co-ordinate, measured from the drop's axis, and s as axial co-ordinate measured from the rear stagnation point towards the drop's centre) the stream function is_

$$\psi_1 = \frac{v_c}{2} w^2 \left(1 - \frac{w^2 + (a - s)^2}{a^2}\right)$$

For small s and w (i.e. in the region of the rear stagnation point) this is approximately:

$$\psi_1 = v_o w^2 \frac{s}{a}$$

Thus the speed in the s direction is

$$\begin{aligned} v_s &= \frac{1}{w} \frac{\partial \psi}{\partial w} \\ &= 2 v_o \frac{s}{a} \text{, approximately.} \end{aligned}$$

i.e.

$$\frac{ds}{dt} = 2 v_o \frac{s}{a}$$

So $$\log \frac{s}{a} = 2v_o \frac{t}{a}$$

s changes from order $a.Pe^{-\frac{1}{2}}$ in the boundary layer to order a in the internal wake so the time T for a particle to cover this distance is given by

$$2v_o \frac{T}{a} \;**\; \log 1 - \log Pe^{-\frac{1}{2}}$$

i.e. $$T \;**\; \frac{a}{U} \log Pe$$

since v_o and U are at the same order of magnitude. The particle will of course take a similar length of time to move through the region near the front stagnation point. The time taken in moving along the central axis from the region of the rear stagnation point to the region of the front stagnation point is of order $\frac{a}{U}$, since this distance is of order a and in this region the flow speed will be of the order of the characteristic velocity of the flow, that is U. For large Peclet number this time will be smaller than the time spent in the stagnation regions so that the order of magnitude of the time spent in moving through the central wake is determined by the length of stay in the stagnation regions.

It is now possible to examine more closely the idea that the concentration of a particle is not significantly altered during its passage through the central wake.

The width of the wake is $a.Pe^{-\frac{1}{4}}$ and its concentration profile can only be altered by molecular diffusion from one stream surface to another. The rate of change of concentration due to diffusion is given by:

$$\frac{\partial c}{\partial t} = D\nabla^2 c$$

so that the time scale T' for diffusion (that is the time taken for the concentration to fall by its own order of magnitude) is given by:

$$\frac{C'}{T'} ** \frac{DC'}{(a.Pe^{-\frac{1}{4}})^2}$$

i.e. $$T' ** \frac{a^2 Pe^{-\frac{1}{2}}}{D}$$

$$= \frac{a}{U} Pe^{\frac{1}{2}}$$

The condition that the concentration should not be significantly altered is that a particle should be convected up the wake in a much smaller time than the time scale of the diffusion,

i.e. $$T \ll T'$$

i.e. $$\frac{a}{U} \log Pe \ll \frac{a}{U} Pe^{\frac{1}{2}}$$

which is always true for sufficiently large Peclet number. It is therefore safe to assume that, in the case of high Peclet number, solute is convected through the internal wake of the drop with negligible diffusion.

The external wake has the same thickness as the internal one and so the time scale for diffusion in it is also given by $\frac{a}{U}\,Pe^{\frac{1}{2}}$. In that time a fluid particle will move a distance $a.Pe^{\frac{1}{2}}$ so this wake therefore has a length of the order of $a.Pe^{\frac{1}{2}}$. Thus the drop has a very thin concentration wake stretching behind it for a distance $a.Pe^{\frac{1}{2}}$. It is from this wake that the extracted solute finally moves into the bulk fluid.

Having described the boundary layer-wake system it is now possible to describe, in general terms, the mechanisms of the transport process. The essential point to realise is that the inner boundary layer forms an extremely effective mechanism for transferring solute to the surface and hence to the external boundary layer. The time scale for the diffusion process in a boundary layer is $\frac{h^2}{D} = \frac{a^2}{D}\,Pe^{-1}$ $= \frac{a}{U}$. On the other hand material can only be transferred into the internal boundary layer from the interior of the drop (here and in following use the word "interior" refers to everything enclosed by the drop's surface, excepting the internal boundary layer-wake system), and in this interior the gradients of concentration are of the order of $\frac{C}{a}$ (since the concentration falls from a value of order C to zero in a distance of order a , where C is the order of magnitude of the concentration at the stagnation ring), so it follows that this diffusion process has the time scale $\frac{a^2}{D} = \frac{a}{U}$ Pe , calculated in the same manner as the diffusion time scale in the wake. Thus the boundary layer is efficient in transferring solute to the exterior of the drop, but the interior is relatively inefficient in transferring solute to the internal boundary layer-wake system. The result of this is that in the initial stage the solute in the boundary layer is transferred to the outside of the drop and, since the rate of transfer from the interior is far too small to replenish this loss, the concentration in the boundary layer-wake falls to a low value. The internal wake also has a low concentration because it consists of fluid which has flowed through the boundary layer. This initial stage lasts only as long as it takes for the material to be transferred out of the boundary layer-wake system - that is for a time of order $\frac{a}{U}$, which is the time taken for the drop to move (relative to the fluid at infinity) through a distance equal to its own radius.

The next stage of the process is one in which solute is slowly transferred from the interior to the boundary layer, and from there transferred to the exterior. During this stage the governing process is the transference of solute within the interior, and the effect of the boundary layer is of minor importance. The time scale of the overall process is therefore given by the time scale of diffusion in the interior, and this is $\frac{a^2}{D}$.

The internal wake plays practically no part in the transfer. Transfer into it from the interior occurs in the same manner as transfer into the internal boundary layer, but its surface area is too small (it is of order $a^2 Pe^{-\frac{1}{4}}$, compared with the boundary layer's area of order a^2) for any significant quantity of solute to be involved. And, as previously described, the wake is too thick for its own structure to be significantly altered.

The role of the external boundary layer is simply to transfer the solute from the drop's surface to the external wake. This boundary layer is also an effective mechanism for the transfer and can remove the solute from the surface at a rate comparable with that with which it is transferred from the internal boundary layer. There is no transfer from the external boundary layer directly to the continuous phase: the external boundary layer is, by definition, the only part of the bulk fluid upstream of the wake to contain any solute that has been extracted from the drop.

Finally, it is possible to estimate the magnitude of the concentration of solute in the boundary layer-wake system in the second stage of the process by considering the mass fluxes into and out of the system.

The mass flux through a stream-surface is given by the integral:

$$- \int D \frac{\partial c}{\partial n} \cdot dS$$

where dS is an element of surface,

$\frac{\partial c}{\partial n}$ is the gradient of concentration in a direction normal to the surface,

and the integral is taken over the surface.

The concentration gradient in the interior is of order $\frac{C}{a}$ and, because the boundary layer is very thin and the surface area of the internal wake is very small, the area of the "surface" dividing the interior from the boundary layer-wake does not differ significantly from the area of the drop's surface, which is of order a^2. Consequently the order of magnitude of the mass flux from the interior into the internal boundary layer-wake system is of order

$$D . \frac{C}{a} . a^2$$

The concentration gradient in the boundary layer is of order $\frac{C'}{h}$, where C' is a characteristic concentration for the boundary layer. Thus the mass flux from the internal boundary layer to the exterior is of order

$$D . \frac{C'}{h} . a^2$$

There being no build up of solute in the boundary layer these two fluxes must be equal, so:

$$C' \ast\ast \frac{h}{a} C$$

$$= C.Pe^{-\frac{1}{2}}$$

The boundary layer-wake system therefore has a concentration which is much less than the concentration of the interior, and in fact is almost zero.

The concentration in the external boundary layer will have the same order of magnitude if it is assumed that the equilibrium constant is of order one.

It is worth emphasising that this result means that there can be no steep gradient of ~~sudden jump in~~ concentration in the boundary layer. The interior and the boundary layer merge smoothly into one another and the gradient of concentration is of order $\frac{C}{a}$ in both regions.

5. Remarks

Calculations of the type used in this chapter are not, of course, intended to be anything more than approximate and, indeed, for a variety of reasons, they can sometimes be completely inaccurate. But they can provide a basis for more detailed investigations - which is the reason they are presented here - and their results should not be ignored without justification. Of particular importance is the result that solute is carried up the internal wake without significant diffusion. As was mentioned in Chapter 2 this contradicts one of the assumptions made by Levich *et al*. (10, 11) and by Ruckenstein (12). The assumption made by these authors (namely that the internal boundary layer is constantly fed with fresh solution in the region of the front stagnation point) should therefore produce an inaccurate picture because it implies that the highly efficient boundary layer transfer is the rate-governing process, instead of the much slower interior transfer that the present theory emphasizes.

CHAPTER 4

Diffusion in the Interior

This chapter describes a way in which a first approximation to the concentration and the mass transfer may be derived.

In their paper (13) Kronig and Brink consider the problem of extraction from a spherical liquid drop falling in Hadamard-type flow, when all the resistance to diffusion is inside the drop. They ignore the possibility of boundary layers being present and they do not consider the internal wake. For these reasons their calculations might be expected to be inaccurate, but in fact this is not so. The reason for this is apparent from the previous chapter - the fact that diffusion in the interior is the rate-governing process means that a first approximation to the concentration field may be found by considering only what happens in the interior. Since the interior is bounded by a thin boundary layer, whose concentration is almost in equilibrium with that of the exterior, only a small error is caused by assuming that the interior region stretches as far as the drop's surface. A complication of course arises because of the internal wake, since this means that the concentration near the central axis is in equilibrium with the exterior (to this degree of approximation). No error is however introduced into Kronig and Brink's solution by this fact because the co-ordinate system that they use is such that the central axis is treated as part of the drop's surface as far as imposing boundary conditions is concerned. In fact the only cause of inaccuracy in Kronig and Brink's work (apart from the inevitable inaccuracies of the numerical work, which was done without the aid of a computer) was the use of an insufficiently precise boundary condition at the drop's stagnation ring.

In this chapter I wish to describe a way in which the problem of diffusion in the interior may be solved. Much of this work closely parallels that done by Kronig and Brink.

Essentially the problem is to solve the diffusion equation:

$$\frac{\partial c}{\partial t} + \underline{v}.\nabla c = D\nabla^2 c$$

Since the situation is axi-symmetric this is a partial differential equation with three independent variables - two in space, and one in time. However, as will be shown, by making use of the properties of mass transfer at high Peclet number, it is possible to eliminate one of the space variables, whereupon the equation reduces to a recognisable type that may be solved by fairly simple numerical means.

The idea behind this approach may perhaps best be grasped by considering a hollow circular cylinder in which a fluid is flowing in such a way that the stream surfaces are concentric circular cylinders - Figure 3a. Suppose that initially there is a non-constant distribution of concentration $c(\psi)$ such that the concentration c at a point is a function only of the stream function ψ which defines the stream surface on which the point lies. Clearly, as time progresses a transfer process will occur but, because of the symmetry of the situation, the concentration remains a function only of the stream function and time - that is, no variation in concentration between different points on the same stream surface can arise.

But now consider a situation in which the stream surfaces are eccentric circular cylinders - Figure 3b. In the region AB the stream surfaces are closer together than in the region AC . The gradient of concentration is therefore higher in the region AB than in the region AC so that diffusion here is more rapid. This will set up variations in concentration between different points on the same stream surface. Thus, at any time after the initial instant the concentration is a function of time, of the stream function, and of position on a stream surface.

If q is the co-ordinate orthogonal to the stream function ψ then

$$c = c(q, \psi, t) .$$

However, this dependence on q can be shown to be very weak when the Peclet number is large. Any variation in concentration from one point on a stream surface to another must be the result of the particles at these points having been in different concentration fields at some time. Now if e is the distance AC and b is the distance AB (both of the same order of magnitude) then the time scales of the diffusion process in these regions are of the order $\frac{e^2}{D}$ and $\frac{b^2}{D}$ respectively. Suppose U is a characteristic speed of the motion and s' is the circumference of a stream surface (and of the same order of magnitude as b and e), then a particle moves from the region AC to the region AB in time of order $\frac{s'}{U}$. In this time the concentration field will not have altered much (by about $\frac{s'}{U} \frac{DC}{e^2}$ or $\frac{s'}{U} \frac{DC}{b^2}$, both of which are small compared with C, provided that the Peclet number - defined by either $\frac{Ue}{D}$ or $\frac{Ub}{D}$ - is much greater than one), nor will the particle's concentration have changed greatly (again by about $\frac{s'}{U} \frac{DC}{e^2}$ or $\frac{s'}{U} \frac{DC}{b^2}$). But it is this change which causes the variation in concentration. The variation brought about in time

$\frac{s'}{U}$ is therefore of the order of $\frac{s'}{U}\frac{DC}{e^2}$ or $\frac{s'}{U}\frac{DC}{b^2}$, and both these are small compared with C.

Even so a variation comparable to C could be built up (since the diffusion process goes on for time $\frac{b^2}{D}$) if one particle were continuously in a privileged position - but this is not so: the particles quickly rotate through the different parts of the flow field and no one particle receives greatly different treatment from its fellows on that particular stream surface.

This illustrative situation is similar to the situation inside a liquid drop. In terms of the example the distances which correspond to b and e are of the same order of magnitude as the drop radius a. The circumference s' is also of this order. Thus the variation in concentration on a stream surface is of order $\frac{a}{U}\frac{DC}{a^2}$, which is equal to $C.Pe^{-1}$.

Thus if $\bar{c}\,(\psi, t)$ is, in some sense (to be made more precise later), the average concentration of a stream surface, then the concentration at any point may be represented by

$$c(q, \psi, t) = \bar{c}(\psi, t) + Pe^{-1}.c^*(q, \psi, t)$$

where $\bar{c}$ and c^* are both of order one.
(Here it is assumed that the situation is axi-symmetric so that there is no dependence on the co-ordinate λ).

Thus for high Peclet number the dependence of the concentration on the co-ordinate q may be neglected.

This argument is not valid if a stream surface passes near a stagnation point, for then the flow speed can no longer be represented by the characteristic speed U, and the flow may be so slow that a significant change in concentration could occur as a particle passes through this region. There are two types of stagnation point in a liquid drop - the stagnation points at the poles, and the ring of stagnation points in the drop's equatorial plane.

Consider firstly the stagnation ring. Here the speed tends to zero, but the circumference of the stream surface tends to zero as well and, as might have been hoped, the time taken for a particle to make one circuit is substantially the same as on a normal stream surface. The rest of the argument is not affected by the slowness of the flow so the approximation remains valid. To be more precise, the time taken for a particle to go once round the stream surface represented by ψ = constant, is:

$$\oint \frac{ds}{v}$$

where ds is an element of length of the particle's path and the integral is taken round the stream surface, on the path of the particle.

This integral is evaluated in Appendix 3 where its value is shown to be:

$$\frac{a}{v_0} \sqrt{2}\,\pi$$

The circulation time is therefore still of order $\frac{a}{U}$, so that the variation remains of order $\frac{a}{U}\cdot\frac{DC}{a^2} = C.Pe^{-1}$. Near the stagnation ring, therefore, the dependence of the concentration on the co-ordinate q remains negligible.

Secondly, there is the effect of passing near the polar stagnation points to be considered. As was seen in the previous chapter in the discussion on diffusion in the internal wake the time that a particle takes to move through a region near a stagnation point has a logarithmic dependence on the closest axial distance from the stagnation point. Suppose s is this distance. Then the time taken to move through the stagnation region is of order $\frac{a}{U}\log\frac{s}{a}$, and in this time the concentration can change by an amount of order $C\ Pe^{-1}\log\frac{s}{a}$ (assuming that the order of the rate of change of concentration is $\frac{D}{a^2}$). This is negligible for all s in the interior - in fact one would have to be a considerable distance into the boundary layer-wake system before this would become of the same order as $\bar{c}$. Thus the region in which diffusion near the stagnation points produces significant variations from the average concentration is contained inside the boundary layer-wake system, and since only the interior of the drop is under consideration here this effect introduces no new restriction and consequently may be ignored.

This discussion has shown that everywhere in the interior the average concentration for the stream surface is a valid approximation to the concentration at any point on the stream surface.

2. The interior equation

The equation describing the diffusion process is the diffusion equation (1), that is:

$$\frac{\partial c}{\partial t} + \underline{v}.\nabla c = D\nabla^2 c$$

Bearing in mind the comments of the previous section it is obviously convenient to use a co-ordinate system in which one of the co-ordinates is constant on a stream surface. For this purpose a non-dimensionalised stream function is suitable. In order to make the system the same as that used by Kronig and Brink, which has the advantage that the co-ordinate is equal to unity at the stagnation ring, the following system is used:

$$\frac{v_o}{8} a^2 m = \psi$$

i.e. $$m = 4\,p^2\,(1 - p^2)\,\sin^2\theta \qquad \ldots \quad (2)$$

where $$ap = r\,.$$

A co-ordinate orthogonal to m in planes containing the axis of symmetry (that is the drop's axis) is given by:

$$q = \frac{p^4 \cos^4\theta}{2p^2 - 1} \qquad \ldots \quad (3)$$

The derivation of a co-ordinate orthogonal to m is described in Appendix 6. This co-ordinate system is illustrated in Figure 4. The third co-ordinate λ (where λ = constant are planes through the axis of symmetry) remains the same as in a spherical polar co-ordinate system.

In this co-ordinate system the diffusion equation (1) becomes:

$$\frac{\partial c}{\partial t} + \frac{v_q}{h_q}\frac{\partial c}{\partial q} + \frac{v_m}{h_m}\frac{\partial c}{\partial m} = \frac{D_1}{a^2 h_m h_q h_\lambda}\left[\frac{\partial}{\partial m}\left(\frac{h_q h_\lambda}{h_m}\frac{\partial c}{\partial m}\right) + \frac{\partial}{\partial q}\left(\frac{h_\lambda h_m}{h_q}\frac{\partial c}{\partial q}\right) + \frac{\partial}{\partial \lambda}\left(\frac{h_m h_q}{h_\lambda}\frac{\partial c}{\partial \lambda}\right)\right] \qquad \ldots \quad (4)$$

where h_m, h_q, h_λ are the scale factors of this co-ordinate system. They are given in full in Appendix 2. Since the flow is almost along surfaces of constant m the velocity in the directions of increasing m , i.e. v_m, is Small ~~zero~~. The fluid is incompressible so that the continuity equation is:

$$\frac{\partial}{\partial m}(h_q h_\lambda v_m) + \frac{\partial}{\partial q}(h_m h_\lambda v_q) = 0$$

(there is no velocity in the λ direction).

Thus:

$$\oint v_q h_m h_\lambda \frac{\partial c}{\partial q}\, dq = \oint \frac{\partial}{\partial q}(v_q h_m h_\lambda c)\, dq - \oint c \frac{\partial}{\partial q}(h_m h_\lambda v_q)\, dq$$

$$= \oint c \frac{\partial}{\partial m}(h_q h_\lambda v_m)\, dq$$

where $\oint ..dq$ indicates integration at constant time round a stream surface along a line on which λ = constant. So, multiplying equation (4) by $h_m h_q h_\lambda$ and integrating results in:

$$\oint h_m h_q h_\lambda \frac{\partial c}{\partial t}\, dq + \oint \frac{\partial}{\partial m}(v_m h_q h_\lambda c)\, dq = \frac{D_1}{a^2} \oint \left[\frac{\partial}{\partial m}\left(\frac{h_q h_\lambda}{h_m} \frac{\partial c}{\partial m}\right) + \frac{\partial}{\partial q}\left(\frac{h_\lambda h_m}{h_q} \frac{\partial c}{\partial q}\right) + \frac{\partial}{\partial \lambda}\left(\frac{h_m h_q}{h_\lambda} \frac{\partial c}{\partial \lambda}\right) \right] dq$$

Using the assumption of axial symmetry, so that $\frac{\partial c}{\partial \lambda} = 0$, and putting

$$\oint \frac{\partial}{\partial q}\left(\frac{h_\lambda h_m}{h_q} \frac{\partial c}{\partial q}\right) dq = 0$$

because of the single valuedness of $\frac{h_\lambda h_m}{h_q} \frac{\partial c}{\partial q}$, the equation is further simplified to:

$$\oint \frac{\partial}{\partial m}(v_m h_q h_\lambda c)\, dq + \oint h_m h_q h_\lambda \frac{\partial c}{\partial t}\, dq = \frac{D_1}{a^2} \oint \frac{\partial}{\partial m}\left(\frac{h_q h_\lambda}{h_m} \frac{\partial c}{\partial m}\right) dq \quad .$$

Now let

$$c = \bar{c}(m, t) + Pe^{-1} c^*(q, m, t)$$

with

$$\oint h_m h_q h_\lambda \, c^*(q,\, m,\, t)\, dq \;=\; 0 \,.$$

$\bar{c}$ and c^* have been mentioned before, when it was explained that $\bar{c}$ is an average of the concentrations on a given stream surface. $\bar{c}$ and c^* are now uniquely defined.

By inverting the order of differentiation and integration (which is permissible because $\frac{\partial c^*}{\partial t}$ is bounded so that the integral of $h_m h_q h_\lambda \frac{\partial c^*}{\partial t}$ is uniformly convergent) it follows from the definition of c^* that

$$\oint h_m h_q h_\lambda \frac{\partial c^*}{\partial t}\, dq$$

is equal to

$$\frac{\partial}{\partial t} \oint h_m h_q h_\lambda c^* dq$$

which equals zero. Also, $\oint \frac{\partial}{\partial m}(v_m h_q h_\lambda \bar{c})\, dq = 0$, by continuity.

On using this result the equation becomes:

$$\frac{\partial \bar{c}}{\partial t} \oint h_m h_q h_\lambda \; dq \;=\; \frac{D_1}{a^2} \oint \left[\frac{\partial}{\partial m} \left(\frac{h_q h_\lambda}{h_m} \frac{\partial \bar{c}}{\partial m} \right) + Pe^{-1} \frac{\partial}{\partial m} \left(\frac{h_q h_\lambda}{h_m} \frac{\partial c^*}{\partial m} \right) - Pe^{-1} \oint \frac{\partial}{\partial m}(v_m h_q h_\lambda c^*)\, dq \right] dq$$

The second and third terms on the right-hand side ~~is~~ are small enough to be neglected

, leaving

$$\frac{\partial \bar{c}}{\partial t} \oint h_m h_q h_\lambda \; dq \;=\; \frac{D_1}{a^2} \oint \frac{\partial}{\partial m} \left(\frac{h_q h_\lambda}{h_m} \frac{\partial \bar{c}}{\partial m} \right) dq \,.$$

Finally, by writing

$$i \;=\; t \frac{D_1}{a^2} \,,$$

$$H = \oint h_m h_q h_\lambda \, dq ,$$

and

$$J = \oint \frac{h_q h_\lambda}{h_m} \, dq ,$$

and reversing the order of integration and differentiation on the right-hand side, the desired form of the equation is obtained:

$$H \frac{\partial \bar{c}}{\partial i} = \frac{\partial}{\partial m} \left(J \frac{\partial \bar{c}}{\partial m} \right) \quad \ldots \quad (5)$$

This is the equation that must be solved to obtain the concentration at any point in the interior.

The functions H and J are described in greater detail in Appendix 2, and the validity of inverting the order of integration and differentiation in obtaining equation (5) is discussed in Appendix 4.

This equation is of the similar form to the one-dimensional heat equation, which is:

$$\frac{\partial c}{\partial t} = \frac{\partial^2 c}{\partial x^2}$$

However there are several complicating factors associated with the behaviour at $m = 0$. These are that the function H(m) has a logarithmic singularity at this point, and that equation (5) may not be valid there. Further description of these matters is deferred to Appendices 2 and 4.

These properties will not be of practical importance because the equation will be applied to solve the problem only in the drop's interior where m is always greater than zero, but the method of solution is such that they may cause difficulty. For the present it suffices to point out that $m = 0$ is a singular point.

3. Boundary and initial conditions

Equation (5) is a parabolic partial differential equation. To solve it therefore requires two boundary conditions in the m direction and one boundary (or initial) condition in the i direction.

Consider firstly the boundary condition in the m direction. One of these will be derived from the conditions at the drop's surface and axis (more exactly at the meeting of the interior with the internal boundary layer-wake system), and the other from the conditions at the stagnation ring.

Near the surface and axis, where $m ** Pe^{-\frac{1}{2}}$, the interior merges into the boundary layer-wake system. Here the concentration is of the order $C.Pe^{-\frac{1}{2}}$. Assuming that the equation's solution does not exhibit an unusual behaviour - an assumption that will be confirmed in Chapter 5 - it is clear that a condition $\bar{c} = 0$ may be imposed in this region (where $m ** Pe^{-\frac{1}{2}}$) and will result in an error of order only $Pe^{-\frac{1}{2}}$, which is negligible as far as this first approximation is concerned.

If a numerical method of solution is to be used it is obviously undesirable that this condition should be imposed at $m = Pe^{-\frac{1}{2}}$ since this would require that the calculation be repeated for different values of the Peclet number. It is therefore preferable to impose the condition at a constant point $m = b$, where b is of the order of $Pe^{-\frac{1}{2}}$. Putting $b = 0$ would be the most convenient value but this might be expected to cause inaccuracies due to it being a singular point. In fact the problem of a singularity in H does not arise because, as will be seen later, the value of H at the boundary is never required for the purpose of the numerical calculation. From the point of view of the numerical calculation, therefore, it makes little difference whether the boundary condition is imposed at $m = 0$ or at some small value. For simplicity the condition is taken to be:

$$\bar{c} = 0 \quad \text{at} \quad m = 0 .$$

Later, in Chapter 5, it will be shown that the solution of equation (5) is well-behaved in the neighbourhood of $m = 0$ and this will confirm the statement that no great inaccuracy is caused by imposing the boundary condition there.

Assuming for the present that the solution is well-behaved the use of this boundary condition may also introduce an error of order $Pe^{-\frac{1}{2}}$, which again may be neglected in the determination of the first approximation.

The condition at the stagnation ring is obtained by assuming that $\bar{c}$ is a regular function of m at this point. That being so it may be represented by a Taylor expansion in the neighbourhood of $m = 1$:

$$\bar{c}(m,i) = \bar{c}(1,i) + (m - 1)\,\bar{c}'(1,i) + O(m - 1)^2$$

where $\bar{c}'$ is the derivative of $\bar{c}$.

The fact that the concentration at the stagnation ring will not be zero whilst the diffusion process lasts means that the first term, namely $\bar{c}(1,i)$, is non-zero.

H and J are regular at $m = 1$ and have Taylor expansions (see Appendix 2). However $J(1)$ is zero, so that:

$$J(m) = (m - 1)\,J'(1) + O(m - 1)^2$$

Substituting these series into equation (5) results in:

$$H(1)\,\frac{\partial\bar{c}}{\partial i}(1,i) + O(m - 1) = \frac{\partial}{\partial m}\Big[(m - 1)\,J'(1)\,c'(1,i) + {} + O(m - 1)^2\Big]$$

and taking the limit as m tends to one gives:

$$H(1)\,\frac{\partial\bar{c}}{\partial i}(1,i) = J'(1)\,\frac{\partial\bar{c}}{\partial m}(1,i)$$

This, as is shown in Appendix 2, is equivalent to:

$$\frac{\partial \bar{c}}{\partial i} = -20\frac{\partial \bar{c}}{\partial m} \quad \text{at} \quad m = 1$$

which is the required boundary condition.

The physical meaning of this condition is that it represents the relationship between the flux through a stream surface which surrounds the stagnation ring and the fall in concentration in the volume enclosed by this stream surface, in the limiting case as m tends to one. The first step is to obtain the mass loss per unit time in terms of the concentration:

The rate of mass loss from a volume enclosed by a stream surface m is given by

$$\frac{\partial}{\partial t} \quad a^3\int_0^{2\pi} \int_{-\infty}^{\infty} \int_m^1 \bar{c}\ h_m h_q h_\lambda \ dm\ dq\ d\lambda\ .$$

For small values of (1-m) the integral with respect to m may be approximately evaluated so that this expression is approximated by

$$(1-m)\ a^3 \frac{\partial \bar{c}}{\partial t} \iint h_m h_q h_\lambda \ dq\ d\lambda$$

which equals

$$(1-m)\left[a^3 \frac{\partial \bar{c}}{\partial t} \int H\ d\lambda\right]_{m=1}$$

The mass flux through the stream surface is:

$$-D_I\ a\int_0^{2\pi}\int_{-\infty}^{\infty} \frac{1}{h_m}\frac{\partial \bar{c}}{\partial m} h_q h_\lambda \ dq\ d\lambda$$

which equals

$$- D_1 \; a \frac{\partial \bar{c}}{\partial m} \iint \frac{h_q h_\lambda}{h_m} \, dq \; d\lambda$$

which is

$$- D_1 \; a \frac{\partial \bar{c}}{\partial m} \int J \; d\lambda$$

Using the Taylor expansion of J near $m = 1$, this expression can be approximated by

$$+ D_1 \; a \frac{\partial \bar{c}}{\partial m} \int (1-m) \; J' \; d\lambda$$

where the derivatives are evaluated at $m = 1$.

Because all the mass lost from the volume enclosed by a stream surface must be diffused through the stream surface the two expressions can be equated, resulting in:

$$\frac{\partial \bar{c}}{\partial i} \; H = \frac{\partial \bar{c}}{\partial m} J' \qquad \text{at} \quad m = 1$$

which is the condition previously derived.

This boundary condition is omitted by Kronig and Brink who use in its place the condition that the concentration profile may be adequately represented by a quadratic function of m. The inaccuracy that this causes seems to have no significant effect.

The initial condition is the state of the concentration profile at $i = 0$. As was described in Chapter 3 the drop will attain terminal velocity before the diffusion effect has penetrated further than a thin layer - that is thin compared with the size of the drop. It is therefore valid to use the following condition:

$$\bar{c} = 1 \quad \text{at} \quad i = 0 , \; m > 0 ,$$

but still retaining the condition

$$\bar{c} = 0 \quad \text{at} \quad m = 0 .$$

To summarize, a first approximation for the concentration at any point in the interior may be obtained by solving the equation

$$H \frac{\partial \bar{c}}{\partial i} = \frac{\partial}{\partial m} \left(J \frac{\partial \bar{c}}{\partial m} \right)$$

with the boundary and initial conditions:

$$\bar{c} = 0 \quad \text{at} \quad m = 0 ,$$

$$\frac{\partial \bar{c}}{\partial i} = - 20 \frac{\partial \bar{c}}{\partial m} \quad \text{at} \quad m = 1 ,$$

and $$\bar{c} = 1 \quad \text{at} \quad i = 0 , \; m > 0 .$$

4. Numerical method

Equation (5) is difficult to solve by analytic means because of the complexity of the functions H and J , and I have therefore obtained a solution by a numerical method. The method of solution is suggested by the strong resemblance of this equation to the heat equation. This suggests that a numerical method that may be used to solve the heat equation may solve equation (5).

The problem can be solved numerically by transforming the equation into finite difference form. Provided that care is taken to ensure stability this will produce a solution.

Considering the left-hand side of the equation first, this is:

$$H \frac{\partial \bar{c}}{\partial i}$$

and may be represented by:

$$H_k \frac{\bar{c}_{k,\ j+1} - \bar{c}_{k,\ j}}{\delta i}$$

where

$\bar{c}_{k,j} = \bar{c}\ (m = (k-1)\delta m,\ \ i = (j-1)\delta i)$

$H_k = H\ (m = (k-1)\delta m)$

δi is the step length in the time direction,

and δm is the step length in the m direction.

In the right-hand side $J \frac{\partial \bar{c}}{\partial m}$ may be represented by

$$J_k \frac{\bar{c}_{k+\frac{1}{2},j} - \bar{c}_{k-\frac{1}{2},j}}{\delta m}$$

So that

$$\frac{\partial}{\partial m} (J \frac{\partial \bar{c}}{\partial m})$$

can be represented by:

$$\frac{1}{\delta m}\left(J_{k+\frac{1}{2}}\frac{\bar{c}_{k+1}-\bar{c}_{k}}{\delta m} - J_{k-\frac{1}{2}}\frac{\bar{c}_{k}-\bar{c}_{k-1}}{\delta m}\right)$$

and this is equal to:

$$\frac{1}{(\delta m)^2}\left\{J_{k+\frac{1}{2}}\,\bar{c}_{k+1,j} - \bar{c}_{k,j}\left(J_{k+\frac{1}{2}}+J_{k-\frac{1}{2}}\right) + \bar{c}_{k-1,j}\,J_{k-\frac{1}{2}}\right\}$$

So that the equation may be represented by:

$$\bar{c}_{k,j+1} = \bar{c}_{k,j} + \frac{(\delta i)}{H_k(\delta m)^2}\left\{J_{k+\frac{1}{2}}\,\bar{c}_{k+1,j} - \bar{c}_{k,j}\left(J_{k+\frac{1}{2}}+J_{k-\frac{1}{2}}\right) + \right.$$
$$\left. + \bar{c}_{k-1,j}\,J_{k-\frac{1}{2}}\right\}$$

This scheme has used forward differences to represent time-wise differentiation and central differences to represent space-wise differentiation.

Similarly the boundary and initial conditions may be transformed into finite difference form:

The condition

$$\bar{c} = 0 \quad \text{at} \quad m = 0 \quad \text{for all } i\ ,$$

becomes

$$\bar{c}_{1,j} = 0 \quad \text{for all } j\ ,$$

whilst

$$\frac{\partial\bar{c}}{\partial i} = -\,20\,\frac{\partial\bar{c}}{\partial m} \quad \text{at} \quad m = 1$$

becomes

$$\frac{\bar{c}_{N,j+1}-\bar{c}_{N,j}}{\delta i} = -\,20\,\frac{\bar{c}_{N,j+1}-\bar{c}_{N-1,j+1}}{\delta m}$$

or

$$\bar{c}_{N,j+1} = \frac{\delta m\ \bar{c}_{N,j} + 20\ \delta i\ \bar{c}_{N-1,j+1}}{\delta m + 20\ \delta i}$$

where N is the value of k that corresponds to $m = 1$, i.e. $(N - 1)\ \delta m = 1$.

The initial condition

$$\bar{c} = 1 \quad \text{at} \quad i = 0\ , \quad m > 0$$

becomes

$$\bar{c}_{k,1} = 1 \quad \text{for all} \quad k > 1\ .$$

To determine a stability criterion use is made of a variable Δ_k defined by:

$$\Delta_k = \frac{\delta i}{H_k\ (\delta m)^2}$$

The equation may therefore be written in the form:

$$\bar{c}_{k,j+1} = \bar{c}_{m,j} \left\{ 1 - \Delta_k (J_{k+\frac{1}{2}} + J_{k-\frac{1}{2}}) \right\} + \Delta_k\ J_{k+\frac{1}{2}} \bar{c}_{k+1,j} + \Delta_k\ J_{k-\frac{1}{2}}\ \bar{c}_{k-1,j}$$

It is to be expected, by analogy with the heat equation, that if Δ_k is too large instability will result. However, it is easy to determine a range for Δ_k in which the equation will be stable. Suppose an error of absolute magnitude less than, or equal to, $|\Sigma|$ occurs in $\bar{c}_{k+1,j}$, $\bar{c}_{k,j}$, or $\bar{c}_{k-1,j}$. Then this produces an error in the determination of $\bar{c}_{k,j+1}$, of magnitude Σ^* , where

$$|\Sigma^*| \leqslant |\Sigma| \left|1 - \Delta_k(J_{k+\frac{1}{2}} + J_{k-\frac{1}{2}})\right| + \left|\Delta_k J_{k+\frac{1}{2}}\right| |\Sigma| + \left|\Delta_k J_{k-\frac{1}{2}}\right| |\Sigma|$$

Since $\Delta_k J_{k+\frac{1}{2}}$ and $\Delta_k J_{k-\frac{1}{2}}$ are known to be positive then, provided that

$$1 - \Delta_k(J_{k+\frac{1}{2}} + J_{k-\frac{1}{2}}) \geqslant 0 ,$$

it follows that

$$|\Sigma^*| \leqslant |\Sigma|$$

In other words the process is stable if

$$1 - \Delta_k(J_{k+\frac{1}{2}} + J_{k-\frac{1}{2}}) \geqslant 0$$

This does not of course demonstrate that the process is unstable if this condition is not satisfied, but it was found in practice that if this condition was not obeyed then instability resulted.

The easiest way to satisfy the condition is to calculate δi in such a way as to ensure that the condition is obeyed for all k. This may be done in the following manner:

The stability criterion is:

$$1 - \frac{\delta i}{(\delta m)^2 H_k} (J_{k+\frac{1}{2}} + J_{k-\frac{1}{2}}) \geqslant 0 \quad \text{for all } k .$$

Therefore

$$\delta i \leqslant \frac{(\delta m)^2 H_k}{J_{k+\frac{1}{2}} + J_{k-\frac{1}{2}}}$$

So let

$$\delta i = \chi (\delta m)^2 \min \frac{H_k}{J_{k+\frac{1}{2}} - J_{k-\frac{1}{2}}}$$

where

$$0 < \chi \leqslant 1$$

and the minimum is to be taken over all values of k.

Since it is desirable to proceed in as large time steps as are compatible with the required accuracy (in order to minimise calculation times) it is natural to chose χ near one, and in the numerical calculations $\chi = 0.9$ was used. $\chi = 1.0$ would be the best value but here the round-off error inherent in any numerical process might produce instability. In practice any instability soon makes its presence obvious and no undetected error of this type can be expected to occur.

A detailed analysis of the errors involved in this numerical work would be superfluous since it is a routine type of calculation. However the magnitude of any errors has been established by some simple checks which will now be described.

That the finite difference approximations are sufficiently accurate can be ensured in the usual way by halving the step length δm until this change produces no significant difference in the solution. In the present case of course decreasing δm automatically results in a decrease in δi, so that there is no need to consider the two variables separately. It was found that decreasing δm from $\frac{1}{40}$ to $\frac{1}{80}$ produced a difference of less than 1% in the concentration at the stagnation ring (the difference at any time being expressed as a percentage of the concentration at that time).

A more comprehensive check is to solve a similar problem analytically as well as numerically. In this way any error that occurs for any reason should become obvious. It has already been remarked that the equation at present under consideration is of the same type as the heat equation. A comparable, but simpler, problem is to find the temperature distribution inside an insulated bar, with uniform initial temperature, whose ends are kept at zero temperature. The equation for this problem is:

$$\frac{\partial c}{\partial t} = \frac{\partial^2 c}{\partial x^2}$$

with the boundary conditions:

$$c = 1 \quad \text{at} \quad t = 0\,, \quad 0 < x < 2\,,$$

$$c = 0 \quad \text{at} \quad x = 0\,, \quad \text{all} \quad t$$

$$\frac{\partial c}{\partial x} = 0 \quad \text{at} \quad x = 1\,, \quad \text{all} \quad t$$

where $x = 1$ is the centre of the bar.

The solution may be determined in the form of an infinite series. Its value at $x = 1$ is:

$$c = \frac{4}{\pi}\exp(-\frac{\pi^2}{4}t) - \frac{4}{3\pi}\exp(-\frac{9\pi^2}{4}t) + \frac{4}{5\pi}\exp(-\frac{25\pi^2}{4}t) + O(\exp(-\frac{49}{4}\pi^2 t))$$

Investigation of the numerical solution shows general agreement with this result. With sufficiently small step length (i.e. $\delta x = \frac{1}{90}$) the error is reduced until it is less than about 3.5% of the analytic solution. In general the error increases with time. This is presumably due to an error accumulating with each time step.

A final check on the calculation utilised the calculation of the mass loss. This may be found either by calculating, from the concentration profile, the amount of solute inside the drop at any moment and subtracting this from the original amount, or by integrating the rate at which mass diffuses through the surface of the drop (which is found from the gradient of concentration at the drop's surface) with respect to time. Ideally these two calculations should produce identical results. In practice certain discrepancies occur. These are partly due to the differing round-off errors involved in the two calculations, but any error in the work that produces an effect similar to a mass source inside the drop (e.g. a mistake in the boundary condition at the stagnation ring) would cause a significant difference between the two results. This is because one method of calculation - that using the concentration profile - assumes that the mass loss at any time is equal to the mass at that time subtracted from the initial mass, and this would be untrue if a mass source were present.

The other method makes no such assumption.

It was found that agreement between the two calculations improved as time increased, and the discrepancy was always of the order of .05% or less of the initial mass of solute in the drop.

6. Results and Discussion

The results of this calculation are given in Tables 1, 2 and 3, and are summarized in graphs (Figures 5, 6 and 7) showing the concentration profile at various times, and the mass loss (calculated from the concentration profile) as a function of time. The concentration at the stagnation ring as a function of time is also shown for the purpose of comparison with Kronig and Brink's work. The calculations were terminated when the concentration at the stagnation ring fell to less than $\frac{1}{20}$ of the initial concentration.

Perhaps the chief characteristic of these results is that the transfer process takes considerably less time than might be expected on order of magnitude considerations. The only property that could be responsible for this effect is the internal circulation, which decreases the effective size of the drop because the diffusion effect merely has to penetrate to the stagnation ring (at a distance $a(1 - \frac{1}{\sqrt{2}})$

from the surface) instead of to the drop's centre (at a distance a) as is the case with a stagnant drop.

From the point of view of obtaining experimental verification of these results it is of importance to note the close agreement between them and the results of Kronig and Brink. This is because many experimenters have commented that the results of experiments are, at least approximately, in agreement with Kronig and Brink's calculation. The fact that the present work imposes a boundary condition at the stagnation ring in place of Kronig and Brink's assumption that the concentration profile may be approximated by a quadratic expression makes the close agreement between the two sets of results surprising. However, the ratio

$$\frac{\partial \bar{c}}{\partial i} \bigg/ \frac{\partial \bar{c}}{\partial m}$$

when calculated from the first term of Kronig and Brink's result has the value -20.24 at $m = 1$, compared with the accurate value of -20, so the different conditions are compatible.

This first approximation is the only part of the solutions produced in this thesis that can be experimentally checked. The difficulties associated with satisfying the necessary assumptions in an experiment are such as to make the detection of second order effects (which are of order

$Pe^{-\frac{1}{2}}$ of the first order effect) almost impossible at the present time. This first approximation is therefore the only part of practical importance in the prediction of mass transfer rates.

This solution, namely that:

$$\begin{aligned} c &= \overline{c} \quad \text{inside the drop,} \\ c &= 0 \quad \text{outside the drop,} \end{aligned}$$

is a uniformly valid first approximation to the concentration field. The errors are everywhere of order $Pe^{-\frac{1}{2}}$ or less. To a first approximation the drop exterior is unaffected by the transfer process, and the transfer process is unaffected by the exterior (except for the presence of the external concentration in the normalisation formulae) - in particular the mass transfer is not dependent on the coefficient of diffusion in the bulk fluid (D_o).

It should be noted that the case where a continuous phase is a pure solute which dissolves into a solvent drop is included in the results of this chapter. In such a situation the drop surface is held at a constant concentration and the solute diffuses into the drop. Mathematically this process is identical (to this first approximation) to the extraction process described here: the physical differences are removed by the use of the normalised concentration. This result is important because it is often easier to obtain experimental results for a system of this type than it is to obtain results for an extraction process.

CHAPTER 5

Diffusion in the boundary layers

1. The boundary layers

There were two principal sources of inaccuracy in the determination of the first approximation, apart from the errors inherent in the numerical process. These were the inaccuracy due to assuming that the concentration was equal to the average concentration on the stream surface, and that due to imposing the condition

$$\bar{c} = 0 \quad \text{at} \quad m = 0 .$$

The latter of these two errors is the larger, for the concentration in the boundary layer is actually of order $C.Pe^{-\frac{1}{2}}$ and the boundary layer has a thickness $a.Pe^{-\frac{1}{2}}$, whilst the variation in concentration round a stream surface was shown in Chapter 4 to be only of order $C.Pe^{-1}$. The purpose of this chapter is to demonstrate how the larger error may be eliminated and so to obtain a more accurate expression for the concentration in the interior. This will involve a more detailed investigation of the boundary layers.

Clearly this search for greater accuracy in solving the diffusion equation should not be taken too far in view of the limited accuracy of the diffusion equation itself, and of the equilibrium condition at the drop's surface but, on the other hand, the boundary layers have an intrinsic interest, not least because they have sometimes been assumed to be the dominant effect in drop diffusion.

The boundary layers have already been described qualitatively in Chapter 3 where the distinction between two different time periods - an initial period and a final period - was made. It is this final period (in which the drop interior dominates the diffusion process) that is under consideration here.

Often the presence of a boundary layer in a system is indicated by the existence in the system of a region of relatively large gradients of some quantity. For example in flow at high Reynolds number past a solid there is a large gradient of velocity near the surface of the solid. Similarly in flow past a dissolving solid at high Peclet number there is a large gradient of concentration. In both these cases the boundary layers are regions of first order perturbations. The case of diffusion from a liquid drop is completely different; here the boundary layers are a region in which only second order terms are perturbed, whilst the first approximation is uniformly valid, instead of being valid only outside the boundary layers. There is therefore no region of high concentration gradients that can be easily identified as a boundary layer.

The practical effect of the boundary layers in the present case is that variation in concentration along a stream surface near the drop's surface affects the concentration field by an amount of order $C.Pe^{-\frac{1}{2}}$. The boundary layers are of thickness $a.Pe^{-\frac{1}{2}}$ and a corresponding change in concentration occurs over that distance scale in the normal direction as occurs over a distance of order a in the tangential direction.

Although the approximation of the previous chapter is no longer possible if the required accuracy is to be achieved, another approximation becomes valid in the boundary layer. This is fortunate since, otherwise, the problem would involve three independent variables (two of space and one of time) and would consequently be intractable.

This other approximation is to neglect the time derivative which appears in the diffusion equation. Recall that the diffusion equation is

$$\frac{\partial c}{\partial t} + v.\nabla c = D\nabla^2 c$$

Consider this equation in spherical polar co-ordinates, with origin at the drop's centre and upstream direction at $\theta = 0$, then one of the terms on the right-hand side is

$$\frac{D}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c}{\partial r}\right)$$

The other term (there are only two because the situation is axi-symmetric) is

$$\frac{D}{r^2 \sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial c}{\partial\theta}\right) .$$

In the boundary layer this term is negligible compared with the former because of the property of the boundary layer that the variation in concentration over a distance $a.Pe^{-\frac{1}{2}}$ in a direction normal to it is comparable to the variation over a distance of order a in the tangential direction, so that the former term is of order $\frac{DC'}{h^2}$ whereas this term is of order $\frac{DC'}{a^2}$.

Still near the surface (i.e. at a distance small compared with a) but in the interior this term remains negligible because it approximately represents the variation along the stream surface, whilst the former term approximately represents the variation normal to the stream surface. (This is not true near the poles where differentiation in the θ direction can correspond to variation normal to the stream surfaces.)

In a region of distance of order aN from the drop's surface the former term will be of magnitude at most

$$\frac{DC'}{a^2 N^2} .$$

(Here the word "region" refers to a group of entire stream surfaces - not parts of stream surfaces - whose least distance from the surface is of order aN .)

The time derivative term is of order

$$\frac{DC'}{a^2}$$

since the time scale for the boundary layer is determined by the time scale of the interior (which is $\frac{a^2}{D}$). Thus

$$\frac{\text{magnitude of time derivative}}{\text{magnitude of diffusion term}} ** N^2$$

so that, for $N ** Pe^{-\frac{1}{2}}$, i.e. in the boundary layer, the time derivative is negligible. (This also shows that it is negligible for some distance into the interior and it is not until N becomes greater than $Pe^{-\frac{1}{4}}$ that the error caused by neglecting the time derivative becomes greater than $Pe^{-\frac{1}{2}}$.)

When the time derivative is omitted the equation becomes:

$$v_r \frac{\partial c}{\partial r} + \frac{v_\theta}{r} \frac{\partial c}{\partial \theta} = \frac{D}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial c}{\partial r})$$

which is the boundary layer equation for drop diffusion. The equations for the internal and external boundary layers are the same, except for the different diffusion coefficients, which have been represented here by the one symbol D. It is only by the omission of the time derivative that this equation differs from the equation for the concentration in the interior.

Now let

$$a\,y = r - a$$

so that y is the non-dimensionalised radial distance from the drop's surface.

The stream function inside the drop ψ_1 is given by:

$$\psi_1 = \frac{v_o}{2}\, r^2 \left(1 - \frac{r^2}{a^2}\right) \sin^2\theta$$

Since the region under consideration is very thin compared with the radius of the drop, it follows that, in this region:

$$y \ll 1$$

So, when ψ_1 is expressed in terms of y, and terms of smaller magnitude than y are neglected, the equation for ψ_1 becomes:

$$\psi_1 = - v_o\, a^2\, y.\sin^2\theta$$

So

$$v_\theta = v_o \sin\theta$$

$$v_r = - 2\, v_o\, y.\cos\theta$$

These will be valid expressions for the velocities outside as well as inside the drop (provided always that $y \ll 1$) since these velocities are continuous at the interface.

Putting these expressions into the diffusion equation one obtains:

$$-2\frac{v_o}{a}\,y\cos\theta\,\frac{\partial c}{\partial y}+\frac{v_o}{a}\sin\theta\,\frac{\partial c}{\partial\theta}=\frac{D}{a^2}\,\frac{\partial^2 c}{\partial y^2}$$

Define a new variable y^* by:

$$y^* = y\,Pe_j^{\frac{1}{2}}$$

where $$Pe_j = \frac{v_o a}{D_j}$$

$j = 1$ represents the inside of the drop

$j = 0$ represents the outside of the drop.

It should be noted that distances in the external boundary layer are scaled differently to distances in the internal boundary layer.

With this scaling the two boundary layer equations (that is the internal and the external one) are identical:

$$-2\,y^*\cos\theta\,\frac{\partial c}{\partial y^*}+\sin\theta\,\frac{\partial c}{\partial\theta}=\frac{\partial^2 c}{\partial y^{*2}}$$

The substitutions (see Harper and Moore (6)):

$$X = -\cos\theta+\frac{\cos^3\theta}{3}+\frac{2}{3}$$

$$Y = y^*\sin^2\theta$$

will reduce this equation to the heat equation:

$$\frac{\partial^2 c}{\partial Y^2}=\frac{\partial c}{\partial X}$$

It is worth noting that Y is closely connected with the non-dimensionalised stream function m - in fact in the boundary layers they differ only by a multiplicative constant:

m is given by

$$m = 4\, p^2\, (1 - p^2) \sin^2\theta$$

$$= -\, 8\, y \sin^2\theta \text{ , approximately.}$$

So that

$$m = -\, 8\, Y\, \mathrm{Pe}_j^{-\frac{1}{2}} \quad \text{approximately.}$$

Also, since

$$q = \frac{p^4 \cos^4\theta}{2\, p^2 - 1}$$

q may, in the boundary layers, be approximated by

$$q = \cos^4\theta$$

So that X is a function of q alone, and Y is a function of m alone.

The only essential difference between the boundary layer equation and the equation for c in the interior is that the former does not involve time as an independent variable (although time will enter, as a parameter, into the boundary conditions). Apart from the omission the two equations are identical when allowance is made for the scaling and for the approximations (i.e. neglect of y^2, etc.)

that are permissible in the boundary layer because of its thinness. Thus for a region sufficiently close to the surface (a distance less than $a.Pe^{-\frac{1}{4}}$) there is no difference between the two equations, since the same approximations and omission of the time derivative are valid assumptions. This does not mean that no new information can be gained from solving the boundary layer equation - on the contrary, the fact that the time has been eliminated means that the dependence of the concentration on both space co-ordinates, X and Y (i.e. q and m) can be examined, whereas the interior solution considered only dependence on one space variable.

Once again it is necessary to solve a parabolic differential equation, although in this case it is of a sufficiently well-known type to be solvable in analytic form. Again three boundary conditions are required - one "initial" condition (corresponding to $X = 0$), and two boundary conditions corresponding to the solution's behaviour in the Y direction. The situation is complicated by the fact that there are really two equations - one for the external, and one for the internal, boundary layer - so that further conditions are necessary at the interface between them.

One boundary equation may be determined by considering the behaviour of the solution of the interior equation in the region near the boundary layer (that is for small values of m). The interior equation is:

$$H \frac{\partial \bar{c}}{\partial i} = \frac{\partial}{\partial m} \left(J \frac{\partial \bar{c}}{\partial m} \right)$$

As is shown in Appendix 2,

at $\quad m = 0, \quad J = \frac{32}{3}$

whilst $\quad H \sim -\frac{1}{8} \log m \quad$ as $\quad m \to 0$.

So that for small m the equation may be approximated by

$$\frac{256}{3} \frac{\partial^2 \bar{c}}{\partial m^2} = (-\log m) \frac{\partial \bar{c}}{\partial i}$$

An approximate solution for this equation may be obtained by taking the Laplace transform with respect to time. If the transform of $\bar{c}$ is defined by:

$$S_1 = \int_0^\infty \bar{c}\, e^{-ki}\, di$$

(here k indicates the variable in the Laplace transform and should not be confused with the earlier use of k in the numerical analysis),

then the transform of the equation is:

$$\frac{256}{3} \frac{d^2 S_1}{dm^2} = \log m - kS_1 \log m .$$

Writing

$$S = S_1 - \frac{1}{k}$$

the equation becomes

$$\frac{256}{3} \frac{d^2S}{dm^2} + kS \log m = 0 .$$

Since the intention is to determine the behaviour in the interior where it meets the boundary layer the region of interest is where m is small.

S is continuous for small m, so it may be expressed by:

$$S(m) = S(0) + W$$

and, by taking m sufficiently near zero, W may be made as small as required.

Then

$$\frac{256}{3} W'' + k\,S(0) \log m = - k\,W \log m$$

where the dashes indicate differentiation with respect to m.

Now $|S(0)| > 0$, because $\overline{c} < \overline{c}(i = 0)$ and so, by taking m sufficiently small, it follows that

$$|W| \ll |S(0)| .$$

The equation is therefore approximately equivalent to:

$$\frac{256}{3} W'' + k\,S(0) \log m = 0 ,$$

which has the solution

$$W = -k\,S(0)\,\frac{3}{256}\,\frac{m^2}{4}\,(2\log m - 3) + A_1 m + F\ .$$

At $m = 0$, $W = 0$ so that $F = 0$, and therefore

$$S_1 = \frac{1}{k} + S(0) + A_1 m - k\,S(0)\,\frac{3}{256}\,\frac{m^2}{4}\,(2\log m - 3)\ .$$

It should be noted that both $S(0)$ and A_1 are functions of k and that the transform cannot be inverted unless they are known. Inversion is not, however, necessary. This solution demonstrates that for sufficiently small m, S_1 may be written in the form

$$S_1 \sim A_1 m + B_1$$

where A_1 and B_1 are functions of k.

Hence $\bar{c}$ may be written in the form

$$\bar{c} \sim A_2 m + B_2 \quad \text{as} \quad m \to 0\ ,$$

where A_2 and B_2 are functions of the time i.

This has justified the assumption made in Chapter 4, that the solution of equation (5) is well-behaved near $m = 0$.

A boundary condition for the boundary layer equations is therefore furnished by requiring that the concentration c must approach a behaviour similar to that of

$$A\,Y + B$$

as Y moves from its value in the boundary layer to its value in the neighbouring part of the interior. This transition from $\bar{c}$ to c is permissible because $\bar{c}$ is a sufficiently accurate approximation for c in the interior.

As usual with equations of the boundary layer type there is no need to be so specific over the values attained by the boundary layer variable; sufficient accuracy is achieved by assuming that a condition that should be imposed at the edge of the boundary layer may instead be imposed in the limit as the variable tends to infinity. With this assumption the boundary condition is:

$$c_1 \sim A\,Y + B \quad \text{as} \quad Y \to -\infty$$

The corresponding condition for the outer boundary layer is that the concentration should tend to the concentration of the bulk fluid:

i.e. $$c_0 \to 0 \quad \text{as} \quad Y \to \infty \,.$$

And there are two conditions to be satisfied at the drop surface in order to link the internal and external solution. The first of these is the relationship between the concentrations on each side of the interface:

$$c_1 = E\,c_0 \quad \text{at} \quad Y = 0 \,,$$

and the second is an equation representing the fact that the mass flux into any part of the interface from the inside of the drop is equal to the mass flux out of the same part of the interface into the exterior of the drop:

$$D_1 \frac{\partial c_1}{\partial r} = D_0 \frac{\partial c_0}{\partial r} \quad \text{at} \quad Y = 0 .$$

This is equivalent to:

$$D_1^{\frac{1}{2}} \frac{\partial c_1}{\partial Y} = D_0^{\frac{1}{2}} \frac{\partial c_0}{\partial Y} \quad \text{at} \quad Y = 0 .$$

Here the derivatives on the left-hand side must be interpreted as being the limiting values of the derivatives as Y tends to zero from below, and those on the right-hand side are the limiting values as Y tends to zero from above.

Two more boundary conditions are required. These relate to the concentration profiles near the front pole of the drop - that is where X equals zero. Outside the drop fresh solvent at zero concentration is swept from the bulk fluid into the boundary layer, so that:

$$c_0 = 0 \quad \text{at} \quad X = 0 , \quad Y > 0 .$$

It is necessary to explain in greater detail what is meant by the statement $X = 0$, $Y > 0$ for, according to the definitions of X and Y this is a self-contradiction. The line $\theta = 0$ is a singular point of the X, Y co-ordinate system in the sense that both X and Y are zero there.

The statement $X = 0$, $Y > 0$ must be interpreted to mean a limiting process in which X tends to zero, whilst Y is kept fixed at a positive value. This means that as X becomes small y^* must become large, and this corresponds to moving along a stream surface in a direction away from the drop. The statement

$$c_o = 0 \quad \text{at} \quad X = 0 , \quad Y > 0$$

should therefore be interpreted to mean

$$c_o \to 0 \quad \text{as} \quad X \to 0 , \quad Y = \text{constant} > 0 .$$

The situation in the interior is more complicated than that in the exterior. In the interior the internal wake feeds solute into the boundary layer. Suppose that the concentration profile where the internal wake flows into the boundary layer is $\overline{Q}(Y)$ - since Y is constant on a stream surface near the surface of the drop, and the concentration profile in the wake is constant with respect to position in the wake it is not necessary to specify exactly at what value of X the wake joins the boundary layer: the profile would be the same at any sufficiently small value of X.

Thus the condition in the interior is:

$$c = \overline{Q}(Y) \quad \text{at} \quad X = 0 , \quad Y < 0$$

and the expression $X = 0$, $Y < 0$ must be interpreted in a similar way to the expression $X = 0,\ Y > 0$. At this stage $\overline{Q}(Y)$ is unknown: it is merely the initial (i.e. at $X = 0$) value of the concentration.

To summarize, the problem is as follows: There are two simultaneous equations to solve (alternatively described as one equation in two regions). These are:

$$\frac{\partial^2 c_1}{\partial Y^2} = \frac{\partial c_1}{\partial X} \qquad Y < 0$$

inside the drop, and

$$\frac{\partial^2 c_o}{\partial Y^2} = \frac{\partial c_o}{\partial X} \qquad Y > 0$$

outside the drop.

The boundary conditions are

$$\begin{array}{lll}
c_1 \sim A\,Y + B & \text{as} & Y \to -\infty \\
c_o \to 0 & \text{as} & Y \to +\infty \\
c_o = 0 & \text{at} & X = 0 \\
c_1 = \overline{Q}(Y) & \text{at} & X = 0 \\
c_1 = E c_o & \text{at} & Y = 0 \\
D_1^{\frac{1}{2}} \dfrac{\partial c_1}{\partial Y} = D_o^{\frac{1}{2}} \dfrac{\partial c_o}{\partial Y} & \text{at} & Y = 0
\end{array}$$

This problem has strong similarities with the one solved by Harper and Moore (6) and a similar method of solution was consequently employed. The details of the method are lengthy and are given in Appendix 1. The solution is:

$$\begin{aligned} c_o = {} & \frac{\sqrt{D_1}\ B}{\sqrt{D_o} + E\sqrt{D_1}}\ \operatorname{erfc} \frac{Y_o}{2\sqrt{X}} \\ & - \frac{2\sqrt{D_1} A}{\sqrt{D_o} + E\sqrt{D_1}}\ \sqrt{X}\ \operatorname{ierfc} \frac{Y_o}{2\sqrt{X}} \\ & + \frac{D_1}{\sqrt{D_o} + E\sqrt{D_1}}\ \frac{1}{\sqrt{\pi X}} \int_{-\infty}^{0} Q(Y') \exp\left(- \frac{(Y_o - Y')^2}{4X}\right) dY' \end{aligned} \qquad \ldots \quad (6)$$

$$\begin{aligned} c_1 = {} & A\,Y_1 + B \\ & - \frac{\sqrt{D_o}\ B}{\sqrt{D_o} + E\sqrt{D_1}}\ \operatorname{erfc} \frac{-Y_1}{2\sqrt{X}} \\ & - \frac{2\,E\sqrt{D_1}\ A}{\sqrt{D_o} + E\sqrt{D_1}}\ \sqrt{X}\ \operatorname{ierfc} \frac{-Y_1}{2\sqrt{X}} \\ & + \frac{1}{2\sqrt{\pi X}} \int_{-\infty}^{0} Q(Y')\ \exp\left(- \frac{(Y_1 - Y')^2}{4X}\right) dY' \\ & + \frac{E\sqrt{D_1} - \sqrt{D_o}}{E\sqrt{D_1} + \sqrt{D_o}}\ \frac{1}{2\sqrt{\pi X}} \int_{-\infty}^{0} Q(Y') \exp\left(- \frac{(Y_1 + Y')^2}{4X} \right) dY' \end{aligned} \qquad \ldots \quad (7)$$

where $Q(Y) = \overline{Q}(Y) - A\,Y - B$. Y_o and Y_1 represent values of Y corresponding to the outside and the inside of the drop, respectively. The function $Q(Y)$ and the constants A and B are still to be determined. (A and B are constant with respect to X and Y , but are functions of time.)

$Q(Y)$ is determined by a similar method to that used to obtain the analogous function in Harper and Moore's paper. Their method uses the fact that the internal wake convects the solute without appreciable diffusion occurring. The concentration profile in the region near the front pole is consequently the same function of the stream function as it is near the rear pole. Since Y_1 is a constant multiple of the stream function this is equivalent to the condition

$$c_1(Y_1 \,,\; X = 0) \;=\; c_1(Y_1 \,,\; X = X_e)$$

where X_e is the value of X at $\theta = \pi$ (the downstream direction) and $c_1(Y_1 \,,\; X = 0)$ should be thought of as the concentration profile for small, but non-zero values of X. Thus

$$Q(Y_1) \;=\; c_1(Y_1 \,,\; X = X_e) \;-\; AY_1 - B \,,$$

so

$$\begin{aligned} Q(Y_1) \;=\; & - \frac{\sqrt{D_o}\; B}{\sqrt{D_o} + E\sqrt{D_1}} \;\operatorname{erfc}\; \frac{-\,Y_1}{2\sqrt{X_e}} \\ & - \frac{2\;E\sqrt{D_1}\;A}{\sqrt{D_o} + E\sqrt{D_1}} \;\sqrt{X_e}\;\; \operatorname{ierfc} \frac{-Y_1}{2\sqrt{X_e}} \\ & + \frac{1}{2\sqrt{\pi X_e}} \int_{-\infty}^{o} Q(Y') \;\; \exp\Big(- \frac{(Y_1 - Y')^2}{4\;X_e} \Big) \;\; dY' \qquad + \end{aligned}$$

$$+ \frac{E\sqrt{D_1} - \sqrt{D_o}}{E\sqrt{D_1} + \sqrt{D_o}} \; \frac{1}{2\sqrt{\pi X_e}} \int_{-\infty}^{o} Q(Y') \exp\left(- \frac{(Y_1 + Y')^2}{4\,X_e}\right) dY' \qquad \ldots \quad (8)$$

This is an integral equation for $Q(Y)$, which can be solved numerically. In order to avoid the presence of the five parameters (A, B, E, D_o, D_1) in the problem it is desirable to re-write the problem as two equations by using suitable transformations.

Let

$$z = \frac{-\,Y_1}{2\sqrt{X_e}} \quad , \qquad z' = \frac{-\,Y_1'}{2\sqrt{X_e}} \quad ,$$

$$p(z) = Q(Y) \quad \text{so that} \quad p(z') = Q(Y') \, ,$$

and

$$n_a = \frac{E\sqrt{D_1} - \sqrt{D_o}}{E\sqrt{D_1} + \sqrt{D_o}} \quad ,$$

$$n_b = \frac{2\,E\sqrt{D_1}\,A\sqrt{X_e}}{E\sqrt{D_1} + \sqrt{D_o}} \quad ,$$

$$n_c = \frac{\sqrt{D_o}\;B}{E\sqrt{D_1}\,{}^{1} + \sqrt{D_o}} \quad .$$

Then, by writing

$$p(z) = n_b\,p_b(z) + n_c\,p_c(z)$$

the equation may be split into two parts:

$$\frac{1}{\sqrt{\pi}} \int_{o}^{\infty} p_b(z') \left[\exp\{-(z - z')^2\} + n_a \exp\{-(z + z')^2\} \right] dz'$$

$$- \; p_b(z) = \operatorname{ierfc} z \qquad \ldots \quad (9)$$

and

$$\frac{1}{\sqrt{\pi}}\int_{0}^{\infty} p_c(z')\left[\exp\{-(z - z')^2\} + n_a \exp\{-(z + z')^2\}\right] dz'$$

$$- p_c(z) = \operatorname{erfc} z \qquad \ldots \quad (10)$$

This leaves only one parameter (namely n_a) in each equation.

The solution of the first of these equations is given in Harper and Moore's paper. It is not expressible as an elementary function and is given only in numerical form (see Table 4). The solution of the second equation is suggested by the obvious fact that if p_c were a constant then the left-hand side of the equation would contain only complementary error functions and constants, which is a similar composition to that of the right-hand side. Thus, putting

$$p_c = L$$

where L is constant, the left-hand side becomes:

$$\frac{L}{\sqrt{\Pi}}(\sqrt{\pi} - \frac{\sqrt{\pi}}{2} \operatorname{erfc} z + n_a \frac{\sqrt{\pi}}{2} \operatorname{erfc} z) - L$$

and this is equal to

$$L \frac{1}{2} (n_a - 1) \operatorname{erfc} z$$

which is a constant multiple of the right-hand side.

Therefore

$$p_c(z) = \frac{2}{n_a - 1}$$

is the solution. Thus

$$p(z) = n_b\, p_b(z) + n_c \frac{2}{n_a - 1}$$

$$= n_b\, p_b(z) - B$$

So $Q(Y)$ is given by

$$Q(Y) = n_b\, p_b\left(-\frac{Y}{2\sqrt{X_e}}\right) - B$$

At this point, although the constants A and B are still unknown, it becomes possible to examine in greater detail the behaviour of the boundary layers in the regions near the stagnation points, and the way in which they merge into the wakes. It is clear from the expressions (6) and (7) for the concentration that the boundary layer thickness is associated with the behaviour of the terms $\frac{-Y_1}{2\sqrt{X}}$ and $\frac{Y_o}{2\sqrt{X}}$. These expressions appear in terms which are, or behave to some extent like, $\operatorname{erfc} \frac{Y_o}{2\sqrt{X}}$. That is these terms cease to change rapidly when

$$\frac{Y_o}{2\sqrt{X}} \quad \left(\text{or } \frac{-Y_1}{2\sqrt{X}} \right)$$

becomes, in some sense, large, and the value at which rapid change ceases gives a measure of the boundary layer thickness. For the purpose of order of magnitude calculations it may be assumed that when

$$\frac{Y_0}{2\sqrt{X}} \quad (\text{ or } \frac{-Y_1}{2\sqrt{X}})$$

is of the order of one, then the edge of the boundary layer has been reached.

Since $$Y = y \, Pe^{\frac{1}{2}} \sin^2\theta \ ,$$

where y is the non-dimensionalised distance from the drop's surface, the value of y at the edge of the boundary layer is given by

$$\frac{y \, Pe^{\frac{1}{2}} \sin^2\theta}{2\sqrt{X}} \quad ** \quad 1$$

i.e.

$$y \quad ** \quad \frac{Pe^{-\frac{1}{2}}\sqrt{X}}{\sin^2\theta} \qquad \ldots \quad (11)$$

which, of course confirms the previously obtained result that the boundary layer is of thickness $a.Pe^{-\frac{1}{2}}$.

In the case of the external boundary layer this is true even in the neighbourhood of the front stagnation point where $\sin\theta$ becomes small, because X also tends to zero in this region.

More exactly

$$X = -\cos\theta + \frac{\cos^3\theta}{3} + \frac{2}{3}$$

So that

$$\frac{X}{\frac{1}{4}\,\theta^4} \rightarrow 1 \quad \text{as} \quad \theta \rightarrow 0$$

with the required result that

$$y ** Pe^{-\frac{1}{2}}$$

in the region of the front stagnation point. This applies only to the external boundary layer because the thickness of the internal boundary layer is determined by the function Q(Y) and the flow pattern.

The significance of this is that the external boundary layer does not start with zero thickness at the front stagnation point: there is a boundary layer of non-zero thickness at all points of the drop's surface. This also means that there will be a finite non-zero mass transfer even at the drop's front pole.

In the neighbourhood of the rear stagnation point the situation is different. Here X is of order one so that equation (11) shows that the boundary layer becomes thick as $\sin \theta$ tends to zero. Diffusion in the boundary layer will therefore be less significant in this region, because the thickening of the boundary layer will cause the concentration gradient to fall. The boundary layer equation, however, remains valid: the only effect is that the convection terms must become dominant over the diffusion term, whereas in the rest of the boundary layer they are of the same order of magnitude. Thus near the rear stagnation point there is a region where diffusion is unimportant and the solute is convected along the stream surfaces.

Because the boundary layer solutions (6) and (7) are well-behaved in the region of the rear stagnation point there can be no separation in the sense of the boundary layer solution breaking down, as happens, for example, in Harper and Moore's solution for the vorticity boundary layers around a drop. However, in this region the flow turns away from the surface either into the interior in the case of the internal boundary layer or away from the drop in the case of the external boundary layer. The fact that near the rear stagnation point the solute is being convected therefore provides a clue as to how the solute may move from the boundary layers into the wakes. Clearly a reasonable hypothesis is that the solute reaches the region in which diffusion becomes unimportant, so that it is convected along until it reaches the region in which the flow turns away from the surface. The solute is then convected by the fluid to form one of the wakes. That this is so can be verified by determining the point at which the fluid turns away from the surface and demonstrating that at this point the solute is being convected with negligible diffusion. This "separation" can, for the purpose of an order of magnitude calculation, be said to occur at the point where the stream surfaces are at an angle of about $\frac{\pi}{4}$ with the drop's surface.

Now the stream function is given by

$$\psi_1 = - v_o a^2 y \sin^2\theta$$

and, at the edge of the boundary layer

$y \ ** \ Pe^{-\frac{1}{2}}$, in the region where $\sin\theta \ ** \ 1$ so that the stream surface that forms the edge of the boundary layer has the equation

$$y \sin^2\theta \ ** \ Pe^{-\frac{1}{2}}$$

Let $$\phi = \pi - \theta$$

then in the region of the rear stagnation point $\sin\theta$ may be approximated by ϕ so that the equation of the stream surface becomes

$$y \phi^2 \ ** \ Pe^{-\frac{1}{2}}$$

The angle that the stream surface makes with the drop's surface is

$$\tan^{-1}\frac{dy}{d\phi}$$

and this is approximately equal to $\frac{\pi}{4}$ when

$$- 2 \frac{Pe^{-\frac{1}{2}}}{\phi^3} \ ** \ 1$$

i.e. $$\phi \ ** \ Pe^{-\frac{1}{6}}$$

So that, from the equation of the stream surface,

$$y \ ** \ Pe^{-\frac{1}{6}} \text{ as well.}$$

Recall that the boundary layer thickness is given by

$$a\,\frac{Pe^{-\frac{1}{2}}\sqrt{X}}{\sin^2\theta}$$

Using the calculated order of magnitude for ϕ it can be seen that this expression for the boundary layer thickness is of order $a.Pe^{-\frac{1}{6}}$ in the region of the rear stagnation point. This is much greater than $a.Pe^{-\frac{1}{2}}$, which is the thickness of the boundary layer in regions where diffusion is significant. It follows that solute is convected through this region and swept away from the drop surface to form the wakes.

In the interior the solute is carried up the internal wake to the region of the front stagnation point where the fluid flow is the mirror image of the flow in the region of the rear stagnation point (the plane through the drop's equator is a plane of symmetry for the flow) so that the solute is convected into the front part of the boundary layer in a similar manner to the way it was convected out of the rear part.

It now remains to determine the two constants A and B. (It should be emphasised that, although A and B are constant with respect to the boundary layer variables, they are functions of time.) It is not possible to obtain the actual value of either constant without referring to the interior solution - this of course is to be expected because diffusion in the interior is the governing process which determines the time dependence of the entire system. If the boundary layer problem could be solved completely without reference to the interior that would imply that the behaviour of the boundary layer was independent of the interior. It would also mean that the mass transfer could be determined from the boundary layer solution alone, which is unlikely in view of the fact that it is the diffusion in the interior that is the important part of the process. It is, however, possible to obtain a relationship between the two constants from the properties of the boundary layer.

The necessary property is that $\overline{Q}(Y)$, which represents the concentration profile "at" $X = 0$, must, like the concentration profile at other values of X, behave like

$$A\,Y + B \quad \text{as} \quad Y \to -\infty$$

So that

$$Q(Y) \to 0 \quad \text{as} \quad Y \to -\infty$$

i.e.

$$n_b\, p_b\left(-\frac{Y}{2\sqrt{X_e}}\right) - B \to 0 \quad \text{as} \quad Y \to -\infty$$

Or

$$\frac{B}{A} = \frac{2\,E\sqrt{D_1 X_e}}{E\sqrt{D_1} + \sqrt{D_0}}\, p_b(\infty) \; .$$

Values of $\frac{B}{A}$ are given in Table 4.

It now remains to determine the actual values of the constants by examining the effect of the interior upon the boundary layer.

The property that connects the two regions is the mass flux - the flux into the boundary layer from the interior can be determined either from the boundary layer solution (in which case it contains the unknown constants) or from the interior solution (in which case the first approximation to it is known). Equating the two expressions provides an equation for the constants. It was shown earlier that in the interior, in the thin region bordering the boundary layer, the concentration behaves like

$$A\,Y + B$$

whilst c may be approximated by $\bar{c}$, so that

$$\bar{c} \sim A\,Y + B \quad \text{as} \quad Y \to -\infty$$

and, therefore

$$\frac{\partial \bar{c}}{\partial Y} \sim A \quad \text{as} \quad Y \to -\infty$$

Since a first approximation to $\bar{c}$ is known, a first approximation to A , and hence to B , may be determined and a first approximation to the boundary layer solution obtained.

In fact $\bar{c}$ is not known as a function of Y but as a function of m . Near the surface these two co-ordinates are merely constant multiples of one another:

$$m = -8\,Y\,Pe_1^{-\frac{1}{2}}$$

So that A is given by:

$$A = -8 \, Pe_1^{-\frac{1}{2}} \frac{\partial \bar{c}}{\partial m}$$

Since $Y \to -\infty$ corresponds to the edge of the boundary layer and m is very small in this region it follows that the derivative $\frac{\partial \bar{c}}{\partial m}$ is to be evaluated at a small value of m. In fact the gradient of $\bar{c}$ is constant near $m = 0$ so the derivative may be evaluated at $m = 0$. $\frac{\partial \bar{c}}{\partial m}$ may be found from the calculated values of $\bar{c}$, and hence A can be determined.

The result of the calculation of $\frac{A}{Pe_1^{-\frac{1}{2}}}$ is given in Table 5 (a) and in graphical form in Figure 8.

Finally, it is worth noting that the fact that $p_c(z)$ is a constant enables the expression for the concentration in the internal boundary layer to be simplified by writing:

$$Q^*(Y) = Q(Y) + B$$

so that

$$Q^*(Y) = \bar{Q}(Y) - AY$$

$$= n_b \, p_b \left(\frac{-Y}{2\sqrt{X_e}} \right)$$

The simplified expression is:

$$c_1 = AY$$

$$- \frac{2 \, E\sqrt{D_1} \, A}{E\sqrt{D_1} + \sqrt{D_o}} \sqrt{X} \; \text{ierfc} \; \frac{-Y_1}{2\sqrt{X}}$$

$$+ \frac{1}{2\sqrt{\pi X}} \int_{-\infty}^{0} Q^*(Y') \exp\left(- \frac{(Y_1 - Y')^2}{4 \, X}\right) dY' \; +$$

$$+ \frac{E\sqrt{D_1} - \sqrt{D_o}}{E\sqrt{D_1} + \sqrt{D_o}} \; \frac{1}{2\sqrt{\pi X}} \int_{-\infty}^{o} Q^*(Y') \exp\left(- \frac{(Y_1 + Y')^2}{4X}\right) dY'$$

2. A second approximation to the concentration in the interior

The first approximation to the concentration in the interior was obtained by imposing the condition

$$\bar{c} = 0 \quad \text{at} \quad m = 0 .$$

The boundary layer solution has shown that this condition is inexact, and that $\bar{c}$ should behave like

$$A\,Y + B \quad \text{as} \quad Y \to -\infty$$

i.e. $\bar{c}$ behaves like $A\,Y + B$ for small m, where B is non-zero, and hence

$$\bar{c} = B \quad \text{at} \quad m = 0$$

is a more exact boundary condition. Of course B can only be determined when the first approximation is known. Thus, let $\bar{c}$ be given by

$$\bar{c} = \bar{c}_a + Pe_1^{-\frac{1}{2}}\, \bar{c}_b$$

(the suffices a and b are intended to distinguish between the first and second terms in this expression for the concentration), where

$$\bar{c}_a = 0 \quad \text{at} \quad m = 0$$

and
$$Pe_1^{-\frac{1}{2}}\,\bar{c}_b = B \quad \text{at} \quad m = 0 .$$

$\bar{c}_a$ is then the first approximation, whilst adding $\bar{c}_b$ (which is possible because the equation is linear) gives a second approximation. $\bar{c}_b$ may be obtained in a similar manner to $\bar{c}_a$, except of course with slightly different boundary conditions. The equation for $\bar{c}_b$ is the same as the equation for $\bar{c}$ (because of the linearity of the equation). Therefore

$$H\,\frac{\partial \bar{c}_b}{\partial i} = \frac{\partial}{\partial m}\left(J\,\frac{\partial \bar{c}_b}{\partial m}\right)$$

At $i = 0$, $\bar{c} = 1$ and $\bar{c}_a = 1$,

so that the initial condition for $\bar{c}_b$ is:

$$\bar{c}_b = 0 \quad \text{at} \quad i = 0 .$$

Whilst at $m = 1$,

$$\frac{\partial \bar{c}}{\partial i} = -20\,\frac{\partial \bar{c}}{\partial m}$$

This condition is also satisfied by $\bar{c}_a$, and hence must be satisfied by $\bar{c}_b$, so that

$$\frac{\partial \bar{c}_b}{\partial i} = -20\,\frac{\partial \bar{c}_b}{\partial m} \quad \text{at} \quad m = 1 .$$

And the boundary condition at $m = 0$ is:

$$Pe^{-\frac{1}{2}}\,\bar{c}_b = B \quad \text{at} \quad m = 0 ,$$

$$\text{i.e.} \quad \bar{c}_b = -\frac{16\, E\sqrt{D_1}\, X_e\, p_b(\infty)}{E\sqrt{D_1} + \sqrt{D_o}} \frac{\partial \bar{c}_a}{\partial m} \quad \text{at} \quad m = 0 \,,$$

$$= F \frac{\partial \bar{c}_a}{\partial m} \,, \quad \text{say.}$$

The equation for $\bar{c}_b$ may therefore be solved in the same way as the equation for $\bar{c}_a$, the only differences being in the boundary condition at $m = 0$, and in the initial condition.

The first approximation has therefore furnished a value for the derivative at the surface which, because of the properties of the boundary layer, can be used to form a more accurate boundary condition at the surface and so produce a second approximation.

For simplicity in numerical calculation it is convenient to solve for $\frac{\bar{c}_b}{F}$ rather than for $\bar{c}_b$.

3. Results and remarks on Chapter 5

The effect of the second term $(\bar{c}_b)$ upon the mass loss is given in Table 6 and in graphical form in Figure 9, and the effect upon A is given in Table 5 (b). In the numerical work it was found that the result of the calculation for the second term (i.e. the term associated with the effect of $\bar{c}_b$) was noticeably less accurate than the results for the first approximation, in the sense that decreasing the step length δm from $\frac{1}{40}$ to $\frac{1}{80}$ resulted in a change in the results for the rate of mass transfer of between 10% (for small values of the diffusion time i) to 3% (for larger values of the time), compared with a change of less than 1% in the first term. It is reasonable to assume that the results could be made more accurate by decreasing the step length further, but this would of course increase the computation time, and in the present work it was not done.

These results have been obtained more in order to demonstrate the effect of the Peclet number and of the parameters D_o , D_1 , and E than for the increased accuracy that they confer to the solution. The fact that the Peclet number typically has a high value means that the second approximation does not differ greatly from the first. Certainly the increased accuracy is too small to be experimentally detectable in most cases.

The process described in this chapter could be repeated to obtain higher approximations - that is the second approximation to the concentration in the interior could be used to give a more accurate value for the derivative $\frac{\partial \bar{c}}{\partial m}$ at the surface and this in turn would provide a boundary condition for a third approximation, and so on. But there is no point in this because the approximation made in the interior - that the concentration at any point may be approximated by the average concentration on the stream surface through that point - causes greater errors than those that are eliminated by this procedure. The present work has therefore achieved as much accuracy as it is possible to attain without a more detailed examination of diffusion in the interior.

It is interesting to note that the situation in which the bulk fluid is a pure solute which dissolves into a solvent drop may be obtained as a special case of the results of this chapter. In such a situation there is no external boundary layer and wake, but the internal system still exists. There is a short initial period in which the solute dissolves into the internal boundary layer and is convected into the internal wake, so that the internal boundary layer-wake system is, to a first approximation, in equilibrium with the exterior. This is followed by a longer period in which the solute dissolves inwards until, finally, even the fluid at the stagnation ring is in equilibrium with the exterior.

It has already been noted that the first approximation theory that was described in Chapter 4 will be applicable to this process. It is not so clear that the internal boundary layer-wake system may be described by the theory developed in the present chapter. If the bulk fluid is pure the boundary condition that equates the mass fluxes on either side of the interface, namely,

$$D_0^{\frac{1}{2}} \frac{\partial c}{\partial Y_0} = D_1^{\frac{1}{2}} \frac{\partial c}{\partial Y_1} \quad \text{at} \quad Y = 0$$

is not applicable: the flux of solute from the pure solute cannot be measured by the gradient of concentration at the outside surface of the drop. Consequently this condition need no longer be satisfied, leaving the remaining boundary conditions, which are

$$\begin{array}{lllll} c_1 & = & 0 & \text{at} & Y = 0 \\ c & = & \overline{Q}(Y) & \text{at} & X = 0\ , \quad Y < 0 \\ c & \to & A\,Y + B & \text{as} & Y \to -\infty\ . \end{array}$$

Under these conditions the solution of the boundary layer equation is:

$$\begin{aligned} c_1 = {} & A\,Y + B \\ & + (-B)\ \text{erfc}\ \frac{-Y}{2\sqrt{X}} \\ & + \frac{1}{2\sqrt{\pi X}} \int_{-\infty}^{0} Q(Y')\ \{e^{\frac{-(Y+Y')^2}{4X}} - e^{\frac{-(Y-Y')^2}{4X}}\}\ dY' \end{aligned}$$

This is equal to the limit, as D_0 tends to infinity, of the expression for c_1 obtained earlier in this chapter. An infinite value of D_0 implies that, in the external fluid, solute is diffused to and from the interface as fast as it is diffused from or to the interface by the internal fluid, and that condition is satisfied by a situation in which the continuous phase is pure solute.

CHAPTER 6

The mass flux

So far the discussion has been limited to determining the value of the concentration at any point. This of course is because the differential equations are simple to formulate in terms of this variable. However, in an experiment the determination of the concentration at any point would present difficulties and most experimenters are content to measure the overall mass transfer. For the purpose of obtaining experimental verification of the theory it is therefore important to obtain an expression for the mass transfer.

This may be done in one of three ways. The local mass transfer at any point on the drop surface may be found from the expression for the concentration in the boundary layer and this result may be integrated over the drop's surface to give the overall mass transfer. Alternatively, the result may be obtained by finding the mass flux in the external boundary layer in the region near the rear stagnation point (that is the flux through a surface perpendicular to the flow in the boundary layer). It was pointed out in Chapter 3 that there is no mass transfer from the external boundary layer directly to the bulk fluid - all the solute is convected into the external wake. Thus, finding the mass flux in the boundary layer at a point just before it feeds into the external wake is equivalent to finding the mass flux from the drop as a whole.

Thirdly the mass transfer may be determined by calculating the mass flux from the interior into the internal boundary layer. This neglects the fact that the internal boundary layer contains a small, but decreasing, amount of solute which accounts for part of the total mass flux. However the concentration in the boundary layer is of order $C.Pe^{-\frac{1}{2}}$ and the volume of the boundary layer is of order $a^3.Pe^{-\frac{1}{2}}$, so that the total mass in the boundary layer is of order $a^3.C.Pe^{-1}$ and this is negligible to the order of accuracy considered here. This method of calculation is by far the simplest of the three, and it will be described first.

The mass flux - that is the mass of solute transferred per unit time - through any surface tangential to the flow must be due entirely to molecular diffusion, and is therefore given by

$$- D \int \frac{\partial c}{\partial n} dS$$

where $\frac{\partial c}{\partial n}$ is the gradient of concentration in the direction of the transfer and perpendicular to the surface,

dS is an element of the surface,

and the integral is taken over all the surface.

In the present case this integral is equal to

$$\int_0^{\pi} 2\pi\, a^2 \sin\theta \left(-\,D_1 \frac{\partial \bar{c}}{\partial r}\right) d\theta$$

where $\frac{\partial \bar{c}}{\partial r}$ is to be evaluated at the surface joining the boundary layer and the interior.

Now $$\frac{\partial c}{\partial r} = \frac{1}{a}\frac{\partial c}{\partial y} = \frac{1}{a}\frac{\partial c}{\partial y^*} Pe^{\frac{1}{2}} = \frac{\partial c}{\partial Y_1}\frac{Pe_1^{\frac{1}{2}} \sin^2\theta}{a}$$

and $\frac{\partial c}{\partial Y_1} = A$ by the argument used in Chapter 5,

so the total mass flux is

$$-\,2\pi\, a^2\, D_1 \frac{Pe_1^{\frac{1}{2}}}{a}\, A \int_0^{\pi} \sin^3\theta\, d\theta$$

$$= -\,\frac{8}{3}\,\pi\, a^{\frac{3}{2}}\, v_o^{\frac{1}{2}}\, D_1^{\frac{1}{2}}\, A$$

This of course refers to the rate of transfer of mass based on the normalised concentration. In terms of the dimensional concentration the rate of transfer of mass from the drop is

$$-\,\frac{8}{3}\,\pi\, a^{\frac{3}{2}}\, v_o^{\frac{1}{2}}\, D_1^{\frac{1}{2}}\, A\,(c_1^{\,i} - Ec_o^{\,i})$$

using the same symbols as were used in Chapter 1.

If a Sherwood number is defined by

$$Sh = \text{Rate of mass transfer} \; X \; \frac{a}{D_1(c_1^{\,i} - Ec_o^{\,i})4\pi a^2}$$

then

$$Sh = -\frac{2}{3}\,\frac{A}{Pe_1^{-\frac{1}{2}}}$$

It is worth re-calculating the result in a different way, just to demonstrate the consistency of the theory. Consider, therefore, the mass flux in the external boundary layer.

The mass flux through a surface perpendicular to the flow is due almost entirely to convection - the fraction that is due to diffusion being of the order of Pe^{-1} of the whole - and hence is given to the required degree of accuracy, by

$$\int c \; v \; dS$$

where v is the velocity normal to the surface,

dS is an element of the surface,

and the integral is taken over the surface.

In the present case it suffices to take a surface perpendicular to the surface of the drop. Such a surface is not exactly perpendicular to the flow but the discrepancy is sufficiently small for the effect of molecular diffusion to be negligible. The integral is then equal to:

$$\int c\ v_\theta\ 2\pi\ a^2\ \sin\theta\ .\ dy$$

where terms of order y and smaller have been neglected and the integral is taken over all values of y in the boundary layer.

v_θ is given by

$$v_\theta = v_o \sin\theta$$

and

$$Y_o = y_o^* \sin^2\theta = y \sin^2\theta\ .\ Pe_o^{\frac{1}{2}}$$

So that the integral becomes

$$2\pi\ a^2\ v_o\ Pe_o^{-\frac{1}{2}} \int_o^\infty c\ dY_o\ .$$

This is the mass flux through a surface at any value of θ (or X) . The total mass flux from the drop may be obtained by finding the limiting value of this integral as θ tends to π (its value at the rear stagnation point, corresponding to $X = X_e$) for in this region diffusion ceases because of the thick boundary layers, and the solute is convected from the external boundary layer into the external wake from where it will diffuse into the bulk fluid.

Since the integral is uniformly convergent in the neighbourhood of $X = X_e$ it follows that

$$\lim_{X \to X_e} \int_o^\infty c\ dY_o = \int_o^\infty (\lim_{X \to X_e} c)\ dY_o$$

and hence the value of c required in the integral is that obtained by substituting X_e for X in the expression (6) for the concentration in the external boundary layer. On carrying out the integration (see Appendix 5 for details) the same result as before is obtained.

The local mass transfer is obtained by calculating the gradient of concentration in either of the boundary layers. It is expressed in the form of the mass flux per unit area and, in the case of the internal boundary layer, is given by:

$$- D_1 \frac{\partial c}{\partial r}$$

where the derivative is evaluated at $r = a$ (the drop's surface). This equals

$$- D_1 \frac{Pe_1^{\frac{1}{2}} \sin^2\theta}{a} \frac{\partial c_1}{\partial Y_1}$$

Substituting the value of the derivative at $Y = 0$ from equation (7) results in the following expression for the local rate of mass transfer:

$$\frac{D_1 Pe_1^{\frac{1}{2}}}{a} \frac{\sqrt{D_o}}{E\sqrt{D_1}+\sqrt{D_o}} \sin^2\theta \, . \, A\left[\frac{4\, E\sqrt{D_1}\ \sqrt{X_e}}{E\sqrt{D_1} + \sqrt{D_o}} \frac{1}{\sqrt{\pi X}} \int_0^\infty p_b(z')z'e^{-z'^2}dz' - 1\right]$$

The overall mass transfer could be found again by integrating this expression over the drop's surface, but the presence of the integral whose value is known only in numerical terms makes this approach less useful than the ones previously described.

CHAPTER 7

Remarks on the theory and its experimental verification

1. Experimental verification

Experimental work with drops has many difficulties. The chief of these is probably the removal of surface active materials. Even a very small quantity of one of these substances will radically alter the flow pattern and this affects the rate of mass transfer.

However the literature contains several reports of observations of mass transfer from drops and bubbles. Most of these experiments have been carried out with the object of investigating an industrial process so that the results are not normally applicable to the verification of a theory like the present one. Usually no attempt is made to remove surface active materials. Or, in the high Reynolds number case, the drops have insufficient interfacial tension to retain a spherical shape and their motion may be unsteady and not in the straight lines predicted by the Hill's vortex solution that has been used here. In addition comparatively few experimenters have considered the case of very low Reynolds number ($Re \ll 1$). And many of the experiments are concerned with pure liquid drops dissolving into a bulk solvent instead of with an extraction process. ~~However, as was remarked in Chapter 4, this type of system is a special case of the present theory.~~

Heertjes, Holve and Talsma (14), Johnson and Hamielec (15), and Skelland and Wellek (21) have measured the rate of mass transfer in such a system. All three groups of experimenters compared their results to those predicted by Kronig and Brink (13).

In these experiments it was found that some systems (e.g. water drops in cyclohexanol, isobutanol drops in water) were in agreement, at least approximately, with Kronig and Brink's results, and others are not. The reason for these discrepancies is not always clear: sometimes the drops are observed to be oscillating and this obviously renders the theory inapplicable, but in other cases (e.g. water drops in n-butanol) the fluids appear to be flowing in accordance with the assumptions of the theory. In the former group there is general agreement between the observed results and those of Kronig and Brink, but the agreement is not sufficiently close to support a claim that Kronig and Brink's results are an accurate prediction of the rate of mass transfer. The observed rates of mass transfer are higher than those predicted by

Kronig and Brink. None of these experiments was done with the flow at Reynolds numbers less than one.

Since the results of the present theory are close to those of Kronig and Brink, at least to the order of accuracy required for comparison with experiments, the same comments apply. In Figure 12 the results of Heertjes, Holve and Talsma for the transfer of water into isobutanol drops are compared with the results of the present work.

Experimental results for an extraction process are rarer than those for a pure bulk fluid dissolving into a drop. Kadenskaya, Zheleznyak, and Brounshtein (16) measured the rate of mass transfer when acetic acid was extracted from water by single drops of ethyl acetate. This system is complicated by the fact that some of the ethyl acetate dissolves in the water and some of the water in the ethyl acetate, but they conclude that there is good agreement (the mass transfer coefficients agree to within about 10%) with the results predicted by Kronig and Brink for drops smaller than 2.7 mm in diameter. It is not clear why the result ceases to be accurate at this point but the fact that the mass transfer approaches that predicted by Handlos and Baron (17), who considered a similar problem with turbulent flow inside the drop indicates that the explanation may lie in an inaccurate expression for the flow.

Kadenskaya, Zheleznyak and Brounshtein do not give the Reynolds numbers at which their experiments were made but a calculation based on their values of drop diameter and velocity, together with an estimate of the viscosity of the liquids involved implies that the Reynolds numbers must have been of the order of 100 to 500.

It can be seen therefore that the experimental results are insufficient to provide verification of the theory, although they do indicate general agreement.

2. Summary and remarks

The principal objective of this thesis has been to give a qualitative description of the extraction of solute from a liquid drop with internal circulation, and this has involved dividing the system into several regions - the boundary layers (internal and external), the wakes (also internal and external) and the interior and exterior of the drop - and describing the various parts that they play in the transfer process. A secondary objective has been to obtain quantitative expressions for the concentration at any point, and for the mass transfer.

From a practical point of view the most important result of the qualitative description was the role of the internal wake in convecting solute from the region of the rear stagnation point to the region of the front stagnation point and the consequential dominance of diffusion in the interior. If molecular diffusion played an important role in the internal wake then fresh solute would be continuously fed into the internal boundary layer. The result of this would be that the relatively fast boundary layer diffusion would determine the time scale of the process, instead of the relatively slow diffusion in the interior which this thesis has shown to be of paramount importance.

Another consequence of the dominance of the interior is that the coefficient of diffusion in the bulk fluid (D_o) is of little importance. The process is almost entirely governed by the coefficient of diffusion in the dispersed phase (D_1).

It has been shown that these circumstances give rise to a problem very similar to that solved by Kronig and Brink (13) except in one boundary condition, and that the solution to this problem is a uniformly valid first approximation to the concentration field. This solution has a time scale significantly shorter than that of diffusion from a non-circulating drop of the same size. There is close agreement between the results of the present work and those of Kronig and Brink.

In the boundary layer there is no inherent time dependence, and time enters into the solution only as a parameter. The boundary layer equation itself is parabolic in form, but in the internal layer this is modified by the condition that the solute is convected up the internal wake from the rear to the front without diffusion. Thus conditions in the "downstream" region (meaning, increasing X) have some effect on conditions in the "upstream" region, which is more characteristic of an elliptic equation than one of parabolic type. This solution in the boundary layer demonstrates the effects of the parameters D_o and E. The boundary layer solution was used to improve the boundary conditions for the interior problem and hence to find a more accurate solution in the interior, and a better approximation to the mass transfer.

It was noted that the results of the theory are applicable to the case of a pure bulk solute diffusing into a solvent drop, the first approximation being identical with the first approximation to the extraction process, and the second approximation being obtained by adding a correction term which is a limiting case (as D_o tends to infinity) of the correction term in the second approximation to the extraction process. This result is of importance in obtaining experimental verification of the theory.

Throughout this thesis the phrase "high Peclet number" has been used to characterize the diffusion, but the meaning of this has not been made precise. The meaning has, however, been implied every time that a statement like "$Pe^{-\frac{1}{4}}$ is much larger than $Pe^{-\frac{1}{2}}$" has been used: "high Peclet number" means that the Peclet number is sufficiently large for the various powers of the Peclet number mentioned to be of distinct orders of magnitude, to the required degree of accuracy.

The approach of this thesis has been entirely theoretical and the experimental results quoted were intended only to demonstrate that the derived results are not wildly at variance with those of experiments. This means that at present the theory lacks the experimental verification that is required to make its results conclusive. The basis for arguing the validity of the theory is that it is a valid mathematical deduction from valid assumptions.

In a practical situation liquid drops are often spheroidal. The problem of mass transfer from such a drop has not been mentioned, except to exclude it from consideration. However, it is obvious that the conclusions of the qualitative theory will apply, at least in the case of flow at sufficiently small Reynolds number (where the flow is known to be only slightly perturbed from the flow around a spherical drop) and it seems likely that this theory will be valid at higher Reynolds numbers when the perturbations are not so small. And, of course, the results of the quantitative theory will be a valid first approximation to the mass transfer at very small Reynolds numbers. It is tempting to assume that the qualitative theory will be valid for spheroidal drops at high Reynolds number, but care should be taken in making this assertion because the concentration boundary layers and wakes formed would be inside the velocity boundary layers and wakes associated with the flow and the nature of these is not yet understood. But it does seem almost certain that a similar theory will be valid and, even without considering the details of the qualitative theory, a quantitative theory could be established in a manner similar to that described here. Since the velocity in the velocity boundary layer is not known such a theory would ignore these boundary layers - just as the first approximation of the present theory ignores the presence of the concentration boundary layers - and would consequently contain inaccuracies of the order of $Re^{-\frac{1}{2}}$ (assuming that $a.Re^{-\frac{1}{2}}$ is the order of the thickness of these layers).

APPENDIX ONE

Solution of the boundary layer equations

The problem is to solve two simultaneous equations, namely,

$$\frac{\partial^2 c_1}{\partial Y^2} = \frac{\partial c_1}{\partial X} \qquad Y < 0$$

$$\frac{\partial^2 c_o}{\partial Y^2} = \frac{\partial c_o}{\partial X} \qquad Y > 0 \quad ,$$

with the following boundary conditions:

$$c_1 \sim A\,Y + B \qquad \text{as} \qquad Y \to -\infty$$

$$c_o \to 0 \qquad \text{as} \qquad Y \to \infty$$

$$c_1 = Ec_o \qquad \text{at} \qquad Y = 0$$

$$D_1^{\frac{1}{2}} \frac{\partial c_1}{\partial Y} = D_o^{\frac{1}{2}} \frac{\partial c_o}{\partial Y} \qquad \text{at} \qquad Y = 0$$

$$c_o = 0 \qquad \text{at} \qquad X = 0$$

$$c_1 = \overline{Q}(Y) \qquad \text{at} \qquad X = 0 \quad .$$

At this stage $\overline{Q}(Y)$ is an unknown function.

The problem is similar to that solved by Harper and Moore (6), and the same method of solution is used. For the sake of mathematical simplicity it is convenient to make some changes in the dependent variables c_o and c_1. These are:

$$K_o = E\, c_o$$

$$K_1 = c_1 - A\, Y - B$$

Then K_o and K_1 satisfy the same equations as c_o and c_1, but with the boundary conditions:

$$K_1 \to 0 \quad \text{as} \quad Y \to -\infty$$

$$K_o \to 0 \quad \text{as} \quad Y \to \infty$$

$$K_1 + B = K_o \quad \text{at} \quad Y = 0$$

$$D_1^{\frac{1}{2}} \frac{\partial K_1}{\partial Y} + D_1^{\frac{1}{2}} A = \frac{D_o^{\frac{1}{2}}}{E} \frac{\partial K_o}{\partial Y} \quad \text{at} \quad Y = 0$$

$$K_o = 0 \quad \text{at} \quad X = 0$$

$$K_1 = Q(Y) \quad \text{at} \quad X = 0$$

$$\text{where } Q(Y) = \overline{Q}(Y) - A\, Y - B$$

Probably the easiest way to solve this problem is to split it into three parts. The three parts will have the same equations but different boundary conditions. Since the equations are linear the final solution can be obtained by summing the solutions of the three parts. These are:

(1) $$K_1 = K_o = 0 \quad \text{at} \quad X = 0$$

$$\frac{D_o^{\frac{1}{2}}}{E} \frac{\partial K_o}{\partial Y} = D_1^{\frac{1}{2}} \frac{\partial K_1}{\partial Y} \quad \text{at} \quad Y = 0$$

$$K_o \to 0 \quad \text{as} \quad Y \to \infty$$

$$K_1 \to 0 \quad \text{as} \quad Y \to -\infty$$

$$\text{and } K_o = K_1 + B \quad \text{at} \quad Y = 0$$

(2)

$$K_o = K_1 = 0 \quad \text{at} \quad X = 0$$

$$K_o = K_1 \quad \text{at} \quad Y = 0$$

$$K_o \to 0 \quad \text{as} \quad Y \to \infty$$

$$K_1 \to 0 \quad \text{as} \quad Y \to -\infty$$

$$\text{and } \frac{D_o^{\frac{1}{2}}}{E}\frac{\partial K_o}{\partial Y} = D_1^{\frac{1}{2}}\frac{\partial K_1}{\partial Y} + D_1^{\frac{1}{2}} A \quad \text{at} \quad Y = 0$$

(3)

$$K_o = 0 \quad \text{at} \quad X = 0$$

$$K_o = K_1 \quad \text{at} \quad Y = 0$$

$$\frac{D_o^{\frac{1}{2}}}{E}\frac{\partial K_o}{\partial Y} = D_1^{\frac{1}{2}}\frac{\partial K_1}{\partial Y} \quad \text{at} \quad Y = 0$$

$$K_o \to 0 \quad \text{as} \quad Y \to \infty$$

$$K_1 \to 0 \quad \text{as} \quad Y \to -\infty$$

$$\text{and } K_1 = Q(Y) \quad \text{at} \quad X = 0$$

It is well known that

$$M \operatorname{erfc} \frac{Y}{2\sqrt{X}} + N$$

is a solution of the diffusion equation. Clearly, with appropriate values for M and N, this will form a solution for part (1). This solution is:

$$K_o = \frac{E\sqrt{D_1}\ B}{E\sqrt{D_1} + \sqrt{D_o}} \operatorname{erfc} \frac{Y_o}{a\sqrt{X}}$$

$$K_1 = \frac{-\sqrt{D_o}\ B}{E\sqrt{D_1} + \sqrt{D_o}} \operatorname{erfc} \frac{-Y_1}{2\sqrt{X}}$$

Part (2) is similar to part of the problem solved by Harper and Moore so that it is reasonable to guess that the solution must be of the form:

$$M\sqrt{X} \ \operatorname{ierfc} \frac{Y}{2\sqrt{X}}$$

On substituting this into the boundary condition the appropriate values of M are found. The solutions are:

$$K_o = \frac{2\ E\sqrt{D_1}\ A}{E\sqrt{D_1} + \sqrt{D_o}} \sqrt{X} \operatorname{ierfc} \frac{Y_o}{2\sqrt{X}}$$

$$K_1 = \frac{2\ E\sqrt{D_1}}{E\sqrt{D_1} + \sqrt{D_o}} \sqrt{X} \operatorname{ierfc} \frac{-Y_1}{2\sqrt{X}}$$

In the same way part (3) is of similar form to part of Harper and Moore's problem, and the solution is therefore:

$$K_o = \frac{E\sqrt{D_1}}{E\sqrt{D_1} + \sqrt{D_o}} \frac{1}{\sqrt{\pi X}} \int_{-\infty}^{o} Q(Y') \exp\left\{ - \frac{(Y_o - Y')^2}{4\ X} \right\} dY'$$

$$K_1 = \frac{1}{2\sqrt{\pi X}} \int_{-\infty}^{0} Q(Y') \exp \{ - \frac{(Y_1 - Y')^2}{4\ X} \} \, dY'$$

$$+ \frac{E\sqrt{D_1} - \sqrt{D_0}}{E\sqrt{D_1} + \sqrt{D_0}} \frac{1}{2\sqrt{\pi X}} \int_{-\infty}^{0} Q(Y') \exp \{ - \frac{(Y_1 + Y')^2}{4\ X} \} \, dY'$$

The complete solutions are obtained by adding the solutions of the three parts.

APPENDIX TWO

The functions H and J

H(m) and J(m) are defined by the following equations:

$$H = \oint h_m h_q h_\lambda \, dq$$

$$J = \oint \frac{h_q h_\lambda}{h_m} \, dq$$

where $\oint$ means that the integration is to be taken around a stream surface (along a line on which λ is constant) and h_m, h_q, h_λ are non-dimensionalised scale factors of the co-ordinate system, so that an infinitesimal displacement of length ds can be represented by:

$$ds^2 = a^2 h_m^2 \, dm^2 + a^2 h_q^2 \, dq^2 + a^2 h_\lambda^2 \, d\lambda^2$$

where dm, dq, $d\lambda$, are the changes in co-ordinate values associated with the displacement. Since m, q, and λ are known in terms of the spherical polar co-ordinate system p, θ, and λ, then h_m, h_q, h_λ may be determined from the expression for ds in spherical polars, which is:

$$ds^2 = a^2 \, dp^2 + a^2 p^2 \, d\theta^2 + a^2 p^2 \sin^2\theta \, d\lambda^2$$

Since $$dp = \frac{\partial p}{\partial m} dm + \frac{\partial p}{\partial q} dq + \frac{\partial p}{\partial \lambda} d\lambda$$

then

$$ds^2 = a^2\{(\frac{\partial p}{\partial m})^2 + p^2 (\frac{\partial \theta}{\partial m})^2 + p^2 \sin^2\theta (\frac{\partial \lambda}{\partial m})^2\} dm$$

$$+ a^2\{(\frac{\partial p}{\partial q})^2 + p^2 (\frac{\partial \theta}{\partial q})^2\} dq^2$$

$$+ a^2p^2 \sin^2\theta \, d\lambda^2$$

since all the cross-product terms involving $\frac{\partial p}{\partial m} \frac{\partial p}{\partial q}$, etc., are equal to zero because of the orthogonality of the system.

Thus

$$a^2h_m^2 = a^2 \left\{ (\frac{\partial p}{\partial m})^2 + p^2 (\frac{\partial \theta}{\partial m})^2 \right\}$$

etc.

In this manner h_m, and h_q may be found. h_λ is not altered from its spherical polar value.

$$h_m = \frac{1}{8 \, p \sin\theta.\Delta}$$

$$h_q = \left| \frac{(2p^2 - 1)^2}{4 \, p^3 \cos^3\theta.\Delta} \right|$$

$$h_\lambda = p \sin \theta$$

where $\Delta^2 = (1 - 2p^2)^2 \sin^2\theta + (1 - p^2)^2 \cos^2\theta.$

The sign of the scale factors is arbitrary and the absolute value has been taken so that h_q is everywhere positive. From these the functions H and J may be determined.

Consider firstly H :

$$H = \oint h_m h_q h_\lambda \, dq$$

$$= \oint \frac{(2p^2 - 1)^2}{32 \, p^3 \cos^3\theta . \Delta} \, dq$$

Since $$dq = \frac{- 4 \, p^3 \cos^2\theta . \Delta^2}{(1 - 2p^2)^2 \; (1 - p^2)} \, dp$$

when the displacement is along a surface on which m is constant, H is equal to

$$- \frac{1}{8} \oint \frac{p\sqrt{1 - p^2}}{(1 - p^2) \sqrt{p^2(1 - p^2) - \frac{1}{4}m}} \, dp$$

where the integral is taken in the direction of increasing q (i.e. decreasing p).

Putting $$u = p^2 ,$$

and letting u_1 , u_2 ($u_1 > u_2$) be the two zeroes of

$$u(1 - u) - \tfrac{1}{4}m$$

(u_1 and u_2 are the two values of p^2 at the points where the stream surface cuts the equatorial plane), this is equal to

$$- \frac{1}{8} \int_{u_1}^{u_2} \frac{du}{\sqrt{(u - 1)(u - u_1)(u - u_2)}}$$

and by making the transformation

$$t = \frac{u - u_2}{u_1 - u_2}$$

this may be transformed into an elliptic integral. Thus

$$H = \frac{1}{4\sqrt{1 - u_2}} \int_0^1 \frac{dt}{\sqrt{(1 - t^2)(1 - k^2t^2)}}$$

where $$k = \sqrt{\frac{u_1 - u_2}{1 - u_2}}$$

In a similar fashion J, which is given by

$$J = \oint \frac{h_q h_\lambda}{h_m} \, dq$$

is equal to

$$2 \oint \frac{(2p^2 - 1)^2 \sin^2\theta}{p \cos^3\theta} \, dq \quad ,$$

which is equal to

$$- 2 \int_{u_1}^{u_2} \frac{m \{(1 - u)^3 + (3u - 2)\tfrac{1}{4}m\}}{\sqrt{(1 - u)\{ u(1 - u) - \tfrac{1}{4}m\}}} \, du \quad .$$

So that

$$J = \frac{4}{3}\left\{ \frac{-m}{\sqrt{1 - u_2}} \int_0^1 \frac{dt}{\sqrt{(1 - t^2)(1 - k^2t^2)}} + 2\sqrt{1 - u_2} \; (4 - 3m) \int_0^1 \sqrt{\frac{1 - k^2t^2}{1 - t^2}} \, dt \right\} .$$

Graphs showing the behaviour of H and J are in Figures 10 and 11.

It is worth drawing attention to the nature of the singularity in H at $m = 0$. It is well known (see, for example Page 522 in (18)) that

$$\int_0^1 \frac{dt}{\sqrt{(1 - t^2)(1 - k^2t^2)}} \sim -\tfrac{1}{2}\log(1 - k^2) \quad \text{as} \quad k \to 1.$$

Now

$$k = \sqrt{\frac{u_1 - u_2}{1 - u_2}}$$

$$\sim 1 - \tfrac{1}{2}m \quad \text{as} \quad m \to 0 .$$

So

$$H \sim -\frac{1}{8}\log m \quad \text{as} \quad m \to 0 .$$

J has no singularities in $[0,1]$.

For the purpose of obtaining the boundary condition at the stagnation ring, namely

$$\frac{\partial\bar{c}}{\partial i} = -20\frac{\partial\bar{c}}{\partial m} \quad \text{at} \quad m = 1 ,$$

it is necessary to know $\frac{\partial J}{\partial m}$ and H at $m = 1$. It is easier to determine this in the spherical co-ordinate system than in the m,q system.

As before

$$J = \oint \frac{h_q h_\lambda}{h_m}\, dq$$

$$= -8\oint \frac{p^2\sin^2\theta\ \Delta^2}{\cos\theta\ (1 - p^2)}\, dp$$

$$= -16\int_{\frac{\sqrt{y}}{2\sqrt{2}}}^{\frac{-\sqrt{y}}{2\sqrt{2}}} \frac{6R^2 + \frac{1}{4}y}{\sqrt{y - 8R^2}}\, dR$$

where $$R = p - \frac{1}{\sqrt{2}}$$

$$y = 1 - m$$

and terms of order R^3, y^3, and smaller have been neglected. This is therefore a valid approximation for J in the neighbourhood of the stagnation ring (which is at $R = 0$, $y = 0$).

This integral is equal to

$$\pi \frac{5}{\sqrt{2}} y .$$

So that $$\frac{\partial J}{\partial m} = -\pi \frac{5}{\sqrt{2}} \quad \text{at} \quad J = 1 .$$

Similarly

$$H = -\frac{1}{8} \oint \frac{dp}{(1 - p^2) \cos \theta}$$

$$= -\frac{1}{2} \int_{\frac{\sqrt{y}}{2\sqrt{2}}}^{\frac{-\sqrt{y}}{2\sqrt{2}}} \frac{dR}{\sqrt{y - 8 R^2}}$$

$$= \frac{1}{4\sqrt{2}} \pi$$

with the required result that

$$\frac{\partial \bar{c}}{\partial i} = -20 \frac{\partial \bar{c}}{\partial m} \quad \text{at} \quad m = 1 .$$

APPENDIX THREE

Evaluation of $\oint \frac{ds}{v}$

The continuity equation in the m, q, λ co-ordinate system is

$$\frac{\partial}{\partial q}(h_\lambda\ h_m\ v_q) = 0 ,$$

there being zero component of velocity in the directions of increasing λ or increasing m .

Thus the velocity component v_q must be given in terms of the stream function m by

$$v_q = \frac{1}{h_\lambda h_m}\ \frac{\partial m}{\partial m}\ K'$$

where K' is some constant. At $\theta = \frac{\pi}{2}$ there is a discontinuity in the direction of increasing q and a consequential change of sign of v_q and hence of K'.

Since the velocity on the surface of the drop at the equator is v_o and since the velocity is in the direction of decreasing q in the hemisphere $0 < \theta < \frac{\pi}{2}$, and in the direction of increasing q in the hemisphere $\frac{\pi}{2} < \theta < \pi$ it follows that

$$K' = -\frac{v_o}{8} \qquad 0 < \theta < \frac{\pi}{2}$$

$$K' = \frac{v_o}{8} \qquad \frac{\pi}{2} < \theta < \pi$$

Hence

$$\oint \frac{ds}{v} = -\int_{S_1} \frac{ds}{v_q} + \int_{S_2} \frac{ds}{v_q}$$

where S_1 is the part of the surface of constant m in the hemisphere $0 < \theta < \frac{\pi}{2}$, and S_2 is the part of the surface in the hemisphere $\frac{\pi}{2} < \theta < \pi$,

so that

$$\oint \frac{ds}{v} = a \int_{S_1} \frac{h_q dq}{v_q} - a \int_{S_2} \frac{h_q dq}{v_q}$$

$$= \frac{8a}{v_o} \int_{S_1} h_m h_q h_\lambda \; dq + \frac{8a}{v_o} \int_{S_2} h_m h_q h_\lambda \; dq$$

$$= \frac{8a}{v_o} \oint h_m h_q h_\lambda \; dq$$

$$= \frac{8a}{v_o} \; H(m)$$

$$= \frac{a}{v_o} \sqrt{2}\, \pi \qquad \text{at} \qquad m = 1 .$$

APPENDIX FOUR

Inversion of order of integration and differentiation

The derivation of equation (5) in Chapter 4 is complete apart from the demonstration of the validity of inverting the order of integration and differentiation, which is given here.

The equation is:

$$\frac{\partial \bar{c}}{\partial t} H = \frac{D}{a^2} \oint \frac{\partial}{\partial m} \left(\frac{h_q h_\lambda}{h_m} \frac{\partial \bar{c}}{\partial m} \right) dq$$

and it is desired to invert the order of differentiation and integration on the right-hand side. It should be noted that q varies from $-\infty$ to ∞ and m varies from 0 to 1 .

The right-hand side becomes simpler in form when written in the same form as is used in Appendix 2 to evaluate J :

$$\frac{4}{3} \frac{D}{a^2} \int_0^1 \frac{\partial}{\partial m} \left[\left\{ - \frac{m}{\sqrt{1 - u_2} \sqrt{(1 - k^2u^2)(1 - u^2)}} + 2 \sqrt{1 - u_2} (4 - 3m) \sqrt{\frac{1 - k^2u^2}{1 - u^2}} \right\} \frac{\partial \bar{c}}{\partial m} \right] du$$

where $$k^2 = \frac{u_1 - u_2}{1 - u_2}$$

and u_1 and u_2 are the two zeroes of

$$u^2 - u + \tfrac{1}{4}m$$

with $$u_1 \geqslant u_2$$

It is now clear that for $k < 1$ (which corresponds to m being greater than zero) this integral is convergent, being equivalent to

$$\frac{D}{a^2} \int_0^1 A(u) \frac{du}{\sqrt{1 - u^2}}$$

where $A(u)$ is bounded in $[0,1]$. (This assumes that $\frac{\partial \bar{c}}{\partial m}$ is a bounded function of u).

It will now be shown that the order of differentiation and integration may be changed for any value of m such that $\Sigma \leqslant m \leqslant 1$, where Σ is any real number such that $0 < \Sigma < 1$.

Let $f(u,m)$ denote $\frac{h_q h_\lambda}{h_m} \frac{\partial \bar{c}}{\partial m}$

and $g(u,m)$ denote $\frac{\partial f}{\partial m}$.

u and m are both space co-ordinates: the dependence of the functions on time is ignored here.

Then f and g are continuous functions defined in

$0 \leqslant u < 1$ and $\Sigma \leqslant m \leqslant 1$, where $1 > \Sigma > 0$.

Then

$$\frac{\partial}{\partial m} \int_0^1 f(u,m)\, du = \lim_{x \to 0} \left\{ \int_0^1 \frac{f(u,m+x)}{x}\, du - \int_0^1 \frac{f(u,m)}{x}\, du \right\}$$

$$= \lim_{x \to 0} \int_0^1 \frac{f(u,m+x) - f(u,m)}{x}\, du$$

$$= \lim_{x \to 0} \int_0^1 g(u,m+\phi x)\, du$$

where $0 \leqslant \phi \leqslant 1$, by the mean value theorem.

It will now be shown that this is equal to

$$\int_0^1 g(u,m)\, du$$

The function $g(u,m+x)$ is a well-behaved function of u except near $u = 1$ where it becomes infinitely large. Since, as was shown above, its integral converges it follows that for every $Z > 0$, there exists $V > 0$ such that

$$\left| \int_{1-V}^{1} g(u,m+x)\, du \right| < Z$$

$g(u,m)$ is uniformly continuous in $0 \leqslant u \leqslant 1 - V$, $\Sigma \leqslant m \leqslant 1$ so that for every $Z > 0$ there exists $x_0 > 0$ such that, for every x satisfying $|x| < x_0$

$$\left| g(u,m+x) - g(u,m) \right| < Z$$

It follows, therefore, that for $|x| < x_o$

$$\left| \int_o^1 g(u,m+\phi x) \, du - \int_o^1 g(u,m) \, du \right|$$

$$\leqslant \left| \int_{1-v}^1 \{g(u,m+\phi x) - g(u,m)\} \, du \right| + \left| \int_o^{1-v} \{g(u,m+\phi x) - g(u,m)\} \, du \right|$$

$$< \quad 2Z \quad + \quad Z(1 - V)$$

$$= (3 - V) Z$$

which proves the required result that

$$\lim_{x \to 0} \int_o^1 g(u,m+\phi x) \, du = \int_o^1 g(u,m) \, du$$

and hence that

$$\int_o^1 g(u,m) \, du = \frac{\partial}{\partial m} \int_o^1 f(u,m) \, du \quad \text{in} \quad \Sigma \leqslant m \leqslant 1$$

For $k = 1$ (corresponding to $m = 0$), the integral of the derivative does not converge, since it contains a term of the form

$$\int_o^1 \frac{du}{1 - u^2}$$

This is of no practical importance since inverting the order of integration and differentiation is valid everywhere else in $[0,1]$.

APPENDIX FIVE

Evaluation of $\int_0^\infty c \, dY$

This appendix demonstrates a method of evaluating

$$\int_0^\infty c \, dY$$

where

$$c = \frac{\sqrt{D_1}\ B}{E\sqrt{D_1} + \overline{D_o}} \operatorname{erfc} \frac{Y}{2\sqrt{X_e}}$$

$$- \frac{2\sqrt{D_1}\ A}{E\sqrt{D_1} + \sqrt{D_o}} \sqrt{X_e} \operatorname{ierfc} \frac{Y}{2\sqrt{X_e}}$$

$$+ \frac{\sqrt{D_1}}{E\sqrt{D_1} + \sqrt{D_o}} \frac{1}{\sqrt{\pi X_e}} \int_{-\infty}^{o} Q(Y') \exp \frac{-(Y - Y')^2}{4\ X_e} \, dY'$$

Clearly the most difficult part of this problem is in integrating this last term, especially as Q(Y) is not known in an analytic form. This term may, however, be integrated by using the integral equation for Q(Y) - equation (8) This method was used by Harper and Moore (6).

The equation is:
T~~his is~~:

$$Q(Y) = - \frac{\sqrt{D_o}\ B}{E\sqrt{D_1} + \sqrt{D_o}} \operatorname{erfc} \frac{-Y}{2\sqrt{X_e}} -$$

$$- \frac{2\,E\sqrt{D_1}\,A}{E\sqrt{D_1} + \sqrt{D_o}} \sqrt{X_e} \;\operatorname{ierfc} \frac{-Y}{2\sqrt{X_e}}$$

$$+ \frac{1}{2\sqrt{\pi X_e}} \int_{-\infty}^{0} Q(Y') \left[\exp\left\{ -\frac{(Y-Y')^2}{4\,X_e} \right\} + n_a \exp\left\{ -\frac{(Y+Y')^2}{4\,X_e} \right\} \right] dY'$$

where

$$n_a = \frac{E\sqrt{D_1} - \sqrt{D_o}}{E\sqrt{D_1} + \sqrt{D_o}} .$$

When the last term in hhis expression is integrated with respect to Y from $-\infty$ to 0 it produces a term which is equal to the right-hand side of the equation (when integrated) and a term which is similar to the last term in the integration of c . In fact:

$$\int_{-\infty}^{0} \int_{-\infty}^{0} Q(Y') \left[\exp\left\{ -\frac{(Y-Y')^2}{4\,X_e} \right\} + n_a \exp\left\{ -\frac{(Y+Y')^2}{4\,X_e} \right\} \right] dY'\, dY$$

equals

$$\int_{0}^{\infty} \int_{-\infty}^{0} Q(Y') \left[\exp\left\{ -\frac{(t+Y')^2}{4\,X_e} \right\} + n_a \exp\left\{ -\frac{(t-Y')^2}{4\,X_e} \right\} \right] dY'\, dt$$

where $t = -Y$.

On reversing the order of integration (which is permissible because the fact that $Q(Y) \to 0$ as $Y \to -\infty$ means that the integration with respect to Y' is uniformly convergent) this becomes:

$$\int_{-\infty}^{0} Q(Y')\ \sqrt{\pi X_e}\left\{2 - \operatorname{erfc}\frac{-Y'}{2\sqrt{X_e}} + n_a \operatorname{erfc}\frac{-Y'}{2\sqrt{X_e}}\right\} dY'$$

which equals

$$2\sqrt{\pi X_e}\int_{-\infty}^{0} Q(Y')\,dY' + \sqrt{\pi X_e}\int_{-\infty}^{0} Q(Y')(n_a - 1)\operatorname{erfc}\frac{-Y'}{2\sqrt{X_e}}\,dY'$$

In the integration of c with respect to Y the last term is equal to

$$\frac{\sqrt{D_1}}{E\sqrt{D_1} + \sqrt{D_0}}\int_{-\infty}^{0} Q(Y')\operatorname{erfc}\frac{-Y'}{2\sqrt{X_e}}\,dY'$$

on reversing the order of integration.

And, by the previous result this must equal

$$-\frac{\sqrt{D_1}\,B}{E\sqrt{D_1}+\sqrt{D_0}}\int_{-\infty}^{0}\operatorname{erfc}\frac{-Y}{2\sqrt{X_e}}\,dY - \frac{E\sqrt{D_1}}{\sqrt{D_0}}\,\frac{2\sqrt{D_1}\,A}{E\sqrt{D_1}+\sqrt{D_0}}\sqrt{X_e}\int_{-\infty}^{0}\operatorname{ierfc}\frac{-Y}{2\sqrt{X_e}}\,dY$$

and this equals

$$-\frac{\sqrt{D_1}\,B}{E\sqrt{D_1}+\sqrt{D_0}}\int_{0}^{\infty}\operatorname{erfc}\frac{Y}{2\sqrt{X_e}}\,dY - \frac{E\sqrt{D_1}}{\sqrt{D_0}}\,\frac{2\sqrt{D_1}A}{E\sqrt{D_1}+\sqrt{D_0}}\sqrt{X_e}\int_{0}^{\infty}\operatorname{ierfc}\frac{Y}{2\sqrt{X_e}}\,dY$$

So that

$$\int_0^\infty c \; dY = - \frac{2\sqrt{D_1}}{\sqrt{D_o}} A\sqrt{X_e} \int_0^\infty \text{ierfc} \frac{Y}{2\sqrt{X_e}} \; dY$$

$$= - 2\frac{\sqrt{D_1}}{\sqrt{D_o}} A \; X_e$$

Since the mass flux is given by

$$2\pi a^2 \; v_o \; Pe_o^{-\frac{1}{2}} \int_0^\infty c \; dY$$

it is equal to

$$- \frac{8}{3} \pi a^2 \; v_o^{\frac{1}{2}} \; D_1^{\frac{1}{2}} \; A$$

which is the required result.

APPENDIX SIX

The co-ordinate q

In order to make the co-ordinate system orthogonal it is necessary to find an orthogonal compliment (q), to the co-ordinate m .

$$m = 4 p^2 (1 - p^2) \sin^2\theta$$

Since q is orthogonal to m it follows that:

$$\frac{\partial q}{\partial p} \frac{\partial m}{\partial p} + \frac{1}{p^2} \frac{\partial q}{\partial \theta} \frac{\partial m}{\partial \theta} = 0$$

that is

$$\frac{\partial q}{\partial p} 8 (p - 2p^3) \sin^2\theta + \frac{\partial q}{\partial \theta} 8 (1 - p^2) \sin\theta \cos\theta = 0$$

This is a Lagrange linear equation and has the solution:

$$q = \text{any function of } \frac{p \cos\theta}{(1 - 2p^2)^{\frac{1}{4}}}$$

In order to be consistent with Kronig and Brink's notation

$$q = \frac{p^4 \cos^4\theta}{2p^2 - 1}$$

is taken.

The co-ordinate system is illustrated in Figure 4. It should be noted that as one moves along a line of constant

m and λ, q decreases as p increases. In other words in the upper hemisphere $(0 < \theta < \frac{\pi}{2})$ the co-ordinate q decreases in the direction of the flow, and in the lower hemisphere $(\frac{\pi}{2} < \theta < \pi)$ q increases in the direction of the flow. This means that there will be a change in the sign of v_q as one moves through the plane $\theta = \frac{\pi}{2}$.

REFERENCES

1. J. Hadamard. Comptes Rendus, Acad. Sci., Paris, 152, 1735, 1911.
2. W. Rybczynski. Bulletin Academie de Sciences de Cracovie (Series A) 1911, pp. 40-46.
3. W.L. Haberman and R.K. Morton. "An experimental investigation of the drag and shape of air bubbles rising in various liquids." Taylor Model Basin Report number 802, Sept. 1953, NS715-102.
4. A. Frumkin and V. Levich. "The influence of substances which lower surface tension on movement at the boundaries of liquid media." Zh. fiz. khim. 21, 1183, 1947.
5. M.J.M. Hill. "On a spherical vortex." Phil. Trans. Roy. Soc. A, clxxxv, 213, 1894.
6. J.F. Harper and D.W. Moore. "The motion of a spherical liquid drop at high Reynolds number." J. Fluid Mech. 32, 367, 1968.
7. T.D. Taylor and A. Acrivos. "On the deformation and drag of a falling viscous drop at low Reynolds number." J. Fluid Mech. 18, 466, 1964.
8. I. Proudman and J.R.A. Pearson. "Expansions at small Reynolds numbers for the flow past a sphere and a circular cylinder." J. Fluid Mech. 2, 237, 1957.

9. L.E. Johns, Jnr. and R.B. Beckmann. "Mechanism of dispersed phase mass transfer in viscous, single drop extraction systems." A.I.Ch.E.J. 12, 10, 1966.

10. V.G. Levich, V.S. Krylov, and V.P. Vorotilin. "Theory of non-stationary diffusion from a moving droplet." Doklady Academii Nauk. SSR 161, 648, 1965.

11. V.G. Levich, V.S. Krylov, and V.P. Vorotilin. "Theory of extraction from a falling drop." Doklady Academii Nauk. SSR 160, 1358, 1965.

12. E. Ruckenstein. "Mass transfer between a single drop and a continuous phase." Int. J. Heat Mass Transfer 10, 1785, 1967.

13. R. Kronig and J.C. Brink. "On the theory of extraction from falling droplets." Appl. Sci. Res. A2, 142, 1951.

14. P.M. Heertjes, W.A. Holve, and H. Talsma. "Mass transfer between isobutanol and water in a spray column." Chem. Eng. Sci. 3, 122, 1954.

15. A.I. Johnson and A.E. Hamielec. "Mass transfer inside drops." A.I.Ch.E.J. 6, 145, 1960.

16. N.I. Kadenskaya, A.S. Zheleznyak, and B.I. Brounshtein. "Mass transfer in extraction of acetic acid by single drops of ethyl acetate." Zhurnal Prikladnoi Khimii 38, 1156, 1965.

17. A.E. Handlos and T. Baron. "Mass and heat transfer from drops in liquid-liquid extraction." A.I.Ch.E.J. 3, 127, 1957.

18. E.T. Whittaker and G.N. Watson. "A course of modern analysis."

19. P.H. Calderbank. "Gas absorption from bubbles." Chemical Engineer 212, CE209 - CE233, 1967.

20. B.I. Brounshtein, A.S. Zheleznyak, and G.A. Fishbein. "Heat and mass transfer in interaction of spherical drops and gas bubbles with a liquid flow." Int. J. Heat Mass Trans. 13, 963-973, 1970.

21. A.H.P. Skelland and R.M. Wellek. "Resistance to mass transfer inside droplets." A.I.Ch.E.J. 10, 491-496, 1964.

TABLE 1

Profiles of the first approximation to the concentration at various times

m =	0.025	0.225	0.425	0.625	0.825	1.000
Time*						
.00009	0.9798	1.	1.	1.	1.	1.
.0004	0.2110	0.9835	1.	1.	1.	1.
.0007	0.1449	0.9085	0.9989	1.	1.	1.
.0011	0.1157	0.8267	0.9923	1.	1.	1.
.0014	0.0983	0.7561	0.9783	0.9996	1.	1.
.0018	0.0866	0.6974	0.9586	0.9986	1.	1.
.0021	0.0779	0.6483	0.9356	0.9963	1.	1.
.0092	0.0317	0.3014	0.5701	0.7942	0.9397	0.9949
.0163	0.0213	0.2067	0.4095	0.5129	0.8029	0.9362
.0234	0.0161	0.1573	0.3173	0.4908	0.6706	0.8253
.0305	0.0128	0.1251	0.2545	0.3991	0.5567	0.7026
.0375	0.0104	0.1016	0.2074	0.3275	0.4611	0.5887
.0446	0.0085	0.0833	0.1704	0.2698	0.3816	0.4897
.0517	0.0070	0.0686	0.1405	0.2227	0.3156	0.4060
.0588	0.0058	0.0567	0.1160	0.1840	0.2610	0.3361
.0659	0.0048	0.0468	0.0959	0.1521	0.2158	0.2781
.0730	0.0039	0.0387	0.0792	0.1258	0.1785	0.2073
.0800	0.0033	0.0320	0.0655	0.1040	0.1476	0.1902
.0871	0.0027	0.0264	0.0542	0.0860	0.1220	0.1573
.0942	0.0022	0.0219	0.0448	0.0711	0.1009	0.1301
.1013	0.0018	0.0181	0.0370	0.0588	0.0834	0.1075
.1084	0.0015	0.0149	0.0306	0.0486	0.0690	0.0889
.1154	0.0013	0.0124	0.0253	0.0402	0.0570	0.0735
.1225	0.0010	0.0102	0.0209	0.0332	0.0472	0.0608
.1296	0.0009	0.0085	0.0173	0.0275	0.0390	0.0503
.1367	0.0007	0.0070	0.0143	0.0227	0.0322	0.0416

* Time $\equiv i = t \frac{D}{a^2}$

TABLE 2

The first approximation to the mass extracted from the liquid drop as a function of time (Initial mass of solute in drop = 1.0)

Time *	Mass loss	Time *	Mass loss
0.00009	0.0504	0.06397	0.8803
0.00053	0.1208	0.06927	0.8962
0.00097	0.1608	0.07458	0.9099
0.00150	0.1968	0.07989	0.9219
0.00204	0.2261	0.08520	0.9323
0.00734	0.3992	0.09051	0.9413
0.01088	0.4712	0.09582	0.9491
0.01442	0.5288	0.10112	0.9558
0.01973	0.5987	0.10643	0.9618
0.02504	0.6554	0.10997	0.9651
0.03035	0.7027	0.11528	0.9698
0.03566	0.7430	0.12059	0.9738
0.04096	0.7776	0.12590	0.9773
0.04627	0.8072	0.13120	0.9803
0.04981	0.8248		
0.05512	0.8482		
0.06043	0.8683		

* Time $\equiv i = t \frac{D}{a^2}$

TABLE 3

The first approximation to the concentration at the stagnation ring as a function of time

Time *	Concentration	Time *	Concentration
0.00009	1.	0.06043	0.3217
0.00053	1.	0.06397	0.2926
0.00097	1.	0.06927	0.2538
0.00150	1.	0.07458	0.2202
0.00204	1.	0.07989	0.1909
0.00734	0.9989	0.08520	0.1656
0.01088	0.9882	0.09051	0.1436
0.01442	0.9592	0.09582	0.1245
0.01973	0.8865	0.10112	0.1080
0.02504	0.7967	0.10643	0.0936
0.03035	0.7047	0.10997	0.0852
0.03566	0.6177	0.11528	0.0739
0.04096	0.5389	0.12059	0.0640
0.04627	0.4689	0.12590	0.0555
0.04981	0.4270	0.13120	0.0482
0.05512	0.3707		

* Time $\equiv i = t \frac{D_1}{a^2}$

TABLE 4

Solution of the integral equation (9)
and values of $\frac{B}{A}$

$\frac{1}{E}\frac{D_0^{\frac{1}{2}}}{D_1^{\frac{1}{2}}}$	0.2	0.5	1.0	2.0	5.0	∞
Z			$p_b\ (z)$			
0.0	-2.543	-1.441	-1.000	-0.7808	-0.6503	-0.5643
0.2	-2.469	-1.358	-0.9150	-0.6941	-0.5620	-0.4741
0.4	-2.424	-1.308	-0.8643	-0.6425	-0.5090	-0.4200
0.6	-2.401	-1.282	-0.8378	-0.6152	-0.4812	-0.3914
0.8	-2.391	-1.271	-0.8263	-0.6034	-0.4690	-0.3788
1.0	-2.387	-1.267	-0.8227	-0.5996	-0.4651	-0.3748
1.2	-2.387	-1.267	-0.8224	-0.5993	-0.4647	-0.3744
1.4	-2.387	-1.268	-0.8229	-0.5999	-0.4654	-0.3751
1.6	-2.389	-1.268	-0.8235	-0.6005	-0.4659	-0.3757
1.8	-	-1.268	-0.8238	-0.6008	-0.4662	-0.3760
2.0	-	-	-0.8239	-0.6009	-0.4664	-
2.2	-	-	-	-	-0.4662	-
∞	-2.389	-1.268	-0.8239	-0.6009	-0.4662	-0.3760
$\frac{B}{A}$ =	4.597	1.953	0.9514	0.4626	0.1794	0.

TABLE 5(a)

(a) The first approximation to $A/Pe_1^{-\frac{1}{2}}$ as a function of time

Time *	$A/Pe_1^{-\frac{1}{2}}$	Time *	$A/Pe_1^{-\frac{1}{2}}$
0.00009	-145.78	0.06043	-1.747
0.00053	- 54.33	0.06397	-1.588
0.00097	- 38.69	0.06927	-1.376
0.00150	- 30.19	0.07458	-1.193
0.00204	- 25.35	0.07989	-1.035
0.00734	- 11.62	0.08520	-0.8971
0.01088	- 8.969	0.09051	-0.7780
0.01442	- 7.372	0.09582	-0.6746
0.01973	- 5.839	0.10112	-0.5850
0.02504	- 4.814	0.10643	-0.5073
0.03035	- 4.057	0.10997	-0.4614
0.03566	- 3.462	0.11528	-0.4001
0.04096	- 2.975	0.12059	-0.3470
0.04627	- 2.567	0.12590	-0.3009
0.04981	- 2.330	0.13120	-0.2609
0.05512	- 2.016		

* Time $\equiv i = t\,\frac{D}{a^2}$

TABLE 5(b)

(b) Effect of $\bar{c}_b$ on the value of $A/Pe_1^{-\frac{1}{2}}$

Second approximation to $A/Pe^{-\frac{1}{2}}$ = First approximation + A_b

Time *	$\frac{1}{F} \times {}^{A_b}/_{Pe_1^{-\frac{1}{2}}}$	Time *	$\frac{1}{F} \times {}^{A_b}/_{Pe_1^{-\frac{1}{2}}}$
0.00009	-385.44	0.06043	-3.324
0.00053	- 97.29	0.06397	-3.183
0.00097	- 60.39	0.06927	-2.971
0.00150	- 42.81	0.07458	-2.762
0.00204	- 33.74	0.07989	-2.556
0.00734	- 10.06	0.08520	-2.357
0.01088	- 8.082	0.09051	-2.166
0.01442	- 6.881	0.09582	-1.984
0.01973	- 5.772	0.10112	-1.813
0.02504	- 5.096	0.10643	-1.652
0.03035	- 4.655	0.10997	-1.550
0.03566	- 4.344	0.11528	-1.407
0.04096	- 4.098	0.12059	-1.275
0.04627	- 3.881	0.12590	-1.153
0.04981	- 3.742	0.13120	-1.041
0.05512	- 3.534		

* Time $\equiv i = t\,\frac{D}{a^2}$

TABLE 6

Effect of $\bar{c}_b$ on the mass loss

Time *	$\frac{1}{F}$ x Mass loss (b)	Time *	$\frac{1}{F}$ x Mass loss (b)
0.00009	-1.559	0.06043	-0.5473
0.00053	-1.407	0.06927	-0.4916
0.00097	-1.339	0.07989	-0.4329
0.00150	-1.285	0.09051	-0.3828
0.00204	-1.244	0.10112	-0.3407
0.00734	-1.077	0.10997	-0.3109
0.01088	-1.013	0.12059	-0.2810
0.01973	-0.8933	0.13120	-0.2565
0.03035	-0.7842		
0.04096	-0.6917		
0.04981	-0.6224		

Second approximation to mass loss

$$= \text{First approximation} + Pe_1^{-\frac{1}{2}} \ (\text{mass loss (b)})$$

* Time $\equiv i = \dfrac{D}{a^2} t$

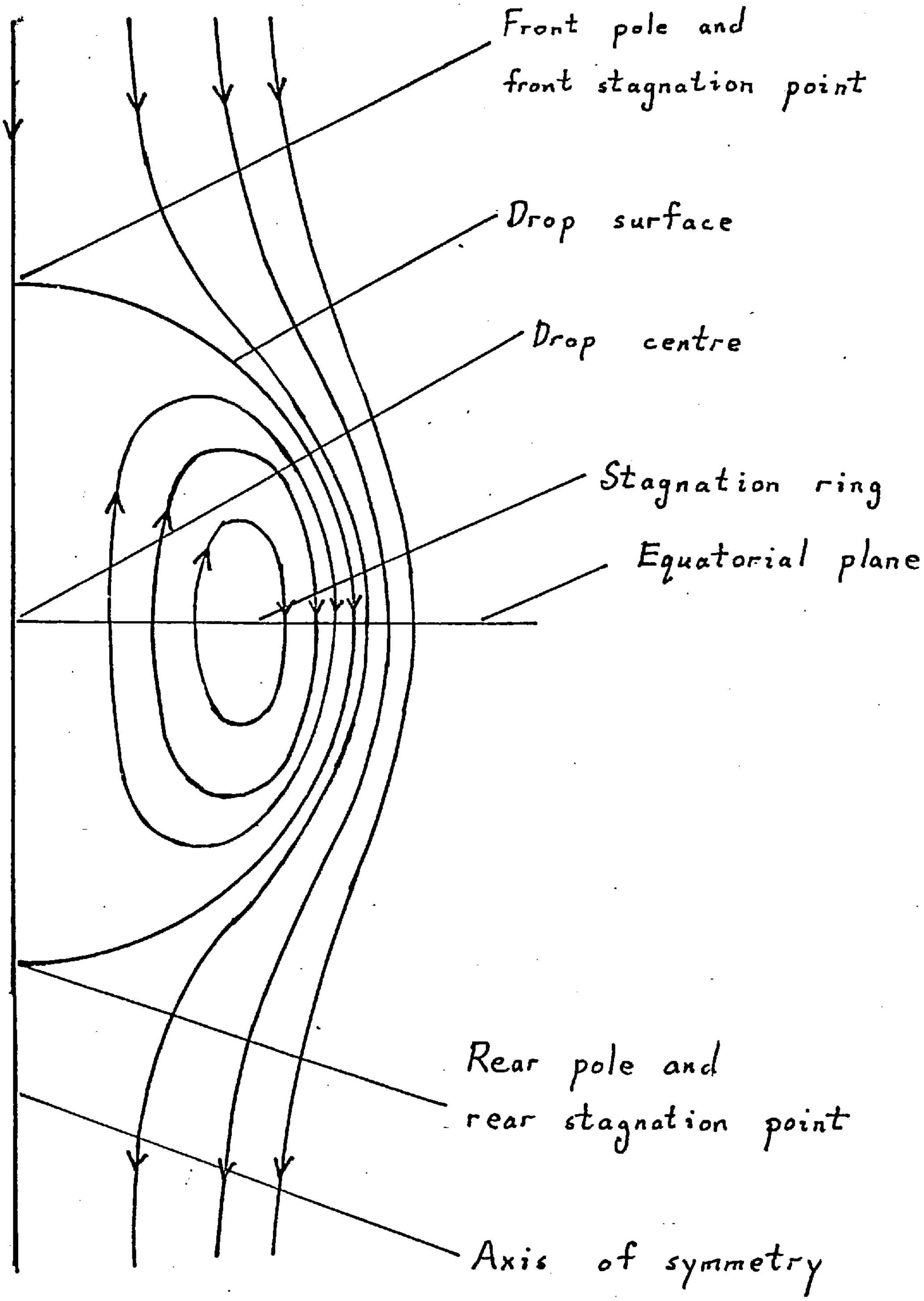


Figure 1 : The flow pattern in and around a liquid drop at low Reynolds number.

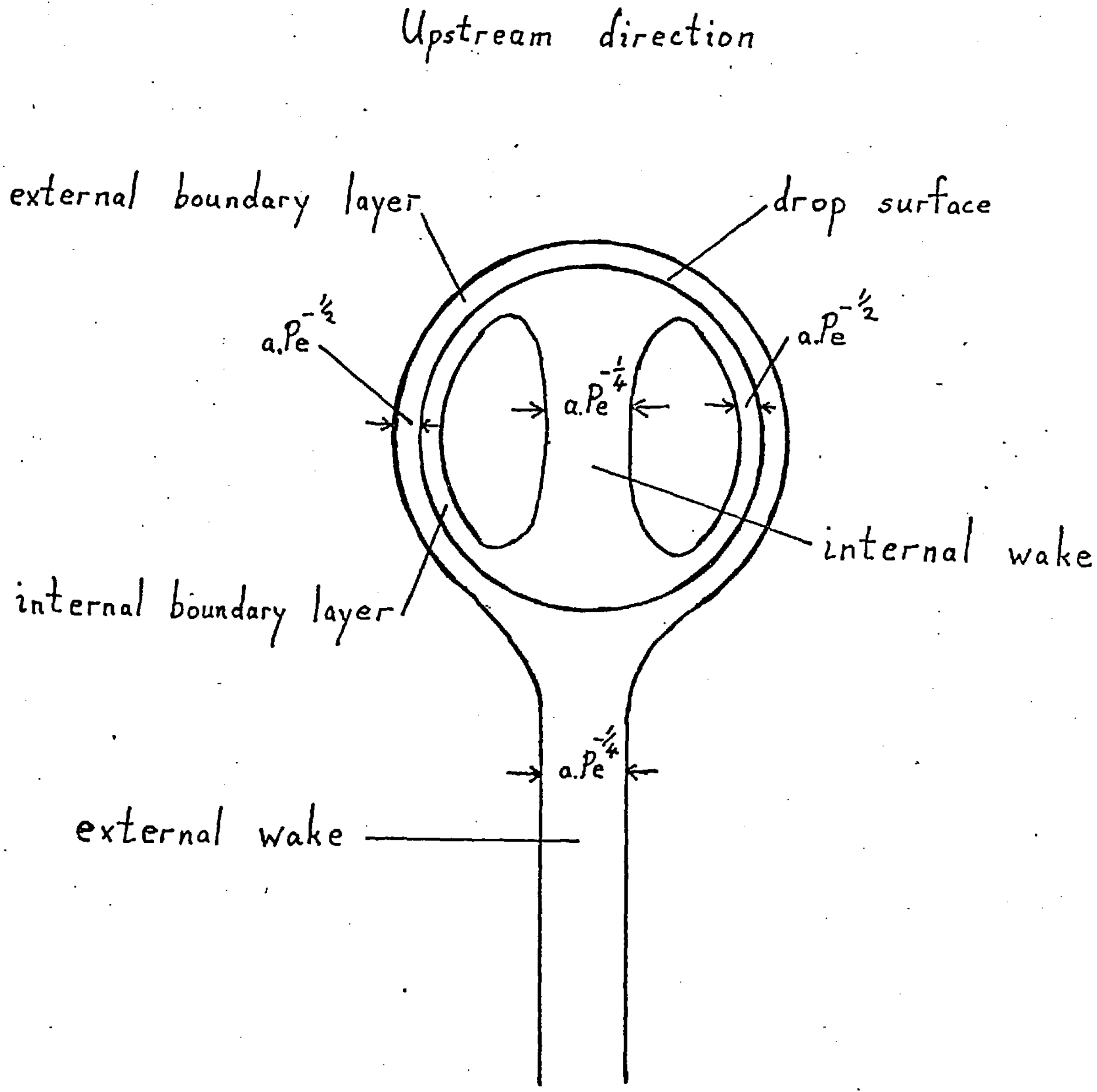
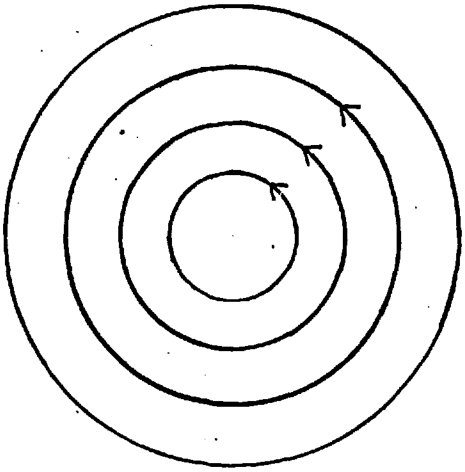
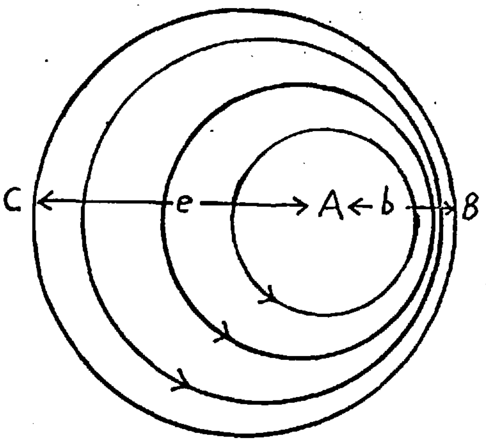


Figure 2 : The boundary layer - wake system.



3a : Concentric flow system



3b : Eccentric flow system

Figure 3 : Diagram to illustrate how variations in concentration may occur.

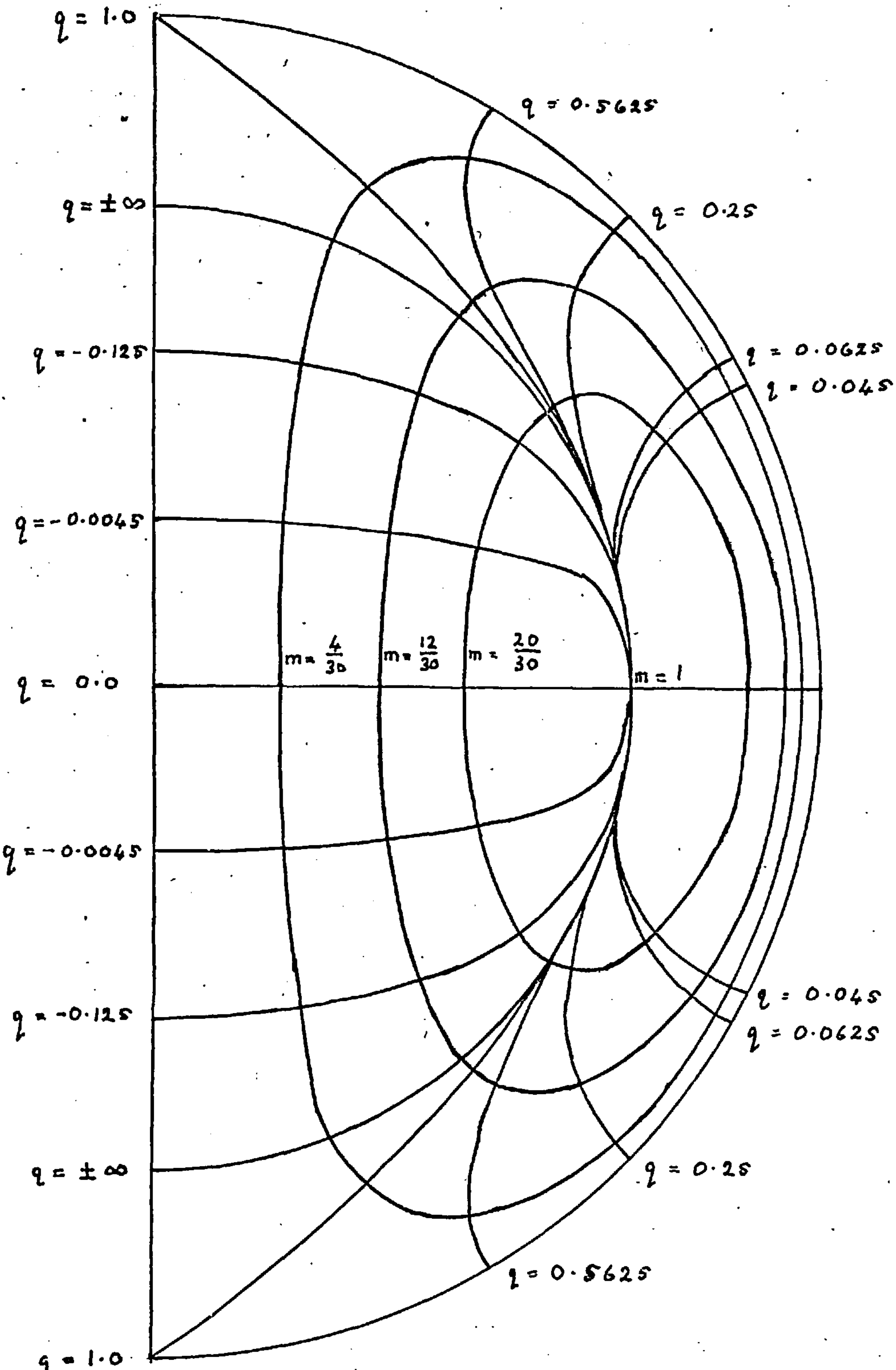


Figure 4

The m-q co-ordinate system

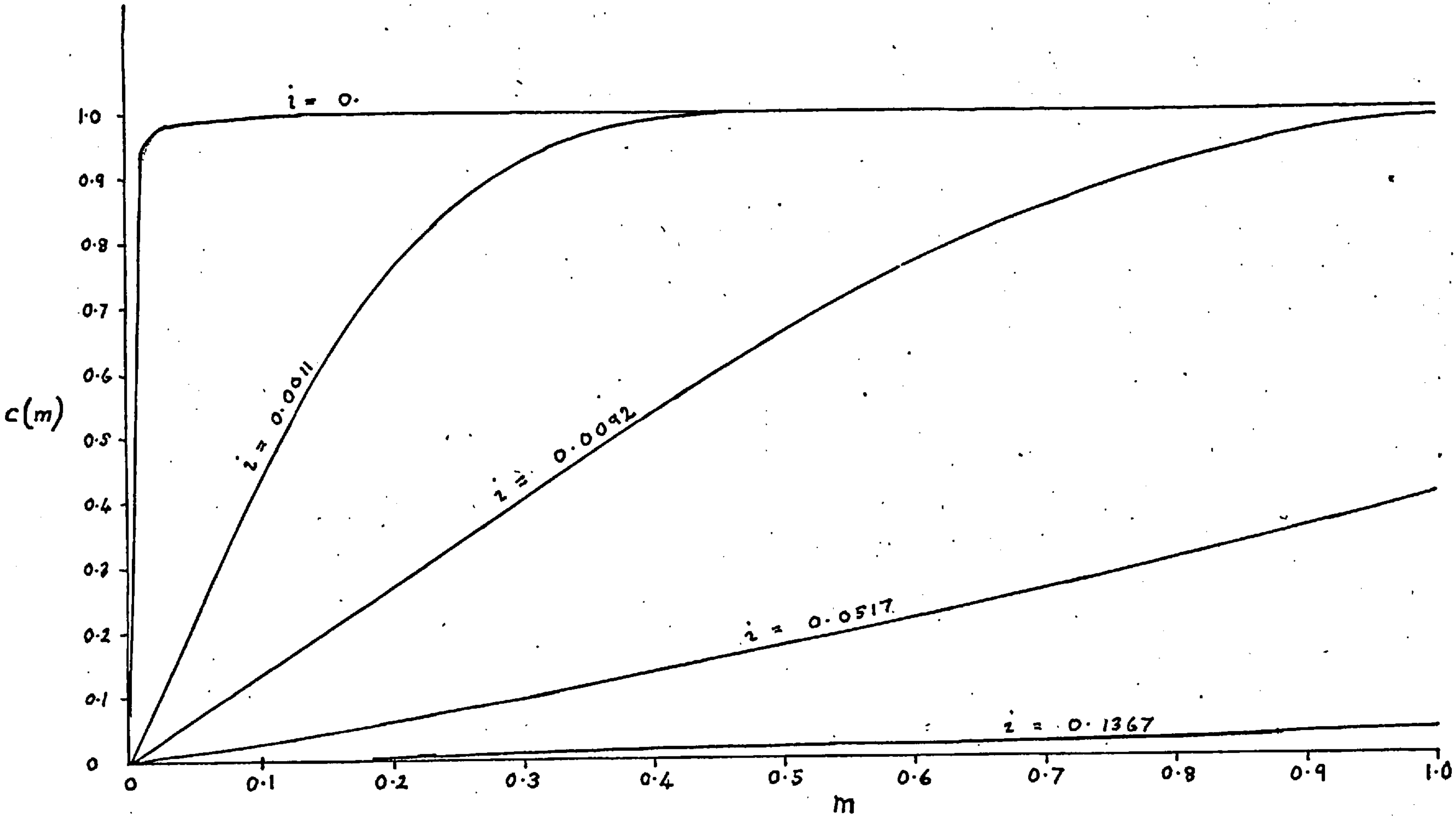


Figure 5 : Concentration profiles at various times

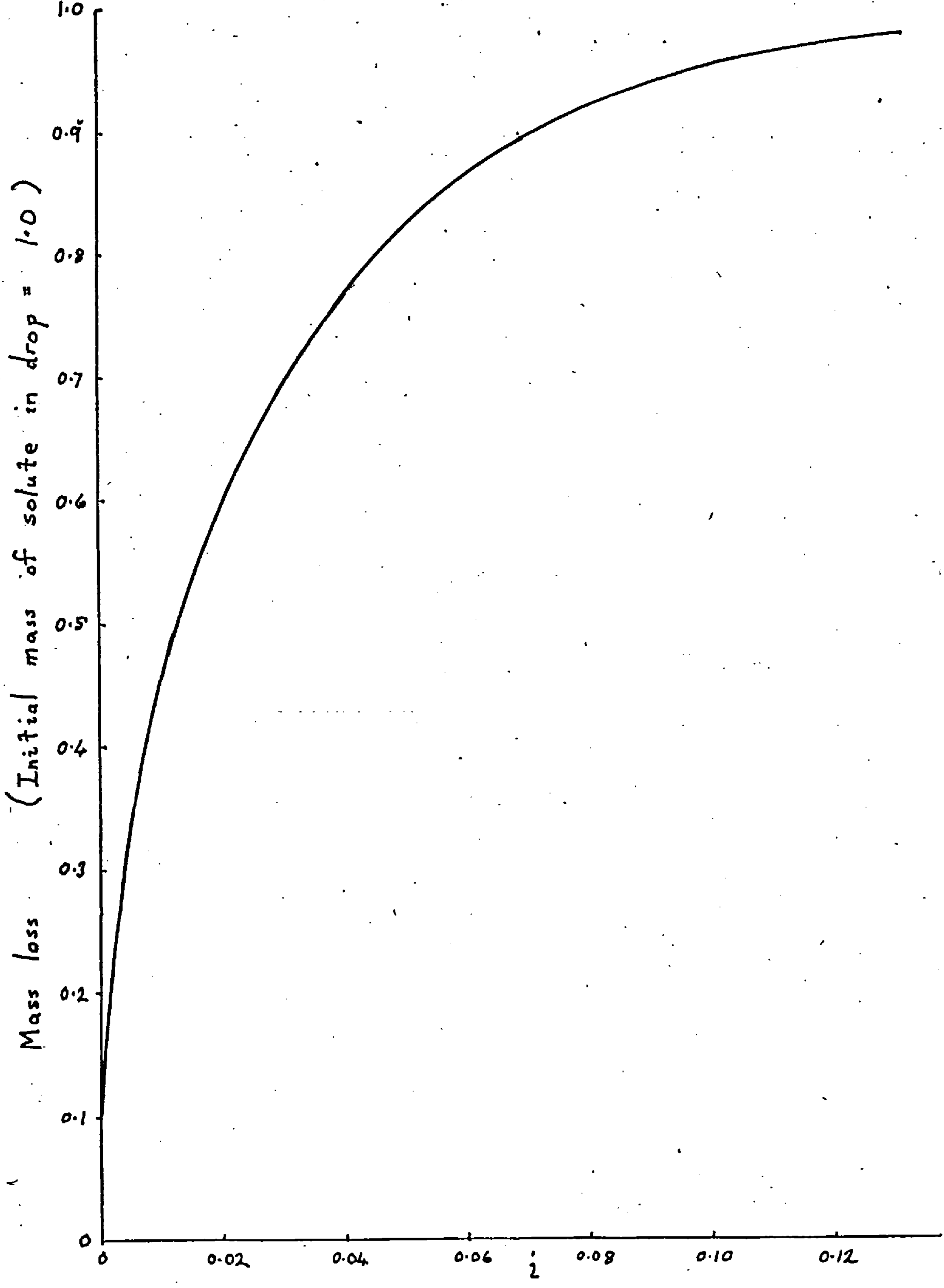


Figure 6 : The first approximation to the mass loss v. time (i)

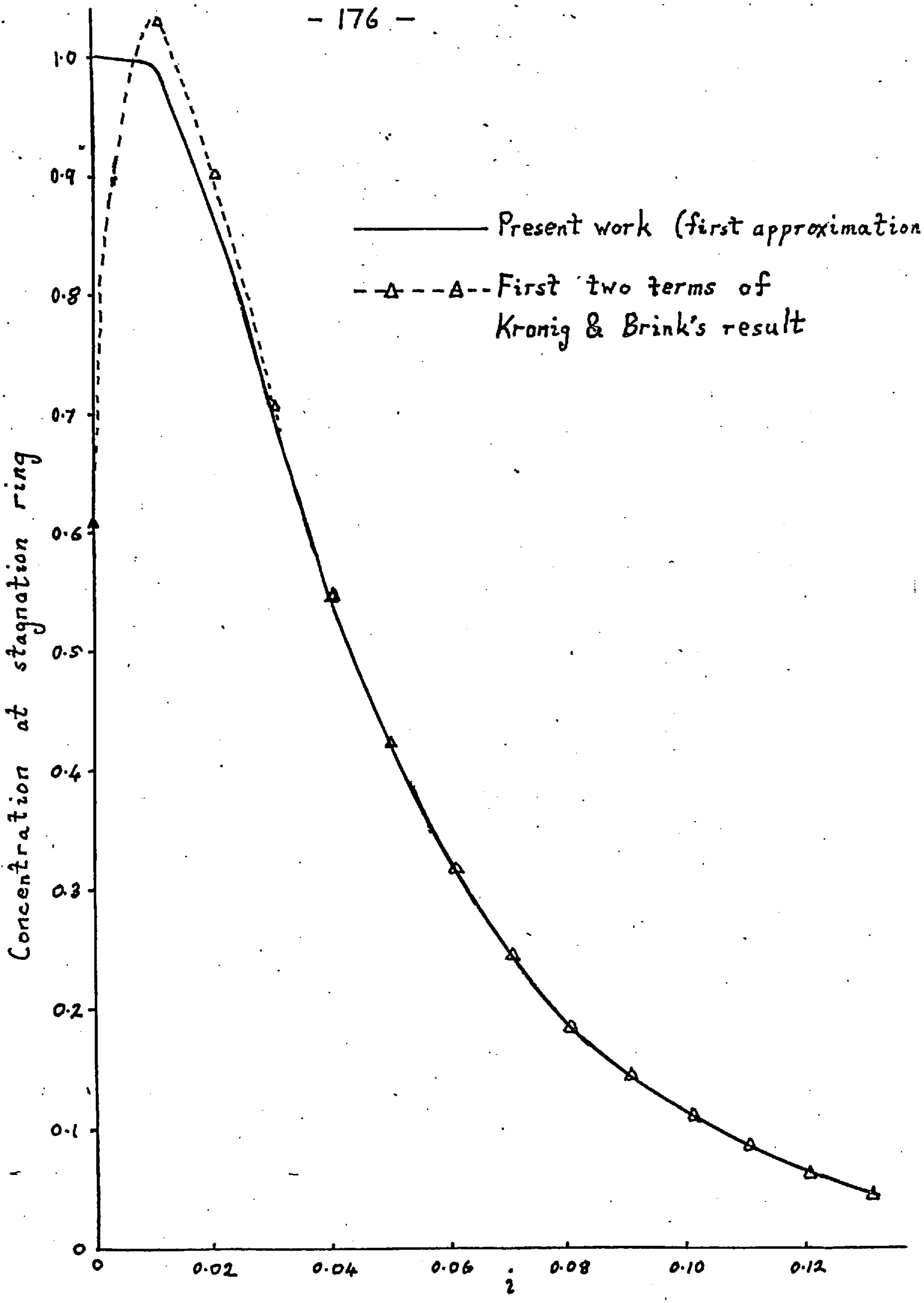


Figure 7: Concentration at stagnation ring v. time (i)

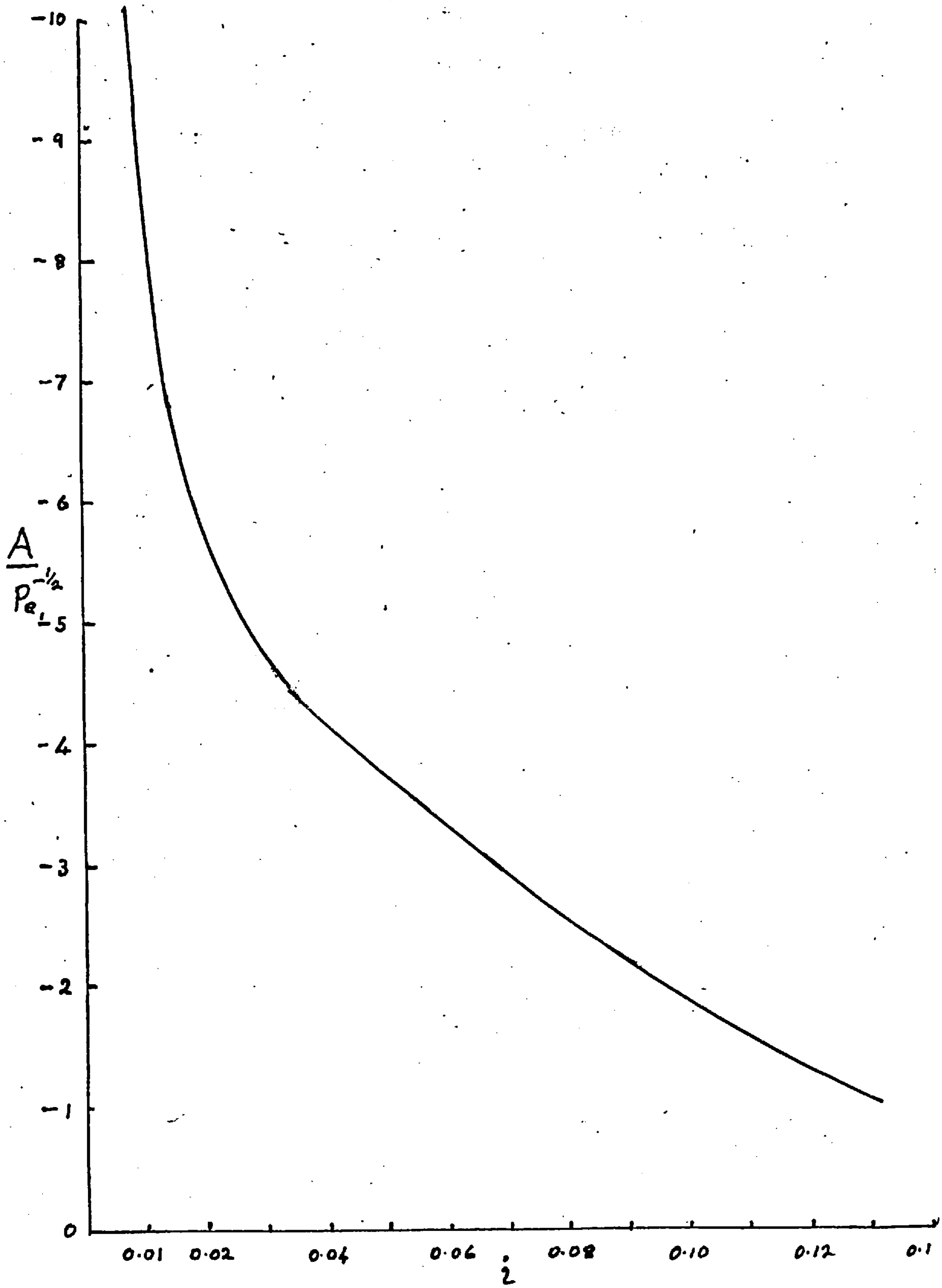
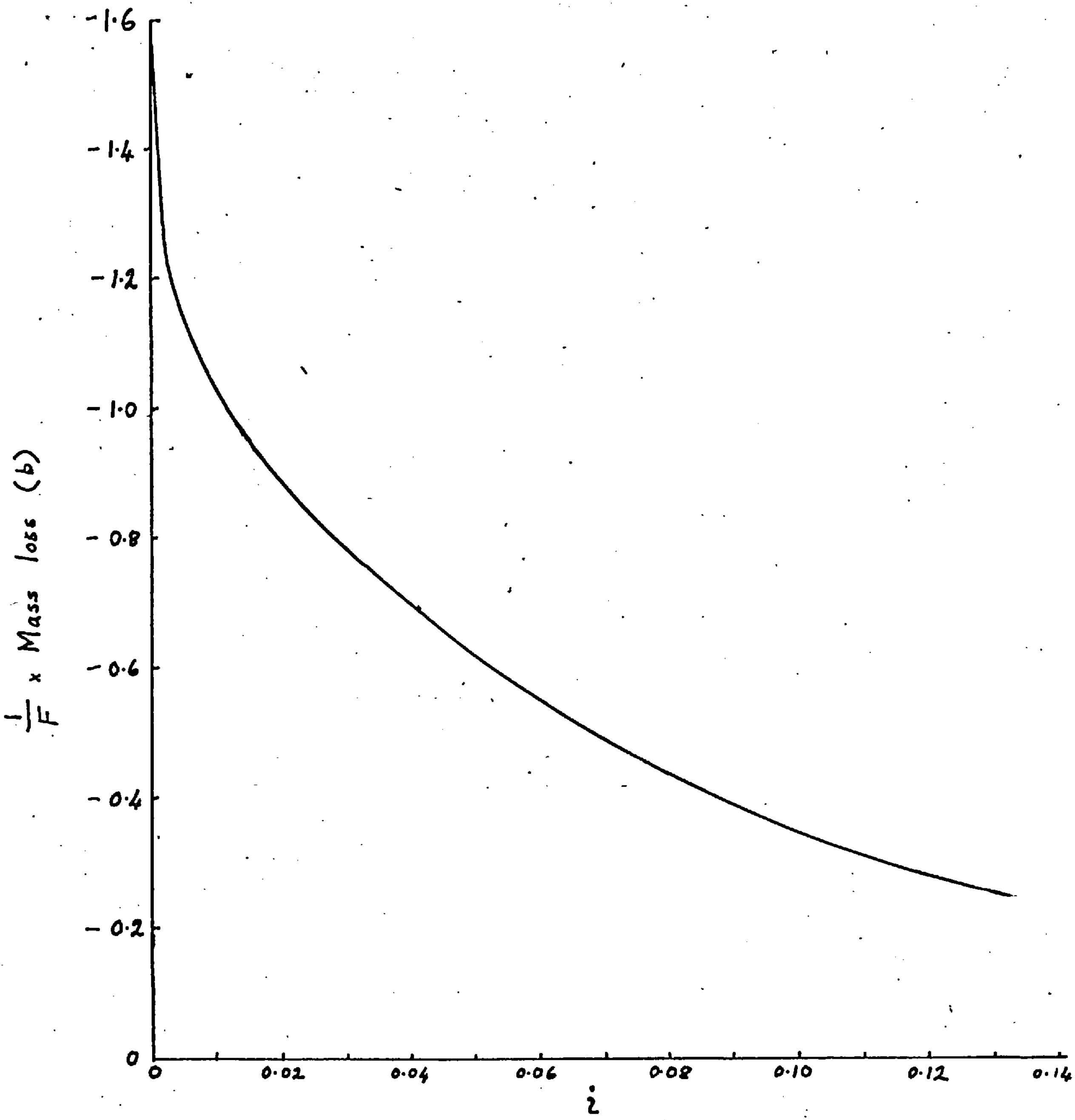


Figure 8 : The first approximation to $\frac{A}{Pe_1^{-1/2}}$ v. time (i)



Second approximation to mass loss
= First approximation + $P_{e_1}^{-\frac{1}{2}}$ × (Mass loss (b)).

Figure 9 : Effect of $\overline{c}_b$ on the mass loss

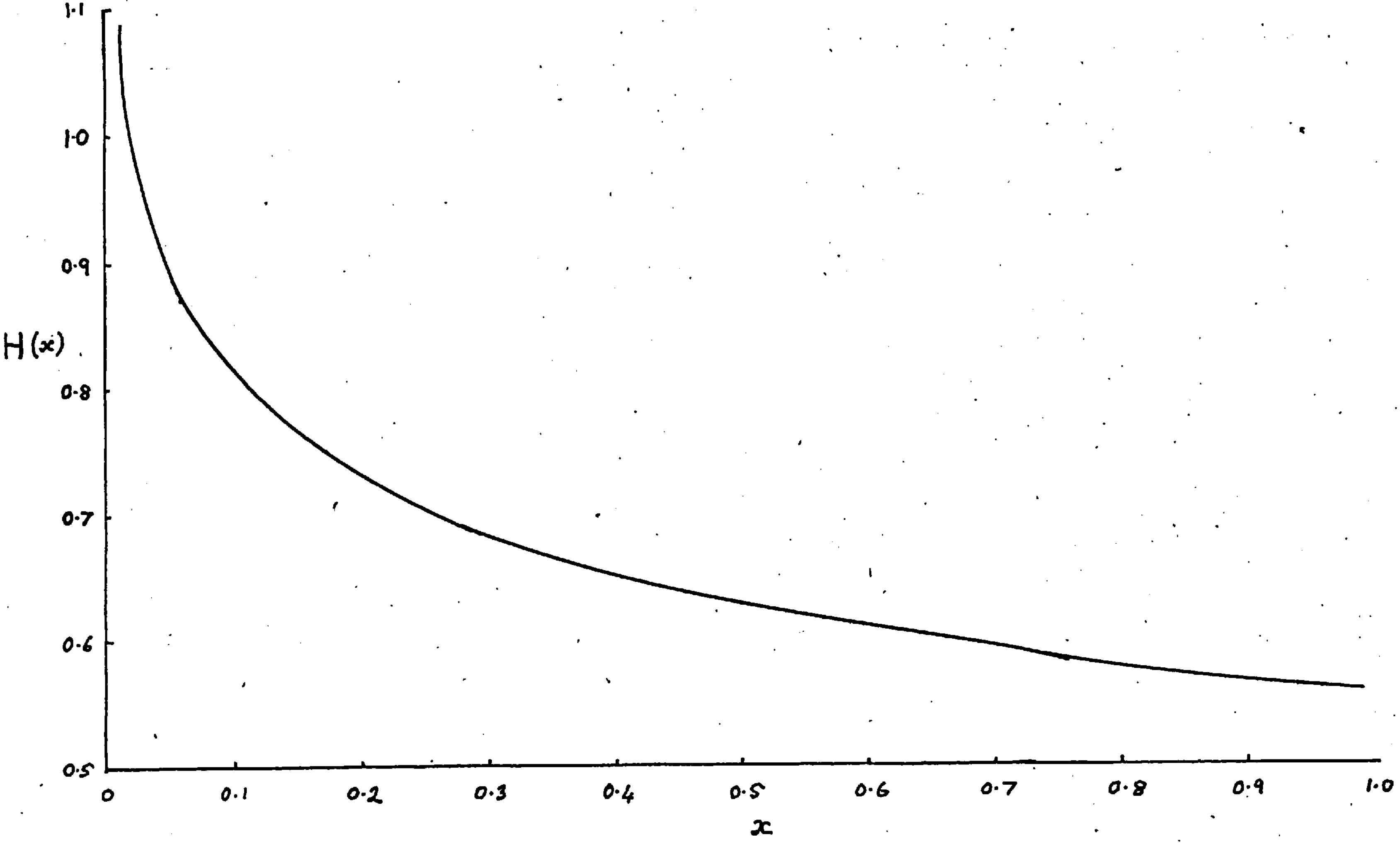


Figure 10 : The function H

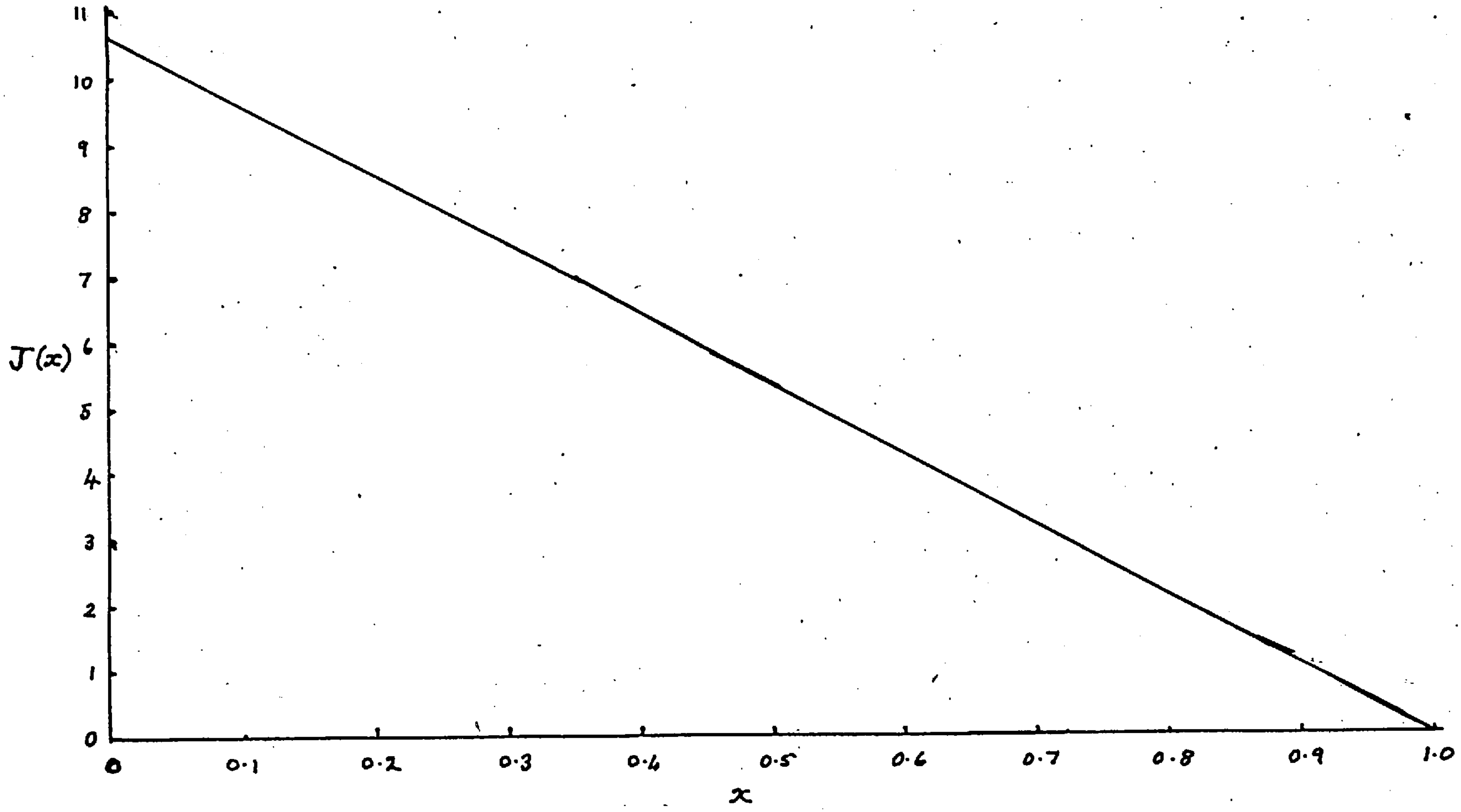


Figure 11 : The function J

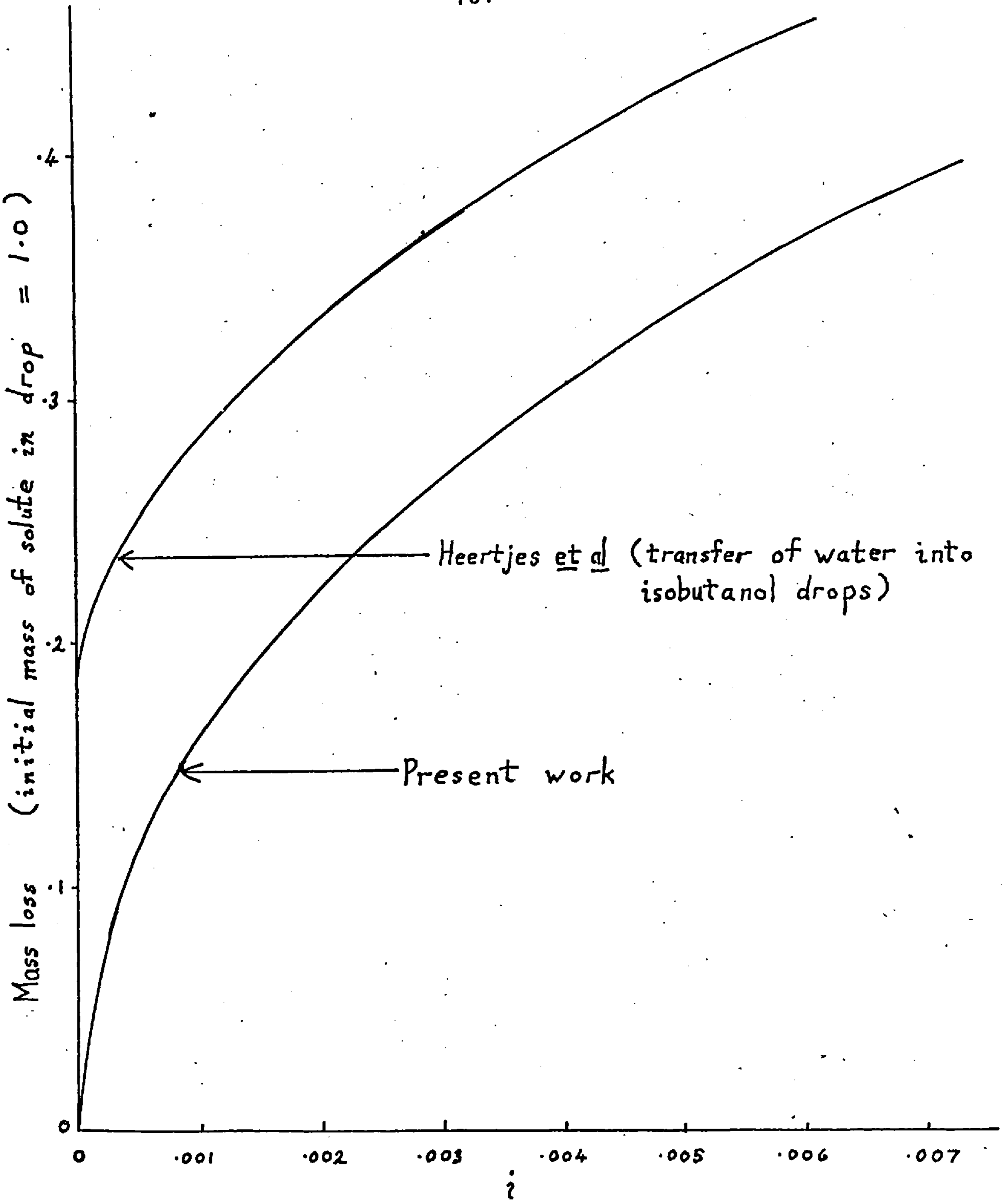


Figure 12 : Mass loss v. time for small values of the time i