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Mass transfer with second-order chemical reaction inside circulating fluid droplets

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MASS TRANSFER WITH SECOND-ORDER CHEMICAL REACTION
INSIDE CIRCULATING FLUID DROPLETS

by

ROY JAMES BRUNSON, 1944-

A DISSERTATION
Presented to the Faculty of the Graduate School of the
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ABSTRACT

The solution of a mathematical model is presented which describes mass transfer accompanied by a second-order chemical reaction inside a circulating, fluid sphere for the laminar flow region. The values for eight different mass transfer indices are presented as a function of the Peclet number, reaction number, diffusivity ratio, concentration ratio, and the dimensionless contact time. The results of this work are compared with the film and penetration theories for mass transfer with reaction as modified to apply inside a fluid sphere. This work corrects the three factors which limit the accuracy of applying previous theories to fluid spheres: geometrical description, fluid flow model, and the possibility of complete depletion of the reactant initially in the fluid sphere. The model assumes that all resistance to mass transfer in the continuous phase is negligible, that the reaction is irreversible, and that the system is isothermal.

Experimental data were obtained for a system which consisted of a continuous phase of n-pentyl formate diffusing into falling aqueous drops which contain one formal sodium sulfate and 0.04 formal sodium hydroxide. The n-pentyl formate and sodium hydroxide undergo a second-order irreversible reaction inside the drop. For this experimental study the reaction numbers ranged from 3023 to 8953. The Peclet number ranged from \(7.14 \times 10^4\) to \(1.15 \times 10^5\). The concentration ratio was 0.335 and the diffusivity ratio was 2.16. The Reynolds number ranged from 490 to 789.

The experimental results for the total mass transferred were two to four times that predicted by the model developed in this work. The
large experimental total mass transferred was due to the fact that the laminar velocity profiles inside the drop were not valid for the drop-let Reynolds numbers encountered experimentally. The experimental results agreed reasonably well with a special combination of empirical correlations by Skelland and Wellek with the film theory combined with second-order chemical reaction.
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LIST OF SYMBOLS

\( a \) = radius of sphere, cm.

\( b \) = reactant initially in continuous phase

\( A \) = dimensionless concentration of \( a \), \( C_a/C_{as} \)

\( \bar{A} \) = space averaged dimensionless concentration of \( a \)

\( \bar{A}_0 \) = space averaged dimensionless concentration of \( a \) for mass transfer without reaction

\( A_1 \) = dimensionless concentration of \( a \) at previous time step

\( A_2 \) = dimensionless concentration of \( a \) at present time step

\( A_3 \) = dimensionless concentration of \( a \) at future time step

\( \bar{A}_r \) = dimensionless amount of solute reacted in the sphere, \( C_{ar}/C_{as} \)

\( \bar{A}_{mt} \) = dimensionless total mass transferred, \( \bar{A} + \bar{A}_r \)

\( \bar{A}_{mt}^e \) = dimensionless total mass transferred with end effects

\( b \) = reactant soluble only in dispersed phase

\( B \) = dimensionless concentration of \( b \), \( C_b/C_{bo} \)

\( \bar{B} \) = space averaged dimensionless concentration of \( b \)

\( B_1 \) = dimensionless concentration of \( b \) at previous time step

\( B_2 \) = dimensionless concentration of \( b \) at present time step

\( B_3 \) = dimensionless concentration of \( b \) at future time step

\( C_a \) = concentration of \( a \), moles/liter

\( C_{ar} \) = moles of \( a \) reacted per volume of sphere, moles/liter

\( C_{as} \) = surface concentration of \( a \), moles/liter

\( C_b \) = concentration of \( b \), moles/liter

\( C_{bo} \) = initial concentration of \( b \), moles/liter

\( C_{bf} \) = final concentration of \( b \), moles/liter

\( \bar{C}_{mt} \) = moles of \( a \) transferred per volume of sphere, moles/liter

\( \bar{C}_{mt}^e \) = moles of \( a \) transferred with end effects per volume of sphere, moles/liter
\[ D_a = \text{diffusivity of component } a, \text{ sq. cm./sec.} \]
\[ D_b = \text{diffusivity of component } b, \text{ sq. cm./sec.} \]
\[ e_1 = \text{intercept for least squares correlation} \]
\[ e_2 = \text{slope for least squares correlation} \]
\[ g = \text{ionic coefficient used in section 7.1} \]
\[ h = \text{distance from the interface, cm.} \]
\[ H = \text{distance from interface wherein diffusion is important: film thickness for film theory and approaching infinity for penetration theory, cm.} \]
\[ i = \text{index of grid point in radial direction} \]
\[ I = \text{ionic strength} \]
\[ j = \text{index of grid point in angular direction} \]
\[ k = \text{index of grid point in time dimension} \]
\[ k_2 = \text{second-order reaction constant, liter/mole/sec.} \]
\[ k_R = \text{dimensionless reaction number, } k_2 a C_{bo}/D_a \]
\[ L = \text{depth of concentration cell, cm.} \]
\[ m_r = \text{number of increments in angular direction} \]
\[ M = \text{number of data points} \]
\[ m_{rr} = \text{number of grid points in angular direction, } m_r + 1 \]
\[ n_r = \text{number of increments in radial direction} \]
\[ N = \text{dimensionless flux of component } a, 2a N_a/D_a \]
\[ \bar{N} = \text{time averaged dimensionless flux of } a \]
\[ N_a = \text{flux of component } a, \text{ mole cm./liter sec.} \]
\[ \bar{N}_a = \text{time averaged flux of } a, \text{ mole cm./liter sec.} \]
\[ N_0 = \text{dimensionless flux of } a \text{ in the absence of a chemical reaction} \]
\[ \bar{N}_o = \text{time averaged dimensionless flux of } a \text{ in the absence of a chemical reaction} \]
\[ N_p = P \text{ group, } \frac{\sigma^3 2}{980 \mu_c (\rho_d - \rho_c)^4} \]
N_{Pe} = \text{Peclet number, } \left( \frac{aV_t}{2D_a} \right) \frac{\mu_c}{(\mu_c + \mu_d)}

N_{Re} = \text{Reynolds number, } 2aV_t \rho_c / \mu_c

n_{rr} = \text{number of grid points in radial direction}

N_{Sc} = \text{dispersed phase Schmidt number, } \frac{\mu_d}{\rho_d D_a}

N_{Sh} = \text{Sherwood number, } N / (1 - \bar{A})

\bar{N}_{Sh} = \text{time averaged Sherwood number}

N_{We} = \text{Weber number, } 2aV_t^2 \rho_c / \sigma

P = 2 \Delta \tau / (\Delta \theta)^2

P_2 = \frac{\Delta \tau}{\Delta \theta}

p = \text{radius of concentration cell, cm.}

q = \text{meniscus depth, cm.}

r = \text{radial distance, cm.}

R = \text{dimensionless radius, } r/a

R_c = \text{concentration ratio, } \frac{C_{as}}{C_{bo}}

R_D = \text{diffusivity ratio, } \frac{D_b}{D_a}

S = 2 \frac{\Delta \tau}{(\Delta R)^2}

S_2 = \frac{\Delta \tau}{\Delta R}

S_o = \text{surface area of transfer, cm}^2.

t = \text{contact time, sec.}

T = \text{temperature, } ^{\circ}\text{C}

V = \text{volume of sphere, cm}^3.

v_r = \text{velocity in radial direction, cm./sec.}

V_R = \text{dimensionless velocity in radial direction}

v_e = \text{velocity in angular direction, cm./sec.}

V_e = \text{dimensionless velocity in angular direction}

V_t = \text{terminal velocity of sphere relative to surrounding fluid, cm./sec.}
\( W \) = parameter in equation (4.12), defined by equation (4.14)

\( x \) = parameter in equation (4.13) = 0.85\( \sqrt{W R_c + W} \)

\( Y \) = parameter in equations (4.6) and (4.8), defined by equation (4.7)

\( z \) = ionic charge

\( Z \) = stoichiometric coefficient

**GREEK SYMBOLS**

\( \Gamma \) = the enhancement factor divided by the enhancement factor for an instantaneous reaction

\( \delta \) = Kronecker delta (one for penetration theory and zero for film theory)

\( \theta \) = angle

\( \mu_c \) = viscosity of continuous phase, poise

\( \mu_d \) = viscosity of dispersed phase, poise

\( \rho_c \) = density of continuous phase, gm./cm.\(^3\)

\( \rho_d \) = density of dispersed phase, gm./cm.\(^3\)

\( \sigma \) = interfacial tension, dyne/cm.

\( \tau \) = dimensionless time, \( tD_a/a^2 \)

\( \phi \) = enhancement factor, \( \bar{N}/N_0 \)

\( \phi^1 \) = instantaneous enhancement factor, \( N/N_0 \)

\( \phi_1 \) = enhancement factor for first-order reaction

\( \phi_\infty \) = enhancement factor for instantaneous reaction
I. INTRODUCTION

A chemical reaction between two solutes which are initially in separate immiscible fluid phases is frequently encountered in industry. In the introduction to his book, Danckwerts (1970) lists forty-two industrial reactions in which one reactant is initially in a liquid phase and the other reactant is in a gas phase. Industrial reactions in which the two reactants are in mutually immiscible liquid phases include:

Extraction of malodorous mercaptans from gasoline by aqueous caustic soda.

Removal of carbonyl sulfide from liquefied C₃ fractions by extraction into aqueous solutions containing caustic soda or alkanolamines.

Hydrolysis or saponification of esters of fatty acid; Saponification of esters such as isobornyl formate or acetate, ethyl fluoroacetate, etc.

Hydrolysis of organic halogen compounds such as amyl chloride, benzyl chloride, 2,4-dinitro chlorobenzene, etc.

Reactions between sparingly soluble carbonyl compounds such as butyraldehyde, cyclohexanone, etc., and hydroxylamine sulfate for the preparation of the corresponding oximes.

Oxidation of a number of organic compounds sparingly soluble in water by aqueous alkaline potassium permanganate solution.

Cannizzaro's reaction.

(Sharma, 1966) and

nitration or sulfonation of olefins


The first two examples, which involve the removal of malodorous mercaptans and carbonyl sulfide, are actually liquid extraction processes which use a simultaneous chemical reaction to enhance the rate of extraction. Possible methods of contacting the immiscible fluid
phases include spray, perforated plate, and rotating disc columns and venturi scrubbers. In these types of contactors and others, one of the fluid phases is dispersed and freely rising or falling in the other fluid.

It is the purpose of this work to develop and test a model which will predict the rate of simultaneous mass transfer and chemical reaction inside a freely rising or falling fluid sphere. The droplet motion must be in the creeping flow regime. The model could be applied to two-phase chemical reactions, gas absorption with reaction, or liquid extraction with reaction.

In order to focus attention on mass transfer and chemical reaction within the dispersed phase, it is assumed that there is no resistance to mass transfer in the continuous phase. In addition, it will be understood that the reactions, considered in this work, are irreversible.

Section II gives the literature background for this study. A model for mass transfer with second-order chemical reaction inside a freely rising or falling fluid sphere is developed in section III. The results of the model developed in section III are discussed in section IV. Section V describes an experimental apparatus and procedure to test the mathematical model. Section VI describes a special study to estimate the interfacial concentration. The results obtained as described in section V with the interfacial concentrations determined in section VI, are discussed in section VII. The conclusions based on this work are given in section VIII.
II. LITERATURE SURVEY

Most of the literature pertinent to this work has been presented as being applicable for mass transfer in either a gas or a liquid. In order to maintain this generality, the terms "fluid sphere" and "dispersed phase" will be used to refer to gas bubbles in a liquid or liquid drops in a gas or another liquid. This review covers selected papers on fluid dynamics, mass transfer inside fluid spheres, and two mass transfer theories adaptable to fluid spheres.

Licht and Conway (1950) cited three zones of interest for a dispersed phase in an unpacked column. The zones are drop formation at a nozzle with the associated drop acceleration, free rise or fall in the continuous phase, and drop coalescence. These zones may occur once, as in a spray tower or a venturi scrubber, or they may be repeated several times, as in a perforated plate column. This work deals primarily with the free rise or fall of the dispersed phase. The other two zones are considered end effects, and their study is beyond the scope of this work. Garner and Skelland (1954) suggested that the effect of mass transfer during end effects can be accounted for by plotting total mass transfer against time of dispersed phase contact. The intercept of this plot extrapolated to zero contact time is the total mass transferred during end effects.

2.1. Fluid Mechanics

After a fluid sphere detaches from the nozzle or forming device, it accelerates until it reaches its terminal velocity. The viscous shear on the surface of the fluid sphere causes the fluid inside the sphere to circulate. Hadamard (1911) solved the linearized Navier
Stokes equation for fluid velocities in a spherical drop. This derivation is valid for a fluid sphere in creeping flow at its terminal velocity.

Olney and Miller (1963) found that a drop reaches its terminal velocity in the first five to ten centimeters of free rise or fall. Heertjes, et al. (1954) qualitatively verified the Hadamard velocity profile for a drop Reynolds number of about five. They based their conclusions on visually observed color changes associated with mass transfer in falling liquid drops. Horton, et al. (1965) used suspended colloidal particles to measure velocity profiles within a liquid drop. Their results compared favorably with the Hadamard theory for Reynolds numbers up to nineteen. Johnson and Hamielec (1960) used suspended aluminum powder to study velocity profiles inside water drops. They found Hadamard type streamlines for Reynolds numbers up to 87. However, at Reynolds numbers above four hundred no distinct flow pattern could be observed.

Fluid velocities within the dispersed phase may differ from the theoretical values predicted by Hadamard, even in the region of low Reynolds numbers, where the assumption of creeping flow should be valid. The deviation may be due to interaction with other fluid spheres or surface active impurities, which collect at the surface of the fluid sphere. Gal-Or (1970) developed stream functions for swarms of fluid spheres, which contain surfactant impurities. This development reduces to the Hadamard stream functions for single drops without surfactants.

For larger Reynolds numbers, a wake forms in the continuous phase at the rear of the fluid sphere. The wake distorts the symmetry of the streamlines, as derived by Hadamard (1911). At large Reynolds numbers,
the internal velocity gradients are greater than predicted by the Hadamard equations. A numerical solution of the Navier Stokes equation at these higher Reynolds numbers has been developed by Hamielec and coworkers (LeClair, et al., 1970).

At very large Reynolds numbers, the wakes in the continuous phase become unstable and shed periodically (Schroeder and Kintner, 1965). This instability causes the shape of the dispersed phase to oscillate from a spherical shape to that of an oblate and/or prolate spheroid. The flow in an oscillating dispersed phase is turbulent and there are no well defined streamlines.

2.2. Mass Transfer

Extensive reviews of mass transfer inside fluid spheres were presented by Johnson and Hamielec (1960), Sideman and Shabtai (1964) and Johns, Beckmann and Ellis (1965). This review will describe two simple mass transfer models, which can be adapted to fluid spheres, as well as correlations which have been proposed for mass transfer in stagnant, circulating, and oscillating dispersed phases.

2.2.1. Mass Transfer Without Chemical Reaction. Whitman (1923) visualized the mass transfer process as molecular diffusion across a stagnant film of empirically determined thickness. This model, which has become known as the film theory, implies a steady state concentration profile.

To avoid the necessity of empirical determination of the film thickness and to allow for unsteady concentration profiles, Higbie (1935) solved for non-steady state mass transfer, in which the stagnant film is assumed to be of infinite extent. This model, known as the penetration theory, can predict the time averaged flux into a stagnant
sphere with an error of less than three per cent for dimensionless times less than 0.001. The standard for comparison was the equation for unsteady state mass transfer in a stagnant fluid sphere as solved by Newman (1931).

The first theoretical prediction of mass transfer in a circulating fluid sphere was made by Kronig and Brink (1950). They assumed fluid velocities inside the sphere to be as derived by Hadamard. Kronig and Brink further assumed that the fluid velocities were much faster than the diffusional process, so that the concentration in a fluid sphere does not vary along any streamline.

At smaller fluid velocities inside the fluid sphere the concentration would vary along each Hadamard streamline. Johns and Beckmann (1966) solved numerically for mass transfer in a circulating fluid drop by assuming the velocity profile was the same as that derived by Hadamard. For Peclet numbers larger than one hundred, their numerical solution agrees with the results obtained by Kronig and Brink (1950). For a Peclet number of zero, the solution of Johns and Beckmann agrees with the stagnant sphere solution by Newmann (1931). Several other theoretical results for mass transfer inside fluid spheres are given in the review by Sideman and Shabtai (1964). In addition, Skelland and Wellek (1964) present an empirical correlation for mass transfer inside circulating liquid drops, which accounts for deviation of experimental results from the available theoretical relationships.

Mass transfer inside an oscillating dispersed phase takes place primarily by turbulent convection. A review of theoretical and empirical correlations for mass transfer in oscillating liquid drops is presented by Brunson and Wellek (1970b). This review found one of the
empirical correlations by Skelland and Wellek (1964) for oscillating drops to be the best available relation for predicting mass transfer data.

2.2.2. Mass Transfer With First-Order Chemical Reaction. All of the theoretical models for mass transfer without chemical reaction presented in section 2.2.1. have been extended to account for mass transfer accompanied by a first-order or pseudo first-order chemical reaction. The film theory for mass transfer with first-order reaction was first solved by Hatta (1932).

The mathematical equation for mass transfer with first-order chemical reaction, according to the penetration theory is identical to the equation for the conduction of heat along a long, thin rod, from which heat is lost at the surface and at a rate proportional to its temperature. The solution to the heat transfer problem was presented by Carslaw and Jaeger (1959). The solution was adapted for mass transfer by Danckwerts (1950).

With advanced mathematical techniques, the other models for mass transfer, presented in this review, could be extended for mass transfer with simultaneous chemical reaction by considering the rate of reaction as a negative generation term in the equation of continuity for the individual component. However, this approach is not necessary for first-order reactions. Danckwerts (1951) proposed a transformation for finding the rate of mass transfer with first-order chemical reaction, when the rate of mass transfer without chemical reaction is known. The only restriction on this transformation is that the velocity profiles not be time dependent. Danckwerts went on to apply his transformation to both the Newman solution for a stagnant sphere and the Kronig and Brink
solution for a fully circulating fluid sphere. Andoe (1968) bridged the gap between the stagnant sphere and fully circulating sphere solutions for mass transfer with first-order chemical reaction by recalculating the Johns and Beckmann (1966) solution for mass transfer without chemical reaction. He then used the Danckwerts transformation to obtain mass transfer indices for the case of a concurrent first-order chemical reaction. The same problem was solved independently by Watada et al. (1970). The limitation of steady state velocity profiles for the Danckwerts transformation was overcome by Stewart (1968).

Wellek, Andoe and Brunson (1971) proposed a special adaptation of the penetration theory to apply to oscillating liquid drops. It predicts mass transfer accompanied by first-order chemical reaction.

2.2.3. Mass Transfer With Second-Order Chemical Reaction. Prior to the initiation of this work, the only mass transfer models, which had been studied in conjunction with a second-order chemical reaction, were the film theory and the penetration theory. Two books have since been published which review both film theory and penetration theory mass transfer with chemical reaction (Astarita, 1967; Danckwerts, 1970). Both the film theory and the penetration theory as described in this section apply strictly to mass transfer across flat interfaces.

Van Krevelen and Hoftijzer (1948) found an approximate solution for the film theory with chemical reaction by assuming the presence of a reaction film, as well as a mass transfer film. The correlation derived by Van Krevelen and Hoftijzer has been altered by most modern reviews (Brian, et al., 1961; Astarita, 1967; and Danckwerts, 1970). A further discussion of this revised correlation is given in Section IV. Peaceman (1951) numerically solved the differential equations for film
theory mass transfer with second-order chemical reaction. He showed that the revised Van Krevelen and Hoftijzer approximation deviated from the true solution by less than eight per cent. Thus, the approximation is sufficiently accurate for engineering work. However, the equation is implicit, and thus, difficult to use. Santiago and Farina (1970) formulated explicit correlations for the film theory for the practically important ranges of parameters.

Several investigators have studied the differential equations for penetration theory mass transfer with second-order chemical reaction. Perry and Pigford (1953) obtained numerical solutions to the simultaneous partial differential equations for mass transfer with a reversible chemical reaction. Their solutions included, as a special case, mass transfer with an irreversible second-order chemical reaction, Brian, et al. (1961) later resolved the penetration model for irreversible chemical reaction and presented results for a greater range of parameters. A final numerical work by Pearson (1963) presented results for the complete range of independent variables.

Gilliland, et al. (1958) and Hikita and Asai (1964) presented approximate equations for penetration theory mass transfer with second-order chemical reaction. However, both of the correlations are implicit and thus, difficult to use. Kishinevskii (1965) obtained an approximate solution for the penetration theory approach with a second-order reaction. Later Kishinevskii and Kornienko (1966) empirically corrected this analytical solution to fit the numerical solution of Brian, et al.

Astarita (1966, 1967) listed four regimes for mass transfer with simultaneous reaction. The purpose of these regimes is to indicate values of independent variables for which asymptotic solutions are
valid. Only three of the regimes are important for mass transfer considerations. These regimes are (1) for a chemical reaction which is infinitely fast compared to the mass transfer process; (2) a chemical reaction which is so slow that the process is essentially mass transfer without reaction; and (3) concentration levels, such that the chemical reaction is pseudo first-order. The solution for the two latter regimes have been discussed in sections 2.2.1. and 2.2.2. respectively.

The solution for mass transfer with instantaneous chemical reaction can be obtained from the corresponding solution for mass transfer without chemical reaction by using the transformation derived by Toor (1962). The same transformation was also derived by Brunson and Wellek (1970a) with more definitive statements of the applicable boundary conditions. The transformation, obtained from both derivations, is dependent on the assumption that the diffusivities of both reactants are equal. Danckwerts (1950) obtained an analytical expression for penetration theory mass transfer with instantaneous chemical reaction. Nijsing (1959) presented a simplification of the Danckwerts results which is much easier to use. The Nijsing simplification is thought to be valid for conditions which approach pseudo first-order reaction, if the diffusivities of the two reactants are not greatly different.

For the intermediate regions, where none of the asymptotic solutions are valid, Yeramian, et al. (1970) suggest a solution for mass transfer with second-order chemical reaction for any geometry or fluid flow model. It is based on the corresponding solutions for first-order reaction and no reaction. This solution also depends on the assumption that the diffusivities of the two reactants are equal.
2.3. Previous Experimental Work

Several workers have studied experimentally liquid extraction without chemical reaction in single drops. Among the more notable are Garner and Skelland (1954), Johnson and Hamielec (1960), and Skelland and Wellek (1964).

Andoe (1968) also studied liquid extraction by single drops this time with a simultaneous first-order chemical reaction. He found the rates of mass transfer to be as much as an order of magnitude greater than expected. Andoe attributed this rapid mass transfer to spontaneous turbulent mixing at the interface. Sherwood and Wei (1957) studied forty different systems, which exhibit interfacial turbulence, and were among the first to visually observe the phenomena. They were able to detect at least three types of turbulence; rippling, drop formation, and spontaneous emulsification. Various criteria have been developed to predict the presence of interfacial turbulence (Sterling and Scriven, 1959; Berg and Morig, 1969; and Ostroviskii, et al., 1967). In general, the criteria are contradictory and are not supported by experimental data (Orell and Westwater, 1962). Seto, et al. (1971) studied mass transfer of low molecular weight esters into sodium hydroxide solutions. They found interfacial turbulence at the interface at long contact times. There was no turbulence at short times. Fernandes and Sharma (1967) found that a stable interface was formed by n-hexyl formate and NaOH solution. Based on previous observations with esters, no interfacial turbulence was anticipated for n-pentyl formate at small contact times.

Three investigators have studied liquid extraction with second-order chemical reaction inside the dispersed phase. Sharma and Nanda (1968) studied swarms of water drops, containing sodium hydroxide, as
they rise through methyl dichloroacetate. They correlated their data with the film theory approximation for second-order reaction, using experimentally determined physical mass transfer rates. No estimation of the contact time was made. Tyroler, et al. (1971) studied aqueous sodium hydroxide drops, falling through cyclohexanol containing acetic acid. They located the reaction surface photographically but did not measure mass transfer rates. Watada (1968) studied aqueous sodium hydroxide drops falling through butyl lactate and through ethyl acetate. Both systems undergo obvious interfacial turbulence, and some of the drops even broke up due to surface tension effects.
III. MATHEMATICAL MODEL

Mass transfer into a fluid sphere which is falling or rising in a continuous fluid medium, can be described by a combination of the equations for fluid flow and heat transfer. The equations of continuity for all components of interest are also required. In general, all of the equations used to describe the mass transfer process must be solved simultaneously.

3.1. Description of Model

The mathematical model for any given problem consists of a set of algebraic and/or differential equations together with assumption made to facilitate the solution of the problem and the boundary conditions, imposed upon the equations which describe the problem. The assumptions and boundary conditions will be listed with their respective differential equations in this section. The validity of these assumptions will be discussed in Section VII.

The geometry of the model is shown in figure 3.1. Component \( a \), initially in the continuous phase, diffuses into the fluid sphere where it reacts with component \( b \), initially in the fluid sphere. The concentrations will be considered symmetrical about the polar axis. This approximation makes it possible to consider only the cross section of a sphere. Any location within the cross section may be specified by the radius, \( r \), and the angle, \( \theta \).

3.1.1. Heat Transfer. The temperature was assumed to be uniform throughout the dispersed phase. In order for this to be true for mass transfer with chemical reaction, it is necessary that:

The heat effects of solute transfer across the interface be negligible.

The heat of reaction is negligible.
Figure 3.1. Geometrical Model
3.1.2. Velocity Profile. The velocity profile within a flowing fluid is dependent upon physical properties which include the viscosity and density of the fluid. Since both viscosity and density are dependent on concentration, the equations for fluid flow can be solved, independently of the equations of mass transfer, only if concentration changes within the system are small. Hadamard (1911) solved the linearized Navier-Stokes equation for flow in and around a fluid sphere in creeping flow (Reynolds number less than one). Hadamard's velocity profiles within the sphere are

\[
v_r = -\frac{V_t}{2} \frac{\mu_c}{\mu_c + \mu_d} (1 - R^2) \cos \theta \tag{3.1}
\]

\[
v_\theta = \frac{V_t}{2} \frac{\mu_c}{\mu_c + \mu_d} (1 - 2 R^2) \sin \theta \tag{3.2}
\]

The streamlines described by equations (3.1) and (3.2) are shown in figure 3.2. The Hadamard development is dependent on the following assumptions:

- The drop shape is spherical.
- The continuous phase is infinitely large.
- The velocity field is independent of time.
- Concentration changes in the drop do not appreciably affect the fluid properties.
- The velocity profile is symmetrical about the polar axis.
- The velocity field is continuous at the phase boundary.
- The velocity field satisfies the linearized equations of motion (Reynolds number less than one).

3.1.3. Mass Transfer. The equations of continuity for individual solutes are given by Bird, et al. (1963). If there is symmetry about the polar axis and if the second-order reaction acts as a negative generation term, the mass balance equations for components \( a \) and \( b \) may be
Figure 3.2. Hadamard Streamlines
expressed as shown by equations (3.3) and (3.4).

\[
\frac{\partial C_a}{\partial t} + v_r \frac{\partial C_a}{\partial r} + \frac{v_\theta}{r} \frac{\partial C_a}{\partial \theta} = D_a \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial C_a}{\partial r} \right) \right] + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial C_a}{\partial \theta} \right) - k_2 C_a C_b \quad (3.3)
\]

and

\[
\frac{\partial C_b}{\partial t} + v_r \frac{\partial C_b}{\partial r} + \frac{v_\theta}{r} \frac{\partial C_b}{\partial \theta} = D_b \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial C_b}{\partial r} \right) \right] + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial C_b}{\partial \theta} \right) - Z k_2 C_a C_b \quad (3.4)
\]

The initial conditions for equations (3.3) and (3.4) are

\[
C_a(r, \theta, 0) = 0 \quad C_b(r, \theta, 0) = C_{b_0} \quad (3.5)
\]

The boundary conditions are, at the surface of the sphere

\[
C_a(a, \theta, t) = C_{as} \quad \frac{\partial C_b}{\partial r} (a, \theta, t) = 0 \quad (3.6)
\]

and at the center of the sphere

\[
\frac{\partial C_a}{\partial r} (0, \theta, t) = 0 \quad \frac{\partial C_b}{\partial r} (0, \theta, t) = 0 \quad (3.7)
\]

The angular boundary conditions stem from the symmetry of the sphere.

\[
\frac{\partial C_a}{\partial \theta} (r, 0, t) = 0 \quad \frac{\partial C_b}{\partial \theta} (r, 0, t) = 0 \quad (3.8)
\]
\[ \frac{\partial C_a}{\partial \theta} (r, \pi, t) = 0 \quad \frac{\partial C_b}{\partial \theta} (r, \pi, t) = 0 \]  

In addition to the assumptions listed in sections 3.1.1. and 3.1.2., the use of equations (3.3) to (3.9) implies:

The solute being transferred reacts irreversibly with a solute in the dispersed phase.

The reaction may be described by a second-order kinetics relationship.

The dispersed phase side of the interface is saturated with solute.

The solute initially in the dispersed phase is not soluble in the continuous phase.

### 3.2. Solution of Concentration Profile

There is no known means to obtain an analytical solution for equations (3.3) and (3.4). The following is a description of a numerical method to obtain concentration profiles.

**3.2.1. Dimensionless Equations.** The first step in obtaining the numerical solution of a problem is to rewrite the differential equations in terms of dimensionless groups. The solution of a problem for one set of dimensionless groups applies for any combination of dimensional variables which correspond to that set of dimensionless groups.

The dimensionless groups which are pertinent to this study are:

\[ \tau = \frac{D_a t}{a^2} \]  
\[ R = \frac{r}{a} \]  
\[ \theta = \theta \]
dimensionless parameters

\[ R_c = \frac{Z C_a s}{C_{bo}} \]  (3.13)

\[ R_D = \frac{D_b}{D_a} \]  (3.14)

\[ k_R = \frac{k_2 a^2 C_{bo}}{D_a} \]  (3.15)

\[ N_{Pe} = \frac{a v_t}{2 D_a} \frac{\mu_c}{\mu_d + \mu_c} \]  (3.16)

dependent variables

\[ A = \frac{C_a}{C_{as}} \]  (3.17)

\[ B = \frac{C_b}{C_{bo}} \]  (3.18)

and the dimensionless velocities

\[ \frac{V_R}{V_t} = \frac{v_r}{V_t} \frac{\mu_c + \mu_d}{\mu_c} \]  (3.19)

\[ \frac{V_\theta}{V_t} = \frac{v_\theta}{V_t} \frac{\mu_c + \mu_d}{\mu_c} \]  (3.20)

In terms of the dimensionless numbers (3.10) through (3.20), equations (3.3) and (3.4) with their initial and boundary conditions become

\[ \frac{\partial A}{2\tau} = -N_{Pe} \left( V_R \frac{\partial A}{\partial R} + \frac{V_\theta}{R} \frac{\partial A}{\partial \theta} \right) + \frac{\partial^2 A}{\partial R^2} + \frac{2}{R} \frac{\partial A}{\partial R} \]

\[ + \frac{1}{R^2} \frac{\partial^2 A}{\partial \theta^2} + \cot \theta \frac{\partial A}{\partial \theta} - k_R A B \]  (3.21)

and
The initial conditions become

\[ A(R,S,O) = 0 \]

The boundary conditions become

\[ A(l,S,T) = 1 \]
\[ \partial A / \partial R (O,S,T) = 0 \] or \[ \partial A / \partial R (R,O,T) = 0 \]
\[ \partial B (R,TC,T) = 0 \] or \[ \partial B (R,TC,T) = 0 \]

where

\[ V_R = -(1 - R^2) \cos \theta \] \hspace{1cm} (3.28)
\[ V_\theta = (1 - 2 R^2) \sin \theta \] \hspace{1cm} (3.29)

Equations (3.21) and (3.22) with conditions (3.23) through (3.27) and the velocity profiles (3.28) and (3.29) constitute the dimensionless statement of the mathematical model to be solved.

3.2.2. Calculational Procedure. A numerical solution does not give a continuous solution. The concentration is defined only at the grid points. A grid point is identified by the indices \( i, j, \) and \( k. \) The symbol \( i \) is the index for the radial direction.

\[ R_i = i \Delta R \] \hspace{1cm} (3.30)
The symbol $j$ is the index for the angular direction.

$$\theta_j = j\Delta\theta$$  \hspace{1cm} (3.31)

The symbol $k$ is the index in the time dimension.

$$\tau_k = k\Delta\tau$$  \hspace{1cm} (3.32)

The number of increments in the radial direction is $nr$.

$$\Delta R = 1.nr$$  \hspace{1cm} (3.33)

The number of increments in the angular direction is $mr$.

$$\Delta\theta = \pi/mr$$  \hspace{1cm} (3.34)

$\Delta\tau$ is chosen as large as possible without sacrificing accuracy. The dimensionless concentrations at the grid point $R_i$, $\theta_j$, $\tau_k$ are written as $A_{i,j,k}$ and $B_{i,j,k}$.

The number of grid points in the radial direction, $nrr$, is one greater than the number of increments in the radial direction, $nr$. The number of grid points in the angular direction, $mrr$, is one greater than the number of increments in the angular direction, $mr$.

The method of solution was a modification of the numerical method developed by DuFort and Frankel (1953). This numerical method was chosen, because an explicit expression is obtained to express the concentration at a future time step. The DuFort-Frankel method requires a knowledge of the concentration at two previous time steps. Therefore, concentrations at three consecutive time steps are all that are used in any numerical calculation. To conserve storage space in the computer, the concentrations were redefined after each time step, so that only three time steps need be stored in the computer. The concentrations currently being calculated are designated $A_{3i,j}$ and $B_{3i,j}$. The concentrations at the two previous time steps are referred to as $A_{1i,j}$ and $A_{2i,j}$ for component $a$ and $B_{1i,j}$ and $B_{2i,j}$ for component $b$. 
The calculational procedure is shown in figure 3.3. The four grid points at the present time step and one at the past time step, all marked by circles, are used to calculate the concentration at the future grid point marked by an x.

3.2.3. Initial Conditions. At a dimensionless time equal to zero, the concentrations are evaluated from the initial and boundary condition expressions given by equations (3.23) and (3.24).

\[ Bl_{i,j} = 1 \quad 1 \leq i \leq \text{nrr} \]
\[ 1 \leq j \leq \text{mrr} \]

and

\[ Al_{i,j} = 0 \quad 1 \leq i \leq \text{nr} \]
\[ 1 \leq j \leq \text{mrr} \]

also

\[ Al_{i,j} = 1 \quad i = \text{nrr} \]
\[ 1 \leq j \leq \text{mrr} \]

Since the DuFort-Frankel method requires concentrations for two previous time steps, it is necessary to use another method to approximate concentrations at the first dimensionless time step. Andoe (1968) used a numerical method to calculate the concentration profile at \( \Delta T \). Inaccuracy in his solution was encountered at small dimensionless times. The forward difference method used by Andoe had the inherent error that it forced the concentration profile at \( \Delta T \) to be identical to the concentration profile at \( \tau = 0 \), except at one radial increment from the surface of the sphere. It is possible to obviate this assumption if, instead, the reaction for component \( a \) is approximated as pseudo first-order for all times up to \( \Delta T \). The pseudo first-order approximation is
Figure 3.3. Calculation Scheme for the Numerical Solution of the Partial Differential Equations
a more valid assumption than the assumption used by Andoe, because the change in the concentration of component \( b \) with time is less than the change in the concentration of component \( a \) with distance, at small times and near the surface.

At very small times, the penetration theory may be used to describe mass transfer in a sphere (Johns and Beckman, 1966). Therefore, the concentration of component \( a \) at the first time step is approximated by the penetration theory with chemical reaction as solved by Carslaw and Jaeger (1959, page 134).

\[
A_{2i,j} = \frac{1}{2} \exp \left( (R_i - 1) \sqrt{k_R} \right) \text{erfc} \left( \frac{1 - R_i}{2 \sqrt{\tau}} - \sqrt{k_R \tau} \right) + \\
\frac{1}{2} \exp \left( (1 - R_i) \sqrt{k_R} \right) \text{erfc} \left( \frac{1 - R_i}{2 \sqrt{\tau}} + \sqrt{k_R \tau} \right)
\]  

(3.38)

For component \( b \) at the first time step, an implicit finite difference method was used. The Crank-Nicolson method (Smith, 1965, p. 17) uses the following finite difference approximations.

\[
\frac{\partial B}{\partial t} = \frac{B_{2i,j} - B_{1i,j}}{\Delta t}
\]  

(3.39)

\[
\frac{\partial B}{\partial R} = \frac{1}{4\Delta R} \left( B_{1i+1,j} - B_{1i-1,j} + B_{2i+1,j} - B_{2i-1,j} \right)
\]  

(3.40)

\[
\frac{\partial^2 B}{\partial R^2} = \frac{1}{2(\Delta R)^2} \left( B_{1i+1,j} - 2B_{1i,j} + B_{1i-1,j} + B_{2i+1,j} - 2B_{2i,j} + B_{2i-1,j} \right)
\]  

(3.41)

and

\[
A B = \frac{1}{2} \left( A_{1i,j} B_{1i,j} + A_{2i,j} B_{2i,j} \right)
\]  

(3.42)
Two ratios of time and space increments evolve when the finite difference approximations (3.39) through (3.42) are substituted into equation (3.22).

\[ S = \frac{2\Delta T}{(\Delta R)^2} \]  

(3.43)

and

\[ S_2 = \frac{\Delta T}{\Delta R} \]  

(3.44)

The Crank-Nicolson numerical method results in a tridiagonal system of equations.

\[-R_D \left( \frac{S}{4} + \frac{S_2}{2 R_i} \right) B_{2i+1,j} + \left( 1 + \frac{R_D S}{2} + \frac{R_c k R \Delta T}{2} A_{i,j} \right) B_{2i,j} \]

\[-R_D \left( \frac{S}{4} - \frac{S_2}{2 R_i} \right) B_{2i-1,j} = 1 - \frac{R_c k R \Delta T}{2} A_{i,j} \]  

(3.45)

for \( i \neq nrr \).

At the surface of the sphere, the boundary condition becomes

\[ B_{2nrr+1,j} = B_{2nrr-1,j} \]  

(3.46)

Thus, at the surface

\[ B_{2i,j} \left( 1 + \frac{R_D S}{2} + \frac{R_c k R \Delta T}{2} A_{i,j} \right) - \frac{R_D S}{2} B_{2i-1,j} = \]

\[ 1 - R_c k R \Delta T / 2 \]  

for \( i = nrr \)  

(3.47)

This system of equations was solved by reducing the tridiagonal matrix.

The Crank-Nicolson method does not take into account any variation in the angular direction. However, it is still an improvement over the method of Andoe (1968) and is considered adequate as an approximation for the concentrations at the first time step.
3.2.4. Finite Difference Equations. For dimensionless times
greater than the first time step, equations (3.21) and (3.22) were
solved by the two step explicit method proposed by DuFort and Frenkel
(1953). The unique feature of the DuFort and Frenkel numerical method
is the finite difference approximation for the partial derivatives.

\[
\frac{\partial A}{\partial T} = \frac{A_{i,j}^3 - A_{i,j}^1}{2\Delta T} \quad (3.48)
\]

\[
\frac{\partial A}{\partial R} = \frac{A_{i+1,j}^2 - A_{i-1,j}^2}{2\Delta R} \quad (3.49)
\]

\[
\frac{\partial A}{\partial \Theta} = \frac{A_{i,j+1}^2 - A_{i,j-1}^2}{2\Delta \Theta} \quad (3.50)
\]

\[
\frac{\partial^2 A}{\partial R^2} = \frac{A_{i+1,j}^2 - 2A_{i,j}^1 + A_{i-1,j}^2 - A_{i,j}^3 + A_{i-1,j}^2}{(\Delta R)^2} \quad (3.51)
\]

\[
\frac{\partial^2 A}{\partial \Theta^2} = \frac{A_{i,j+1}^2 - 2A_{i,j}^1 + A_{i,j-1}^2 - A_{i,j}^3 + A_{i,j-1}^2}{(\Delta \Theta)^2} \quad (3.52)
\]

The substitutions for the derivatives of component \( b \) are analogous to
equations (3.48) through (3.52).

For the nonlinear reaction term, DuFort and Frenkel suggest a space
average approximation. Due to the boundary conditions for this problem,
this type of substitution led to an unstable numerical method. However,
a time average for part of the nonlinear term did lead to a stable solu-
tion. The substitution for equation (3.21) was

\[
A \cdot B = \left(\frac{A_{i,j}^1 + A_{i,j}^3}{2}\right) B_{2i,j} \quad (3.53)
\]

and for equation (3.22)
\[ A B = A_{2i,j} \left( \frac{B_{1i,j} + B_{3i,j}}{2} \right) \] (3.54)

In addition to equations (3.43) and (3.44), two more ratios of increments become important.

\[ p = \frac{2 \Delta \tau}{(\Delta \theta)^2} \] (3.55)

\[ p_2 = \frac{\Delta \tau}{\Delta \theta} \] (3.56)

The finite difference form of equation (3.21) for component \( a \) is

\[ A_{3i,j} \left( 1 + S + \frac{P}{R_1} + k_\tau B_{2i,j} \right) = \]

\[ A_{1i,j} \left( 1 - S - \frac{P}{R_1} - k_\tau B_{2i,j} \right) + \]

\[ A_{2i+1,j} \left( \frac{2 S_2}{R_1} - S_2 N_\text{Pe} V_{R i,j} + S \right) + \]

\[ A_{2i-1,j} \left( S - \frac{2 S_2}{R_1} + S_2 N_\text{Pe} V_{R i,j} \right) + \]

\[ A_{2i,j+1} \left( \frac{P}{R_1^2} \cot \theta_j - \frac{P_2 N_\text{Pe} V_{\theta i,j}}{R_1} \right) + \]

\[ A_{2i,j-1} \left( \frac{P}{R_1^2} - \frac{P_2 \cot \theta_j}{R_1^2} + \frac{P_2 N_\text{Pe} V_{\theta i,j}}{R_1} \right) \] (3.57)

The same substitutions in equation (3.22) yield the finite difference equation for component \( b \).

\[ B_{3i,j} \left( 1 + S_{RD} + \frac{P \cdot RD}{R_1^2} + R_c k_\tau A_{2i,j} \right) = \]
Equations (3.57) and (3.58) are valid for all interior points and at times equal to or greater than the second time step.

At the center of the sphere, the concentration gradients are zero due to the assumption of symmetry in the sphere. This symmetry is expressed in the boundary conditions (3.25). At the center, all angular dependence becomes meaningless. At the center, one term in equation (3.21) becomes indeterminant.

\[
\frac{1}{R} \frac{\partial^2 A}{\partial R^2} \bigg|_{R = 0} = \text{indeterminant} \tag{3.59}
\]

The indeterminant can be resolved by the L'Hospital rule

\[
\lim_{R \to 0} \frac{1}{R} \frac{\partial A}{\partial R} = \frac{\partial^2 A}{\partial R^2} \tag{3.60}
\]

Thus, at the center, equation (3.21) becomes

\[
\frac{\partial A}{\partial \tau} = 3 \frac{\partial^2 A}{\partial R^2} - k_R A B \tag{3.61}
\]
An analogous limiting process for equation (3.22) results in the following expression for the time derivative of the dimensionless concentration of component b

\[ \frac{\partial \bar{b}}{\partial t} = 3R \frac{\partial^2 \bar{b}}{\partial \bar{r}^2} - R_c k_R A \bar{b} \quad \text{(3.62)} \]

The finite difference form of equation (3.61), for component a, is

\[ A^{3}_{1,j} (1 + 3 S + k_R \Delta \tau \quad A_{21,j}) = 6 S A_{22,j} + \]
\[ A^{1}_{1,j} (1 - 3 S - k_R \Delta \tau \quad B_{21,j}) \quad \text{(3.63)} \]

The finite difference form of equation (3.62), for component b, is

\[ B^{3}_{1,j} (1 + 3 R_D S + R_c k_R \Delta \tau \quad A_{21,j}) = \]
\[ B^{1}_{1,j} (1 - 3 R_D S - R_c k_R \Delta \tau \quad A_{21,j}) + \]
\[ 6 R_D S B^{2}_{2,j} \quad \text{(3.64)} \]

At the surface, the concentration of component a is a constant.

\[ A^{3}_{nrr,j} = 1 \quad \text{(3.65)} \]

At the surface, the finite difference equation for component b can be reduced. The boundary condition given by equation (3.24) leads to

\[ B^{2}_{nrr+1,j} = B^{2}_{nrr-1,j} \quad \text{(3.66)} \]

The concentration of component b at the surface can thus be calculated as

\[ B^{3}_{nrr,j} (1 + P R_D + R_D S + R_c k_R \Delta \tau) = \]
\[ B_{nrr,j}^1 (1 - P_R^D \cdot R_D^D S - R_c k_R \Delta \tau) + \]
\[ B_{nrr,j+1}^2 (P_R^D + R_D^D P_2 \cot \theta_j - N_{P_2} \theta_{i,j}^2) + \]
\[ B_{nrr,j-1}^2 (P_R^D - R_D^D P_2 \cot \theta_j + N_{P_2} \theta_{i,j}^2) + \]
\[ 2 R_D^D S B_{nrr-1,j}^2 \]  

At each of the angular limits, the boundary conditions again contain terms which are indeterminant. Again, the application of L'Hospital's limiting process is straightforward.

\[ \lim_{\theta \to 0 \text{ or } \pi} \cot \theta \frac{\partial^2 A}{\partial \theta^2} \]  

The finite difference approximation for either equation (3.26) or (3.27) is

\[ A_{i+1,j}^2 = A_{i,j+1}^2 \]  

The special conditions given by equations (3.67) and (3.68) reduce the finite difference equation (3.57) for component \( \theta \) at the angular limits to

\[ A_{i,j}^3 (1 + \frac{2 P_{R_1}}{R_1^D} + S + k_R \Delta \tau B_{i,j}^2) = \]
\[ A_{i,j}^1 (1 - \frac{2 P_{R_1}}{R_1^D} - S - k_R \Delta \tau B_{i,j}^2) + \]
\[ A_{i+1,j}^2 (S + \frac{2 S_2}{R_1^D} - S_2 N_{P_2} V_R^i,j) + \]
\[ A_{i-1,j}^2 (S - \frac{2 S_2}{R_1^D} + S_2 N_{P_2} V_R^i,j) + \]
\[ A_{i,j+1}^2 \left( \frac{4 P_{R_1}}{R_1^D} \right) \]  

The plus or minus sign on the subscript of the last term of the above equation is for the two angular limits. When \( j \) is one, the sign
is positive. When \( j \) is \( mrr \), the sign is negative.

The finite difference equation for component \( b \) at the angular limits follows by the same logic as for component \( a \).

\[
B_{3i,j} (1 + \frac{2 \ P \ R_D}{R_i^2} + S \ R_D + R_c \ k_{R,AT} A_{2i,j}) = \\
B_{1i,j} (1 - \frac{2 \ P \ R_D}{R_i^2} - S \ R_D - R_c \ k_{R,AT} A_{2i,j}) + \\
B_{2i+1,j} (S \ R_D + \frac{2 \ S_2 \ R_D}{R_i} - S_2 \ N_{Pe} V_{R,i,j}) + \\
B_{2i-1,j} (S \ R_D - \frac{2 \ S_2 \ R_D}{R_i} + S_2 \ N_{Pe} V_{R,i,j}) + \\
B_{2i,j+1} (\frac{4 \ P \ R_D}{R_i^2})
\]

Equation (3.71), like the equation for component \( a \), applies at both angular limits.

The only grid points which remain to be specified are the two points to which both the surface boundary condition and the angular boundary condition apply. These points are located at either end of the polar axis. At these points

\[
B_{3nrr,j} (1 + 2 \ P \ R_D + S \ R_D + R_c \ k_{R,AT}) = \\
B_{1nrr,j} (1 - 2 \ P \ R_D - S \ R_D - R_c \ k_{R,AT}) + \\
2 \ S \ R_D B_{2nrr-1,j} + 4 \ P \ R_D B_{2i,j+1}
\]

The complete computer program used to solve the circulating drop model is given in Appendix A.

### 3.3. Calculation of Mass Transfer Indices

The concentration profile calculated by the finite difference method
described in the preceding sections was used to calculate various dimensionless quantities which indicate the extent of the mass transfer process.

3.3.1. Average Concentration of Component $a$. The space averaged concentration is defined by

$$\overline{A} = \frac{1}{V} \int_V A \, dV$$

(3.73)

For an axisymmetric sphere the space averaged concentration becomes

$$\overline{A} = \frac{3}{2} \int_0^1 \int_0^1 A R^2 \sin \theta \, dR \, d\theta$$

(3.74)

Equation (3.74) can be evaluated by the trapezoidal rule.

$$\overline{A} = \frac{3}{2} \Delta R \Delta \theta \sum_{j=2}^{mR} \sin \theta_j \left( \frac{A_{nR, i}}{2} + \sum_{i=2}^{nR} A_{i, j} R_i^2 \right)$$

(3.75)

3.3.2. Average Concentration of Component $b$. The method to average the concentration of component $b$ is analogous to the method described for component $a$ in section 3.3.1.

$$\overline{B} = \frac{3}{2} \Delta R \Delta \theta \sum_{j=2}^{mR} \sin \theta_j \left( \frac{B_{nR, i}}{2} + \sum_{i=2}^{nR} B_{i, j} R_i^2 \right)$$

(3.76)

3.3.3. Total Mass Transferred. The total amount of component $a$ transferred into the dispersed phase is the sum of the amount of component $a$ present and the amount of component $a$ which has already reacted with component $b$.

The amount of component $a$ per unit volume of dispersed phase is the average concentration, $\overline{A}$. The amount of component $a$ which has reacted per unit volume of dispersed phase is related to the depletion
of component \( b \) by the stoichiometric ratio. Therefore, the total mass transferred is given by

\[
\bar{A}_{\text{mt}} = \bar{A} + \frac{(1-B)}{R_c}
\]  

(3.77)

### 3.3.4. Flux of Component \( a \)

The instantaneous flux of component \( a \) can be calculated from the concentration gradient of \( a \) at the surface or from the rate of increase of the total mass transferred. By the concentration gradient

\[
N_a = -\frac{D_a}{S_0} \int_{S_0} \left. \frac{\partial C_a}{\partial r} \right|_{r=a} dS_0
\]  

(3.78)

The dimensionless form of equation (3.78) is

\[
N = -\frac{2}{S_0} \int_{S_0} \left. \frac{\partial A}{\partial r} \right|_{r=1} dS_0
\]  

(3.79)

For a sphere this becomes

\[
N = -\int \left. \frac{\partial A}{\partial R} \right| \sin \theta d\theta
\]  

(3.80)

The above can be evaluated by a finite difference approximation for the derivative followed by integration by the trapezoidal rule.

\[
N = \frac{\Delta \theta}{2 \Delta R} \sum_{j=2}^{mr} \sin \theta_j (3 - 4 A_{nr,j} + A_{nr-1,j})
\]  

(3.81)

The flux of component \( a \) can be calculated from the rate of change of the total mass transferred with time.

\[
N_a = \frac{V}{S_0} \frac{d\bar{C}_{\text{mt}}}{dt}
\]  

(3.82)
From equation (3.82) the dimensionless flux is

\[ N = \frac{2}{3} \frac{d\bar{A}_{mt}}{d\tau} \]  
(3.83)

In finite difference form, Equation (3.83) becomes

\[ N = \frac{2}{3\Delta\tau} \left( \bar{A}_{mt}\bigg|_{\tau} - \bar{A}_{mt}\bigg|_{\tau + \Delta\tau} \right) \]  
(3.84)

As an internal check for the computer program, the instantaneous flux was calculated by both equations (3.81) and (3.84).

3.3.5. Time Averaged Flux of a. The time averaged flux of \( a \) is defined by

\[ \bar{N}_a = \frac{1}{t} \int_0^t N_a \, dt \]  
(3.85)

From the second method to calculate the flux of component \( a \) (Equation 3.82) the time averaged flux of component \( a \) can be found.

\[ \bar{N}_a = \frac{\bar{C}_{mt} V}{t \bar{S}_o} \]  
(3.86)

In terms of dimensionless variables, equation (3.86) becomes

\[ \bar{N} = \frac{2}{3} \frac{\bar{A}_{mt}}{\tau} \]  
(3.87)

3.3.6. Sherwood Number. The Sherwood number is defined as

\[ N_{Sh} = \frac{N_a}{C_{as} - C_a} \]  
(3.88)

In dimensionless terms, the Sherwood number becomes

\[ N_{Sh} = \frac{N}{1 - \bar{A}} \]  
(3.89)
3.3.7. Time Averaged Sherwood Number. The time averaged Sherwood number is defined

\[ \bar{N}_{Sh} = \frac{1}{t} \int_0^t N_{Sh} \, dt \]  
(3.90)

In dimensionless terms, equation (3.90) is written,

\[ \bar{N}_{Sh} = \frac{1}{\tau} \int_0^\tau N_{Sh} \, d\tau \]  
(3.91)

For calculational purposes the integral may be divided into two parts.

\[ \bar{N}_{Sh} = \frac{1}{\tau} \left( \int_0^{\Delta\tau} N_{Sh} \, d\tau + \int_{\Delta\tau}^\tau N_{Sh} \, d\tau \right) \]  
(3.92)

The division of the integral is necessary, because the numerical method is unable to predict accurately the large Sherwood numbers encountered at very small contact times. The first integral can be evaluated by assuming that there is negligible depletion of component \( b \) during the first time step. For negligible depletion the Sherwood number would be the same as for a pseudo first-order reaction. Andoe (1968) found that in circulating spheres mass transfer with pseudo first-order reaction can be approximated at short contact times by the penetration theory. Thus, the first integral can be approximated thus

\[ \int_0^{\Delta\tau} N_{Sh} \, d\tau = 4 \sqrt{\frac{\Delta\tau}{\pi}} \left( 1 + \frac{k_R \Delta\tau}{3} \right) \]  
(3.93)

The second integral can be evaluated by the trapezoidal rule.

Therefore,
3.3.8. Instantaneous Enhancement Factor. The effect of chemical reaction on a mass transfer process can be described by the ratio of the rate of mass transfer with reaction to the rate of mass transfer without reaction. (Perry and Pigford, 1953).

\[ \phi_1 = \frac{N_a}{N_{ao}} \]  

(3.95)

In dimensionless terms, equation (3.95) becomes

\[ \phi_1 = \frac{N}{N_0} \]  

(3.96)

The dimensionless flux of component \( a \) for a finite reaction rate constant was calculated as described in section 3.3.4.

The concentration profile of component \( a \) for a zero reaction rate constant has been solved analytically by Newman (1931) for a stagnant sphere. The dimensionless flux can be calculated from the concentration profile.

\[ N_0 = 4 \sum_{n=1}^{\infty} \exp(-n^2 \pi^2 \tau) \]  

(3.97)

The instantaneous enhancement factor was used to check the accuracy of the numerical solution and was only calculated for stagnant spheres.
3.3.9. **Enhancement Factor.** The enhancement factor may be defined as the ratio of the time averaged fluxes with and without reaction. (Brian, et al., 1961).

\[ \phi = \frac{N_a}{N_{ao}} \]  

(3.98)

and, making all terms dimensionless

\[ \phi = \frac{N}{N_o} \]  

(3.99)

The numerator of the right hand side of equation (3.99) was evaluated numerically as described in section 3.3.5. The denominator has been evaluated by different investigators for stagnant and circulating fluid spheres. Newman's development leads to the following expression for the time averaged flux of component \( a \) in a stagnant sphere.

\[ \overline{N_o} = \frac{2}{3\tau} \left( 1 - 6 \sum_{n=1}^{\infty} \frac{1}{\pi^2 n^2} \exp \left( -n^2 \frac{2}{\tau} \right) \right) \]  

(3.100)

Johns (1964) solved the partial differential equation for mass transfer (without chemical reaction) in the circulating drop model. Andoe (1968) later recalculated the values originally found by Johns. The time averaged flux taken from the work of Johns and of Andoe differ by less than one per cent for dimensionless times greater than 0.02. However, at small dimensionless times the two results differ by as much as ten per cent. For a Peclet number of zero (stagnant sphere) and at a dimensionless time of \( 10^{-3} \), the time averaged flux was 67.47 by Johns and 74.00 by Andoe. The analytical solution by Newman (1931) predicts a time averaged flux of 69.37. The flux was recalculated using the
program written for second-order reaction with the reaction constant set equal to zero and for the increments $\Delta R = 1/80$, $\Delta \theta = \pi/31$ and $\Delta \tau = 10^{-4}$. The numerical program gave a value of 70.52 for the time averaged flux in a stagnant sphere at $\tau = 10^{-3}$. For dimensionless times greater than $10^{-3}$, the flux calculated in this work for the stagnant sphere differed from the analytical solution by less than one per cent.

Thus, the time averaged flux for mass transfer without reaction, for use in the calculation of the enhancement factors was calculated by equation (3.100) for zero Peclet number. For Peclet numbers greater than zero the time averaged flux for dimensionless time up to two-tenths was calculated by equation (3.87) for the increments $\Delta \tau = 0.0001$, $\Delta \theta = \pi/31$, and $\Delta R = 1/80$. For dimensionless time greater than two-tenths, the time averaged flux was computed by the method developed by Andoe (1968). The values for the time averaged flux for mass transfer without reaction, shown in Table 3.1, were used in equation (3.99).
TABLE 3.1

TIME AVERAGED FLUX FOR MASS TRANSFER WITHOUT REACTION, $N_0$

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</tr>
</tbody>
</table>

(1) For $N_{pe} = 0$ the Time Averaged Flux was calculated from the analytical solution.

(2) For $N_{pe} \neq 0$ the Time Averaged Flux for Dimensionless Time less than or equal to two-tenths was calculated by the equations in this work using the increments $\Delta \tau = 0.0001$, $\Delta \theta = \pi/31$ and $\Delta R = 1/80$. For Dimensionless Time greater than two-tenths the Time Averaged Flux was as calculated by Andoe.
IV. DISCUSSION OF MATHEMATICAL SOLUTION

The different mass transfer indices calculated numerically are tabulated in Appendix B. Two of these indices are shown graphically in this chapter. The total mass transferred, $\bar{A}_{mt}$, is shown as a function of dimensionless time for various parameters in figures 4.1 through 4.22. The ratio of the time averaged enhancement factor, $\phi$, to the enhancement factor for an instantaneous reaction, $\phi_\infty$, is shown as a function of dimensionless time. Parameters of dimensionless reaction rate constant are shown in figures 4.23 through 4.28.

4.1. Accuracy of Numerical Solution

For each combination of dimensionless parameters, the instantaneous flux was calculated by two different methods: the time rate of change of the total mass transferred; and the average concentration gradient at the surface, as described in section 3.3.4. The deviation between the results for the two methods to calculate the instantaneous flux would be less than two per cent if the time and space increments are small enough.

As an additional check on the accuracy of the numerical solution, calculated results were compared with analytical results for the asymptotic regimes defined by Astarita (1966, 1967). All comparisons made for this preliminary study were for mass transfer in a stagnant sphere. The mass transfer index used for comparison was the instantaneous enhancement factor as defined by equation (3.96).

By setting the dimensionless reaction rate constant equal to zero, the finite difference equations reduce to the equations for mass transfer without chemical reaction. If there is no error in the numerical solution, the instantaneous enhancement factor will always have a value
of one. A reaction rate constant of zero, a Peclet number of zero, a
diffusivity ratio of one, and a concentration ratio of one were chosen
for the particular solution studied. The radius was divided into forty
increments, and the dimensionless time step size was 0.0002. The en-
hancement factor at the first time step was 1.166. All other enhance-
ment factors differed from one by less than four per cent, except at
the third time step, where the enhancement factor was 1.061. For all
dimensionless times greater than 0.003, the maximum deviation of the
enhancement factor from one was less than one per cent, and the average
absolute per cent deviation was less than one-tenth of a per cent.

For very large reaction rate constants, $k_R$, concentration ratios, $R_c$,
and/or dimensionless times, $\tau$, the asymptotic solution by Toor (1962)
and Brunson and Wellek (1970a) for $\phi_\infty$ is valid. For this region, the
instantaneous enhancement factor is equal to $1 + 1/R_c$. To test the
numerical solution at this extreme, the program was run for a concen-
tration ratio of five, a diffusivity ratio of one, a Peclet number of zero,
and a dimensionless reaction rate constant of 640. The dimensionless
radius was divided into one hundred increments, and the step size for
the dimensionless time was 0.0001. For this concentration ratio, the
asymptotic enhancement factor is 1.20. This asymptotic region was ap-
proached for dimensionless times greater than 0.01. Within the range
of dimensionless times between 0.01 and 0.18, the maximum deviation of
the instantaneous enhancement factor from 1.20 was less than one per
cent. The average absolute per cent deviation was two tenths of a per
cent.

The Danckwerts (1951) transformation of the Newman (1931) solution
for stagnant sphere results in a series solution for mass transfer with
first-order reaction inside a stagnant sphere. The same problem was also solved numerically by Andoe (1968). These two previous solutions were used to test the accuracy of the numerical method used in this study. The parameters, used for the numerical solution were concentration ratio of zero, the Peclet number of zero, diffusivity ratio of one, and dimensionless reaction rate constant of 160. The instantaneous enhancement factors, calculated by the analytical and the two numerical methods, are shown in Table 4.1. Andoe's results were the most accurate of the two numerical methods for large dimensionless times. Andoe imposed a network of rectangular grids upon the cross section of a sphere to obtain his numerical results. Andoe added an arbitrary constant to his numerical solution to force his results to conform to the analytical equations. The numerical solution, presented in this work, is more accurate than Andoe's solution at small times. Over the complete range of dimensionless times, the instantaneous enhancement factor calculated in this work differed from the analytical results by less than three per cent. If the entire time range is considered, the numerical solution of this work was as accurate as Andoe's solution. Andoe's numerical solution and this work both agree well with the analytical results.

A further check of the accuracy of the program was made by testing the effect of changes in the size of the time and space increments on the instantaneous enhancement factor. Two computer calculations were executed for a concentration ratio of one, a diffusivity ratio of one, and a dimensionless reaction rate constant of 160. The first program used forty increments in the radial direction and a dimensionless time step size of 0.0002. For the second program, the number of increments in the radial direction was increased to two hundred, and the size of
TABLE 4.1
COMPARISON OF ANALYTICAL INSTANTANEOUS ENHANCEMENT
FACTOR WITH VALUES CALCULATED NUMERICALLY
BY ANDOE (1968) AND BRUNSON (THIS WORK)

\[ k_R = 160 \quad R_D = 1 \quad N_{Pe} = 0 \quad (\text{Stagnant Sphere}) \quad R_c = 0 \]

<table>
<thead>
<tr>
<th>Time ( \tau )</th>
<th>Analytical</th>
<th>Andoe</th>
<th>Brunson</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>1.162</td>
<td>1.215</td>
<td>1.207</td>
</tr>
<tr>
<td>0.002</td>
<td>1.326</td>
<td>1.374</td>
<td>1.313</td>
</tr>
<tr>
<td>0.003</td>
<td>1.488</td>
<td>1.535</td>
<td>1.469</td>
</tr>
<tr>
<td>0.005</td>
<td>1.803</td>
<td>1.840</td>
<td>1.767</td>
</tr>
<tr>
<td>0.006</td>
<td>1.957</td>
<td>1.986</td>
<td>1.912</td>
</tr>
<tr>
<td>0.007</td>
<td>2.107</td>
<td>2.131</td>
<td>2.060</td>
</tr>
<tr>
<td>0.008</td>
<td>2.256</td>
<td>2.273</td>
<td>2.202</td>
</tr>
<tr>
<td>0.009</td>
<td>2.401</td>
<td>2.413</td>
<td>2.345</td>
</tr>
<tr>
<td>0.010</td>
<td>2.545</td>
<td>2.551</td>
<td>2.484</td>
</tr>
<tr>
<td>0.011</td>
<td>2.686</td>
<td>2.687</td>
<td>2.623</td>
</tr>
<tr>
<td>0.012</td>
<td>2.826</td>
<td>2.822</td>
<td>2.758</td>
</tr>
<tr>
<td>0.013</td>
<td>2.963</td>
<td>2.955</td>
<td>2.893</td>
</tr>
<tr>
<td>0.014</td>
<td>3.099</td>
<td>3.087</td>
<td>3.026</td>
</tr>
<tr>
<td>0.015</td>
<td>3.324</td>
<td>3.217</td>
<td>3.157</td>
</tr>
<tr>
<td>0.020</td>
<td>3.888</td>
<td>3.852</td>
<td>3.796</td>
</tr>
<tr>
<td>0.030</td>
<td>5.142</td>
<td>5.073</td>
<td>5.020</td>
</tr>
<tr>
<td>0.045</td>
<td>6.993</td>
<td>6.881</td>
<td>6.827</td>
</tr>
<tr>
<td>0.060</td>
<td>8.904</td>
<td>8.752</td>
<td>8.719</td>
</tr>
<tr>
<td>0.090</td>
<td>13.177</td>
<td>12.939</td>
<td>12.864</td>
</tr>
<tr>
<td>0.120</td>
<td>18.437</td>
<td>18.096</td>
<td>17.999</td>
</tr>
<tr>
<td>0.150</td>
<td>25.204</td>
<td>24.734</td>
<td>24.606</td>
</tr>
<tr>
<td>0.180</td>
<td>34.124</td>
<td>33.484</td>
<td>33.314</td>
</tr>
<tr>
<td>0.210</td>
<td>46.013</td>
<td>45.150</td>
<td>44.921</td>
</tr>
<tr>
<td>0.240</td>
<td>61.941</td>
<td>60.780</td>
<td>60.471</td>
</tr>
</tbody>
</table>
the dimensionless time increments was reduced to 0.00002. The deviation between the two solutions was less than two per cent for all dimensionless times of 0.001 or greater. The deviation was less than one per cent for all dimensionless times of 0.01 or greater. Therefore, the time increment size, $\Delta \tau$, of 0.0002 and forty increments in the radial direction which were used in this work were considered adequate to give accurate results.

4.2. Effect of Dimensionless Parameters

It was found that the mass transfer indices, calculated in the theoretical portion of this work were a function of five dimensionless parameters: a diffusivity ratio, $R_D$, a concentration ratio, $R_c$, a reaction number, $k_R$, the Peclet number, $N_{Pe}$, and the dimensionless contact time, $\tau$. If the complete range of dimensionless independent variables is studied, conclusions can be made concerning the importance and effect of each dimensionless parameter on the mass transfer indices. A knowledge of the relative influence of each dimensionless parameter makes it possible to establish certain guidelines for the design and operation of industrial reactor-contactors. The range of dimensionless independent variables studied is shown in Table 4.2.

The most important dependent variable for use in comparing theoretical results with experimental data or for use in designing reactor-contactors is the total mass transferred, $\bar{A}_{mt}$ for a given contact time. The total mass transferred, $\bar{A}_{mt}$, is the moles of component $a$ present in the sphere (in the reacted and unreacted state) divided by the product of the volume of the sphere and the surface concentration of component $a$. Figures 4.1 through 4.22 show curves of $\bar{A}_{mt}$ versus dimensionless time for various parametric values. Figures 4.23 through 4.28 show
### TABLE 4.2a
VALUES OF DEPENDENT VARIABLES STUDIED
(all possible combinations)

<table>
<thead>
<tr>
<th>RD</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>N_Pe</td>
<td>0 40 100</td>
</tr>
<tr>
<td>R_c</td>
<td>0 0.2 1 ∞</td>
</tr>
<tr>
<td>k_R</td>
<td>0 40 160 640 ∞</td>
</tr>
</tbody>
</table>

### TABLE 4.2b
SPECIAL COMBINATIONS OF VARIABLES STUDIED

<table>
<thead>
<tr>
<th>Special Study Number</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>RD</td>
<td>5</td>
<td>0.2</td>
<td>5</td>
<td>0.2</td>
<td>0</td>
<td>∞</td>
</tr>
<tr>
<td>N_Pe</td>
<td>100</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>R_c</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>k_R</td>
<td>640</td>
<td>640</td>
<td>640</td>
<td>640</td>
<td>640</td>
<td>640</td>
</tr>
</tbody>
</table>

### TABLE 4.2c
A SPECIAL STUDY OF HIGH PECLET NUMBERS

For RD = 1, R_c = 0.2, k_R = 40, and N_Pe = 150, 200, 300, 400, 500

### TABLE 4.2d
A SPECIAL STUDY OF LOW CONCENTRATION RATIOS

For RD = 1, R_c = 0.1, k_R = 640, and N_Pe = 0, 40, 100
curves of the time averaged enhancement factor divided by the enhancement factor for an instantaneous reaction, $\Gamma$, as a function of dimensionless time, $\tau$, for various values of dimensionless reaction rate constant. Tabular values for the total mass transferred, the time averaged enhancement factor, and six other dependent variables are shown in Appendix B for representative values of the independent variables.

Figures 4.1 through 4.6 show the effect of reaction number on the total mass transferred. When the reaction number is zero, the solution reduces to mass transfer without reaction as presented by Johns and Beckmann (1966).

For an infinitely fast reaction ($k_R \to \infty$) and a diffusivity ratio of one, the expression for the enhancement factor developed by Brunson and Wellek (1970a) and Toor (1962) applies. Thus, the total mass transferred to the dispersed phase when the reaction is instantaneous is the same as the product of the mass transferred without reaction and $(1 + 1/R_c)$. Curves for some intermediate values of reaction number, $k_R$, are shown to allow interpolation.

The curves for the total mass transferred are plotted against dimensionless time. The rate of mass transfer or the flux of component $a$ is proportional to the slope of these curves. Thus, from figures 4.1 through 4.6, it can be seen that at small dimensionless times, the flux increases with increasing reaction number. At large times, the $b$ reactant inside the dispersed phase has been depleted if the reaction is rapid but some $b$ reactant is still present for slow reactions. Thus, the flux for mass transfer with a slow reaction is larger than the flux for mass transfer with a fast reaction; however, the total mass transferred at any given time increases with increasing reaction number.
Figure 4.1. Total Mass Transferred, $\bar{A}_{mt}$, as a Function of Dimensionless Time, $\tau$, for Parametric Values of the Reaction Number, $k_R$ ($R_D = 1, N_{Pe} = 0, R_c = 0.2$)

$$R_D = 1$$
$$N_{Pe} = 0$$
$$R_c = 0.2$$

$$k_R = \frac{k_2 C_{bo} a^2}{D_o}$$

Total Mass Transferred, $\bar{A}_{mt}$, as a Function of Dimensionless Time, $\tau$, for Parametric Values of the Reaction Number, $k_R$ ($R_D = 1, N_{Pe} = 0, R_c = 0.2$)
Figure 4.2. Total Mass Transferred, $\bar{A}_{mt}$, as a Function of Dimensionless Time, $\tau$, for Parametric Values of the Reaction Number $k_R$ ($R_D = 1.0, N_{Pe} = 0, R_C = 1$)

\[
R_D = 1.0 \\
N_{Pe} = 0 \\
R_C = 1 \\
k_R = \frac{k_1 C_{bo} a^2}{D_o}
\]
Figure 4.3. Total Mass Transferred, \( \bar{A}_{mt} \), as a function of Dimensionless Time, \( \tau \), for Parametric Values of the Reaction Number, \( k_R \) 
\( (R_D = 1, N_{Pe} = 40, R_C = 0.2) \)
Figure 4.4. Total Mass Transferred, $\bar{A}_{mt}$, as a Function of Dimensionless Time, $\tau$, for Parametric Values of the Reaction Number, $k_R$ ($R_D = 1, N_{Pe} = 40, R_c = 1$)
Figure 4.5. Total Mass Transferred, $\overline{A}_m$, as a Function of Dimensionless Time, $\tau$, for Parametric Values of the Reaction Number, $k_R$ ($R_D = 1$, $N_{Pe} = 100$, $R_c = 0.2$)
\[ R_D = 1 \]
\[ \text{R}_{\text{Pe}} = 100 \]
\[ R_c = 1 \]
\[ k_R = k_2 C_{b_0} \sigma^2 \]

Figure 4.6. Total Mass Transferred, $\bar{A}_{mt}$, as a Function of Dimensionless Time, $\tau$, for Parametric Values of the Reaction Number, $k_R$
\( (R_D = 1, \text{R}_{\text{Pe}} = 100, R_c = 1) \)
Figures 4.7 through 4.15 show the dependence of the total mass transferred on parametric values of concentration ratio, $R_c$. For a concentration ratio of zero, the $\text{b}$ reactant is in such excess that the reaction is pseudo first-order. At the other extreme when the concentration ratio becomes infinite, there is no $\text{b}$ reactant present; and the total mass transferred can be found from the case of mass transfer without reaction as originally solved by Johns and Beckmann (1966). Each of the curves in Figures 4.7 through 4.15 for immediate values of the concentration ratio approach an asymptotic value of $1 + 1/R_c$ as the dimensionless time becomes large.

The dependence of the total mass transferred, $\overline{A}_{\text{mt}}$, on the diffusivity ratio, $R_D$, is indicated in Figure 4.16. For a given value of dimensionless time, the total mass transferred increases with increasing diffusivity ratio, $R_D$. The rate of reaction is fastest if the $\text{b}$ reactant is mobile enough to maintain a large concentration near the surface of the sphere. The two extremes of the diffusivity ratio, zero and very large, may not be of practical importance; however, they are included in the figure to show the complete range of parameters. The solution for an infinite diffusivity ratio was obtained numerically by setting, after each time iteration, the concentration of $\text{b}$ at each grid point at the average concentration of $\text{b}$.

For a pseudo first-order reaction, the concentration of component $\text{b}$ remains constant; therefore, the effect of the diffusivity ratio disappears when the concentration ratio becomes zero. The importance of the diffusivity ratio is also small for large concentration ratios because the total mass transferred, $\overline{A}_{\text{mt}}$, approaches an asymptotic value within the time range studied. For a concentration ratio, $R_c$, of unity and a diffusivity ratio, $R_D$, of unity, the total mass transferred is
Figure 4.7. Total Mass Transferred, $\bar{A}_{mt}$, as a Function of Dimensionless Time, $\tau$, for Parametric Values of the Concentration Ratio, $R_c$ ($R_D = 1$, $N_{Pe} = 0$, $k_R = 40$)

$R_c = R_z \frac{C_{os}}{C_{bo}}$

$R_D = 1$

$N_{Pe} = 0$

$k_R = 40$

$R_c = 0$

$R_c = 0.2$

$R_c = 1$

$R_c \rightarrow \infty$ (NO REACTION)
Figure 4.8. Total Mass Transferred, $\bar{A}_{mt}$, as a Function of Dimensionless Time, $\tau$, for Parametric Values of the Concentration Ratio, $R_c$ ($R_D = 1$, $k_R = 160$, $N_{Pe} = 0$)
Figure 4.9. Total Mass Transferred, $\bar{\Delta}_{mt}$, as a Function of Dimensionless Time, $\tau$, for Parametric Values of the Concentration Ratio, $R_c$ ($R_D = 1, k_R = 640, N_{Pe} = 0$)
Figure 4.10. Total Mass Transferred, $\bar{A}_{mt}$, as a Function of Dimensionless Time, $\tau$, for Parametric Values of the Concentration Ratio, $R_c$ ($R_D = 1, N_{Pe} = 40, k_R = 40$)
Figure 4.11. Total Mass Transferred, $\bar{A}_{mt}$, as a Function of Dimensionless Time, $\tau$, for Parametric Values of the Concentration Ratio, $R_c$ ($R_D = 1, N_{Pe} = 40, k_R = 160$)
Figure 4.12. Total Mass Transferred, $\bar{A}_{mr}$, as a Function of Dimensionless Time, $\tau$, for Parametric Values of the Concentration Ratio, $R_c$ ($R_D = 1$, $N_{Pe} = 40$, $k_R = 640$)
Figure 4.13. Total Mass Transferred, $\overline{A}_{mt}$, as a Function of Dimensionless Time, $\tau$, for Parametric Values of the Concentration Ratio, $R_c$ ($R_D = 1, N_{Pe} = 100, k_{R} = 40$)
Figure 4.14. Total Mass Transferred, $\bar{\Delta}_{mt}$, as a Function of Dimensionless Time, $\tau$, for Parametric Values of the Concentration Ratio, $R_c$ ($R_D = 1$, $N_{Pe} = 100$, $k_R = 160$)
Figure 4.15. Total Mass Transferred, $\bar{A}_{mt}$, as a Function of Dimensionless Time, $\tau$, for Parametric Values of the Concentration Ratio, $R_c$ ($R_D = 1$, $N_{Pe} = 100$, $k_R = 640$)
Figure 4.16. Total Mass Transferred, $\bar{A}_{mt}$, as a Function of Dimensionless Time, $\tau$, for Parametric Values of the Diffusivity Ratio, $R_D$ ($R_C = 0.2, k_R = 640, N_{Pe} = 0$)
within one per cent of its asymptotic value at a dimensionless time, \( \tau \), of 0.24. The asymptotic restriction does not allow a larger diffusivity ratio to greatly increase the total mass transferred. Thus, the effect of the diffusivity ratio is most important for concentration ratios, \( R_c \), between zero and one.

Since the reactants become depleted by a fast reaction the rapidity with which the reactants diffuse toward each other becomes more important as the reaction rate increases.

The effect of the diffusivity ratio decreases as the Peclet number increases. As the Peclet number increases, transfer by bulk flow becomes more important than solute transfer by diffusion. The diffusivity ratio, \( R_D \), was increased from 0.2 to 5 for a concentration ratio, \( R_c \), of 0.2, a dimensionless reaction rate constant, \( k_R \), of 640, and a Peclet number, \( N_{Pe} \), of 100. The variation of the diffusivity ratio changed the total mass transferred by less than one part in four thousand.

Figures 4.17 through 4.22 show the effect of internal circulation on the total mass transferred as predicted by the model. To avoid unnecessary clutter the complete extensions of all of the curves are not shown in these figures.

No attempt was made in this work to solve analytically for mass transfer with reaction for a Peclet number approaching infinity.

Kronig and Brink (1950) made that computation for mass transfer without chemical reaction. However, it was possible to increase the Peclet number until the total mass transferred, \( \bar{A}_{mt} \), approached a constant value with respect to increasing Peclet number. This constant value was reached at a Peclet number about one hundred for both mass transfer without reaction and mass transfer with a rapid chemical reaction. Larger Peclet numbers were required to reach the asymptotic
Figure 4.17. Total Mass Transferred, $\bar{A}_{mt}$, as a Function of Dimensionless Time, $\tau$, for Parametric Values of the Fluid Flow Model $(R_D = 1, R_c = 1, k_R = 40)$
Figure 4.18. Total Mass Transferred, $\tilde{A}_{\text{mf}}$, as a Function of Dimensionless Time, $\tau$, for Parametric Values of the Fluid Flow Model ($R_D = 1, R_c = 1, k_R = 160$)
$R_D = 1$

$R_c = 1$

$k_R = 640$

$N_{Pe} = \frac{\alpha V t}{2D_0} \frac{\mu_c}{\mu_d + \mu_c}$

Figure 4.19. Total Mass Transferred, $A_{mt}$, as a Function of Dimensionless Time, $\tau$, for Parametric Values of the Fluid Flow Model ($R_D = 1$, $R_c = 1$, $k_R = 640$)
Figure 4.20. Total Mass Transferred, $\bar{A}_{mt}$, as a Function of Dimensionless Time, $\tau$, for Parametric Values of the Fluid Flow Model ($R_D = 1, R_C = 0.2, k_R = 40$)
Figure 4.21. Total Mass Transferred, $\bar{A}_{mt}$, as a Function of Dimensionless Time, $\tau$, for Parametric Values of the Fluid Flow Model ($R_D = 1$, $R_c = 0.2$, $k_R = 160$)
Figure 4.22. Total Mass Transferred, $\bar{A}_{mt}$, as a Function of Dimensionless Time, $\tau$, for Parametric Values of the Fluid Flow Model ($R_D = 1$, $R_c = 0.2$, $k_R = 640$)
effect of Peclet number for intermediate reaction numbers, especially if the concentration ratio was small. Mass transferred at a given dimensionless time increased with increasing Peclet number up to a Peclet number of five hundred for the following example where \( k_R = 40 \), \( R_C = 0.2 \), \( R_D = 1.0 \), and \( \tau = 0.05 \):

<table>
<thead>
<tr>
<th>( N_{Pe} )</th>
<th>0</th>
<th>100</th>
<th>200</th>
<th>300</th>
<th>400</th>
<th>500</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_{mt} )</td>
<td>1.0026</td>
<td>1.1816</td>
<td>1.2863</td>
<td>1.3350</td>
<td>1.3616</td>
<td>1.3762</td>
</tr>
</tbody>
</table>

### 4.3. Other Mass Transfer Models

The film theory (Whitman, 1923) and the penetration theory (Higbie, 1935) are theoretical models for mass transfer across a flat interface. When the depth which the transferring solute penetrates into the sphere is much smaller than the radius of curvature, these theories may be applied to interfaces which are not flat. The following sections describe the film theory and the penetration theory with second-order irreversible chemical reaction as applied to fluid spheres. The reaction involves one mole of component a and Z moles of component b.

\[
a + Z b \rightarrow \text{products} \tag{4.1}
\]

Both models are based on the following simultaneous, differential solute balance equations for components a and b respectively:

\[
\frac{\partial c_a}{\partial t} = D_a \frac{\partial^2 c_a}{\partial h^2} - k_2 c_a c_b \tag{4.2}
\]

\[
\frac{\partial c_b}{\partial t} = D_b \frac{\partial^2 c_b}{\partial h^2} - Z k_2 c_a c_b \tag{4.3}
\]

and the boundary conditions
\[ C_a(0,h) = 0 \quad \text{and} \quad C_b(0,h) = C_{b0} \quad (4.4) \]
\[ C_a(t,0) = C_{as} \quad \text{and} \quad \frac{\partial C_b}{\partial h}(t,0) = 0 \quad (4.5) \]
\[ C_a(t,H) = 0 \quad \text{and} \quad C_b(t,H) = C_{b0} \quad (4.6) \]

For the film theory, \( \delta \) is zero and \( H \) is the film thickness. For the penetration theory, \( \delta \) is unity and \( H \) approaches infinity. The results of these theories are shown in figures 4.17 through 4.22.

### 4.3.1. Film Theory

Van Krevelen and Hoftijzer (1948a) solved numerically equations (4.2) through (4.6) with the restrictions for the film theory. From their numerical solution, they deduced that there is not only a mass transfer film thickness, but also a chemical reaction film thickness. The concentration of component b was almost constant throughout the reaction film thickness. Van Krevelen and Hoftijzer used this approximation to obtain an analytical solution for the film theory model. Their expression for the enhancement factor, \( \phi \), may be written as

\[
\phi = \frac{Y}{\tanh Y} \left[ 1 - \frac{Y}{2kR} \left\{ \frac{\sinh Y \cosh Y}{\sinh^2 Y} + \frac{Y}{\tanh Y} \right\} \right] \quad (4.7)
\]

\[
Y = \frac{2\sqrt{K_R}}{N_o} \sqrt{1 + (1-\phi)R_c/R_D} \quad (4.8)
\]

The term in brackets in equation (4.7) has a value very close to unity except for conditions where the flux without reaction, \( N_o \), is very large. Under these conditions, the presence of a chemical reaction is relatively unimportant in the mass transfer process, and the term in brackets causes the predicted enhancement factor to be less than one. An enhancement factor less than one is not a physical possibility. Peaceman (1951) also obtained numerical solutions of the equations for
film theory mass transfer with second-order chemical reaction and found that the Van Krevelen and Hoftijzer approximation was more accurate if the term in brackets was left off. Thus:

$$\phi = \frac{Y}{\tanh Y} \quad (4.9)$$

The reason the dimensionless flux, $\overline{N}_o$, is used in equation (4.8) is discussed in section 4.4.1.

In this work, equations (4.8) and (4.9) were used to generate the curves for the film theory. Since these equations were implicit in terms of $\phi$, the enhancement factor can only be obtained by an iteration process using an initial estimate of the enhancement factor. Santiago and Farina (1970) formulated the following two explicit expressions for certain ranges of film theory mass transfer.

$$\phi = \frac{2 \sqrt{k R / \overline{N}_o}}{\tanh \left(2 \sqrt{k R / \overline{N}_o}\right)} \quad (4.10)$$

$$\phi = \frac{2 \sqrt{k R}}{\overline{N}_o} \left[\sqrt{\frac{k R C}{\overline{N}_o^2 R_D^2}} + \frac{R_C}{R_D} + 1 \right] - \frac{R_C \sqrt{k R}}{R_D \overline{N}_o} \quad (4.11)$$

As applied to fluid spheres, equation (4.10) is used for short contact times, and equation (4.11) is used for long contact times. For this work, equations (4.10) and (4.11) were used for initial approximations in order to solve equation (4.9) for $\phi$. The smallest value of $\phi$ predicted by either equation (4.10) or (4.11) was taken as an initial approximation for the enhancement factor. This approximation was successively improved by using equations (4.8) and (4.9) in a scheme of linear iteration (Conte, 1965, p. 19).

In order that the results of the film theory could be compared with the results of the next section, the dimensionless flux without chemical reaction was calculated from the following penetration theory
relation:

$$\bar{N}_0 = \frac{4}{\sqrt{\pi \tau}}$$  \hspace{1cm} (4.12)

The use of the penetration theory in conjunction with the film theory was suggested by Rose and Kintner (1966).

4.3.2. Penetration Theory. It was mentioned in the Literature Survey that several investigators had solved equations (4.2) through (4.6) with the specifications of $\delta$ of unity and $H$ approaching infinity (Perry and Pigford, 1953; Brian, et al., 1961; Pearson, 1963). The most comprehensive numerical work was done by Pearson (1963). Tabular results in terms of a specially defined total mass transferred for the parameters studied by Pearson (1963) are available by writing Dr. Pearson.

The semiempirical correlation by Kishinevskii and Kornienko (1966) was the easiest approximation to use to predict total mass transferred since a digital computer was available for the calculations. Their semiempirical correlation for the enhancement factor can be expressed as

$$\phi = 1 + \frac{W[1 - f(0.85 \sqrt{W R_c + W})]}{R_c W + \exp (-0.35 W R_c)}$$  \hspace{1cm} (4.13)

where the function, $f$, is defined by

$$f(x) = \frac{\exp(-x^2)}{x} \int_{0}^{x} \exp(x^2) \, dx$$  \hspace{1cm} (4.14)

and

$$W = \sqrt{\frac{\pi K R \tau}{4}}$$  \hspace{1cm} (4.15)

4.3.3. Discussion of Film and Penetration Theories. The dependent variable plotted in figures 4.17 through 4.22 is the total mass transferred, $\bar{A}_{mt}$. If the rate of mass transfer without chemical reaction is consistent with that predicted by the penetration theory, the total mass
transferred without chemical reaction can be expressed as a function of dimensionless time.

\[ A_o = 6 \sqrt{\tau/\pi} \]  \hspace{1cm} (4.16)

From equation (4.16) the total mass transferred with reaction can be obtained from either equation (4.9) or (4.13) by the following relation:

\[ A_{mt} = 6 \Phi \sqrt{\tau/\pi} \]  \hspace{1cm} (4.17)

The results for the film theory and the penetration theory are tabulated in Appendix B. The curves for the empirical solution of the penetration theory by Kishinevskii and Kornienko and the film theory approximation by Van Krevelen and Hoftijzer agree with the curve for the numerical solution based on the penetration theory and obtained by Pearson within eight per cent.

For dimensionless times less than 0.001, the total mass transferred, as calculated by the fluid sphere model developed in Section III, differs from that predicted by either the film theory or the penetration theory by less than five per cent. This small dimensionless time is the range of dimensionless time important in many liquid extraction applications. Thus the film theory or the penetration theory, as described in the proceeding sections, are sufficiently accurate replacements for the fluid sphere model for most work in liquid extraction with irreversible, second-order chemical reactions. At higher contact times, the assumption of a flat interface which is basic to both of the above mentioned theories is no longer valid. At large dimensionless times ($\tau > 0.02$), dimensionless times important for gas absorption, both the film theory and the penetration theory overestimate values of the total mass transfer. The film theory and the penetration theory predict values of total
mass transfer greater than those which are possible from equilibrium considerations because neither theory is able to allow for the effect of eventual depletion of the reactant within the sphere on the assumed boundary conditions.

4.4. Approximations to the Fluid Sphere Model

4.4.1. Revised Film Theory. One of the shortcomings which result when the film theory is applied to a fluid sphere as described in section 4.3.1. is the use of the penetration theory to approximate the dimensionless flux for mass transfer without reaction. The use of the penetration theory as described in section 4.3.1. is actually a use of the penetration theory to approximate the film thickness. The actual presence of a stagnant film next to a well mixed bulk of fluid, as assumed in the film theory, probably never occurs in a fluid sphere. However, the film theory may still be used to approximate mass transfer rates. The best approximation for the film thickness in a stagnant sphere would come from the theory for mass transfer in a stagnant sphere without chemical reaction. Thus, to predict mass transfer with second-order chemical reaction inside a stagnant sphere, the mass transfer indices for mass transfer without reaction should be those derived by Newman (1931). The average concentration of the solute diffusing into the sphere inside a stagnant sphere without chemical reaction is

\[
\bar{A}_o = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{n^2}{\pi^2} \tau\right)
\]

Equation (4.18) may be used to calculate the enhancement factor, using equations (4.8) and (4.9) based on the film theory because

\[
\bar{N}_o = \frac{2}{3} \frac{\bar{A}_o}{\tau}
\]

Equation (4.19) was used in conjunction with equations (4.8) and (4.9)
to find the enhancement factor. The enhancement factor was then used to find the total mass transferred.

\[ \bar{A}_{mt} = 4 \bar{A}_o \] (4.20)

The value for \( \bar{A}_o \) used in equation (4.20) was as calculated by equation (4.18). Values of the total mass transferred as calculated by the method above are listed in Table 4.3 alongside analogous values calculated by the circulating sphere model developed in Section III for the parameters \( R_c = 0.2, k_R = 640, N_{pe} = 0, \) and \( R_D = 1 \). The results of the film theory model deviate from the circulating sphere model by less than 6.1 per cent for the entire range of dimensionless time.

For the film theory and the penetration theory, the dimensionless flux and the Sherwood number are numerically equal. Therefore, for these theories there is no need to differentiate between the two quantities. However, for mass transfer inside a confined geometry, such as a sphere, the dimensionless flux and the Sherwood number are not equal. The Van Krevelen and Hoftijzer (1948a) derivation does not designate which of the dimensionless numbers should be used to calculate the enhancement factor. If the Sherwood number were used, equation (4.8) becomes

\[ Y = \frac{2 \sqrt{k_R}}{N_{Sh}} \sqrt{1 + (1 - \phi) \frac{R_c}{R_D}} \] (4.21)

However, when the time averaged Sherwood number was used in conjunction with the film theory, the resultant total mass transferred was as much as fifty per cent less than the corresponding numbers in Table 4.3. Based on this test, it was concluded that the dimensionless flux, not the Sherwood number, was the proper variable to be used in equation (4.8).
### Table 4.3

Comparison of Numerical Results with Approximation by Ronco and with Film Theory Using Stagnant Sphere, Dimensionless, Time Averaged Flux

<table>
<thead>
<tr>
<th>Time</th>
<th>Numerical Solution</th>
<th>Film Theory Approximation</th>
<th>Yeramian Approximation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>0.1274</td>
<td>0.1213</td>
<td>0.1225</td>
</tr>
<tr>
<td>0.002</td>
<td>0.2025</td>
<td>0.1918</td>
<td>0.1948</td>
</tr>
<tr>
<td>0.003</td>
<td>0.2732</td>
<td>0.2575</td>
<td>0.2619</td>
</tr>
<tr>
<td>0.004</td>
<td>0.3415</td>
<td>0.3212</td>
<td>0.3265</td>
</tr>
<tr>
<td>0.005</td>
<td>0.4081</td>
<td>0.3835</td>
<td>0.3890</td>
</tr>
<tr>
<td>0.006</td>
<td>0.4732</td>
<td>0.4448</td>
<td>0.4502</td>
</tr>
<tr>
<td>0.007</td>
<td>0.5369</td>
<td>0.5050</td>
<td>0.5100</td>
</tr>
<tr>
<td>0.008</td>
<td>0.5995</td>
<td>0.5642</td>
<td>0.5685</td>
</tr>
<tr>
<td>0.009</td>
<td>0.6609</td>
<td>0.6224</td>
<td>0.6260</td>
</tr>
<tr>
<td>0.010</td>
<td>0.7212</td>
<td>0.6798</td>
<td>0.6823</td>
</tr>
<tr>
<td>0.011</td>
<td>0.7806</td>
<td>0.7362</td>
<td>0.7376</td>
</tr>
<tr>
<td>0.012</td>
<td>0.8389</td>
<td>0.7917</td>
<td>0.7920</td>
</tr>
<tr>
<td>0.013</td>
<td>0.8963</td>
<td>0.8464</td>
<td>0.8454</td>
</tr>
<tr>
<td>0.014</td>
<td>0.9529</td>
<td>0.9002</td>
<td>0.8979</td>
</tr>
<tr>
<td>0.015</td>
<td>1.0085</td>
<td>0.9532</td>
<td>0.9496</td>
</tr>
<tr>
<td>0.020</td>
<td>1.2750</td>
<td>1.2066</td>
<td>1.1964</td>
</tr>
<tr>
<td>0.025</td>
<td>1.5236</td>
<td>1.4422</td>
<td>1.4259</td>
</tr>
<tr>
<td>0.030</td>
<td>1.7565</td>
<td>1.6621</td>
<td>1.6403</td>
</tr>
<tr>
<td>0.040</td>
<td>2.1814</td>
<td>2.0613</td>
<td>2.0307</td>
</tr>
<tr>
<td>0.050</td>
<td>2.5593</td>
<td>2.4146</td>
<td>2.3778</td>
</tr>
<tr>
<td>0.060</td>
<td>2.8970</td>
<td>2.7297</td>
<td>2.6886</td>
</tr>
<tr>
<td>0.070</td>
<td>3.1998</td>
<td>3.0122</td>
<td>2.9683</td>
</tr>
<tr>
<td>0.080</td>
<td>3.4718</td>
<td>3.2667</td>
<td>3.2210</td>
</tr>
<tr>
<td>0.090</td>
<td>3.7167</td>
<td>3.4966</td>
<td>3.4496</td>
</tr>
<tr>
<td>0.100</td>
<td>3.9374</td>
<td>3.7050</td>
<td>3.6577</td>
</tr>
<tr>
<td>0.120</td>
<td>4.3162</td>
<td>4.0662</td>
<td>4.0200</td>
</tr>
<tr>
<td>0.150</td>
<td>4.7575</td>
<td>4.4959</td>
<td>4.4532</td>
</tr>
<tr>
<td>0.180</td>
<td>5.0831</td>
<td>4.8230</td>
<td>4.7846</td>
</tr>
<tr>
<td>0.210</td>
<td>5.3230</td>
<td>5.0729</td>
<td>5.0389</td>
</tr>
<tr>
<td>0.240</td>
<td>5.4997</td>
<td>5.2646</td>
<td>5.2347</td>
</tr>
</tbody>
</table>
Despite the good agreement of the film theory with the numerical solution shown in Table 4.3, the film theory is not recommended for use at large dimensionless times (τ > 0.1) if the diffusivity ratio is much different from unity. For diffusivity ratios other than one the total mass transferred predicted by this revised film theory approaches an asymptotic value of 1 + R_D/R_C instead of the correct value of 1 + 1/R_C (Toor, 1962). This error is not significant at small dimensionless times, when the diffusivities of the two reactants are about equal (i.e. 0.2 < R_D < 5).

4.4.2. Yeramian Approximation. The numerical results for the Yeramian et al. (1970) approximation are shown in Table 4.3. The overall accuracy of this approximation is slightly better than the film theory approximation described in section 4.4.1. This approximation is better possibly because the Yeramian approximation uses previous knowledge of both mass transfer without chemical reaction and mass transfer with first-order chemical reaction. The approximation proposed by Yeramian, et al. (1970) is shown

\[
\phi = \frac{R_C}{2} \phi_1^2 \left[ \sqrt{1 + \frac{4}{R_C} \left( 1 + \frac{1}{R_C} \right)} - 1 \right]
\] (4.22)

where \( \phi_1 \) is the enhancement factor for mass transfer with a first-order chemical reaction.

The Danckwerts (1951) transformation of the Newman solution yields the following expression for the total mass transferred inside a stagnant sphere with first order reaction (Wellek, et al., 1970)
This allows the enhancement factor for first order reaction to be evaluated as

$$\phi_1 = \frac{\bar{A}_{mt}}{\bar{A}_0}$$

(4.24)

The total mass transferred can then be calculated by equation (4.20) for a second-order reaction.

The Yeramian approximation is also limited in its application, because its development assumes that the diffusivities of the two reactants are equal.

4.5. Enhancement Factor

The enhancement factor, as defined in this work, was calculated as the ratio of the dimensionless average flux with reaction to the dimensionless average flux without reaction. The enhancement factor is also equal to the total mass transferred with reaction divided by the average concentration without reaction.

$$\phi = \frac{N}{N_0} = \frac{\bar{A}_{mt}}{\bar{A}_0}$$

(4.25)

Thus, the enhancement factor is a measure of the fractional increase in the total mass transferred caused by the introduction of a chemical reaction. For a diffusivity ratio of unity the range of the enhancement factor is from unity, for no enhancement, to 1+1/Rc, for enhancement due to an instantaneous reaction (Brunson and Wellek, 1970a). A reduced enhancement factor, Γ, is defined as the enhancement factor
divided by the quantity $1 + 1/R_c$.

$$\Gamma = \frac{\phi}{1 + \frac{1}{R_c}}$$  \hspace{1cm} (4.26)

The reduced enhancement factor has a maximum value of one. This reduction of the enhancement factor was done to make possible a less cluttered graphical presentation. The reduced enhancement factor is shown as a function of dimensionless time for parametric values of the dimensionless reaction rate constant in figures 4.23 through 4.28. The curves for the parametric values of reaction rate constant show that the effect of the reaction rate constant varies with the concentration ratio. Figures 4.23 through 4.25 show the results for a set of solutions in which a concentration ratio, $R_c$, of 0.2 is used. The distance between adjacent curves in each of these figures indicates that each successive increase in the dimensionless reaction rate constant brings a corresponding increase in the enhancement due to reaction. The same is true at small dimensionless times for figures 4.26 through 4.28 where the concentration ratio, $R_c$, is one. However, at large dimensionless times even the slowest reaction studied is fast enough to deplete all of the reactant initially inside the fluid sphere. Thus, the curves for various reaction rate constants converge as the mass transfer process approaches equilibrium.

Johns (1964) in a study of mass transfer in circulating drops, found that the dimensionless flux oscillated with time. The oscillation was due to the fact that at large Peclet numbers the fluid initially at the surface of the sphere is carried through the interior of the sphere and reappears at the other end of the axis of the sphere. The
Figure 4.23. Reduced Enhancement Factor as a Function of Dimensionless Time for Parametric Values of Reaction Rate Constant ($R_D = 1, N_{Pe} = 0, R_C = 0.2$)
Figure 4.24. Reduced Enhancement Factor as a Function of Dimensionless Time for Parametric Values of a Reaction Rate Constant ($R_D = 1, N_{Pe} = 40, R_c = 0.2$)
$R_D = 1$
$N_{Pe} = 100$
$R_C = 0.2$

$k_R = \frac{k_2 C_{bo} \sigma^2}{D_o}$

Figure 4.25. Reduced Enhancement Factor as a Function of Dimensionless Time for Parametric Values of Reaction Rate Constant ($R_D = 1$, $N_{Pe} = 100$, $R_C = 0.2$)
Figure 4.26. Reduced Enhancement Factor as a Function of Dimensionless Time for Parametric Values of Reaction Rate Constant ($R_D = 1, N_{Pe} = 0, R_C = 1$)
Figure 4.27. Reduced Enhancement Factor as a Function of Dimensionless Time for Parametric Values of Reaction Rate Constant ($R_D = 1, N_{pe} = 40, R_C = 1$)
Figure 4.28. Reduced Enhancement Factor as a Function of Dimensionless Time for Parametric Values of Reaction Rate Constant ($R_D = 1, N_{Pe} = 100, R_c = 1$)

$$k_R = \frac{k_2 C_{bo} a^2}{D_o}$$
cyclic reappearance of solute-rich fluid at the surface reduces the rate of mass transfer. Andoe (1968) found the same type of oscillation in his numerical solution for mass transfer with first-order chemical reaction. However, Andoe found the oscillations to be less pronounced as the reaction rate constant increased. Some of the solute reacted before reappearing on the surface. Thus, the enhancement factor for second-order reaction is the ratio of one number (dimensionless flux with reaction) undergoing damped oscillation and another number (dimensionless flux without reaction) undergoing regular oscillation. Therefore, some of the curves in figures 4.23 through 4.28 appear irregular. The effect is more pronounced for large reaction numbers, because the oscillation of the dimensionless flux with reaction is more completely damped out. Since the flux does not oscillate for a stagnant sphere the irregularity of the enhancement factor curves disappears as the Peclet number approaches zero.

4.6. Application of Results

As with any model the results of this work are limited by the assumptions made in Section III. However, several guidelines can be drawn from this work and the results of this work may apply qualitatively or even quantitatively beyond the limitations imposed by the assumptions incorporated into the mathematical model.

4.6.1. Materials. If reaction is used to enhance the rate of solute transfer to a separating phase, the designer is usually free to choose both the identity and the concentration of reactant $b$. The most important factors to consider in selection of component $b$ are cost and rate of reaction. From figures 4.1 through 4.6 and 4.23 through 4.28,
it can be seen that even a moderate reaction rate is sufficient to enhance interphase mass transfer in gas bubbles; whereas for a liquid droplet, it is important to have as high a reaction rate as possible. As an approximate rule of thumb, one can conclude from this work that it is advantageous to pay twice as much for a reactant if the reaction rate constant can be increased by an order of magnitude. (See figures 4.1 through 4.6.)

Since the total mass transferred becomes insensitive to the diffusivity ratio at large Peclet numbers, the diffusivity of component \( b \) is not important. However, it is important that component \( b \) does not greatly increase the viscosity of the dispersed phase. In many cases it will be important that component \( b \) can be regenerated and used again.

The effect of the concentration of the \( b \) reactant is related to both the dimensionless reaction number and the concentration ratio; however, the effect is most pronounced as a result of changes in the concentration ratio shown in figures 4.7 through 4.15. In general, the total mass transferred increases as the initial concentration of component \( b \), \( C_{bo} \), is increased. However, a large concentration of reactant \( b \), could greatly change the viscosity of the dispersed phase. Therefore, if possible, \( C_{bo} \) should be just large enough to approach a pseudo first-order reaction. For the complete range of variables studied, the total mass transferred could not be increased by as much as five per cent, no matter how much the concentration ratio was reduced below two-tenths for dimensionless times less than 0.01, the time region of interest when the dispersed phase is a liquid.

4.6.2. Equipment. After the chemicals and concentrations for a contactor are selected, the size of the drops formed depend on the
nozzle design and operating conditions. Reducing the drop size increases the dimensionless time but reduces the dimensionless reaction constant and the Peclet number. Because of the way the dimensionless reaction constant varies with drop size, the reduction of drop size is not as important for mass transfer with reaction as it is for mass transfer without reaction. Despite this effect it is still desirable to form small drops. Although the drops formed will not be of uniform size, work by Gal-Or and Hoelscher (1966) for transfer from drops with and without reaction indicates that there is little error if the mean drop size is used.

Reaction inside the fluid sphere keeps the driving force for mass transfer from decreasing rapidly with time. For example, at a Peclet number of one hundred if there is no chemical reaction, the dimensionless flux of \( \dot{a} \) reduces from 29.77 at a dimensionless time of 0.001 to 0.02 at a dimensionless time of 0.24. However, if there is a chemical reaction (e.g. \( R_c = 0 \) and \( k_R = 160 \)) the dimensionless flux of \( \dot{a} \) has a value of 35.89 at a dimensionless time of 0.001 and has only reduced to 23.79 at a dimensionless time of 0.24. The large flux at large dimensionless times can be seen graphically by examining figures 4.7 through 4.15. The slope of the graph of the total mass transferred plotted against dimensionless time (which is proportional to the flux of \( \dot{a} \)) is initially large for all values of \( R_c \). At large times, the slope of the graph for \( R_c = 0 \) is still large; but the curve representing no reaction is almost horizontal. Since the presence of a chemical reaction reduces the effect of the time of contact on the flux of \( \dot{a} \) it is not necessary to redisperse the extracting phase as often as must
be done when there is no reaction present. This means that if back-mixing can be tolerated (as is the case with nitration, sulfonation and saponification) fewer perforated plates are needed per unit length of column. This fact also makes the spray tower feasible for more applications.
V. EXPERIMENTAL

The experimental portion of this work was intended to test the theory developed in Section III and a semi-theoretical relation developed in Section VII. The results of the comparison of theory and experiment are discussed in Section VII.

5.1. Experimental Design

The theoretical model developed in Section III is presented as being valid for a wide range of parameters for small Reynolds numbers. In the experimental part of this work, it is possible to test the theory for only a narrow range of experimental conditions. It was decided to study mass transfer with simultaneous second-order chemical reaction inside single liquid drops which fall through an immiscible liquid phase. The experimental design would make it possible to test the theory at small dimensionless times only. This was because the column height was restricted to less than one-half meter by room heights of the building.

The chemical system chosen for this study consisted of water drops containing 0.04 formal sodium hydroxide and one formal sodium sulfate. The choice of these concentrations will be discussed later. The aqueous drops formed at a single nozzle and fell freely through a stagnant column filled with n-pentyl formate. The n-pentyl formate is only slightly soluble in water and reacts with sodium hydroxide by the class of reactions known as ester saponification.

\[
\text{n-pentyl formate + sodium hydroxide = n-pentyl alcohol + sodium formate}
\]
Sharma and Nanda (1963) studied ester saponification inside swarms of aqueous drops. They did not directly measure droplet size or contact time. This work was planned to study a system similar to those studied by Sharma and Nanda. This work differs from the work by Sharma and Nanda in that single drops were studied and droplet sizes and contact times were measured. N-pentyl formate was chosen as the ester for the reaction because it reacts rapidly with sodium hydroxide and is only slightly soluble in aqueous solutions.

5.1.1. Equipment. The experimental apparatus is shown in figure 5.1. Most of the equipment was made of Pyrex glass. The burette, which held the phase to be dispersed, was made by fusing together two fifty milliliter graduated burettes. A ground glass fitting was fused to the top of the burette to allow for an air tight seal. The only vent for the burette was a capillary tube, which was connected to the outside of the burette and extended from the top of the burette to about halfway down the burette.

The burettes which were previously used as reservoirs for the dispersed phase (Andoe, 1968) were closed at the top by a tapered polyethylene stopper. The polyethylene stopper did not fit well enough to make an air tight seal with the burette. Air leaks about the polyethylene stopper allowed the pressure at the bottom of the burette to vary. The variation of the pressure made it difficult to hold the frequency of drop formation constant. The use of a ground glass stopper in this work eliminated the problem of pressure leaks about the stopper.

The vent in the burette used by Andoe was a capillary tube which passed through the polyethylene stopper and into the burette. Since
Figure 5.1. Experimental Apparatus
the capillary tube used by Andoe was inside the burette, a correction was necessary for all volume measurements read from the burette. The need for a correction was negated in this work because the capillary vent was external to the burette.

The burette used in this work was twice as tall as the burette used by Andoe (1968). The extra height of the burette allowed a greater constant pressure on the drop forming nozzle than was possible with the burette length used by Andoe. The greater height made the burette cumbersome and limited the height of column which could be used in a laboratory with a low ceiling.

The bottom of the burette was fused to a glass fitting which could be connected to a teflon needle valve used to regulate the flow from the burette. At the other end of the needle valve another glass connector was fused to the barrel of a hypodermic syringe. The use of a syringe fitting allowed the use of different nozzles to form the aqueous drops in the continuous ester phase. The nozzles were made from stainless steel hypodermic needles. The points of the needles were carefully sanded off to form blunt ends. Four nozzle sizes were used; 15, 20, 24, and 27 gauge.

The column where the actual contact took place was constructed from a seven and one-half centimeter pyrex glass tube. There were three different columns made from tubes of different lengths to allow for different times of contact of the aqueous drops. The column lengths used were 5, 25, and 45 centimeters. The bottoms of the columns were tapered and fused to another glass fitting. This fitting held a teflon needle valve to regulate the flow rate of the coalesced drops out of
the bottom of the column. Another glass fitting at the bottom of the valve provides an exit tube where the coalesced drops could be collected in a sample bottle.

5.1.2. Experimental Procedure. Just prior to a droplet extraction experiment in the extraction column, an aqueous solution was prepared which was one formal in sodium sulfate and a little more than 0.04 formal in sodium hydroxide. This solution was titrated with standard oxalic acid solution (0.02 Normal) in order to determine the sodium hydroxide concentration. The basic solution was then diluted with one formal sodium sulfate solution, until it was 0.04 formal base.

About one hour before an experimental run, the n-pentyl formate to be employed as the continuous phase was also prepared. The n-pentyl formate for the first runs was poured into four-liter separatory funnels and saturated with carbon dioxide free water. Later in the experimental work, it was suggested (Dr. D. S. Wulfman, private communication) that one hour was sufficient to allow the water to significantly hydrolize the ester.

\[
\text{n-pentyl formate} + \text{water} = \text{n-pentyl alcohol} + \text{formic acid}
\]

The hydrolysis is especially important since this reaction is autocatalytic.

After the possibility of hydrolysis was suggested, all ester was stored over dry calcium carbonate and molecular sieves. This ester was not saturated with water, but was filtered to remove any suspended solids, and used dry. The results of runs with both wet and dry ester are presented in Section VII.
After both solutions were prepared, the burette and the column were cleaned with acid cleaning solution and rinsed with the solution which they would contain during the run. Then, the burette was filled to above the top graduation with the aqueous solution. The column was filled to a predetermined height with n-pentyl formate. Then the desired nozzle was attached to the bottom of the burette and positioned over the column so that the nozzle extended about one millimeter into the ester phase.

With all of the equipment assembled as shown in figure 5.1, the valve just above the nozzle was opened to allow water drops to form in the ester phase and fall to the bottom of the column. A stopwatch was used to check the frequency of drop formation. The frequency was held constant at one drop per second.

After drops began to form at the nozzle, the reduced liquid level in the burette caused air bubbles to be drawn in through the capillary vent. Care was taken to see that the ground glass stopper was in place so that the only vent to the atmosphere was the capillary tube. The purpose of the capillary vent was to keep the pressure at the nozzle constant.

After several drops had been formed at the nozzle, they began to coalesce at the bottom of the column. The needle valve at the bottom of the column was opened slightly to allow some of the coalesced drops to exit. The level of the coalesced phase at the bottom of the column was kept constant at a level, where the outside diameter of the tapered column was three-fourths of an inch, as determined by a circle template.
When ten to twelve milliliters of aqueous drops had passed through the column and were discarded, a sample bottle was placed below the exit tube and the sample collection began. During the time that the sample was being collected, an electric stop watch was used to record the time for a drop to fall from the nozzle to the coalesced phase at the bottom of the column. Ten readings were taken, and the average was considered the contact time of the drop. The room temperature was held constant by manual adjustment of an air conditioner and two portable electric heaters. During sample collection, the room temperature and the frequency of drop formation were checked frequently and adjusted as need be. During a run, the droplet radius and terminal velocity were also determined as described in Appendix D.

After about twelve milliliters of sample were collected, the burette was removed from over the column and an additional sample of the uncontacted droplet phase was drawn directly from the burette. This sample was used as a check of the formality of the uncontacted aqueous solution.

The samples were shaken and allowed to sit for at least five minutes to allow all of the ester in the water sample time to react with the excess of sodium hydroxide. Ten milliliters of the sample were then placed in a flask with an excess of standard oxalic acid solution (0.02 Normal) and back titrated using uncontacted sodium hydroxide solution. The indicator for the titration was phenolphthalein. The total moles of n-pentyl formate transferred per unit volume of dispersed phase, $C_{e}^{m}$, is the difference between the initial concentration of sodium hydroxide, $C_{bo}$, and the final concentration of sodium hydroxide, $C_{bf}$. 

Throughout each experiment the temperature in the room was kept at twenty-five degrees centigrade, plus or minus one-half degree. The results of these experiments are tabulated and discussed in Section VII.
VI. INTERFACIAL CONCENTRATION APPROXIMATIONS

Interfacial concentrations for mass transfer without chemical reaction are taken from equilibrium data. When all of the resistance to mass transfer exists in one phase, the interfacial concentration of the transferring solute is its solubility in the extracting phase. However, when there is also a chemical reaction at the interface, the concentration of the transferring solute may be some value less than the solubility. This portion of the experimental investigation was performed to measure the concentration of n-pentyl formate, \( C_{as} \), on the water side of the water-ester interface.

6.1. Theory

There are no published data for the solubility of n-pentyl formate in water or water solutions. However, experimentally measured surface concentrations for n-pentyl formate can be compared with solubilities for i-pentyl formate. The solubility of i-pentyl formate in water is 0.0256 mole per liter at twenty-two degrees centigrade (Seidell, 1941, p. 436) and 0.0282 mole per liter at thirty degrees centigrade (Sharma and Nanda, 1968).

When ionic compounds are added to water, the solubility of the ester is reduced by a process known as "salting out". This reduced solubility can be estimated by the method of van Krevelen and Hofstijzer (1948b) as reported by Danckwerts (1970).

\[
\log \left( \frac{C_{as\circ}}{C_{as}} \right) = g I
\]  

(6.1)

\( C_{as\circ} \) is the surface concentration in water and \( C_{as} \) is the surface concentration in the ionic solution. The symbol \( I \) represents the ionic
strength defined by

\[ I = \frac{1}{2} \sum c_i z_i^2 \]  

(6.2)

where \( c_i \) is the concentration of an individual ion and \( z_i \) is the corresponding ionic charge. The concentrations of sodium hydroxide and ester are too small to enter into these calculations. From equation (6.2) the ionic strength of one formal sodium sulfate is three. The coefficient \( g \) is an empirical constant.

\[ g = g_+ + g_- + g_e \]  

(6.3)

where (Danckwerts, 1970)

\[ g_+ , \text{ sodium ion contribution} = 0.091 \]
\[ g_- , \text{ sulfate ion contribution} = 0.022 \]
\[ g_e , \text{ ester contribution} = \text{negligible} \]

6.2. Concentration Cell

The interfacial concentration of n-pentyl formate in various aqueous solutions was measured. A large diameter burette (3 to 3.5 cm.) fitted with a teflon stopcock and a capillary exit tube was used. This especially made burette is referred to in this work as a concentration cell.

The same type of concentration cell was used by Andoe (1968). The exit tube for the concentration cell used by Andoe was a large diameter glass tube. The capillary exit tube used in this work made it possible to make a more accurate separation of the two phases than was possible with the concentration cell used by Andoe.

Fifty milliliters of aqueous solution were drained from a pipette into a clean concentration cell. Then twenty-five milliliters of
n-pentyl formate was added to the concentration cell from a pipette. The ester drained slowly down the side of the concentration cell. The time for an interfacial concentration determination was considered to begin when the ester first covered the free surface of the aqueous solution. After a desired portion of an hour, the stopcock of the concentration cell was opened and the aqueous phase was slowly drained into a sample bottle. The stopwatch was stopped when the interface between the ester and water reached the small portion of the concentration cell just above the stopcock. The length of a run was approximately one-half hour or one hour. The capillary exit tube allowed the collection of virtually all of the aqueous phase. During each run, the depth of the meniscus between the ester and the water was measured by a cathetometer. The depth of the meniscus was used to calculate the transfer area for the concentration cell.

Interfacial concentrations were measured for three aqueous solutions. The aqueous phase for series A was 0.02 formal sodium hydroxide solution. For series B, the aqueous phase was one formal sodium sulfate. The aqueous phase for series C was one formal sodium sulfate and 0.04 formal sodium hydroxide.

Expressions for interfacial concentrations with and without chemical reaction were derived in Appendix E. The method of least squares was applied in the developments. Thus, for series B

\[ C_{as} = \frac{V}{2} \sqrt{\frac{\pi}{D_a}} \left( \frac{4}{9} \frac{C_m}{S_o} \sqrt{t} \right) \]

and for series A and C
The interfacial concentration was calculated for each individual run and compared to the "least squares" value for the four runs in a series. The comparison was in the form of the average absolute percent deviation, AAPD (see Tables 6.1 and 6.2).

The area for mass transfer in the concentration cell was calculated from the equation for one-half the surface area of an oblate ellipsoid

$$S_o = \pi \left( \frac{p^2}{2} + \frac{q^2}{e} \right) \ln \left( \frac{1 + e}{1 - e} \right)$$

(6.6)

where

$$e = \sqrt{(p^2 - q^2)/p}$$

$$p = \text{radius of concentration cell, cm.}$$

$$q = \text{meniscus depth, cm. (see Tables 6.1, 6.2, and 6.3)}$$

6.3. Discussion of Method

The use of the penetration theory to develop the least squares expression for the interfacial concentration requires the assumption that the aqueous side of the interface is stagnant. A stagnant interface is not completely true at the start of a run when the n-pentyl formate is drained onto the top of the aqueous phase. Care was taken to let the ester run slowly down the side of the concentration cell to avoid mixing at the interface. Despite this care, the impact of the entering ester always caused visible mixing at the interface. The error from
this mixing is probably small, since the mixing effect is limited to about the first minute of contact when rates of mass transfer by diffusion are so large that they are probably comparable to mass transfer rates in non-stagnant fluids.

There is a possibility of mixing at the interface during withdrawal of the aqueous sample. However, the sample was withdrawn very slowly through the capillary exit tube. It required about three minutes to collect the fifty milliliter sample and there was no mixing observed at the interface. There was, therefore, no reason to believe that the sample was not withdrawn in plug flow.

The time required to obtain an appreciable concentration change in the concentration cell raises a question of the applicability of the interfacial concentration data to droplet studies. The shortest time used in the concentration cell experiments was one-half hour. The longest contact time in the droplet studies was six seconds. If the interfacial concentration changes with time, the values obtained at large times would not apply to short time droplet studies. However, it is not likely that the interfacial concentration is time dependent for the system studied in this work. Since the organic phase is pure n-pentyl formate, there are no diffusional considerations in the organic phase. Thus, n-pentyl formate is always present on the organic side of the interface at a constant concentration value. It will be shown in the next section that for Series A and Series B the experimentally determined interfacial concentration did not change as the contact time was varied from one-half hour to one hour. Hence it was safely assumed that the concentration of n-pentyl formate on the aqueous side of the interface is constant with time.
6.4. Results

The data for the study of the interfacial concentration of n-pentyl formate in 0.02 formal sodium hydroxide solution (Series A) is given in Table 6.1. The least squares fit of the data indicates an interfacial concentration, $C_{as}$, of 0.0278 moles per liter with an average absolute per cent deviation of six per cent. Within experimental error this concentration compares with the solubilities of i-pentyl formate in water given in the introduction to this section (Seidell, 1941, p. 436 and Sharma and Nanda, 1968). Despite the chemical reaction, the interfacial concentration is essentially the same as the solubility in water.

With 0.0278 moles per liter as the solubility of n-pentyl formate in water, equation (6.1) predicts the solubility of n-pentyl formate in one formal sodium sulfate to be 0.0127 moles per liter. Table 6.2 (Series B) shows the interfacial concentration of n-pentyl formate in one formal sodium sulfate to be 0.0134 moles per liter (with an AAPD of four per cent). Therefore, the van Krevelen and Hoftijzer correlation is valid for this case of interfacial concentration determination.

6.5. Interfacial Turbulence

The actual concentrations in the bulk of the aqueous phase used in the droplet studies are 0.04 formal sodium hydroxide and one formal sodium sulfate. Series C of the interfacial concentration studies was designed to measure the interfacial concentration of n-pentyl formate in 0.04 formal sodium hydroxide and one formal sodium sulfate aqueous solution. The results for series C are shown in Table 6.3. The concentration of sodium hydroxide for series C is too small to cause any
### TABLE 6.1
INTERFACIAL CONCENTRATION DETERMINATION--SERIES A

**Light Phase:** n-pentyl formate saturated with water

**Dense Phase:** 0.02 f sodium hydroxide solution

\[ V = 50 \text{ cm}^2, \quad \rho = 1.746 \text{ cm}, \quad D_b = 1.56 \times 10^{-5} \text{ cm}^2/\text{sec}, \quad D_a = 0.692 \times 10^{-5} \text{ cm}^2/\text{sec} \]

<table>
<thead>
<tr>
<th>Sample</th>
<th>time (sec)</th>
<th>meniscus depth (mm)</th>
<th>area (cm$^2$)</th>
<th>initial concentration ($C_{bo}$, mole/liter)</th>
<th>mass transferred ($\overline{C}_{mt}$, mole/liter)</th>
<th>interfacial concentration ($C_{as}$, mole/liter)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-1</td>
<td>3607</td>
<td>3.1</td>
<td>8.61*</td>
<td>0.0187</td>
<td>0.0024</td>
<td>0.0266</td>
</tr>
<tr>
<td>A-2</td>
<td>3478</td>
<td>2.5</td>
<td>10.1</td>
<td>0.0228</td>
<td>0.0030</td>
<td>0.0258</td>
</tr>
<tr>
<td>A-3</td>
<td>3660</td>
<td>0.8</td>
<td>9.59</td>
<td>0.0202</td>
<td>0.0031</td>
<td>0.0307</td>
</tr>
<tr>
<td>A-4</td>
<td>1788</td>
<td>0.9</td>
<td>9.59</td>
<td>0.0204</td>
<td>0.0021</td>
<td>0.0285</td>
</tr>
</tbody>
</table>

*p = 1.587 cm

by least squares $C_{as} = 0.0278 \quad \text{AAPD} = 6\%$
**TABLE 6.2**

**INTERFACIAL CONCENTRATION DETERMINATION--SERIES B**

Light Phase: dry n-pentyl formate

Dense Phase: 1 f sodium sulfate solution

\[ V = 50 \, \text{cm}^3, \quad p = 1.746 \, \text{cm}, \quad D_a = 0.469 \times 10^{-5} \, \text{cm}^2/\text{sec} \]

<table>
<thead>
<tr>
<th>Sample</th>
<th>time (t)</th>
<th>meniscus depth (q)</th>
<th>area (S_0)</th>
<th>mass transferred (\bar{c}_{mt} \times 10^4)</th>
<th>interfacial concentration (C_{as})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>sec</td>
<td>mm</td>
<td>cm²</td>
<td>mole/liter</td>
<td>mole/liter</td>
</tr>
<tr>
<td>B-1</td>
<td>3595</td>
<td>0</td>
<td>9.59</td>
<td>3.96</td>
<td>0.0141</td>
</tr>
<tr>
<td>B-2</td>
<td>1810</td>
<td>0</td>
<td>9.59</td>
<td>2.58</td>
<td>0.0130</td>
</tr>
<tr>
<td>B-3</td>
<td>3598</td>
<td>3.3</td>
<td>10.37</td>
<td>4.04</td>
<td>0.0134</td>
</tr>
<tr>
<td>B-4</td>
<td>1815</td>
<td>3.2</td>
<td>10.37</td>
<td>2.72</td>
<td>0.0127</td>
</tr>
</tbody>
</table>

by least squares \(C_{as} = 0.0134 \, \text{moles/liter} \) AAPD = 4%
TABLE 6.3

INTERFACIAL CONCENTRATION DETERMINATION--SERIES C

Light Phase: dry n-pentyl formate

Dense Phase: 0.04 f sodium hydroxide, 1 f sodium sulfate solution

\[ V = 50 \, \text{cm}^2, \quad p = 1.746 \, \text{cm}, \quad D_a = 0.469 \times 10^{-5} \, \text{cm}^2/\text{sec}, \quad D_b = 1.01 \times 10^{-5} \, \text{cm}^2/\text{sec}, \quad C_{bo} = 0.0399 \]

<table>
<thead>
<tr>
<th>Sample</th>
<th>time</th>
<th>meniscus depth</th>
<th>area</th>
<th>mass transferred</th>
<th>interfacial concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>t</td>
<td>q</td>
<td>( S_0 )</td>
<td>( \bar{C}_{mt} )</td>
<td>( C_{as} )</td>
</tr>
<tr>
<td></td>
<td>sec</td>
<td>mm</td>
<td>( \text{cm}^2 )</td>
<td>mole/liter</td>
<td>mole/liter</td>
</tr>
<tr>
<td>C-1</td>
<td>1806</td>
<td>2.8</td>
<td>10.13</td>
<td>0.0032</td>
<td>0.137</td>
</tr>
<tr>
<td>C-2</td>
<td>1809</td>
<td>3.0</td>
<td>10.20</td>
<td>0.0036</td>
<td>0.165</td>
</tr>
<tr>
<td>C-3</td>
<td>3614</td>
<td>3.0</td>
<td>10.20</td>
<td>0.0062</td>
<td>0.218</td>
</tr>
<tr>
<td>C-4</td>
<td>3596</td>
<td>3.1</td>
<td>10.24</td>
<td>0.0066</td>
<td>0.237</td>
</tr>
</tbody>
</table>
appreciable salting out of the ester in comparison to the salting out of the ester by the sodium sulfate. In addition, the results of Series A of the interfacial concentration studies have shown that the reaction between sodium hydroxide and n-pentyl formate is too slow to appreciably deplete n-pentyl formate from the interface. Therefore, the experimentally determined interfacial concentration of n-pentyl formate for Series C should be about 0.0134 moles per liter, as measured in Series B. However, as seen in Table 6.3, the interfacial concentration obtained in Series C is at least an order of magnitude greater than the interfacial concentration from Series B. The unexpectedly high results for Series C could not result from increased solubility, but might be due to mixing in the aqueous phase. The mixing is thought to be surface tension driven interfacial turbulence as observed by Seto, et al. (1971) for flat interfaces. In agreement with the observations by Seto, the data in Table 6.3 indicate that the effect of mixing is more pronounced at longer times. Seto found that, although their systems did exhibit turbulence for contact times greater than twenty minutes, the same systems did not exhibit turbulence at contact times comparable to the times involved in the droplet studies described in this work. Therefore, the presence of turbulence at long contact times does not support the conclusion that turbulence is present at short contact times. Bupara (1964) showed that the criteria for interfacial turbulence at a curved surface is different from the criteria at a flat interface. Thus, interfacial turbulence could be important for mass transfer with chemical reaction in the concentration cell, but not important in the freely falling drops.
The values given in Table 6.3 were not thought to be representative of the true interfacial concentration. Therefore, the value of the interfacial concentration was taken to be 0.0134 moles per liter as found for mass transfer without chemical reaction in Series B.

An attempt was made to detect optically the presence of spontaneous interfacial turbulence at a flat interface. A laser grating interferometer, described by Griffin and Throne (1968), was assembled by Mr. Ron Cannon as a special research project. When a liquid-liquid interface was optically aligned with the laser beam, the concentration gradients appeared as dark lines on a screen. Unless interfacial turbulence or other concentration dependent phenomena were present, the lines would be straight and horizontal. Any irregularities in the lines could be identified as interfacial turbulence or density driven convective currents. Turbulence was observed in the ethyl acetate-aqueous sodium hydroxide system studied by Seto et al. (1971) in the form of ripples in the concentration gradient lines. Turbulence in the t-butyl chloride in benzene-water system studied by Andoe (1968) was observed as jets of organic phase which penetrated one to two centimeters into the water.

The same laser optical test was applied to n-pentyl formate in contact with aqueous sodium hydroxide solutions which contained one formal sodium sulfate or no sodium sulfate. Turbulence in the form of occasional jets was observed for one-tenth formal sodium hydroxide solution which did not contain sodium sulfate. However, no turbulence was visually observed at the flat interface if the aqueous phase contained one formal sodium sulfate for sodium hydroxide concentrations which varied from 0.02 formal to one formal.
Turbulence was detected in the interfacial concentration studies for an aqueous phase which contained 0.04 formal sodium hydroxide and one formal sodium sulfate. For the same concentrations no turbulence was detected by the optical method. The interfacial concentration studies were more effective in detecting turbulence than was the optical study because the criteria for turbulence was based on a numerical calculation rather than a visual judgement.
VII. EXPERIMENTAL DISCUSSION

The droplet mass transfer results were obtained as described in Section V and are tabulated in Tables 7.3 through 7.6. In addition, the physical properties of the chemicals used are described in Appendix D. This chapter explains the way the experimental results were treated to eliminate end effects and compared with theory. The parameters for this experimental study are shown in Table 7.1. The physical properties used to calculate the parameters are given in Appendix D. The terminal velocity was measured for 1 formal Na$_2$SO$_4$ and 0.04 formal NaOH solution falling through n-pentyl formate presaturated with water. All other physical properties were measured for dry n-pentyl formate. A more complete description of the means by which the physical properties were measured is given in Appendix D.

7.1. Theoretical Assumptions

This section will discuss the extent to which the experimental system described in Section V, satisfies the assumptions which are basic to the theory developed in Section III.

7.1.1. Heat Transfer. Seto, et al. (1965) used fine thermocouple probes inserted at various points in a system of ethyl acetate in contact with NaOH solution. They found temperature differences of no more than half a degree Centigrade to exist throughout the system. The concentration changes for n-pentyl formate in contact with sodium hydroxide solution would be smaller than if the ester were ethyl acetate. The ethyl acetate is much more soluble in water. Since the concentration changes are smaller, the heat effects would also be expected to
TABLE 7.1

DIMENSIONLESS VARIABLES IN THE EXPERIMENTAL STUDY
BASED ON PHYSICAL PROPERTIES FOR DRY N-PENTYL FORMATE

\[ R_c = 0.335 \quad N_p = 7.63 \times 10^9 \]
\[ R_D = 2.16 \quad T = 25.0 \pm 0.5^\circ C \]
\[ N_{Sc} = 2960 \]

<table>
<thead>
<tr>
<th>Nozzle Gauge</th>
<th>( k_R )</th>
<th>( N_{Pe} \times 10^{-4} )</th>
<th>( N_{Re} )</th>
<th>( N_{We} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>27</td>
<td>3023</td>
<td>7.14</td>
<td>490</td>
<td>3.03</td>
</tr>
<tr>
<td>24</td>
<td>3979</td>
<td>8.35</td>
<td>573</td>
<td>3.61</td>
</tr>
<tr>
<td>20</td>
<td>5437</td>
<td>9.82</td>
<td>674</td>
<td>4.27</td>
</tr>
<tr>
<td>15</td>
<td>8953</td>
<td>11.50</td>
<td>789</td>
<td>4.60</td>
</tr>
</tbody>
</table>
be less. The temperature gradients in the experimental system will thus be considered negligible.

7.1.2. Velocity Profile. The shape of the aqueous drops was visually observed as the drops fell through the continuous phase. The drops formed with the 27 gauge nozzle appeared to be spherical. All of the other drop sizes studied were larger and deviated from a spherical shape. The shape of the two largest sized drops oscillated from almost spherical to ellipsoidal. Therefore, if the theory developed in Section III is valid for this experimental system, it would apply only for the smallest drop size.

The second fluid flow assumption requires that wall effects be insignificant. The nozzle was always located so that the drops fell through the central part of the column. The ratio of the column diameter to the diameter of the largest liquid drop was greater than fifteen. Therefore, wall effects should not have been significant.

The assumption of a steady state velocity profile within the droplets is not valid in the oscillating drop sizes. The oscillation sets up turbulent fluid motion which fluctuates with time. In non-oscillating drops the laminar fluid flow approaches steady state after detachment from the nozzle. As the velocity profile inside the drop approaches steady state, the falling drop approaches a terminal velocity. The proximity of a drop velocity to its terminal velocity can be approximated by comparing the ratios of column height to contact time for successive columns. Between the 25 and 45 centimeter columns, this ratio changes by five to ten per cent for the various drop sizes. However, the ratio of the column height over the contact time is not a true
measure of the velocity, because it includes end effects. Therefore, the velocity after 25 centimeters probably differs from the velocity at 45 centimeters by less than five or ten per cent.

The variation in concentrations in the drop is less than 0.04 formal for sodium hydroxide and 0.0134 formal for n-pentyl formate. This variation would not significantly alter the viscosity or density of the dispersed phase. The constant density and viscosity allows the assumption that the mass transfer equations and the fluid flow equations are independent.

If a nozzle was formed or cleaned improperly the forming drop would be skewed to one side. A drop so formed would not fall straight down the column. All nozzles which did not form the drops properly were discarded. If the nozzles were not checked for drop formation, the assumption that the velocity profile is symmetrical about the polar axis would be invalid.

If no impurities collect at the interface, the velocity field is continuous at the phase boundary. Extreme care was taken to exclude all polar organic impurities. These characteristically collect at the interface.

The final hydrodynamic assumption is the least likely to apply to the experimental system. The Hadamard streamlines have been shown to be qualitatively valid for Reynolds numbers approaching one hundred (Johnson and Hamielec, 1960), but all Reynolds numbers for this study were over four hundred. Photographic evidence indicates that the Hadamard results are not valid in this flow regime.

7.1.3. Mass Transfer. The reaction of sodium hydroxide with an ester is irreversible (Groggins, 1952, p. 668). The reaction is also
first-order with respect to the ester and first order with respect to sodium hydroxide.

The continuous phase was primarily or entirely n-pentyl formate, depending on the type of experiment. Since each water drop was completely surrounded by essentially pure material to be extracted, the surface of the drop was always saturated, as assumed. Further substantiation of this fact is given by the results in Section VI.

It is vital to the sample analysis as well as the development of the theory that the sodium hydroxide is not soluble in the continuous phase. In general, ionic substances are not soluble in organic solutes. Seto (1969) studied sodium hydroxide solutions in contact with various esters and found no trace of either sodium hydroxide or sodium formate in the ester phase.

7.1.4. Limitations and Other Models. The three previous sections discussed the validity of the assumptions used in Section III, as applied to the experimental system. All of the assumptions for the circulating drop model are valid for this system, except the limitations on the fluid flow model. The most important limitation is probably the use of velocity profiles for creeping flow in the theoretical model. At present, a computer program is being processed under the direction of Dr. R. M. Wellek to calculate velocity profiles which would be valid for much higher Reynolds numbers. This revised velocity profile would be valid for the smallest drop size used in this study. No attempt is currently underway to treat mass transfer with reaction in turbulent drops.
The penetration theory for mass transfer is strictly valid only for quiescent fluids. Therefore, the experimental hydrodynamic conditions rule out the strict application of this theory. In other words, the determination of the proper characteristic contact time in this problem is very difficult.

The film theory fits all experimental conditions except that a circulating drop does not exactly fit the idealized model for the film mass transfer model. However, an empirical approximation of the film thickness based on a similar system will be compared with the experimental results.

7.2. Data Correlation by Least Squares Technique.

The total mass transferred per unit droplet volume, $A_{mt}$, found by analysis of the samples as described in Section V, includes the mass transferred during drop formation and coalescence. Johnson, et al. (1958) suggest accounting for end effects by plotting the fraction extracted against the square root of the contact time. The intercept of this curve, extrapolated to zero contact time, is an approximation of the total mass transferred during drop formation and coalescence. The form of a straight line equation for the total mass transferred with end effects, $A_{mt}$, as a function of the square root of the dimensionless time, $\tau$, is

$$
\frac{A_{mt}}{A_{mt}} = e_1 + e_2 \tau^{\frac{1}{2}}
$$

(7.1)

The intercept of equation (7.1), $e_1$, is the total mass transferred during end effects. The coefficients for equation (7.1) were evaluated by a least squares fit of the experimental data (Miller and Freund, 1965, p. 230).
These coefficients are shown in Table 7.2 for each nozzle size. The average absolute per cent deviation (AAPD) of the quantity predicted by equation 7.1 from the experimental total mass transferred with end effects is shown in Table 7.2. The least squares correlation and the experimental mass transferred, with end effects, are shown in figures 7.1 through 7.4. From these results, the total mass transferred during free fall of the drop is computed

\[ \bar{A}_{mt} = \bar{A}_{mt} - e_{1} \]  

(7.4)

These experimental results are shown in Tables 7.3 through 7.6.
Figure 7.1. Total Mass Transferred with End Effects as a Function of the Square Root of Dimensionless Time for a Reynolds Number of 490
Figure 7.2. Total Mass Transferred with End Effects as a Function of the Square Root of Dimensionless Time for a Reynolds Number of 573
Figure 7.3. Total Mass Transferred with End Effects as a Function of the Square Root of Dimensionless Time for a Reynolds Number of 674
Figure 7.4. Total Mass Transferred with End Effects as a Function of the Square Root of Dimensionless Time for a Reynolds Number of 789
### TABLE 7.3

MASS TRANSFER DATA FOR 27 GAUGE NOZZLE

\[ V_t = 16.1 \text{ cm/sec} \quad a = 0.129 \text{ cm} \]

<table>
<thead>
<tr>
<th>Column Height</th>
<th>Contact Time</th>
<th>( \tau \times 10^4 )</th>
<th>Total Moles Transferred</th>
<th>Total Mass Transferred</th>
</tr>
</thead>
<tbody>
<tr>
<td>cm</td>
<td>t (sec)</td>
<td>Dimensionless</td>
<td>( \overline{C}_{mt} )</td>
<td>( \overline{A}_{mt} )</td>
</tr>
<tr>
<td>5*</td>
<td>0.24</td>
<td>0.82</td>
<td>0.0064</td>
<td>0.156</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.0051</td>
<td>0.059</td>
</tr>
<tr>
<td>45*</td>
<td>2.99</td>
<td>10.24</td>
<td>0.0087</td>
<td>0.328</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.0085</td>
<td>0.313</td>
</tr>
<tr>
<td>5</td>
<td>0.24</td>
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<td>0.0056</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.0052</td>
<td>0.067</td>
</tr>
<tr>
<td>25</td>
<td>1.59</td>
<td>4.48</td>
<td>0.0068</td>
<td>0.186</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.0071</td>
<td>0.209</td>
</tr>
<tr>
<td>45</td>
<td>3.22</td>
<td>9.08</td>
<td>0.0092</td>
<td>0.365</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.0086</td>
<td>0.320</td>
</tr>
</tbody>
</table>

*n-pentyl formate presaturated with water

\( a = 0.117 \text{ cm} \)
TABLE 7.4

MASS TRANSFER DATA FOR 24 GAUGE NOZZLE

\( V_t = 16.4 \text{ cm/sec} \)

<table>
<thead>
<tr>
<th>Column Height</th>
<th>Contact Time</th>
<th>Total Moles Transferred With End Effects</th>
<th>Total Mass Transferred</th>
</tr>
</thead>
<tbody>
<tr>
<td>cm</td>
<td>t (sec)</td>
<td>( \tau \times 10^4 )</td>
<td>( \overline{c_{mt}} ) (mole/liter)</td>
</tr>
<tr>
<td>5*</td>
<td>0.22</td>
<td>0.55</td>
<td>0.0046</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.0034</td>
</tr>
<tr>
<td>45*</td>
<td>2.65</td>
<td>6.62</td>
<td>0.0074</td>
</tr>
<tr>
<td>5</td>
<td>0.22</td>
<td>0.47</td>
<td>0.0038</td>
</tr>
<tr>
<td>25</td>
<td>1.39</td>
<td>2.98</td>
<td>0.0052</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.0052</td>
</tr>
<tr>
<td>45</td>
<td>2.91</td>
<td>6.23</td>
<td>0.0070</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.0070</td>
</tr>
</tbody>
</table>

* \( n \)-pentyl formate presaturated with water

\( a = 0.137 \text{ cm} \)
TABLE 7.5
MASS TRANSFER DATA FOR 20 GAUGE NOZZLE

\[ v = 16.5 \text{ cm/sec} \quad a = 0.173 \text{ cm} \]

<table>
<thead>
<tr>
<th>Column Height</th>
<th>Contact Time</th>
<th>Total Moles Transferred with End Effects</th>
<th>Total Mass Transferred</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( t \times 10^4 )</td>
<td>( \bar{C}_{mt} )</td>
<td>( \bar{A}_{mt} )</td>
</tr>
<tr>
<td>cm</td>
<td>sec</td>
<td>Dimensionless</td>
<td>mole/liter</td>
</tr>
<tr>
<td>5*</td>
<td>0.19</td>
<td>0.34</td>
<td>0.0026</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.34</td>
<td>0.0028</td>
</tr>
<tr>
<td>45*</td>
<td>2.64</td>
<td>4.72</td>
<td>0.0058</td>
</tr>
<tr>
<td>5</td>
<td>0.19</td>
<td>0.30</td>
<td>0.0026</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.30</td>
<td>0.0024</td>
</tr>
<tr>
<td>25</td>
<td>1.35</td>
<td>2.12</td>
<td>0.0040</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.12</td>
<td>0.0040</td>
</tr>
<tr>
<td>45</td>
<td>2.67</td>
<td>4.18</td>
<td>0.0060</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.18</td>
<td>0.0062</td>
</tr>
</tbody>
</table>

* n-pentyl formate presaturated with water

\( a = 0.162 \text{ cm} \)
<table>
<thead>
<tr>
<th>Column Height</th>
<th>Contact Time</th>
<th>Total Moles Transferred</th>
<th>Total Mass Transferred</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>t &amp; ( \tau \times 10^4 )</td>
<td>( \bar{C}_{mt} )</td>
<td>( \bar{A}_{mt} )</td>
</tr>
<tr>
<td>cm</td>
<td>sec</td>
<td>Dimensionless</td>
<td>mole/liter</td>
</tr>
<tr>
<td>5*</td>
<td>0.24</td>
<td>0.27</td>
<td>0.0022</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.27</td>
<td>0.0018</td>
</tr>
<tr>
<td>45*</td>
<td>2.90</td>
<td>3.24</td>
<td>0.0044</td>
</tr>
<tr>
<td>25</td>
<td>1.42</td>
<td>1.35</td>
<td>0.0032</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.35</td>
<td>0.0032</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.35</td>
<td>0.0029</td>
</tr>
<tr>
<td>45</td>
<td>2.69</td>
<td>2.56</td>
<td>0.0044</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.56</td>
<td>0.0048</td>
</tr>
</tbody>
</table>

*\( n\)-pentyl formate presaturated with water

\[ a = 0.205 \text{ cm} \]
The data for individual experimental runs are shown in Tables 7.3 through 7.6. For all column lengths except the shortest, the individual data points were repeated with a maximum absolute deviation of less than eleven per cent from the average of a set of data points. For the shortest column length some data points deviated from the average by as much as 64 per cent. A possible reason for the greater deviation for the shortest column length is given in section 7.3.2.

7.3. Comparison With Theory

The values of the dimensionless expression for total mass transferred, $\tilde{A}_{mt}$, are listed in Tables 7.3 through 7.6 and are plotted in figures 7.5 through 7.8. The data points, obtained for those runs in which the n-pentyl formate was presaturated with water, are designated by circles, and the data points for dry n-pentyl formate are designated by triangles. The least squares equations developed in section 7.2 are also shown in figures 7.5 through 7.8.

The experimental data will be discussed with respect to the laminar fluid sphere model developed in Section III and an adaptation of the film theory developed in section 7.3.2.

7.3.1. Fluid Sphere Model. It was shown in Section IV that for dimensionless times less than 0.001 the fluid sphere model could be closely approximated by the penetration theory. Yeramian, et al. (1970) found their approximation, which was discussed in section 4.4.2. of this work, to predict mass transfer with second-order reaction by the penetration theory with less than eight per cent error. Because of the simplicity of the Yeramian approximation, equation (4.22) was used in figures 7.5 through 7.8 to generate the curves for the fluid sphere model. The enhancement factor for mass transfer with first-order reaction, predicted by the penetration theory (Wellek, et al.,
Figure 7.5. Experimental Total Mass Transferred as a Function of Dimensionless Time for a Reynolds Number of 490 (Non-Oscillating)
Figure 7.6. Experimental Total Mass Transferred as a Function of Dimensionless Time for a Reynolds Number of 573 (Non-Oscillating)
Figure 7.7. Experimental Total Mass Transferred as a Function of Dimensionless Time for a Reynolds Number of 674 (Oscillating)
Figure 7.8. Experimental Total Mass Transferred as a Function of Dimensionless Time for a Reynolds Number of 789 (Oscillating)
was
\[
\phi_1 = 1 + k_2 C_{bo} t/3
\]  (7.5)

The value of the enhancement factor given by equation (7.5) was used in conjunction with equations (4.17) and (4.22) for the Yeramian approximation. The value of t used in equation (7.5) was the droplet contact time.

The total mass transferred, as calculated by the penetration theory, is consistently less than that experimentally observed. For the smallest drop size, shown in figure 7.5, only two of the experimental data points are significantly greater than twice the total mass transferred predicted by the penetration theory. For the oscillating drops, the experimental total mass transferred is as much as four times that predicted by the penetration theory. (i.e., equations (4.17), (4.22) and (7.5)). The even greater deviation of the oscillating drop data from the penetration theory is probably due to the turbulent mixing inside the drop. As mentioned in section 7.1, the velocity profile used to develop the fluid sphere model was probably inadequate for even the smallest drop size, since the droplet Reynolds number was in all cases much greater than unity.

7.3.2. Film Theory Approximation. The best available correlations for mass transfer in drops, for the Reynolds numbers encountered in this study, were empirical correlations developed by Skelland and Wellek (1964). Their correlations were for Sherwood numbers. For non-oscillating, circulating drops the following expression is obtained for the Sherwood number:

\[
N_{Sh} = 31.4 \tau^{0.34} S_{Sc}^{0.12} W_{We}^{0.37}
\]  (7.6)
Equation (7.6) was based on data taken for Reynolds numbers which ranged from nineteen to three hundred and four. The average absolute per cent deviation of the Sherwood number predicted by equation (7.6) from the experimental data by Skelland and Wellek was 34 per cent. For oscillating drops Skelland and Wellek proposed two correlations. Brunson and Wellek (1970b), in a study of mass transfer inside oscillating drops, found the following correlation to be better than the other.

\[ \bar{N}_{\text{Sh}} = 0.320 \frac{N_0^{0.68}}{Re^{0.10}} \frac{P}{\tau^{0.14}} \]  

Equation (7.7) was based on data taken for Reynolds numbers which ranged from four hundred and eleven to three thousand one hundred and fourteen. The average absolute per cent deviation of the Sherwood number predicted by equation (7.7) from the experimental data by Skelland and Wellek was 10.5 per cent.

As indicated in section 4.4.1., the mass transfer index to use with the film theory is the dimensionless flux, \( \bar{N} \), not the Sherwood number, \( \bar{N}_{\text{Sh}} \). The dimensionless flux can be calculated from the empirical Sherwood number by equation (4.19).

Since

\[ \bar{A}_0 = 1 - \exp \left( -\frac{3}{2} \tau \bar{N}_{\text{Sh}} \right) \]  

(7.8)

The dimensionless flux can then be calculated from equations (7.8) and (4.19).

\[ \bar{N}_0 = \frac{2}{3\tau} \left[ 1 - \exp \left( -\frac{3}{2} \tau \bar{N}_{\text{Sh}} \right) \right] \]  

(7.9)
A semi-empirical correlation for the enhancement factor for a second-order chemical reaction can be obtained by combining equation (7.9) with the film theory development described by equations (4.8) and (4.9). The enhancement factor may be used to calculate the total mass transferred, $A_{mt}$, from equation (7.8) by use of equation (4.17). Equation (7.6) was used to evaluate the Sherwood number for circulating drops. Equation (7.7) was used for oscillating drops. (A sample calculation for the case of a circulating drop is given in Appendix F.) The drops formed by the 27 gauge nozzle appeared to remain spherical so the correlation for circulating drops, equation (7.6), was used. Both of the larger drops (formed by the 15 and 20 gauge nozzles) were observed to oscillate. The data for the oscillating drops were treated by the correlation developed from equation (7.7). The drops formed by the 24 gauge nozzle were not observed to oscillate and were thus compared with the empirical correlation for circulating drops. However, since the drops formed by the 24 gauge nozzle were the largest drops which were not observed to oscillate, they were probably part of a transition region between circulating drops and oscillating drops. For this reason, the empirical curves for both circulating and oscillating drops are shown on figure 7.6, which represents data from the 24 gauge nozzle.

The average absolute per cent deviation, AAPD, of the experimental data points, from the empirical film theory model developed here was calculated for each nozzle size. The total moles transferred per unit volume was experimentally determined by subtracting the final sodium hydroxide concentration from the initial sodium hydroxide concentration as described in section 5.1.2. For the shortest column length this
subtraction involved two large numbers very close to each other. The subtraction of two numbers close to each other is a situation which could lead to substantial error in the experimental total mass transferred. The cause for this error can be seen from the following development. Equation (7.4) may be rewritten.

\[ \bar{A}_{mt} = \frac{C_{bo} - C_{bf}}{C_{as}} - e_1 \]  

(7.10)

Equation (7.10) can be rearranged

\[ \bar{A}_{mt} = \left( \frac{C_{bo}}{C_{as}} \right) - \left( \frac{C_{bf}}{C_{as}} + e_1 \right) \]  

(7.11)

For the shortest column length, the total mass transferred, \( \bar{A}_{mt} \), is as small as two and one-half per cent of either term in parentheses on the right hand side of equation (7.11). A one per cent error in either term in parentheses may lead to an error of forty per cent or more in the total mass transferred. For this reason, the AAPD was also calculated for each nozzle size except for the shortest column (in which case the error would be greatest).

The experimental values of total mass transferred for the smallest drop size (27 gauge nozzle) were all greater than predicted by the film theory using the Skelland and Wellek correlation. The AAPD of the experimental total mass transferred from the theoretical total mass transferred for all ten data points was 53.4%. By excluding the data for the shortest column length, the AAPD for the remaining six data points was 24.6%.

The film theory solution for mass transfer with second-order chemical reaction cannot be expected to be any better than the equation
used for mass transfer without reaction. The Skelland and Wellek correlation for mass transfer in non-oscillating drops predicted their data with an average absolute per cent deviation of 34% for the Sherwood number. As estimated from typical physical properties, an AAPD of 34 per cent for the Sherwood number would correspond to an AAPD of about twenty per cent for total mass transferred without reaction.

The AAPD of the experimental total mass transferred from the theoretical (equation 7.6) for the eight data points for the 24 gauge nozzle was 91.8%. The AAPD was reduced to 53.3% by excluding the three data points for the shortest column height. The data for the 24 gauge nozzle seem to be closer to the empirical curve for oscillating drops than they are to the empirical curve for circulating drops. The relationship of the data to the empirical curves lends weight to the opinion that this drop size is somewhat unstable and on the verge of oscillation. This transition would explain why the data for the 24 gauge nozzle has a more pronounced deviation from theory than is exhibited for any other size.

The drops from the two largest nozzles oscillated. There was no trend as to the relative magnitude of the theoretical and experimental results for the next to largest drop. The theoretical results were generally higher than the experimental results for the largest drops. The AAPD for all nine of the drops formed at the 20 gauge nozzle was 45.3. The AAPD for the same nozzle excluding the four data points for the shortest column was 14.9%. The agreement for the 15 gauge nozzle was even better. The AAPD for eight points was 28.0 per cent. For the six data points for the larger columns, the AAPD was 11.2 per cent.
These figures compare well with an AAPD of 15.6 per cent which Brunson and Wellek (1970b) found for the Skelland and Wellek oscillating drop correlation for experimental data without reaction.

Andoe (1968) studied an experimental system for mass transfer with first-order chemical reaction. He found the experimental total mass transferred to be seven to ten times as great as predicted by the penetration theory. Andoe attributed this phenomena to surface tension driven turbulent mixing at the interface where mass transfer occurred. The possible presence of this type of interfacial turbulence is mentioned in Section VI in connection with the interfacial concentration determination. Good agreement between experimental data and the modified film theory as described by equation (7.9) for this work seems to rule out vigorous interfacial turbulence as an important factor.
VIII. SUMMARY AND CONCLUSIONS

8.1. Theoretical

A mathematical model was described for solute transfer with second-order chemical reaction in a fluid sphere, which is circulating, as described by the Hadamard stream function. In Section IV, it was shown that for dimensionless times less than 0.001, which are common in liquid extraction, the circulating sphere model is closely approximated by either the film theory or the penetration theory for mass transfer with second-order chemical reaction. The penetration theory is never valid for dimensionless times greater than 0.2. The film theory can be valid at large dimensionless times if all of the parameters for mass transfer without chemical reaction are properly evaluated from a hydrodynamically similar system.

Due to the large Reynolds numbers encountered in the experimental portion of this work, it was not possible to test the mathematical model with actual laboratory data.

The portion of the discussion of experimental results presented in section 4.6 led to the establishment of some design guidelines. It was found that it is not as important to finely disperse a system for mass transfer with chemical reaction as it is for mass transfer without chemical reaction. A larger mean diameter of the dispersed phase will result in less backmixing of the dispersed phase. It was also found in section 4.6 that the contact time had less of an effect on the rate of mass transfer with chemical reaction than for the case of no reaction. For liquid extraction, the effect of the contact time was not important if the concentration ratio was not greater than 0.2.
The possible reduction of backmixing in the dispersed phase and the diminished effect of the contact time lead to the generally applicable conclusion that the distance between trays can be much larger for mass transfer with chemical reaction than for mass transfer without reaction.

8.2. Experimental

The conclusions for the experimental portion of this work are based on the work described in Sections V, VI, and VII. The system studied was n-pentyl formate diffusing into an aqueous phase which contains 0.04 formal sodium hydroxide and one formal sodium sulfate. The n-pentyl formate and sodium hydroxide react irreversibly and second-order.

The abnormally high mass transfer results obtained in the last series of runs described in Section VI indicate that spontaneous interfacial turbulence might be present for long contact times at a flat interface. The agreement of the data for mass transfer to falling droplets with an adaptation of published empirical correlations as described in section 7.3.2 would indicate that spontaneous interfacial turbulence is not significant for the curved interface and short contact time of the droplet studies.

The experimentally observed mass transfer into the falling aqueous drops was shown in section 7.3.1 to be two to four times larger than predicted by the fluid sphere (laminar) model. This deviation can probably be attributed to the fact that since droplet Reynolds numbers ranged from 490 to 789 the fluid motion inside the falling drop was probably faster than predicted by the Hadamard model (for Reynolds numbers less than one) or was turbulent instead of laminar as assumed in the development of the model.
The experimental data did agree well with the film theory for mass transfer with chemical reaction when used in conjunction with the empirical mass transfer relations presented by Skelland and Wellek (section 7.3.2).

The problem of mass transfer with second-order chemical reaction has been solved for a limited number of geometries and flow conditions. In the absence of a valid model for mass transfer with second-order chemical reaction, a prediction of mass transfer rates for design purposes may be obtained from the corresponding results for mass transfer with no reaction and with first-order reaction by the use of the Yeramian correlation. If there are no predictions for mass transfer with first- or second-order chemical reaction, a prediction may be obtained by combining the film theory for mass transfer with second-order chemical reaction and the mass transfer results for the case of no chemical reaction. Such a procedure has been demonstrated with reasonable success in this study of liquid extraction to single droplets with a second order reaction. The same procedure should be applicable to other systems.
VITA

Roy James Brunson was born on July 10, 1944, in Mountain Home, Arkansas, where he received his primary and secondary education. His college freshman year he attended Arkansas State College, in Jonesboro, Arkansas. He completed requirements for a Bachelor of Science in Chemical Engineering in June, 1966, at the University of Missouri-Rolla, in Rolla, Missouri.

He has been enrolled in the Graduate School of the University of Missouri-Rolla since September, 1966. He completed the requirements for a Master of Science in Chemical Engineering in January, 1968.
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APPENDIX A

COMPUTER PROGRAM FOR NUMERICAL SOLUTION OF MASS TRANSFER WITH SECOND ORDER CHEMICAL REACTION INSIDE A CIRCULATING FLUID SPHERE

The finite difference equations, derived in Section III, were solved on an IBM 360 computer. The following pages show a listing of the program in FORTRAN language. Each computer statement is numbered in the left margin. These numbers will be used in the explanation of the computer program.

Lines 10 through 24 define the input variables for the computer program. The values shown are an example of one set of input variables. The complete range of input variables used in this study are shown in Table 4.2.

Lines 26 through 71 calculate quantities used in the bulk of the program. Statements 26 through 38 define the space increments and ratios of increments used in the finite difference method. Statements 40 through 48 define the coordinates at the grid points in the sphere. Statements 50 through 57 and statements 66 and 67 calculate the velocity profiles inside the circulating fluid sphere. This program was written to use the Hadamard velocity profiles defined by equations (3.28) and (3.29). However, the program could be changed to use other velocity profiles by removing the above statements and substituting statements which would calculate or read in the desired velocities. The statements 59 through 71, excluding statements 66 and 67, calculate quantities which are used over and over in the program. These quantities were calculated and stored to save computing time.

Statements 74 through 154 calculate the concentration profiles and the mass transfer indices at the first two time steps. Statements
C MASS TRANSFER WITH SECOND ORDER CHEMICAL REACTION
C SOLUTION BY EXPLICIT METHOD IN SPHERICAL COORDINATES
DIMENSION A1(55,33),A2(55,33),A3(55,33)
DIMENSION B1(55,33),B2(55,33),B3(55,33)
DIMENSION Q1(81),Q2(81),Q3(81,33),Q4(81,33),Q5(81,33)
DIMENSION X1(12),X2(12),X3(12),X4(12),X5(12)
DIMENSION VR(81,33),VT(81,33)
DIMENSION R(81),TH(64)

C DIMENSIONLESS INPUT VARIABLES
RD=DIFFUSIVITY RATIO
RD=1.0
RC=CONCENTRATION RATIO
RC=0.2
PE=PECLET NUMBER
PE=40.0
RX=REACTION NUMBER
RX=160.0
DTA=TIME INCREMENT
DTA=0.0002
MR=NUMBER OF INCREMENTS IN ANGULAR DIRECTION
MR=31
NR=NUMBER OF INCREMENTS IN RADIAL DIRECTION
NR=40

C EVALUATION OF VALUES USED IN CALCULATIONS
DR=1.00/NR
PI=3.141593
DTH=PI/MR
EL=1.00
P2=DTA/DTH
S=2.0*DTA/(DR*DR)
P=2.0*DTA/(DTH*DTH)
S2=DTA/DR
NRR=NR+1
MRR=MR+1
37 Y1=RX*DTA
38 Y2=RD*(S+P)
39 C
40 C EVALUATION OF SPACE COORDINATES
41 R(1)=0.000
42 R(NRR)=1.000
43 TH(1)=0.00
44 TH(MRR)=PI
45 DO 2 J=2, MR
46 2 TH(J)=DTH*(J-1)
47 DO 3 I=2,NR
48 3 R(I)=DR*(I-1)
49 C
50 C CALCULATE OR READ VELOCITY PROFILES
51 DO 100 J=2, MR
52 CN=COS(TH(J))
53 SN=SIN(TH(J))
54 DO 100 I=2,NRR
55 R2=R(I)*R(I)
56 VR(I,J)=(R2-1.0)*CN
57 VT(I,J)=(1.0-2.0*R2)*SN
58 C
59 C FACTORS TO SAVE CALCULATION TIME
60 Q3(I,J)=P2*PE*VT(I,J)/R(I)
61 Q4(I,J)=P2*CN/(SN*R2)
62 Q5(I,J)=S2*PE*VR(I,J)
63 100 CONTINUE
64 DO 101 I=2,NRR
65 R2=R(I)*R(I)
66 VR(I,1)=R2-1.0
67 VR(I,MRR)=1.0-R2
68 Q5(I,1)=S2*PE*VR(I,1)
69 Q5(I,MRR)=S2*PE*VR(I,MRR)
70 Q1(I)=P/(R(I)*R(I))
71 101 Q2(I)=2.0*S2/R(I)
72 C
73 C
INITIAL CONDITIONS
FOR TAU=0 AND DTA

DO 4 J=1,MRR
DO 5 I=1,NRR
A1(I,J)=0.0
B1(I,J)=1.0
A2(I,J)=0.0
B2(I,J)=1.0
A3(I,J)=0.0
B3(I,J)=1.0
CONTINUE

A1(NRR,J)=1.0
A2(NRR,J)=1.0
A3(NRR,J)=1.0
CONTINUE

PENETRATION THEORY TO FIND A2(I,J)

NZ=NR-10
Z1=SQRT(RX)
Z2=SQRT(DTA)
N3=NR-3
DO 26 I=N3,NR
Z3=1.0-R(I)
Z4=EXP(Z3*Z1)
Z5=ERFC(Z3/(2.0*Z2)-Z1*Z2)
Z6=ERFC(Z3/(2.0*Z2)+Z1*Z2)
DO 26 J=1,MRR
A2(I,J)=(Z5/Z4+Z4*Z6)/2.0

FINITE DIFFERENCE METHOD TO FIND B2(I,J)

X2(1)=1.0+RD*S/2.0+RC*Y1/2.0
X3(1)=RD*S/2.0
X3(1)=-X3(1)
X4(1)=1.0-RC*Y1/2.0
X1(10)=-RD*(S/4.0+S2/(2.0*R(NRR-9)))
X2(10)=1.0+RD*S/2.0+RC*Y1*A2(NRR-9,1)/2.0
DO 50 I=2,9

X1(L)=-RD*(S/4.0+S2/(2.0*R(NRR-L+l)))

X2(L)=1.0+RD*S/2.0+RC*Y1*A2(NRR-L+l,1)/2.0

X3(L)=-RD*(S/4.0-S2/(2.0*R(NRR-L+l)))

50 X4(L)=1.0

X2(1)=X2(1)/X3(1)

X4(1)=X4(1)/X3(1)

DO 23 I=2,10

X2(L)=(X2(L)-X1(L)/X2(L-1))/X3(L)

X4(L)=(X4(L)-X1(L)/X2(L-1)*X4(L-1))/X3(L)

23 CONTINUE

X5(10)=X4(10)/X2(10)

DO 25 L=2,10

M=11-L

25 X5(M)=(X4(M)-X5(M+1))/X2(M)

DO 51 J=1,MRR

DO 51 J=1,10

51 B2(NRR-L+1,J)=X5(L)

C C MASS TRANSFER INDICES FOR FIRST TIME STEP

IF(RX-1.0)16,16,17

17 Z1=ERF(SQRT(Y1))

Z2=EXP(Y1)

SHA=2.0*((Y1+0.5)*Z1+SQR(Y1/PI)/Z2)/DTA*SQR(RX))

SH=2.0*SQR(RX)*(Z1+1.0/(Z2*SQR(PI*Y1))

GO TO 18

16 SHA=4.0/SQR(PI*DTA)

Sh=2.0/SQR(PI*DTA)

18 SSH=SHA+SH/2.0

SB=0.0

SA=0.0

DO 19 J=2,MRR

SBB=B2(NRR,J)/2.0

SAA=0.50
DO 20 I=2,NR
  SBB=SBB+R(I)*R(I)*B2(I,J)
20  SAA=SAA+R(I)*R(I)*A2(I,J)
SB=SB+SBB*DR*SIN(TH(J))
SA=SA+SAA*DR*SIN(TH(J))
AAV=1.50*DTH*SA
BAV=1.50*DTH*SB
AMT=AAV+(1.0-BAV)/RC
PAMT=AMT
C
ITERATION TO FIND CONCENTRATION PROFILE
KS1=0.01/DTA+0.05
TAUF=0.24
KS2=TAUF*100.0+0.5
DO 6 KSS=1,KS2
DO 7 KS3=1,KS1
NTM=(KSS-1)*KS1+KS3+1
C
INNER PART OF THE SPHERE
C
INNER PART
DO 21 J=2,MR
DO 8 I=2,NR
ZA=(1.0-S-Q1(I)-Y1*B2(I,J))*A1(I,J)
ZB=(Q2(I)-Q5(I,J)+S)*A2(I+1,J)+(S-Q2(I)+Q5(I,J))*A2(I-1,J)
ZC=(Q1(I)+Q4(I,J)-Q3(I,J))*A2(I,J+1)
ZD=(Q1(I)-Q4(I,J)+Q3(I,J))*A2(I,J-1)
A3(I,J)=(ZA+ZB+ZC+ZD)/(1.0+S+Q1(I)+Y1*B2(I,J))
ZA=(1.0-RD*(S+Q1(I))-RC*Y1*A2(I,J))*B1(I,J)
ZB=(RD*(S-Q2(I))-Q5(I,J))*B2(I+1,J)+(RD*(S-Q2(I))+Q5(I,J))*B2(I-1,J)
ZC=(RD*(Q1(I)+Q4(I,J))-Q3(I,J))*B2(I,J+1)
ZD=(RD*(Q1(I)-Q4(I,J))+Q3(I,J))*B2(I,J-1)
B3(I,J)=(ZA+ZB+ZC+ZD)/(1.0+RD*(S+Q1(I))+RC*Y1*A2(I,J))
8 CONTINUE
SURFACE OF THE SPHERE

\begin{align*}
A3(NRR,J) &= 1.0 \\
ZA &= (1.0 - RD*(P+S) - RC*Y1)*B1(NRR,J) + 2.0*RD*S*B2(NR,J) \\
ZB &= (RD*(P+Q4(NRR,J)) - Q3(NRR,J))*B2(NRR,J+1) \\
ZC &= (RD*(P-Q4(NRR,J)) + Q3(NRR,J))*B2(NRR,J-1) \\
B3(NRR,J) &= (ZA + ZB + ZC)/(1.0 + RD*(P+S) + RC*Y1)
\end{align*}

CONTINUE

ANGULAR LIMITS

\begin{align*}
& \text{DO } 9 \text{ I}=2, NR \\
ZA &= (1.0 - RD*(2.0*Q1(I)+S) - RC*Y1*A2(I,1))*B1(I,1) \\
ZB &= (RD*(S+Q2(I))-Q5(I,1))*B2(I+1,1) \\
ZC &= (RD*(S-Q2(I))+Q5(I,1))*B2(I-1,1)+4.0*RD*Q1(I)*B2(I,2) \\
B3(I,1) &= (ZA + ZB + ZC)/(1.0 + RD*(2.0*Q1(I)+S) + RC*Y1*A2(I,1)) \\
ZA &= RD*(2.0*Q1(I)+S)+RC*Y1*A2(I,MRR) \\
ZB &= (1.0-ZA)*A1(I,MRR)+(S+Q2(I)-Q5(I,MRR))*A2(I+1,MRR) \\
ZC &= (S-Q2(I)+Q5(I,MRR))*A2(I-1,MRR)+4.0*Q1(I)*A2(I,MR) \\
A3(I,MRR) &= (ZB+ZC)/(1.0+ZA) \\
ZA &= (2.0*Q1(I)+S+Y1*B2(I,1)) \\
ZB &= (1.0-ZA)*A1(I,1)+(S+Q2(I)-Q5(I,1))*A2(I+1,1) \\
ZC &= (S-Q2(I)+Q5(I,1))*A2(I-1,1)+4.0*Q1(I)*A2(I,2) \\
A3(I,1) &= (ZB+ZC)/(1.0+ZA) \\
ZA &= (2.0*Q1(I)+S+Y1*B2(I,MRR)) \\
ZB &= (1.0-ZA)*A1(I,MRR)+(S+Q2(I)-Q5(I,MRR))*A2(I+1,MRR) \\
ZC &= (S-Q2(I)+Q5(I,MRR))*A2(I-1,MRR)+4.0*Q1(I)*A2(I,MR) \\
A3(I,MRR) &= (ZB+ZC)/(1.0+ZA)
\end{align*}

COMBINED SURFACE AND ANGULAR BOUNDARY

\begin{align*}
ZA &= RD*(2.0*P+S)+RC*Y1 \\
ZB &= (1.0-ZA)*B1(NRR,1) + 2.0*S*RD*B2(NR,1) + 4.0*P*RD*B2(NRR,2) \\
B3(NRR,1) &= ZB/(1.0+ZA) \\
ZB &= (1.0-ZA)*B1(NRR,MRR) + 2.0*S*RD*B2(NR,MRR) \\
ZC &= 4.0*P*RD*B2(NRR,MR) \\
B3(NRR,MRR) &= (ZB+ZC)/(1.0+ZA)
\end{align*}

CENTER OF THE SPHERE
c
Z1=3.0RD*S+RC*Y1*A2(1,1)
Z2=(1.0-Z1)*B1(1,1)+6.0RD*S*B2(2,1)
Z3=Z2/(1+Z1)
Z1=3.0*S+Y1*B2(1,1)
Z2={(1.0-Z1)*A1(1,1)+6.0*S*A2(2,1)}/(1.0+Z1)

DO 10 J=1,MRR
10 A3(1,J)=Z2
B3(1,J)=Z3
CONTINUE

C PREPARE FOR NEXT TIME STEP
DO 11 I=1,NRR
DO 11 J=1,MRR
A1(I,J)=A2(I,J)
A2(I,J)=A3(I,J)
B1(I,J)=B2(I,J)
B2(I,J)=B3(I,J)
11 CONTINUE

C MASS TRANSFER INDICES FOR EACH TIME STEP AFTER THE FIRST
SB=0.0
SA=0.0
SFLX=0.0
DO 12 J=2,MRR
SBB=B3(NRR,J)/2.0
SAA=0.5
SN=SIN(TH(J))
DO 14 I=2,NR
SBB=SBB+R(I)*R(I)*B3(I,J)
SAA=SAA+R(I)*R(I)*A3(I,J)
14 SB=SB+SBB*DR*SN
12 SFLX=SFLX-(-3.0+4.0*A3(NR,J)-A3(NR-1,J))*SN/(2.0*DR)
AAV=1.50*DTH*SA
BAV=1.50*DTH*SB
F2=DTH*SFLX
TAU = (KSS - 1.0) * 0.01 + KS3 * DTA + DTA * 1.005
AMT = AAV + (1.0 - BAV) / RC
F1 = 2.0 / 3.0 * (AMT - PAMT) / DTA
FAV = 2.0 / 3.0 * AMT / TAU
SH = F1 / (1.0 - AAV)
SSH = SSH + SH / 2.0
SHAV = SSH * DTA / TAU
SSH = SSH + SH / 2.0
PAMT = AMT

C PRINTOUT OF MASS TRANSFER INDICES
C TAU = DIMENSIONLESS TIME
C AAV = AVERAGE CONCENTRATION OF COMPONENT A
C BAV = AVERAGE CONCENTRATION OF COMPONENT B
C AMT = TOTAL MASS TRANSFERRED
C F1 = INSTANTANEOUS FLUX CALCULATED BY TIME DERIVATIVE OF
C TOTAL MASS TRANSFERRED
C F2 = INSTANTANEOUS FLUX CALCULATED BY RADIAL DERIVATIVE OF
C CONCENTRATION OF COMPONENT A
C FAV = TIME AVERAGED FLUX
C SH = INSTANTANEOUS SHERWOOD NUMBER
C SHAV = TIME AVERAGED SHERWOOD NUMBER
WRITE(3,15) TAU, AAV, BAV, AMT, F1, F2, FAV, SH, SHAV
15 FORMAT(10F12.5)
CONTINUE
CONTINUE STOP
END
78 through 83 set all concentrations for the first three time steps equal to the initial conditions. Then, statements 85, 86 and 87 establish the surface condition for component \( a \). Statements 90 through 101 calculate the concentration of component \( a \) at the second time step, according to equation (3.38). Statements 103 through 129 calculate the concentration of component \( b \) at the second time step, according to equations (3.45) and (3.47). The variables \( X_1 \), \( X_2 \) and \( X_3 \) represent the three diagonal rows of the tridiagonal matrix. The computer program, as written, only calculates the concentrations at the ten grid points closest to the surface of the fluid sphere, because concentrations further from the surface were essentially the same as the initial conditions. Statements 131 through 154 calculate the mass transfer indices for the first time step, as described in the Section III.

The remainder of the computer program is repeated for each time step. Statements 157 through 163 and statements 278 and 279 control the iteration of the enclosed statements. The final value of the dimensionless time is \( \text{TAUF} \). Statements 165 through 180 calculate the concentrations for the bulk of the sphere, according to equations (3.57) and (3.58). Statements 182 through 188 calculate the concentrations at the surface of the sphere, according to equations (3.65) and (3.67). Statements 190 through 207 calculate the concentrations at the angular limits of the sphere, according to equations (3.70) and (3.71). Statements 209 through 215 calculate the concentrations at the combined angular and surface boundary conditions, according to equation (3.72). Statements 217 through 226 calculate the concentrations at the center of the sphere, according to equations (3.63) and (3.64).
To save computer storage space, the concentrations are redefined after each time step. Statements 228 through 234 are for this purpose. Statements 237 through 262 calculate the average concentrations of components $a$ and $b$, the total mass transferred, the instantaneous flux, the time averaged flux, and the instantaneous and time averaged Sherwood numbers by the equations derived in Section 3.3. These mass transfer indices are printed out by statements 264 through 277. The results of the computer study are given in Appendix B.
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AAV</td>
<td>average concentration of component $a$, $\bar{A}$</td>
</tr>
<tr>
<td>AMT</td>
<td>total mass transferred per unit volume, $\bar{A}_{mt}$</td>
</tr>
<tr>
<td>A1</td>
<td>concentration of component $a$ at previous time step, $A_1$</td>
</tr>
<tr>
<td>A2</td>
<td>concentration of component $a$ at present time step, $A_2$</td>
</tr>
<tr>
<td>A3</td>
<td>concentration of component $a$ at future time step, $A_3$</td>
</tr>
<tr>
<td>BAV</td>
<td>average concentration of component $b$, $\bar{B}$</td>
</tr>
<tr>
<td>B1</td>
<td>concentration of component $b$ at previous time step, $B_1$</td>
</tr>
<tr>
<td>B2</td>
<td>concentration of component $b$ at present time step, $B_2$</td>
</tr>
<tr>
<td>B3</td>
<td>concentration of component $b$ at future time step, $B_3$</td>
</tr>
<tr>
<td>CN</td>
<td>cosine of $\theta$</td>
</tr>
<tr>
<td>DR</td>
<td>size of increment in radial direction, $\Delta R$</td>
</tr>
<tr>
<td>DTA</td>
<td>size of increment in time dimension, $\Delta T$</td>
</tr>
<tr>
<td>DTH</td>
<td>size of increment in angular direction, $\Delta \theta$</td>
</tr>
<tr>
<td>EL</td>
<td>dummy variable for the number one</td>
</tr>
<tr>
<td>FAV</td>
<td>time averaged dimensionless flux, $\bar{N}$</td>
</tr>
<tr>
<td>F1</td>
<td>dimensionless flux calculated by equation (3.84), $N$</td>
</tr>
<tr>
<td>F2</td>
<td>dimensionless flux calculated by equation (3.81), $N$</td>
</tr>
<tr>
<td>KS1</td>
<td>number of iterations between each printout</td>
</tr>
<tr>
<td>KS2</td>
<td>number of printouts</td>
</tr>
<tr>
<td>M</td>
<td>dummy counter in a do loop</td>
</tr>
<tr>
<td>MR</td>
<td>number of increments in the angular direction, $mr$</td>
</tr>
<tr>
<td>MRR</td>
<td>number of grid points in the angular direction, $mrr$</td>
</tr>
<tr>
<td>NR</td>
<td>number of increments in the radial direction, $nr$</td>
</tr>
<tr>
<td>NRR</td>
<td>number of grid points in the radial direction, $nrr$</td>
</tr>
</tbody>
</table>
NTM = index in time dimension, \( k+l \)

NZ = number of grid points from the center of the sphere where the concentration of component b does not change before the second time step

N3 = number of grid points from the center of the sphere where the concentration of component a does not change before the second time step

P = ratio of angular and time increments, \( P \)

PAMT = previous total mass transferred, \( \bar{A}_{mt} \)

PE = Peclet number, \( N_{Pe} \)

PI = \( \pi \)

P2 = ratio of angular and time increments, \( P_2 \)

Q1 = function of radius and angle used to minimize the number of calculations

Q2 = function of radius and angle used to minimize the number of calculations

Q3 = function of radius and angle used to minimize the number of calculations

Q4 = function of radius and angle used to minimize the number of calculations

Q5 = function of radius and angle used to minimize the number of calculations

R = radius, \( R \)

RC = concentration ratio, \( R_c \)

RD = diffusivity ratio, \( R_D \)

RX = dimensionless reaction rate constant, \( k_R \)

R2 = square of radius, \( R^2 \)

S = ratio of radial and time increments, \( S \)

SA = summation of A

SAA = summation of A in radial direction

SB = summation of B
$S_{BB}$ = summation of B in radial direction

$S_{FLX}$ = summation to calculate dimensionless flux

$S_H$ = Sherwood number, $N_{Sh}$

$S_{HA}$ = time average Sherwood number at first time step, $\overline{N_{Sh}}$

$S_{HAV}$ = time averaged Sherwood number, $\overline{N_{Sh}}$

$S_{N}$ = sine of $\theta$

$S_{SH}$ = summation to calculate time averaged Sherwood number

$S_{2}$ = ratio of radial and time increments, $S_2$

$T_{AUF}$ = final value of dimensionless time

$T_H$ = angle, $\theta$

$T_{AU}$ = dimensionless time, $\tau$

$V_R$ = velocity in radial direction, $V_R$

$V_T$ = velocity in angular direction, $V_\theta$

$X_1$ = element of matrix

$X_2$ = element of matrix

$X_3$ = element of matrix

$X_4$ = element of matrix

$X_5$ = element of matrix

$Y_1$ = factor to save calculation time

$Y_2$ = factor to save calculation time

$Z_A$ = factor used to calculate $A_3$ and $B_3$

$Z_B$ = factor used to calculate $A_3$ and $B_3$

$Z_C$ = factor used to calculate $A_3$ and $B_3$

$Z_D$ = factor used to calculate $A_3$ and $B_3$

$Z_1$ = factor used to calculate $A_3$ and $B_3$

$Z_2$ = factor used to calculate $A_3$ and $B_3$

$Z_3$ = factor used to calculate $A_3$ and $B_3$
\[ Z_4 = \text{factor used to calculate } A_3 \text{ and } B_3 \]
\[ Z_5 = \text{factor used to calculate } A_3 \text{ and } B_3 \]
\[ Z_6 = \text{factor used to calculate } A_3 \text{ and } B_3 \]
Figure A.1. Flow Diagram of Computer Program
calculation of velocities and factors to save calculation time

Figure A.1. (Continued)
specification of initial concentrations of components $a$ and $b$

specification of boundary conditions for component $a$

calculation of parameters for penetration theory

Figure A.1. (Continued)
Figure A.1. (Continued)
Figure A.1. (Continued)
Figure A.1. (continued)
Figure A.1. (continued)
Figure A.1. (continued)
Figure A.1. (Continued)
Figure A.1. (Continued)
Figure A.1. (Continued)
APPENDIX B
NUMERICAL RESULTS FOR MASS TRANSFER WITH
SECOND-ORDER CHEMICAL REACTION

B.1. Fluid Sphere Results.

The mass transfer indices described in Section 3.3 were calculated numerically by the computer program described in Appendix A. The dimensionless mass transfer indices were:

- $\bar{A}$, Average concentration of component $a$
- $\bar{B}$, Average concentration of component $b$
- $\bar{A}_{mt}$, Dimensionless total mass transferred
- $N$, Dimensionless flux of component $a$
- $\bar{N}$, Time average dimensionless flux of component $a$
- $N_{Sh}$, Sherwood number
- $\bar{N}_{Sh}$, Time average Sherwood number
- $\phi$, Enhancement factor

The range of independent variables studied is shown in Table 4.2.

A representative sample of the computer results is presented in Tables B.1 through B.4. A much more detailed listing of the tabular results has been deposited as document no. 01456 with the ASIS National Auxiliary Service, c/o CCM Information Sciences, Inc., 909 Third Avenue, New York 10022 and may be obtained in the form of microfiche or photocopies.

B.2. Film and Penetration Results.

The total mass transferred, as calculated by the film theory and the penetration theory, are tabulated shown in Tables B.5 through B.10. The results for the film theory were calculated from equations (4.7),
### TABLE B.1

**FLUID SPHERE MASS TRANSFER INDICES**

$(R_d=1 \quad R_c=0.1 \quad N_{Pe}=0 \quad k_R=640)$

<table>
<thead>
<tr>
<th>$R_d=1$</th>
<th>$R_c=0.1$</th>
<th>$N_{Pe}=0$</th>
<th>$k_R=640$</th>
<th>$\Delta\tau=0.0001$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau$</td>
<td>$\bar{A}$</td>
<td>$\bar{B}$</td>
<td>$\bar{A}_{mt}$</td>
<td>$N$</td>
</tr>
<tr>
<td>0.001</td>
<td>0.0897</td>
<td>0.9962</td>
<td>0.1275</td>
<td>54.03</td>
</tr>
<tr>
<td>0.002</td>
<td>0.1056</td>
<td>0.9902</td>
<td>0.2037</td>
<td>49.30</td>
</tr>
<tr>
<td>0.003</td>
<td>0.1123</td>
<td>0.9836</td>
<td>0.2764</td>
<td>47.96</td>
</tr>
<tr>
<td>0.004</td>
<td>0.1156</td>
<td>0.9768</td>
<td>0.3474</td>
<td>47.03</td>
</tr>
<tr>
<td>0.005</td>
<td>0.1176</td>
<td>0.9700</td>
<td>0.4174</td>
<td>46.32</td>
</tr>
<tr>
<td>0.006</td>
<td>0.1190</td>
<td>0.9632</td>
<td>0.4866</td>
<td>45.98</td>
</tr>
<tr>
<td>0.007</td>
<td>0.1202</td>
<td>0.9565</td>
<td>0.5550</td>
<td>45.48</td>
</tr>
<tr>
<td>0.008</td>
<td>0.1212</td>
<td>0.9498</td>
<td>0.6228</td>
<td>44.99</td>
</tr>
<tr>
<td>0.009</td>
<td>0.1221</td>
<td>0.9432</td>
<td>0.6900</td>
<td>44.64</td>
</tr>
<tr>
<td>0.010</td>
<td>0.1230</td>
<td>0.9366</td>
<td>0.7565</td>
<td>44.16</td>
</tr>
<tr>
<td>0.015</td>
<td>0.1271</td>
<td>0.9046</td>
<td>1.0812</td>
<td>42.36</td>
</tr>
<tr>
<td>0.020</td>
<td>0.1308</td>
<td>0.8737</td>
<td>1.3940</td>
<td>41.04</td>
</tr>
<tr>
<td>0.025</td>
<td>0.1344</td>
<td>0.8438</td>
<td>1.6962</td>
<td>39.76</td>
</tr>
<tr>
<td>0.030</td>
<td>0.1379</td>
<td>0.8149</td>
<td>1.9888</td>
<td>38.37</td>
</tr>
<tr>
<td>0.040</td>
<td>0.1447</td>
<td>0.7596</td>
<td>2.5482</td>
<td>36.22</td>
</tr>
<tr>
<td>0.050</td>
<td>0.1514</td>
<td>0.7075</td>
<td>3.0763</td>
<td>34.29</td>
</tr>
<tr>
<td>0.060</td>
<td>0.1582</td>
<td>0.6582</td>
<td>3.5759</td>
<td>32.50</td>
</tr>
<tr>
<td>0.070</td>
<td>0.1615</td>
<td>0.6116</td>
<td>4.0492</td>
<td>30.71</td>
</tr>
<tr>
<td>0.080</td>
<td>0.1722</td>
<td>0.5674</td>
<td>4.4979</td>
<td>29.14</td>
</tr>
<tr>
<td>0.090</td>
<td>0.1795</td>
<td>0.5256</td>
<td>4.9235</td>
<td>27.66</td>
</tr>
<tr>
<td>0.100</td>
<td>0.1870</td>
<td>0.4860</td>
<td>5.3270</td>
<td>26.21</td>
</tr>
<tr>
<td>0.120</td>
<td>0.2030</td>
<td>0.4131</td>
<td>6.0718</td>
<td>23.51</td>
</tr>
<tr>
<td>0.150</td>
<td>0.2298</td>
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### TABLE B.3

**FLUID SPHERE MASS TRANSFER INDICES**

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(4.8), (4.11), and (4.15). The results predicted by Kishinevskii were as calculated by equations (4.12) through (4.15). The results attributed to Pearson were taken from computer printouts supplied by Dr. Pearson.

The range of variables studied was \( R_D = 1; R_C = 0.2 \) and 1; and \( k_R = 40, 160, \) and 640.
TABLE B.5
TOTAL MASS TRANSFERRED, $\bar{A}_{mt}$
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<tr>
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</table>
TABLE B.6

TOTAL MASS TRANSFERRED, $\tilde{A}_{mt}$
($R_D = 1$ $R_c = 0.2$ $k_R = 160$)

<table>
<thead>
<tr>
<th>$\tau$/Theory</th>
<th>$R_D = 1$</th>
<th>$R_c = 0.2$</th>
<th>$k_R = 160$</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Pearson</td>
<td>Kishinevskii</td>
<td>Film</td>
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<tr>
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<tr>
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</tbody>
</table>
TABLE B.7

TOTAL MASS TRANSFERRED, $\bar{A}_{\text{m}}$

$(R_D = 1 \quad R_c = 0.2 \quad k_R = 640)$

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<thead>
<tr>
<th>$\tau$/Theory</th>
<th>$R_D = 1$</th>
<th>$R_c = 0.2$</th>
<th>$k_R = 640$</th>
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</table>
TABLE B.8

TOTAL MASS TRANSFERRED, $\bar{A}_{\text{mt}}$
($R_D = 1$, $R_c = 1$, $k_R = 40$)

<table>
<thead>
<tr>
<th>$\tau$/Theory</th>
<th>Pearson</th>
<th>Kishinevskii</th>
<th>Film</th>
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</thead>
<tbody>
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<td>0.002</td>
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<tr>
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<td>$R_c = 1$</td>
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<tr>
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<tr>
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<td>Pearson</td>
<td>Kishinevskii</td>
<td>Film</td>
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<td>Kishinevskii</td>
<td>Film</td>
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<td>3.0508</td>
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<tr>
<td>0.240</td>
<td>3.3529</td>
<td>3.3048</td>
<td>3.2681</td>
</tr>
</tbody>
</table>
APPENDIX C
REAGENT AND APPARATUS SPECIFICATIONS

C.1. Reagent Specifications

**Formic Acid**: Distributed by Fisher Scientific Company, Chemical Manufacturing Division, Fair Lawn, New Jersey. Certified A.C.S. Assay 90.4% HCOOH, F. W. = 46.03, Lot 702557, Catalogue number A-118.


**Water**: Ion exchange water was obtained from the University of Missouri-Rolla Nuclear Reactor. All water was boiled for one hour and allowed to cool before use.


**Sodium Hydroxide**: Distributed by Fisher Scientific Company, Chemical Manufacturing Division, Fair Lawn, New Jersey. USP F. W. = 40.00, NaOH, Lot 792935, Catalogue number S-315.


**Acid Cleaning Solution**: 400 cc. concentrated sulfuric acid was slowly added to 46 grams sodium dichromate in 229 cc. of tap water.

**Basic Cleaning Solution**: Concentrated solutions of sodium hydroxide in ethyl alcohol were used to remove greases from ground glass equipment.

Molecular Sieves: Manufactured by Davison Chemical Company, Baltimore, Maryland. Grade 564, effective pore size 3 Å, 8-12 mesh beads.

Sulfuric Acid: Manufactured by Matheson Scientific Company, Certified A.C.S. Reagent Grade, F. W. = 98.08, Assay 95 to 98% H₂SO₄, specific gravity at 60⁰/60°F is 1.84, Lot MS 4067.


n-Pentyl Formate: Manufactured by Eastman Organic Chemicals, Distillation Products Industries, Rochester, New York. Highest purity,
F. W. = 116.16, HCOO(CH₂)₄CH₃, B. P. = 131-132°C, Catalogue number 8737.

Used for preliminary studies.

**n-Pentyl Formate:** Student Preparation. A mixture of two moles formic acid per mole of n-pentyl alcohol was refluxed, and the aqueous product removed by means of a Dean-Stark separator (Vogel, 1951).

\[
\text{acid} + \text{alcohol} = \text{ester} + \text{water}
\]

The ester was dried with anhydrous sodium sulfate and transferred to a boiling flask. The distillate was collected at 132°C and redistilled through a Vigreux column. Care was taken to eliminate the alcohol-water azeotrope, which boils at 131.4°C.

The purity of the student prepared ester was compared with the purity of the commercial preparation by the means of a chromatograph. A three foot Porapak Q column was used for the chromatographic separation. The major impurities in n-pentyl formate are water, formic acid, and n-pentyl alcohol. The location of the peak for each of these impurities was identified by the addition of excess water, formic acid, and n-pentyl alcohol to three separate samples of n-pentyl formate. Equal volumes of student prepared ester and commercially prepared ester were passed through the chromatograph, one at a time. The size of the peak for n-pentyl formate in the two samples was about the same, but the peaks for all of the impurities in the student preparation were smaller than the corresponding peaks for the commercial preparation. Thus, the student prepared ester was considered to be as pure as the commercial preparation.

**C.2. Apparatus Specifications**

**Cathetometer:** Manufactured by Eberbach Corporation, Ann Arbor,
Michigan. Vernier readable to 0.1 mm. Telescope magnification of 20X at 30 cm.

**Electric Stop Clock:** Manufactured by the A. W. Haydon Company, Waterbury, Connecticut. Model number K15140. Readable to 0.01 sec.

**Mechanical Stop Clock:** Distributed by Fisher Scientific Company. Readable to 0.1 sec.

**DuNouy Tensiometer:** Manufactured by Central Scientific Company, Chicago, Illinois. Vernier readable to 0.1 dyne/cm. Serial number 630.

**Platinum Ring for Tensiometer:** Manufactured by Central Scientific Company, Chicago, Illinois. Mean circumference is 5.999 cm., R/r = 53.3.

**Ostwald Viscometer:** Manufactured by A. S. Aloe Company.

**Sample Bottles:** Distributed by Fisher Scientific Company. 3 dram (about 12 ml.). Catalogue number 3-338.

**Separatory Funnels:** Distributed by Fisher Scientific Company. 4 liter capacity. Catalogue number 10-427B.

**Distilling Column:** Manufactured by Ace Glass Company, Louisville, Kentucky. Vigreaux, 0.2 meter indentions. Catalogue number 9224-04.

**Thermometer:** Manufactured by Ace Glass Company, Louisville, Kentucky. Ground glass, one inch immersion. Range: -10 to 250°C. One degree divisions.
APPENDIX D  
PHYSICAL AND CHEMICAL DATA

All properties shown here represent conditions at twenty-five degrees centigrade.

Density of Ester. Washburn (1926) lists the density of n-pentyl formate to be 0.870 grams per cubic centimeter. The density of n-pentyl formate, saturated with water, was measured with a pycnometer and found to be 0.875 grams per cubic centimeter.

Density of Water Solution. Perry, et al. (1963) lists the following densities of water and its solutions:

<table>
<thead>
<tr>
<th>solution</th>
<th>density (gm/cm³)</th>
<th>page</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>0.9971</td>
<td>3-70</td>
</tr>
<tr>
<td>0.02 f NaOH</td>
<td>0.9980</td>
<td>3-77</td>
</tr>
<tr>
<td>0.04 f NaOH</td>
<td>0.9988</td>
<td>3-77</td>
</tr>
<tr>
<td>1 f Na₂SO₄</td>
<td>1.1155</td>
<td>3-78</td>
</tr>
</tbody>
</table>

Viscosity of Ester. The ester viscosities were measured with an ostwald viscometer. The viscosity of dry n-pentyl formate is 0.738 centipoise. The viscosity of n-pentyl formate saturated with water is 0.756 centipoise.

Viscosity of Water Solutions. The published viscosities of water and its solutions are as follows:

<table>
<thead>
<tr>
<th>solution</th>
<th>viscosity (centipoise)</th>
<th>source</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>0.8937</td>
<td>Perry, 1963, page 3-201</td>
</tr>
<tr>
<td>0.02 f NaOH</td>
<td>1.0046</td>
<td></td>
</tr>
<tr>
<td>0.04 f NaOH</td>
<td>1.0089</td>
<td>Hueckel and Schaff (1959)</td>
</tr>
<tr>
<td>1 f Na₂SO₄</td>
<td>1.55</td>
<td></td>
</tr>
</tbody>
</table>
**Diffusivity of Ester.** Wilke and Chang (1955) proposed an empirical equation for diffusivity.

\[ D_a = \frac{7.4 \times 10^{-8} (\phi M)^{0.5} T}{\mu \nu_A^{0.6}} \]

where

- \( D_a \) = diffusivity of n-pentyl formate in water, cm\(^2\)/sec
- \( M \) = molecular weight of solvent = 18
- \( T \) = temperature = 298°K
- \( \mu \) = solution viscosity, centipoise
- \( \phi \) = association factor for solvent = 2.6
- \( \nu_A \) = solute molal volume = 170 cm\(^3\)/g mole

in 1 f Na\(_2\)SO\(_4\)

\[ D_a = 0.469 \times 10^{-5} \text{ cm}^2/\text{sec} \]

**Diffusivity of NaOH.** From the correlation of Wilke and Chang (1955), the product of the diffusivity and the viscosity divided by the temperature is constant. This approximation was used to extrapolate experimental values for the diffusivity of sodium hydroxide given by Washburn (1926). For 0.04 f NaOH in 1 f Na\(_2\)SO\(_4\),

\[ D_b = 1.01 \times 10^{-5} \text{ cm}^2/\text{sec} \]

**Interfacial Tension.** The interfacial tension between n-pentyl formate and various aqueous solutions were measured with a Du Nouy Interfacial Tensiometer. The interfacial tensions, corrected for the weight of liquid lifted by the ring are
aqueous interfacial solution tension

<table>
<thead>
<tr>
<th></th>
<th>dyne/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>17.5</td>
</tr>
<tr>
<td>1 f Na₂SO₄</td>
<td>20.0</td>
</tr>
<tr>
<td>0.04 f NaOH, 1 f Na₂SO₄</td>
<td>19.2</td>
</tr>
</tbody>
</table>

**Reaction Rate Constant.** There is no published reaction rate constant for alkaline hydrolysis of n-pentyl formate. However, certain estimates can be made concerning its value. Leimu, et al. (1946) measured reaction rate constants for alkaline hydrolysis of a homologous series of formic esters.

<table>
<thead>
<tr>
<th>formate</th>
<th>molecular weight</th>
<th>Reaction Rate Constant liter/mole-sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>methyl</td>
<td>60</td>
<td>36.67</td>
</tr>
<tr>
<td>ethyl</td>
<td>74</td>
<td>25.67</td>
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<tr>
<td>n-propyl</td>
<td>88</td>
<td>22.83</td>
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<tr>
<td>n-butyl</td>
<td>102</td>
<td>21.83</td>
</tr>
<tr>
<td>n-pentyl</td>
<td>116</td>
<td></td>
</tr>
</tbody>
</table>

The reaction rate constants decrease with increasing molecular weight. Therefore, the reaction rate constant for n-pentyl formate is less than 21.83. The reaction rate constants decrease by diminishing amounts with each successive increase in molecular weight. Therefore, the reaction rate constant for n-pentyl formate is greater than 20.83. Thus, the reaction rate constant is 21.3 plus or minus 0.5 liters per mole-second. According to Dr. D. S. Wulfman, at large molecular weights properties such as the reaction rate constant begin to
oscillate with increasing molecular weight. However, the value of the reaction rate constant would not oscillate beyond the stated limits. For the limits given above, the error is less than three per cent.

**Droplet Radius.** The volume of the aqueous drops formed in the droplet studies was measured by counting the number of drops formed for a given volume change in the buret. The droplet radius was calculated by assuming the drop was a sphere. For 0.04 f NaOH, 1 f Na₂SO₄ drops in dry n-pentyl formate and n-pentyl formate saturated with water, the following data were obtained:

<table>
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<tr>
<th>Nozzle Gauge</th>
<th>Droplet Radius, cm.</th>
<th></th>
</tr>
</thead>
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<td>saturated ester</td>
<td>dry ester</td>
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<td>0.117</td>
<td>0.129</td>
</tr>
<tr>
<td>24</td>
<td>0.137</td>
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<tr>
<td>20</td>
<td>0.162</td>
<td>0.173</td>
</tr>
<tr>
<td>15</td>
<td>0.205</td>
<td>0.220</td>
</tr>
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</table>

**Droplet Velocity.** The terminal velocity of 0.04 f NaOH, 1 f Na₂SO₄ drops in n-pentyl formate were measured in a 105 centimeter column. A reference mark was made fifty-five centimeters above the bottom of the column and another mark five centimeters above the bottom of the column. The average time for a drop to fall from one mark to the other was used to calculate the terminal velocity.

<table>
<thead>
<tr>
<th>Nozzle Gauge</th>
<th>terminal velocity cm.</th>
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<tbody>
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<td>16.1</td>
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<td>16.4</td>
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<td>16.5</td>
</tr>
<tr>
<td>15</td>
<td>15.2</td>
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</table>
APPENDIX E

DERIVATION OF LEAST SQUARES EXPRESSION
FOR INTERFACIAL CONCENTRATION

Higbie (1935) developed a model for mass transfer in a quiescent liquid of semi-infinite extent. This model, known as the penetration theory, would be applicable to the concentration cell if the contact time for each run is small enough that there is not an appreciable concentration change at the bottom of the cell.

To test this assumption, the concentration profile for the penetration theory with no chemical reaction is

\[
A = 1 - \text{erf} \sqrt{\frac{L^2}{4D_a}} t
\]

(E.1)

The depth, L, of the water in the concentration cell was a little over five centimeters. Therefore, from equation (E.1) the time necessary for a one per cent change in the concentration at the bottom of the concentration cell is about thirteen hours. For enhancement factors less than five the time for mass transfer with chemical reaction would be of the same order of magnitude. Therefore, for contact times up to one hour, as used in this study, the penetration theory is applicable in the concentration cell.

E.1. Interfacial Concentration with no reaction

The total mass transferred without chemical reaction as solved by Higbie is given by

\[
\overline{C_{mt}} = C_{as} \left( \frac{2S}{V} \sqrt{\frac{D_a t}{\pi}} \right)
\]

(E.2)

Thus a plot of the total mass transferred, \(\overline{C_{mt}}\), as a function of the term in parenthesis would be a straight line with zero intercept and a slope equal to the interfacial concentration. By least squares
E.2. Interfacial Concentration with Reaction

At large times, the total mass transferred in the presence of an irreversible second-order reaction is increased over the case of mass transfer without chemical reaction by the following enhancement factor (Nijsing, 1959)

\[
\phi = \sqrt{\frac{D_a}{D_b}} + \sqrt{\frac{D_b}{D_a}} \frac{C_{bo}}{Z} \frac{C_{as}}{C_{bo}}
\]  

(E.4)

Since the rate of reaction was considered infinite, the value of the reaction rate constant did not appear in the curve fit expression. Astarita (1967), page 61, found that the above enhancement factor was applicable if the contact time was much greater than \( \frac{1}{k_2 C_{bo} R_c^2} \). The concentration ratio, \( R_c \), was expected to vary from one-third to four-thirds. For the systems studied here the contact times should be much larger than twenty seconds. The contact times used for interfacial concentration determinations were two orders of magnitude greater than this limit. Therefore, the total mass transferred in the concentration cell can be taken to be

\[
\overline{C_{mt}} = C_{as} \left( \frac{2 S_o D_a}{V} \sqrt{\frac{t}{\pi D_b}} \right) + \left( \frac{2 S_o C_{bo}}{V Z} \sqrt{\frac{D_b t}{\pi}} \right)
\]  

(E.5)

If the terms in parenthesis are considered to be two independent variables, the above equation can be curve fit for \( C_{as} \) by multiple regression (Miller and Freund, 1965, page 245).
\[ C_{as} = \frac{V}{2D_a} \sqrt{\pi D_b} \frac{4}{\sum l} C_{mt} \sqrt{t} - \frac{D_b}{D_a} \frac{4}{\sum l} S_{ot}^{t} C_{bo} \]  

(E.6)
APPENDIX F
SAMPLE CALCULATION FOR FILM APPROXIMATION

The Skelland and Wellek (1964) correlation which predicts the Sherwood number for non-oscillating drops is given by equation (7.6). The dimensionless parameters for the Skelland and Wellek correlation are given in Table 7.1. The dispersed phase Schmidt number, $N_{Sc}$, is 2960. For the smallest drop size the Weber number, $N_{We}$, is 3.03. A sample calculation is given here for a dimensionless time, $\tau$, equal to $8 \times 10^{-4}$.

\[
\begin{align*}
\bar{N}_{Sh} &= 31.4 \tau^{-0.34} N_{Sc}^{-0.12} N_{We}^{0.37} \\
&= 31.4 \left(8 \times 10^{-4}\right)^{-0.34} (2960)^{-0.12} (3.03)^{0.37} \\
&= 31.4 (11.3) (0.383) (1.51) \\
&= 205
\end{align*}
\]

The average dimensionless concentration without reaction, $\bar{A}_o$, can be calculated from equation (7.8).

\[
\begin{align*}
\bar{A}_o &= 1 - \exp\left[-\left(\frac{3}{2}\right) \tau \bar{N}_{Sh}\right] \\
&= 1 - \exp\left[-\left(\frac{3}{2}\right) (8 \times 10^{-4}) (205)\right] \\
&= 1 - \exp(0.246) \\
&= 1 - 0.782 \\
&= 0.218
\end{align*}
\]

The dimensionless flux without reaction, $\bar{N}_o$, is most easily calculated by equation (4.19)

\[
\begin{align*}
\bar{N}_o &= \frac{2}{3} \frac{\bar{A}_o}{\tau} \\
&= \frac{2}{3} \frac{0.218}{8 \times 10^{-4}} \\
&= 182
\end{align*}
\]
The Sherwood number, average dimensionless concentration, and dimensionless flux as calculated above are based on the empirical correlation by Skelland and Wellek for mass transfer without chemical reaction.

The enhancement factor for a second-order reaction can be calculated by the film theory (Van Krevelen and Hoftijzer, 1948b). From Table 7.1, the concentration ratio, $R_c$, is 0.335, the diffusivity ratio, $R_D$, is 2.16, and the dimensionless reaction rate constant, $k_R$, is 3023. An initial estimate of the enhancement factor can be calculated by equation (4.10).

$$\phi = \frac{2\sqrt{k_R}}{N_o} \frac{1}{\tanh(2\sqrt{k_R}/N_o)}$$

$$= \frac{2\sqrt{3023}}{182} \frac{1}{\tanh(2\sqrt{3023}/182)}$$

$$= \frac{0.605}{\tanh(0.605)}$$

$$= \frac{0.605}{0.544}$$

$$= 1.11$$

The above estimate of the enhancement factor is used to calculate the quantity $Y$ defined by equation (4.8).

$$Y = \frac{2\sqrt{k_R}}{N_o} \sqrt{1 + (1 - \phi) \frac{R_c}{R_D}}$$

$$= \frac{2\sqrt{3023}}{182} \sqrt{1 + (1 - 1.11) \frac{0.335}{2.16}}$$

$$= 0.605 \sqrt{0.983}$$

$$= 0.600$$

The quantity $Y$ is used, as described by equation (4.9) to calculate a better approximation of the enhancement factor.
\[ \phi = \frac{y}{\tanh(y)} \]
\[ = \frac{0.600}{\tanh(0.600)} \]
\[ = 0.600/0.537 \]
\[ = 1.12 \]

This enhancement factor is then used to obtain a better approximation of the quantity \( y \), and so forth. The next iteration shows that the enhancement factor has converged at 1.12. The total mass transferred with chemical reaction can now be found from equation (4.20).

\[ \bar{A}_{mt} = \phi \bar{A}_o \]
\[ = (1.12)(0.218) \]
\[ = 0.244 \]

This value is plotted in figure 7.5.
BIBLIOGRAPHY


