Mass transfer in heterogeneous systems and velocity and gas absorption studies for single bubbles

Amitava Mukerjee

Iowa State University
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\( K_L^0 \) mass transfer coefficient of the liquid side resistance film for 'pure' gas absorption, \( \frac{\text{cms}}{\text{sec}} \)

\((K_La)_e\) effective oxygen transfer coefficient, \( \text{min.}^{-1} \)

\( Q \) amount of solute absorbed per unit surface area in time \( t \), \( \frac{\text{moles}}{\text{cm}^2} \)

\( r \) rate of reaction per unit volume, \( \frac{\text{moles}}{\text{cm}^3 \cdot \text{sec}} \)

\( R \) instantaneous rate of absorption of solute per unit surface area, \( \frac{\text{moles}}{\text{cm}^2 \cdot \text{sec}} \)

\( \bar{R} \) average rate of absorption of solute in time \( t^* \), \( \frac{\text{moles}}{\text{cm}^2 \cdot \text{sec}} \)

\( R_l \) rate of solute uptake per unit area of the particle surface, \( \frac{\text{moles}}{\text{cm}^2 \cdot \text{sec}} \)

\( s \) particle concentration (volume/volume)

\( s' \) Danckwerts' rate of surface renewal, \( \text{sec}^{-1} \)

\( t \) time, secs.

\( t^* \) Higbie's equal time of exposure of surface elements, secs.

\( t_d \) equivalent diffusion time, secs.

\( t_r \) reaction time, secs.

\( V \) volume of reacting liquid, \( \text{cm}^3 \)

\( x \) distance from gas-liquid interface, cm

\( X \) volume of diluted cell sample used in the expression for dilution, \( \text{cm}^3 \)

\( Y \) caustic consumption rate, \( \frac{\text{mls NaOH}}{\text{min}} \)

Greek:

\( \delta \) film thickness in Whitman's film theory, \( \text{cms} \)
Abbreviations:

D.O.  dissolved oxygen

BOD  biological oxygen demand

phy. abs.  physical absorption

erf  error function

NRRL B65  code name for culture Acetobacter rancens

NRRL B72  code name for culture Acetobacter suboxydans

NRRL B42  code name for culture Acetobacter xylinum
NOMENCLATURE - PART II

A  surface area of bubble, cm$^2$
a  interfacial area per unit volume of liquid, cm$^{-1}$
B  temperature gradient, °K/cm
c  instantaneous concentration of oxygen, ppm
c*  saturation concentration of oxygen, ppm
c_b  bulk concentration of oxygen in water, ppm
D  coefficient of diffusivity, cm$^2$/sec
D_c  diameter of bubble, cm
D_c  column diameter, cm
g  acceleration due to gravity, cm/sec$^2$
g_c  dimensional number required for dimensional consistency, $\frac{1.0 \text{dyne sec}^2}{\text{gm cm}}$
h  total depth of lake, cm
K_L  mass transfer coefficient due to absorption, cm/sec
K_L  time average mass transfer coefficient due to absorption, cm/sec
k_v  ratio of actual interfacial speed to the potential flow interfacial speed
L  total lake depth, cm
n  instantaneous number of moles of gas in the bubble
P  instantaneous pressure of gas in the bubble, dynes/cm$^2$
P  pressure of gas in the bubble at zero depth, dynes/cm$^2$
R  radius of bubble, cm
R (also used as) ideal gas law constant, $\frac{\text{dyne cm}}{\text{gm mole °K}}$
$r$ spherical coordinate system, cm

$s$ Laplatian conversion variable

$T$ instantaneous temperature of lake water, °K

$T^0$ temperature of water at zero depth, °K

$t$ instantaneous time after bubble release, sec

$t$ time coordinate, sec

$t_c$ contact time, sec

$u$ instantaneous velocity of rise of bubble, cm/sec

$u_x$, $u_y$, $u_z$ instantaneous components of velocity of rise of bubble in x, y and z directions respectively, cm/sec

$u_t$ terminal velocity of bubble, cm/sec

$V$ instantaneous bubble volume, cm$^3$

$V_0$ initial bubble volume, cm$^3$

$x$ distance from water surface in lake (positive measured downwards), cm

$x$, $y$, $z$ Cartesian coordinate system

Greek letters:

$\gamma$ surface tension of component, dyne/cm

$\gamma$ retarding coefficient due to surface active material

$\delta$ convective diffusion boundary layer thickness, cm

$\delta_0$ hydrodynamic boundary layer thickness, cm
\( \xi/\xi_0 \) ratio of concentration boundary layer thickness with interfacial flow to that without interfacial flow

\( \mu \) viscosity of continuous phase, gm/cm sec

\( \mu' \) viscosity of dispersed phase, gm/cm sec

\( \rho \) density of continuous phase, gm/cm³

\( \nu \) kinematic viscosity \((\mu/\rho)\)

\( \theta \) spherical coordinate system, radians

\( \pi \) ratio \( \frac{355}{113} \) \((= 3.14159292)\)

\( \sigma \) surface tension, dyne/cm

**Dimensionless parameters derived for lake problem:**

\( z \) dimensionless depth, \( x/L \)

\( \phi \) dimensionless volume of bubble, \( V/V_0 \)

\( \alpha \) dimensionless parameter, \( P^o/(L\rho g/g_c) \)

\( \beta \) dimensionless parameter, \( T^o/(BL) \)

\( \gamma \) dimensionless parameter, \( (P^o/RBL)\frac{1}{\nu} \)

\( \delta \) dimensionless parameter, \( (\rho g/Rg_B)\frac{1}{\nu} \)

\( \nu = \frac{K_e F L}{V_0} (c^*-c_b) \), gm moles/cm³ (not dimensionless)

**Dimensionless numbers:**

\( \text{Re} \) Reynold's number, \( \frac{Du \mu}{\nu} \)

\( \text{Sc} \) Schmidt's number, \( \frac{\nu}{\rho \beta} \)

\( \text{Pe} \) Peclet number (= Re·Sc), \( \frac{Du}{\beta} \)

\( \text{Sh} \) Sherwood's number, \( \frac{K_e D}{L \beta} \)

\( \text{Nu} \) Nusselt's number for mass transfer, \( \frac{K_e D}{L \beta} \)

\( \gamma^* \) Dimensionless surface tension, \( \frac{\gamma}{\mu \nu} \)
PART I. GAS ABSORPTION WITH SIMULTANEOUS CHEMICAL REACTION IN A HETEROGENEOUS SYSTEM
INTRODUCTION AND LITERATURE REVIEW

Recently an increased emphasis has been placed on the effect of a simultaneous chemical reaction on the rate of gas absorption. This is due to an increasing number of industrial applications of biochemical oxidation in which gas absorption rate is appreciably affected by a simultaneous chemical reaction. In aerobic fermentation oxygen is an indispensable nutrient and has to be supplied continuously. The rate of oxygen supply often becomes the controlling factor in the fermentation process. Submerged fermentation methods are employed extensively in the development of new antibiotics and in other important industrial fermentation products. The problem of supplying adequate oxygen to fermentors arises because of the limited solubility of oxygen in water. Fine dispersion of oxygen in the liquid broth becomes a natural recourse, which introduces agitation as another important variable from the biological-engineering point of view.

Papers related to oxygen transfer and agitation in submerged fermentation by Hixson and Gaden (1) and Bartholomew et al. (2) essentially pioneered the systematic engineering studies of oxygen transfer and agitation in fermentation systems. Since then numerous researchers have examined the interaction of gases and liquids in biochemical and other systems. In most cases the gas is absorbed by a solution of a
substance with which the dissolved gas reacts. A comprehensive list of examples of industrial importance is given in the book 'Gas-Liquid Reactions' by Danckwerts (3). An extensively studied inorganic system is the oxidation of sodium sulphite by air or oxygen, which is used for establishing the characteristics of absorption equipment. An added advantage in investigating the rates of gas-absorption is that it can be used to determine such physico-chemical quantities as reaction-rate constants (4, 5) and diffusivities, and such physical quantities as mass transfer coefficients and interfacial areas (6).

Gas absorption with simultaneous chemical reaction has also been studied in heterogeneous systems containing suspended small particles which participate in the absorption and the reaction. Some examples of such systems are oxygenation of blood and blood cells by air bubble swamps, heterogeneous catalytic reactions of liquids such as hydrogenation of aniline using platinum-on-carbon catalyst, hydrogenation of fatty oils catalyzed by noble metal and nickel particles and aerobic fermentation. In the studies with heterogeneous systems a very significant factor seems to have been overlooked, namely, the effect of the small catalyst particles on the gas absorption rate with simultaneous chemical reaction. Tsao (7, 8, 9, 10, 11, 12) first drew attention to this aspect of the problem and has elucidated the theoretical and
practical implications of the particulate effect.

The present investigation is an attempt to exhibit the effect of bacterial cell particles on the mass transfer rate of oxygen in the simultaneous oxidation of glucose to gluconic acid. This approach is particularly applicable to biochemical systems as most of the physical assumptions are satisfied. Experiments conducted with three cultures Acetobacter rancens (B65), Acetobacter suboxydans (B72) and Acetobacter xylinum (B42) evidence the marked effect of surface activity of cellular particles on mass-transfer coefficients.

Theoretical Development of the Mass-Transfer Equation

A phenomenon of mass-transfer with chemical reaction occurs whenever two or more phases which are not in chemical equilibrium with one another are brought into contact. In multi-phase reactions such as biological waste treatment, the microbiological cells are the final receivers of the solute. The overall transfer of the solute (gas) is considered as a sequence of a number of elementary transfer steps (11), illustrated in Figure 1.

Step 1: from the bulk gas phase across the gas side resistance film to the gas-liquid interface.
Figure 1. Elementary transfer steps in mass transport

NOTE: DOTTED LINES SHOW RESISTANCE FILMS
Step 2: across the liquid side resistance film next to the gas-liquid interface.

Step 3: across the liquid bulk to the vicinity of a microbial cell.

Step 4: across the liquid resistance film adjacent to the cell surface.

Step 5: transfer into the cell.

Each of these steps offers a resistance to mass transfer. The effective overall resistance is a sum of the individual resistances in series.

\[
\frac{1}{K_{\text{overall}}} = \frac{1}{K_1} + \frac{1}{K_2} + \frac{1}{K_3} + \frac{1}{K_4} + \frac{1}{K_5} \quad (1)
\]

In most industrial gas-liquid-particle reaction systems, the resistance of the liquid film next to the interface is considerably more than the other resistances. Therefore, \(\frac{1}{K_2}\) becomes the rate-controlling resistance, neglecting the other resistances.

\[
\frac{1}{K_{\text{overall}}} = \frac{1}{K_2} = \frac{1}{K_L} \quad (2)
\]

The rate of solute transfer per unit gas-liquid interface area = \(K_L(c^* - c_b)\) \quad (3)

In systems involving a very rapid chemical reaction, such as those with active microbial cells, the solute (oxygen) gas is
quickly depleted and the DO in the liquid drops nearly to zero. Also in systems with a relatively large liquid film resistance, Equation (3) reduces to

\[
\text{rate of solute transfer per unit interface area} = K_L (c^*)
\]  

Equations (3) and (4) indicate, the mass transfer rate of the solute is essentially dependent on \( K_L \). The presence of the microbial cells have no effect on the mass-transfer unless the cells influence the value of \( K_L \) in a direct manner.

The gas film offers negligible resistance and the solute gas can diffuse easily through the bulk gas phase to the interface. Consequently, the resistance due to Step 1 is usually neglected in theoretical considerations, and it is often assumed that the interface is saturated with the solute. In mathematical modelling of mass-transfer processes, this fact is included as a boundary condition.

**Theoretical Analysis of Mass-Transfer Coefficient (\( K_L \))**

**Interfacial mass transfer without chemical reaction**

Several theories have been proposed to explain the mechanism of mass transfer by physical absorption between two phases, without any simultaneous chemical reaction. Foremost among which is the Whitman Film Theory. This theory assumes that there is a stagnant film of thickness \( \delta \) adjacent to the
interface through which the mass transfer process occurs by molecular conduction.

The mass transfer rate per unit area

\[ \frac{1}{A} \frac{\partial c}{\partial t} \bigg|_{\text{absorption}} = -D \left( \frac{\partial c}{\partial x} \right)_{x=0} \]  

(5)

where \( c \) is the concentration of the absorbing component in the liquid phase, \( x \) is the distance from the interface (taken as positive within the liquid). The bulk concentration \( c_b \) is considered to be constant, with the exception of the stagnant film itself, so that the overall driving force is entirely used up by the phenomenon of molecular transport in the film. Also since the concentration at the interface is assumed to be saturated, \((c^*)\)

\[ -(\frac{\partial c}{\partial x})_{x=0} = \frac{c^* - c_b}{\delta} \]

Equation (5) becomes,

\[ \frac{1}{A} \frac{\partial c}{\partial t} \bigg|_{\text{abs}} = \frac{c^* - c_b}{\delta} = K_L^O (c^* - c_b) \]  

(6)

\[ \therefore K_L^O = \frac{D}{\delta} \]  

(7)

The value of \( \delta \) depends upon the hydrodynamic conditions of the liquid phase. Equation (7) suggests that under identical hydrodynamic conditions

\[ K_L^O \propto D \]
Empirical correlations in liquid-side controlled absorption seem to indicate that

\[ K_L^O \propto \sqrt{A} \]

and if the liquid phase is in contact with a solid or more viscous fluid,

\[ K_L^O \propto (A)^{2/3} \]

both of which are in contrast with Equation (7).

The Higbie Penetration Theory. In 1935 Higbie proposed a hydrodynamic model in which he suggested that various liquid elements drift up through the bulk to the gas-liquid interface and reside at the interface for an equal amount of time \( t^* \), during which time mass transfer occurs through the interface. The concentration of the dissolved gas in the liquid element may be considered to be uniformly equal to the bulk concentration when the element is brought to the surface.

The partial differential equation governing the unsteady state molecular diffusion process within each element is

\[ \frac{\partial}{\partial t} \left( \frac{\partial^2 c}{\partial x^2} \right) = \frac{\partial c}{\partial t} \quad (8) \]

where \( t \) is the time elapsed since the element arrived at the interface.

Equation (8) is derived by a material balance of the transferring solute through an element of differential thick-
ness, \( dx \), and of unit cross-sectional area, disposed perpendicular to the \( x \)-axis.

The boundary conditions associated with Equation (8) are:

\[
\begin{align*}
  c &= c_b, \quad x > 0, \quad t = 0 \\
  c &= c^*, \quad x = 0, \quad t > 0 \\
  c \text{ is bounded}, \quad x \to \infty, \quad t > 0
\end{align*}
\]

The solution is,

\[
 c - c_b = (c^* - c_b) \text{erfc}\left(\frac{x}{2\sqrt{\Delta t}}\right)
\]

or

\[
 c - c_b = (c^* - c_b) \left[1 - \text{erf}\left(\frac{x}{2\sqrt{\Delta t}}\right)\right]
\]

(9)

where 'error function' is defined as,

\[
 \text{erf}(y) = \frac{2}{\sqrt{\pi}} \int_0^y \exp(-z^2) \, dz
\]

The concentration gradient is obtained from Equation (9)

\[
 -(\frac{\partial c}{\partial x})_{x=0} = \frac{c^* - c_b}{\sqrt{\Delta \pi t}}
\]

The instantaneous absorption rate in an element is given by

\[
 R = -\Delta (\frac{\partial c}{\partial x})_{x=0} = (c^* - c_b) \sqrt{\frac{\Delta}{\pi t}}
\]

(10)

The amount of solute absorbed by unit area of surface in time \( t \) is

\[
 Q = \int_0^t R \, dt = (c^* - c_b) \ 2\sqrt{\frac{\Delta t}{\pi}}
\]

(11)
The average absorption rate over the whole "life" $t^*$ of a liquid element is

$$ \bar{R} = \frac{Q}{t^*} = \frac{2(c^*-c_d)}{t^*} \sqrt{\frac{\Delta t^*}{\pi}} = 2(c^*-c_d) \sqrt{\frac{\Delta}{\pi t^*}} $$

(12)

From the definition of mass transfer coefficient given in Equation (3)

Average rate of transfer of gas = $K_L^O(c^*-c_d) = 2(c^*-c_d) \sqrt{\frac{\Delta}{\pi t^*}}$ per unit area

\[ \therefore K_L^O = 2\sqrt{\frac{\Delta}{\pi t^*}} \] (13)

Equation (13) suggests that $K_L^O = \sqrt{2}$ which bears out experimentally for bubbles of medium size. The equation also serves as Higbie's definition of the equivalent life of surface elements.

The Danckwerts' Penetration Theory. In 1951 Danckwerts (3) asserted that Higbie's assumption of 'equal life' for all surface elements of liquid was unrealistic. Accordingly, Danckwerts hypothesized a theory based on surface renewal considerations in which it was assumed:

(i) the chance of a liquid element being replaced with fresh liquid is independent of the length of time for which it has been exposed. Alternatively, $t^*$ is not a constant for all liquid elements.

(ii) the fraction of the surface which has been exposed for times between $t$ and $t + dt$ is $s' \exp (-s't)dt$
so that a first order decay pattern exists.

The average rate of absorption in the value of $R$ averaged over all elements of the surface, having ages between 0 and $\infty$.

$$\bar{R} = \int_0^\infty R \ F(t) \, dt$$

(14)

where $F(t)$ is the age distribution function and is a measure of the fraction of elements which reside at the interface for a period of time $t$.

$$F(t) = s' \ \text{exp}(-s't)$$

(15)

$$\therefore \ \bar{R} = s' \int_0^\infty \ R \ \text{exp}(-s't) \, dt$$

$$\bar{R} = s'(c^*-c_b) \int_0^\infty \sqrt{\frac{4}{\pi t}} \ \text{exp}(-s't) \, dt$$

$$\bar{R} = (c^*-c_b) \sqrt{(4s')^{-1}}$$

(16)

Comparing with Equation (3)

$$\bar{R} = K_L^O (c^*-c_b) = (c^*-c_b) \sqrt{(4s')^{-1}}$$

$$K_L^O = \sqrt{(4s')^{-1}}$$

(17)

Equation (17) suggests that whatever the age-distribution function, $K_L^O = \sqrt{\bar{R}}$. Also, the hydrodynamic properties of the system are accounted for by the single parameter $s'$, which signifies the rate of surface renewal and has the dimensions of reciprocal time. In fact, $\frac{1}{s'}$ may be regarded as an
'average' life of surface elements.

The Astarita Theory. Astarita (13) unified the two approaches of the Penetration Theory due to Higbie and Danckwerts. An 'equivalent diffusion time' \( t_d \) was postulated through the equation

\[
(K_L^o)^2 = \frac{\delta}{t_d}
\]  

(18)

Interfacial mass-transfer with chemical reaction

The theories used to explain 'pure' mass transfer could be extended to include situations encountering simultaneous chemical reaction. In each case the gas is absorbed by the liquid phase at the interface and a chemical reaction follows. Whether the gas absorption or the reaction rate will be the controlling factor will depend on the relative magnitudes of the rates.

The general differential equation governing such a process is

\[
\Delta \frac{d^2c}{dx^2} = r(x,t), \text{ for the film theory model}
\]

and

\[
\frac{\partial^2 c}{\partial x^2} = \frac{\partial c}{\partial t} + r(x,t),
\]

for the penetration theory model where \( r(x,t) \) is the rate (per unit volume of liquid) at which the reaction is destroying the solute gas at time \( t \) and at a distance \( x \) below the surface.
A first-order irreversible reaction of the dissolved gas can be used to demonstrate the effect of a chemical reaction, on the basis of the three models.

The local rate of reaction per unit volume is

\[ r = k_1 c \]

\( k_1 \) being the first-order reaction-rate constant and \( c \) the local concentration of the dissolved gas.

**Whitman's film model**

Mathematically,

\[ \mathcal{D} \left( \frac{d^2 c}{dx^2} \right) = k_1 c \]  \hspace{1cm} (19)

Boundary conditions: \( c = c^*, x = 0 \)

\[ c = c_b, x = \delta \]

With the assumptions that the temperature, values of physico-chemical quantities as solubilities, diffusivities and reaction-rate constants remain uniform and constant, we have with reference to Figure 2.

\[ \frac{dc}{dt} = K_L^0 a(c^* - c_b), \text{ without reaction} \]  \hspace{1cm} (20)

\[ \frac{dc}{dt} = K_L a(c^* - c_b'), \text{ for slow reaction} \]  \hspace{1cm} (21)

\[ \frac{dc}{dt} = K_L a(c^* - 0), \text{ for fast reaction} \]  \hspace{1cm} (22)

Since \( c_b' < c_b \), the driving force is more with simultaneous reaction. Thus, the mass transfer rate will increase due
Figure 2. Film theory model
to the reaction. For a slow reaction $K_L = \frac{\delta}{\delta} K_L^0$ (remains unchanged). For a very rapid reaction $c_b = 0$, hence the mass transfer rate increases further.

If the reaction is extremely rapid, the gas may not have sufficient time to diffuse through the film thickness into the bulk of the liquid, then a reduced film thickness $\delta'$ is obtained ($\delta' < \delta$).

$$K_L = \frac{\delta}{\delta} > K_L^0$$

**Higbie's surface renewal model** The governing differential equation in the case of an irreversible first-order reaction is

$$\frac{\partial c}{\partial t} + k c = 0,$$  \hspace{1cm} (24)

with boundary conditions: $c = 0$, $x > 0$, $t = 0$

$$c = c^*, \hspace{0.2cm} x = 0, \hspace{0.2cm} t > 0$$

$$c = 0, \hspace{0.2cm} x = \infty, \hspace{0.2cm} t > 0$$

(the bulk concentration of dissolved gas is here taken to be zero, which will be the case if the reaction is rapid at the interface). The solution to this equation is given (3) as

$$\frac{c}{c^*} = \frac{1}{2} \exp\left[-x\sqrt{\frac{k_1}{D}}\right] \text{erfc}\left[\frac{x}{2\sqrt{(Dt)}}\right] - \sqrt{k_1 t} \left[ \right]$$

$$+ \frac{1}{2} \exp\left[x\sqrt{\frac{k_1}{D}}\right] \text{erfc}\left[\frac{x}{2\sqrt{(Dt)}} + \sqrt{(k_1 t)}\right]$$

(25)
From which the instantaneous rate of absorption is

\[ R = c* \sqrt{(\frac{g}{k_1})} \left[ \text{erf}(k_1 t) + \frac{\exp(-k_1 t)}{\sqrt{\pi k_1 t}} \right] \]  \hfill (26)

and the amount absorbed by unit area of surface in time \( t \) is

\[ Q = c* \sqrt{\left(\frac{g}{k_1}\right)} \left[ (k_1 t + \frac{1}{2}) \text{erf}(k_1 t) + \sqrt{\left(\frac{k_1 t}{\pi}\right)} \exp(-k_1 t) \right] \]  \hfill (27)

Therefore the average rate of absorption in time \( t^* \) by unit area of surface (with chemical reaction) is

\[ \bar{R} = \frac{Q}{t^*} = c* \sqrt{\frac{g}{k_1}} \left[ (k_1 t^* + \frac{1}{2}) \text{erf}(k_1 t^*) + \sqrt{\left(\frac{k_1 t^*}{\pi}\right)} \exp(-k_1 t^*) \right] \]  \hfill (28)

where \( t^* \) is Higbie's time of exposure which is the same for all liquid elements and is given by

\[ t^* = \frac{\frac{4\Phi}{\pi (K_L^0)^2}}{, \text{ from Equation (13)}.} \]

It has been found convenient to express the effect of a chemical reaction in terms of the 'enhancement factor' \( E \), which is the ratio of the average amount of gas absorbed in a given time \( t^* \) into a reacting liquid, to the amount which would be absorbed if there was no reaction.

\[ \therefore E = \frac{(Q/t^*)_{\text{reaction}}}{(Q/t^*)_{\text{physical absorption}}} \]

For Higbie's model, from Equations (12) and (28)
There is sufficient evidence now that simultaneous chemical reaction does enhance gas absorption. Appropriate examples have been listed by Danckwerts (3) and Astarita (13). Theoretical studies by Brian (14), Danckwerts (3, 15) and Astarita (13) considering chemical reactions of various types have shown that rapid chemical reactions increase the rate of gas absorption.

**Danckwerts surface renewal model** The governing equation, boundary conditions and the analyses in Danckwerts' model is similar to Higbie's model. The only modification is that of exposure time.

The solution is

\[
\text{Laplace } (c) = \overline{c} = c^* \exp\left[- \frac{xK_L^O}{D \sqrt{(1 + \frac{Dk_1}{(K_L^O)^2})}}\right]
\]

(30)

making use of the fact that

\[
s' = \frac{(K_L^O)^2}{D}
\]

Enhancement factor \(E = \frac{\overline{c}}{K_L^O c^*}\)

(31)

which is basically the same as in Higbie's model.
Interfacial mass transfer and uptake by small particles

In the realm of gas diffusion another type of problem is becoming increasingly important—that of mass-transfer in a heterogeneous system. In gas-liquid-particle reactions, the solute from the gas phase diffuses through the liquid to the suspended particles. Processes in biochemical systems are some of the best examples of mass transfer in a heterogeneous phase, such as absorption of oxygen from air bubbles in aerobic fermentation and biological waste treatment. Oxygenation of whole blood (16) is another example.

The presence of the small particles seem to increase the gas absorption rate, by directly affecting the mass transfer coefficient \(K_{L'a}\). Evidence to this effect has been observed by Hunt et al. (17) showing the rate of oxygen absorption is proportioned to cell concentration. Phillips and Johnson (18) noted that the presence of cells enhanced the oxygen-transfer coefficient. Tsao (11) has shown that rate of oxidation more than tripled with increase in catalyst concentration in the air oxidation of carbohydrates catalyzed by noble metal. Freeman and Tsao (12) demonstrated the increase in rate of iodine absorption in the presence of suspended starch granules.

The increase in the rate of gas absorption was attributed to the direct effect of the participating small particles on \(K_{L'a}\) by Tsao (7, 8). The effect of surface activity of the
particles is pronounced in that the particles, bacterial cells for example, have a tendency to agglomerate at the surface. The concentrations of cells at the surface is as much as 2.5 times the concentration of cells in the bulk of the liquid. This property of bacterial cells is often employed in foam fractionation (19). The thickness of the liquid-side resistance film is of the order of $10^{-3}$ cm. The small catalyst particles or cells are of the order of $10^{-4}$ cm. in diameter and so there could be total or partial submergence of the individual particles in the resistance film. Tsao (7) proposed a direct absorption process by which the particles on the surface absorb the gas almost directly from the gas bulk phase and enter it into reaction.

Tsao's theoretical model Tsao (8) developed a differential equation considering the surface activity of the small particles and also the rapid uptake of the solute by the particles at the surface. This does not exclude the possibility of the consumption of solute in the bulk of the liquid. Whether or not the solute gas will be able to diffuse through into the liquid bulk will depend upon the rapid rate of reaction at the interface.

The gas-side resistance at the interface is much smaller than the liquid-side resistance. A consequent assumption is that the surface of the liquid is saturated with the transferring solute.
With reference to Figure 3, \( x = 0 \) is at the interface. The area of the interface is normalized to unity. The shaded section represents the space occupied by the particles. When there is no surface absorption of particles at the interface, the variable \( s \) becomes a constant and is the fraction of the total volume occupied by the small particles. In Figure 3 \( s \) is shown as a variable \( s = s(x) \), which signifies the surface active nature of the particles. There is, in fact, a 'concentration profile' for the particles due to surface activity, mathematically \( s = s(x) \). The rate of solute transfer across any plane of constant \( x \) in the direction of increasing \( x \) is

\[
\left( \frac{dQ}{dt} \right)_x = -D \frac{\partial c}{\partial x} x
\]

A material balance of the solute for the volume between planes \( x \) and \( x + dx \) gives (Figure 3)

Input by diffusion = \(-D(1-s) \frac{\partial c}{\partial x}\)

Output by liquid phase

diffusion = \(-D(1-s+ds)\left( \frac{\partial c}{\partial x} + \frac{d}{dx} \left( \frac{\partial c}{\partial x} \right) dx \right)\)

Output due to uptake by small particles = \(a_l R_1 (s - \frac{1}{2} ds) dx\)

Accumulation of the solute in the liquid

\[
= (1-s + \frac{1}{2} ds) dx \left( \frac{\partial c}{\partial t} \right)
\]

where,

\( a_l = \) surface area of particles per unit volume of particles.
Figure 3. Outline of the interface with particles
\[ a_1 = \frac{6}{d} \] for uniform rigid spherical particles of diameter \( d \).

\[ R_1 = \text{rate of solute uptake per unit area of particle surface.} \]

The overall material balance of the solute yields,

\[
(1-s + \frac{1}{2} ds) \frac{dx}{\partial x} \left( \frac{\partial c}{\partial x} \right) = -D(1-s) \left( \frac{\partial c}{\partial x} \right)
\]

\[ + D(1-s+ds) \left[ \frac{\partial^2 c}{\partial x^2} + \left( \frac{\partial}{\partial x} \right) \left( \frac{\partial c}{\partial x} \right) dx \right] \]

\[ - a_1 R_1 (s - \frac{1}{2} ds) dx \]

Eliminating the terms involving the products of two or more differentials, the following equation is obtained.

\[
\frac{\partial c}{\partial t} = D \left( \frac{\partial^2 c}{\partial x^2} \right) + D \left( \frac{\partial c}{\partial x} \right) \left[ \frac{1}{1-s} \frac{ds}{dx} \right] - \frac{a_1 s R_1}{(1-s)} \tag{32}
\]

In Equation (32) special cases are obtained by substituting particular functions for \( R_1 \) depending upon the kinetics of the reaction and so also for \( s = s(x) \) depending upon the surface activity of the particles concerned.

Tsao (8) has theoretically studied the case of surface activity with linear particle concentration profile. Schierholz (20) also studied various cases of particle concentration profile with zero and first order reactions. The evidence to date indicates that the surface active particles indeed have a positive effect on mass-transfer coefficient (\( K_L a \)) in that it enhances the value in processes involving
simultaneous chemical reaction with gas absorption.

Production of D-gluconic acid  The oxidation of glucose to gluconic acid by acetic acid bacteria was first noted by Brown and later confirmed by numerous workers on various strains. As documented by Asai (21), *Acetobacter rancens* (B65), *Acetobacter suboxydans* (B72) and *Acetobacter xylinum* (B42) were specially noted for their high gluconic acid production. The optimal temperature and pH for gluconic acid production are according to Asai, about 25°C and pH 4.0-6.0. Glucose oxidation was apparently mediated by a cytochrome system. There is also a possibility that a cytochrome-independent enzyme system is partly responsible for glucose oxidation.
EXPERIMENTAL EQUIPMENT AND PROCEDURE

General

To study the effect of suspended particles on mass transfer coefficient ($K_La$) experimentally, a system had to be devised in which gas diffusion occurred simultaneously with chemical reaction in the presence of small particles acting as catalysts. The particles would, therefore, appear prominently in the diffusion process as physical barriers and in the heterogeneous chemical reaction as the catalysts.

With this aim in mind, the system chosen was the oxidation of glucose to gluconic acid in the presence of microorganisms which facilitate this reaction.

\[
\begin{align*}
&\text{CHO} \\
&\text{H - C - OH} \\
&\text{HO - C - H} \quad \frac{1}{2} \text{O}_2 \\
&\text{H - C - OH} \\
&\text{H - C - OH} \\
&\text{CH}_2\text{OH} \\
\text{D-Glucose} \\
\end{align*}
\]

\[
\begin{align*}
&\text{COOH} \\
&\text{H - C - OH} \\
&\text{HO - C - H} \\
&\text{H - C - OH} \\
&\text{H - C - OH} \\
&\text{CH}_2\text{OH} \\
\text{D-Gluconic Acid} \\
\end{align*}
\]

The microorganisms used were Acetobacter rancens (NRRL B-65), Acetobacter suboxydans (NRRL B-72) and Acetobacter xylinum (NRRL B-42) in three separate sets of experiments. As described by Asai (21) in great detail, these representa-
tive aerobic bacteria are important for biochemical studies of the oxidation mechanisms of ethanol, polyalcohols and sugars. The cells being largely proteinous and surface active agglomerate at the surface of the liquid, thus obstructing physical diffusion. The oxygen of the atmosphere was utilized in the oxidation reaction.

Culture Preparation

The cultures were obtained from the Northern Regional Research Laboratory, USDA, Peoria, Illinois. Stock cultures were maintained on slants and stored in the refrigerator at 5°C, for future use. Cells from the slants were transferred to shaker flasks and incubated for twenty hours at room temperature for use in the experiments. Repeated trials with cells grown in a homogeneous liquid phase medium indicated that the cell population was insufficient to yield perceptible readings. This necessitated cell growth in biphasic media. This technique was first introduced by Tyrrell et al. (22). The 'liquid' medium was composed of 1.3 gms. yeast extract and 0.65 gms. glucose in 65 mls. distilled water. The 'solid' phase had the same nutrient composition with 20 gms./liter of agar base. All media solutions were sterilized in the autoclave at 15 psig for 15 minutes. The nutrient composition in the slants was the same as the solid phase of the shaker medium. Cultures were transferred on new slants frequently
to ascertain fresh growth and 'young cells' for experimental use.

In preparation for each run, the biphasic medium was uniformly composed of 325 mls. of 'solid phase' and 650 mls. of 'liquid phase.' Also, the inoculum was uniformly maintained at 50 mls. of 24-hour shaker culture grown in liquid medium of identical composition. These procedures were repeated as consistently as possible so as not to inadvertently introduce variables which might be related to the culturing of cells.

Experimental Equipment

The experimental assembly was intentionally made simple to avoid any physical variables affecting the results, (Figure 4).

The reacting vessel was a regular 4-1/2 inch ID one liter pyrex glass beaker. The glucose solution and the suspended cells were well stirred by a magnetic stirrer, to ensure complete mixing without creating a vortex. The reaction solution was kept exposed to the atmosphere. The oxygen probe from a DO Analyzer was partially immersed in the solution to record continuously the DO level. The pH electrodes from a Heath pH recorder were also partially immersed in the solution to continuously monitor the pH of the solution. The oxygen probe and the pH electrodes were carefully located so as to act as baffles and destroy any vortex formation due to stirring.

The location and position of the probe and electrodes were
Figure 4. Experimental apparatus
maintained the same from run to run, to keep the physical parameters invariant. A narrow tygon tubing was used to pump caustic (NaOH) from a burette, by a microflow pump. The pump was triggered by a relay, which in turn was actuated by a microswitch on the pH recorder.

Experimental Procedure

Culture preparation was preplanned before a run was conducted. A day before the run, a mixture of biphasic medium was prepared as described and inoculated. The biphasic culture was then put on the shaker for exactly 20 hours, at which time the cell population was found to be adequate for a run.

Before each run certain procedures were followed:

a) The pH electrodes were washed and dipped in fresh pH 7.0 solution and the pH recorder was standardized.

b) The magnetic stirrer unit was kept on, so as not to give variations in stirrer speed.

c) The oxygen meter was switched on and kept ready at standby for immediate use.

d) The oxygen recorder was switched on and the pen was primed.

e) Some caustic was allowed to flow through to remove any trapped air bubbles in the line.

Ten gms. of anhydrous dextrose (glucose) was weighed out accurately on a Mettler scale in the clean, dry pyrex beaker.
A solution of glucose was made with distilled water. The amount of water added varied in each run, reason for which will be given later.

The solution was stirred at 180 RPM. The stirring speed was checked by a stroboscope. This speed was found to be the maximum allowable speed which will prevent a vortex formation with the help of the baffles and yet ensure complete mixing.

After positioning the oxygen probe, the meter was switched on to operate mode and the solution was saturated with oxygen from an oxygen cylinder. The recorder continuously recorded the oxygen concentration level in the solution, at a chart speed of 1"/min. The pH electrodes were partially immersed in the solution.

A measured volume of the 20-hour 'biphasic' culture was poured into the glucose solution and a good suspension of cells occurred by stirring. The volume of cells varied in each run as was the glucose solution. The principal variable in the experiment was 'cell concentration.' This was achieved by diluting the initial cell-solution with varied amounts of glucose solution, but keeping the total volume consistently at 400 mls.

The pH recorder was switched on and the solution pH was adjusted to the control pH of 6.12 by adding a few drops of concentrated NaOH.

On adding the cell solution, the DO level dropped from
saturation to zero. The rate at which this decrease took place depended on the initial concentration of cells. Usually it took between ten to twenty minutes for the DO level to drop to 0% saturation, in which time the pH recorder had stabilized. The caustic relay was switched on and the caustic level in the burette was raised to the 50.0 ml mark for convenient reading. A three-way stop-cock allowed the flow of caustic from a raised reservoir to the burette.

The readings merely comprised of reading the caustic level in the burette in ten minute intervals. The caustic consumption rate monitored the oxidation reaction rate with simultaneous oxygen absorption from the atmosphere. From this data, \( K_L a \) can be evaluated, as will be shown in the analysis. Every half hour a sample of the 'cell-population' was taken and a few drops of concentrated HCl were added to stop cell growth in the sample. The density of cells was obtained as percent transmittance on a Beckman DU Spectrophotometer.

The least turbid cell sample was examined for transmittance first. Consecutively higher turbid cell samples were diluted accurately with distilled water to read the same transmittance. Accordingly, cell concentration was recorded as 1:X, where 1 ml. of the cell sample was diluted with \((X-1)\) mls. of distilled water. Before and after each turbidity reading the transmittance for the standard (distilled water) was read off at 100%.
As the cells were seen to multiply in the two hour duration of each run, the caustic consumption rate was seen to increase appropriately. For this reason, each run was effectively divided into four divisions of one-half hour each, in which the cell population was practically constant. The caustic data were later examined, grouped together and attributed to the appropriate cell concentration.

A brief description of the accessory apparatus used will be given.

**Dissolved oxygen measurement**

Model DOA oxygen analyzer of the Fermentation Design Co. contains an amplifier and direct reading meter (0 to 100%) capable of accepting DO signals from a galvanic electrode (probe). A span-adjustment potentiometer knob adjusts electrode output to 100% during calibration. It can be electrically zeroed. Zero adjustment was made by the simple expedient of adding a small amount of sodium sulphite. The amount of sodium sulphite was slightly more than required to react with all the dissolved oxygen, in the presence of Co²⁺ catalyst. An ON-OFF switch facilitates operation, standby modes as well as connection to a Polarographic probe which may also be used. The advantage of the galvanic probe used is that it can be sterilized with the fermenter assembly and functions within a large temperature range. It is now used widely in fermentation industry and in water pollution studies.
**pH measurement**

Beckman reference electrode (39402) and glass electrode (39301) were used to monitor the pH of the reacting solution. The electrodes were connected to a Heath pH Recording Electro-meter (Model EUW-301) which amplifies the signal received from the electrode and drives a recorder pen. The recorder was converted to a pH-controller by installing a microswitch at the controlled pH value of 6.12. As glucose gets oxidized to gluconic acid, the penholder moves and closes the switch. This in turn activates the relay which supplies 110 volts to an Emdeco micro flow tubing pump (Model No. 102-130), which pumps caustic from the burette through tygon tubing to the reacting solution. The continuous pumping rate was 6.0 ml/10 minutes. The normality of the caustic and the pumping rate had to be adjusted by repeated trials to make the caustic rate compatible with the acid formed and also to obtain convenient readings between the ranges of cell concentration used.

**Turbidity measurement**

A Beckman 2400 DU Spectrophotometer was used in conjunction with a Beckman 73600 AC DU Power Supply unit. Measurements for transmittance were made on each of the 'cell concentration' samples at 610 μm wavelength and a slit opening of 0.065 mm. The spectrophotometer was equipped with a tungsten lamp which provides energy in 320-1000 μm range and a
standard phototube housing containing red-sensitive phototube (position 1) with 600-1000 μm response range. The samples were contained in standard silica absorption cells (Beckman 75184).
RESULTS AND DISCUSSION

Determination of Mass Transfer Coefficient \((K_L a)\) (with Chemical Reaction)

The caustic consumption rate in each run monitored the rate of oxygen uptake. The caustic consumption/time data from each section of each run was fitted in a least-squares program in the computer to give the best slope. The unit for this slope was \(\frac{\text{mols. NaOH}}{\text{min.}}\). This was converted to \(\frac{\text{mgms. O}_2}{\text{min.}}\) by taking into consideration the normality of the NaOH used and the stoichiometry of the reaction

\[
\text{HOCH}_2\text{CH (CHOH)}_4\text{O} + \frac{1}{2}\text{O}_2 \rightarrow \text{HOCH}_2\text{(CHOH)}_4\text{COOH}
\]

Glucose Gluconic acid

Oxygen consumption rate = \(y (0.1496 \times 16.0) \frac{\text{mgms. O}_2}{\text{min.}}\) \((33)\)

where \(y\) is in \(\frac{\text{mols. NaOH}}{\text{min.}}\) and the normality of NaOH used for B65 and B72 runs was 0.15N.

The mass transfer equation describing the process is

\[
V \frac{dc}{dt} = K_L a(c^*-c)V - \text{(oxygen consumption rate)}
\]

Since \(c = 0\), through the duration of the runs

\[0 = K_L a(c^*-c) V - \text{oxygen consumption rate}\]

\[\therefore K_L a(c^*-c) V = \text{oxygen consumption rate}\]

or, \(K_L a = \frac{\text{oxygen consumption rate}}{(c^*-c)V}\) \((34)\)
In the experiments with the cultures B65, B72 and B42, c* was the saturation concentration of oxygen in air at 25°C, 
\[ c^* = 8.5 \text{ ppm.} = \frac{8.5 \text{ mgms. O}_2}{\text{liter}} \]

c the dissolved oxygen concentration in the bulk was 0% saturated, \( c = 0 \)

\( V \), the volume of reacting liquid was maintained at 400 mls., \( V = 0.4 \text{ liter} \)

\[ K_L a = \frac{y(0.1496 \times 16.0)}{8.5 \times 0.4} \text{ min}^{-1} \]

For B65 and B72 runs, \( K_L a = (0.704)y \text{ min}^{-1} \) \hspace{1cm} (35)

By similar calculations, for B42 runs, \( K_L a = (1.505)y \text{ min}^{-1} \) where NaOH used was 0.32N. \hspace{1cm} (36)

The turbidity measurement of the sample taken in each section gave a relative measure of the concentration of cells present at that time. The turbidity values are expressed as dilutions.

From such \( K_L a/\text{cell concentration} \) data, Figures 5, 6 and 7 were constructed to indicate the dependence of mass transfer coefficient on the presence of tiny particulate matter, bacterial cells in this case.
Figure 5. Effect of relative cell concentration (B65) on oxygen absorption rate
Figure 6. Effect of relative cell concentration (B72) on oxygen absorption rate
Figure 7. Effect of relative cell concentration (B42) on gas absorption rate
Determination of Mass Transfer Coefficient ($K_{L}^{Oa}$) (due to physical absorption only)

The data for physical absorption was collected at the end of each run, by deactivating the cells and allowing the DO level to build up by physical absorption.

Theoretically, the equation governing physical absorption is

$$V \frac{dc}{dt} = (K_{L}^{Oa})(c^{*}-c)V \quad (37)$$

or,

$$\int_{c_{1}}^{c_{2}} \frac{dc}{c^{*}-c} = (K_{L}^{Oa}) \int_{t_{1}}^{t_{2}} dt$$

$$\therefore \ln \frac{c^{*}-c_{1}}{c^{*}-c_{2}} = (K_{L}^{Oa})(t_{2}-t_{1}) \quad (38)$$

From this equation ($K_{L}^{Oa}$) can be evaluated as the slope of the straight line obtained by plotting $\ln \frac{c^{*}-c_{1}}{c^{*}-c_{2}}$ against time.

The data from the oxygen recorder was analyzed and fitted to a straight line. The average slope, in each run was the value for $K_{L}^{Oa}$ in min$^{-1}$. $K_{L}^{Oa}$ values were plotted against average cell concentrations for each run in Figures 8, 9 and 10.

As expected $K_{L}^{Oa}$ values decrease with increase in cell concentration. The deactivated cells being surface active agglomerate on the surface, thereby impeding the passage of oxygen from the atmosphere to the bulk of the liquid. This
Figure 8. Effect of relative cell concentration (B65) on $K_L^{o}a$
Figure 9. Effect of relative cell concentration (B72) on $K_L^o$
Figure 10. Effect of relative cell concentration (B42) on $K_L^{OA}$
impedance is more with increased cell concentration, thereby decreasing \( K_{L}^{Oa} \).

From Figures 8, 9 and 10, it is seen that \( K_{L}^{Oa} \) decreases slightly in the range of cell concentration studied. An average value of \( K_{L}^{Oa} \) was used in further analyses.

\[
(K_{L}^{Oa}) \text{ for } B65 = 3.03 \times 10^{-2} \text{ min}^{-1} \\
(K_{L}^{Oa}) \text{ for } B72 = 3.02 \times 10^{-2} \text{ min}^{-1} \\
(K_{L}^{Oa}) \text{ for } B42 = 3.11 \times 10^{-2} \text{ min}^{-1}
\]

**Determination of Rate Constant of Reaction \( k_{1} \)**

\[
\begin{align*}
\text{HO} & \quad \text{OH} \\
\text{H - C - OH} & \quad \text{H - C - OH} \\
\text{HO - C - H} & \quad \text{HO - C - H} \\
\text{H - C - OH} & \quad \text{H - C - OH} \\
\text{H - C - OH} & \quad \text{CH}_{2}\text{OH} \\
\text{CH}_{2}\text{OH} & \quad \text{CH}_{2}\text{OH}
\end{align*}
\]

D-glucose  \quad \text{D-gluconic Acid}

It has been determined (21) that the aerobic oxidation of glucose to gluconic acid is a relatively fast pseudo-first order reaction with respect to oxygen, in the presence of excess glucose. This reaction is enhanced markedly by acetic acid bacteria B65, B72 and B42, the oxidation being partly mediated by a cytochrome-dependent enzyme system.
The experiments were conducted at the optimal conditions of temperature (25°C) and pH (6.12), under which the reaction was found to be considerably rapid. The data for reaction rate determination were recorded at the start of each run. The rate at which the DO level decreased from 100% saturation to 0% saturation is a measure of the reaction rate.

Since the reacting vessel was exposed to the atmosphere, under strict considerations, simultaneous oxygen absorption from the atmosphere should be accounted for together with the rapid chemical reaction. The unsteady-state equation governing such a process is,

$$\frac{dc}{dt} = K^o_L (c^*-c) - k_1 c$$  \hspace{1cm} (39)$$

The reaction rate being much greater than the mass transfer coefficient, the simultaneous oxygen absorption term was neglected, giving

$$\frac{dc}{dt} = -k_1 c, \quad c=c^*, \quad t=0$$

from which $-\ln \frac{c}{c^*}$ = $k_1 t$, which is an equation of a straight line. \hspace{1cm} (40)

From the recorded output of the O₂-recorder the oxygen concentration/time points were analyzed and fitted in a least-squares program on the computer to give the best slope. This slope was the value of $k_1$ in min⁻¹.
Figures 11, 12 and 13 were constructed to show the dependence of rate constant on the amount of catalyst added, in this case bacterial cells. The rate constant seems to increase sharply with increase in cell concentration, for the region observed. This suggests an active reaction system in which the mass transfer due to physical absorption is much smaller than the reaction rate. It is conceivable that the cells accumulated on the surface consume oxygen directly from the atmosphere, thereby increasing the rate constant. This feature will be discussed in more detail later.

Comparison with Danckwerts' Solution

Danckwerts in his book (3) analyzed theoretically the case of a first-order irreversible reaction of the dissolved gas in a homogeneous phase.

Mathematical expression:

\[
\frac{\partial c}{\partial t} = \frac{\partial^2 c}{\partial x^2} - k_1 c
\] (41)

Boundary conditions: 
- \( c = c^*, x = 0, t > 0 \)
- \( c = c^0, x > 0, t = 0 \)
- \( c = c^0, x = \infty, t > 0 \)

Danckwerts' solution, for \( c^0 = 0 \) (which was the case in the experiments conducted) conforming to Higbie's model is
Figure 11. Effect of relative cell concentration (B65) on reaction rate constant
Figure 12. Effect of relative cell concentration (B72) on reaction rate constant
Figure 13. Effect of relative cell concentration (B42) on reaction rate constant
\[
\frac{c}{c^*} = \frac{1}{2} \exp[-x\sqrt{\frac{k_1}{\Delta}}] \text{erfc}\left[\frac{x}{2\sqrt{\Delta t}} - \sqrt{k_1 t}\right] \\
+ \frac{1}{2} \exp[x\sqrt{\frac{k_1}{\Delta}}] \text{erfc}\left[\frac{x}{2\sqrt{\Delta t}} + \sqrt{k_1 t}\right]
\] (42)

Also the amount of solute absorbed with chemical reaction by a unit area of surface in time \(t^*\) is given by

\[
\left(\frac{Q}{t^*}\right)_r = c^* \sqrt{\frac{\Delta}{k_1}} \left[(k_1 t^* + \frac{1}{2}) \text{erf}\sqrt{k_1 t^*} + \sqrt{\frac{k_1 t^*}{\pi}} \exp(-k_1 t^*)\right]
\]

\[
= K_L a (c^* - 0)
\] (43)

The amount of solute absorbed by pure physical absorption is given by

\[
\left(\frac{Q}{t^*}\right)_{\text{phy. abs.}} = 2 c^* \sqrt{\frac{\Delta}{\pi t^*}} = K_L^0 a (c^* - 0)
\] (44)

Danckwerts introduced the concept of enhancement factor \(E\), which is the factor by which the chemical reaction increases the rate of absorption compared to physical absorption.

With \(c^0 = 0\) in both cases,

\[
E = \frac{\left(\frac{Q}{t^*}\right)_r}{\left(\frac{Q}{t^*}\right)_{\text{phy. abs.}}}
\] (45)

\[
\therefore E = \frac{1}{2} \sqrt{\frac{\pi}{k_1 t^*}} \left[(k_1 t^* + \frac{1}{2}) \text{erf}\sqrt{k_1 t^*} + \sqrt{\frac{k_1 t^*}{\pi}} \exp(-k_1 t^*)\right]
\]

\[
= K_L a / K_L^0 a
\] (46)

This is the solution in the case of simultaneous physical absorption with reaction in the homogeneous phase. \(E\) will
vary with \((k_t t^*)\) according to Equation (46).

One way to study a similar situation in a heterogeneous phase would be to compare the experimentally obtained enhancement factor \((E = K_L a/K_L^0 a)\) with Danckwerts' theoretical model (homogeneous phase). This is demonstrated in Figures 14, 15 and 16. The resulting difference will be discussed shortly.

The time element \(t^*\) in Equations (43) and (44) is the time elapsed from the moment the surface element considered has been brought to the surface. This is in conformity with Higbie's Penetration Theory in which the variety of small liquid elements, which comprise the gas-liquid interface, are continuously brought up to the surface by bulk motion. Higbie assumed the 'exposure time' of each of these surface liquid elements to be the same. This is the time \(t^*\) under consideration.

This uniform exposure time is determined by the hydrodynamic properties of the system. For physical absorption, the average rate of absorption per unit area,

\[
\frac{Q}{t^*}_{\text{phy. abs.}} = 2(c^* - c^0) \sqrt{\frac{2a}{\pi t^*}} = K_L^0(c^* - c^0) \tag{47}
\]

when

\[
c^0 = 0, \quad t^* = \frac{4\phi}{\pi(K_L^0)^2} \tag{48}
\]

Surface area per unit volume \(a = \frac{\pi d^2/4}{V} \tag{49}\)
Table 1. Theoretical enhancement factors for the various systems

<table>
<thead>
<tr>
<th>Relative cell conc.</th>
<th>Acetobacter rancens (B65)</th>
<th>Acetobacter suboxydans (B72)</th>
<th>Acetobacter xylinum (B42)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Relative Enhancement factor<strong>E</strong></td>
<td>Relative Enhancement factor<strong>E</strong></td>
<td>Relative Enhancement factor<strong>E</strong></td>
</tr>
<tr>
<td>7.0</td>
<td>1.001</td>
<td>1.0</td>
<td>4.5</td>
</tr>
<tr>
<td>9.0</td>
<td>1.002</td>
<td>6.0</td>
<td>5.5</td>
</tr>
<tr>
<td>17.0</td>
<td>1.005</td>
<td>18.0</td>
<td>11.3</td>
</tr>
<tr>
<td>31.0</td>
<td>1.016</td>
<td>31.0</td>
<td>17.6</td>
</tr>
<tr>
<td>33.0</td>
<td>1.030</td>
<td>40.0</td>
<td>26.4</td>
</tr>
<tr>
<td>55.0</td>
<td>1.043</td>
<td>60.0</td>
<td>35.7</td>
</tr>
</tbody>
</table>

*Theoretical enhancement factor calculated according to Equation (46).
Figure 14. Comparison of experimental and theoretical enhancement factor ($B_65$)
Figure 15. Comparison of experimental and theoretical enhancement factor (B72)
Figure 16. Comparison of experimental and theoretical enhancement factor (B42)
Under the conditions of the experiments \( a = 0.2112 \text{ cm}^{-1} \).

Therefore, 
\[
K_L^0 = \frac{K_L^0 a}{a}
\]

\[
K_L^0 = 0.24 \times 10^{-2} \text{ csm/sec. for B65 runs}
\]
\[
K_L^0 = 0.24 \times 10^{-2} \text{ csm/sec. for B72 runs}
\]
\[
K_L^0 = 0.25 \times 10^{-2} \text{ csm/sec. for B42 runs}
\]

The diffusivity of oxygen in water (or dilute glucose solution) is taken to be \( 2.0 \times 10^{-5} \text{ cm}^2/\text{sec} \) and the value verified by applying the Wilke and Chang equation for diffusivity.

From Equation (48) the exposure time of liquid elements 
\[
t^* = 4.45 \text{ secs for B65 systems,}
\]
\[
t^* = 4.49 \text{ secs for B72 system and}
\]
\[
t^* = 4.22 \text{ secs for B42 system.}
\]

Knowing \( t^* \) and the rate constant (\( k_1 \)) values, \( E \) can be plotted against (\( k_1 t^* \)) according to Equation (46). Figures 14, 15 and 16 are plots of \( E \) vs. relative cell concentration which are effectively the same as \( E \) vs. (\( k_1 t^* \)) plots.

Discussion

It is clear from Figures 14, 15 and 16 that Danckwerts' theoretical solution of mass transfer occurring in the homogeneous phase does not explain the situation in the heterogeneous phase. This is borne out by the fact that the experimentally determined enhancement factors are manifold
more than that predicted by the theoretical solution, Equation (46).

As pointed out by Tsao (8) this anomaly could be attributed to the surface active property of the bacterial cells. Microbial cells being proteinous tend to concentrate at the surface in a dynamic manner, in the sense that the cellular particles are continuously circulated like the hypothetical liquid elements in Higbie's penetration theory. The interfacial zone is heavily concentrated with cells and thus renders the physical possibility of direct absorption of oxygen from the air by the cells to occur, thereby increasing \( K_L a \). The size of the cell is comparable to the film thickness at the interface (1 micron) and it is conceivable that the volume contained at the interface is heavily packed with rapidly reactive cells. If the oxidation reaction is fast enough at the interface, the oxygen may not be able to travel through the interface into the bulk, thus yielding a zero DO concentration which was observed in the experiments (Figure 17). The direct absorption model does not exclude the possibility of oxygen reaching the bulk, but if it did a nonzero finite oxygen concentration would build up in the bulk.

According to the film theory, there is a stagnant film of thickness \( \delta \) through which transport process takes place by simple molecular conduction. With substantially rapid chemical reaction in the interface, a reduction can occur in the dif-
Figure 17. Dissolved oxygen concentration profile

Figure 18. Overlapping of interfacial films
Case I: No chemical reaction
Case II: Diffusion with rapid simultaneous biochemical reaction

1. Direct absorption into mechanism
2. Reaction in the liquid bulk
fusional path of the absorbed molecules of oxygen. This can also contribute to an increased interfacial mass-transfer coefficient. The penetration of this film suggests an overlapping of the gas-liquid film and the cell-liquid and cell-air films (Figure 18). The net effect due to this could amount to a reduction in the impedance offered to mass transfer by the entire film.

Indeed, the concentration of cells at the interface can cause a significant physical barrier to the transport of oxygen from the atmosphere. This is evidenced in the pure physical absorption part of each experiment. Mass transfer coefficient decreased with the increase in cell concentration (Figures 8, 9, 10). Whether the $K_L^a$ due to simultaneous chemical reaction is more than $K_L^0a$ will, therefore, depend on the relative impetus the reaction renders. If it is rapid enough to overcome the physical resistance, an enhancement factor of 1.0 or more will be observed.

Tsao's model

In order to explain the phenomenon of simultaneous gas-liquid interfacial mass transfer and uptake by small particles, Tsao (8) developed the following differential equation,

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} + D \frac{\partial c}{\partial x} \left( \frac{1}{1-s} \right) \frac{ds}{dx} - \frac{a_l s R_l}{(1-s)}$$

(50)

where $s$ is the fraction of the total volume occupied by the
small particles. Due to the surface active nature of these particles \( s \) is considered as a variable and not a constant.

Here, \( s \) as a function of \( x \), \( s = s(x) \) is unknown and \( R \) as a function of solute concentration, \( R_1 = R_1(c) \) is unknown. Though \( R_1 = R_1(c) \) can be determined by careful kinetic studies, the particle concentration profile \( s = s(x) \) is still experimentally difficult to establish.

The fact that the oxygen concentration in the bulk of the liquid was zero, suggests a rapid chemical reaction in the interfacial zone. Since microbial cells act as catalysts in this study, it is quite probable that the cells penetrate the interfacial zone and lodge in the film thickness in a concentrated manner for short periods of time. It is, therefore, quite reasonable to expect that the unsteady state differential Equation (50) developed by Tsao (8) is valid and does describe the physical situation, including the mechanism of direct absorption by surface-active particles.

The purpose of obtaining a solution to the Equation (50) is to be able to predict an effective oxygen-transfer coefficient \( (K_L a)_e \) which includes the broader perspective of the process.

Then the rate of oxygen transfer at the surface can be described by

\[
(K_L a)_e (c^* - c) = -\frac{\partial (\frac{3c}{2})}{\partial x} \bigg|_{x=0} \tag{51}
\]
A mathematical and statistical evaluation of the situation should be possible if more is known about the ratio of cell population at the interface to that in the bulk, hydrodynamics of fluid properties and necessary molecular dimensions.

**Diffusion and reaction times**

As described by Astarita (13), Higbie's hypothesis of equal life $t^*$ for all surface elements and Danckwerts' "average" life $\frac{1}{s}$ can be unified into an "equivalent diffusion time" $t_d$ through the equation

$$ (K_L^o)^2 = \frac{D}{t_d} $$

$$ \therefore t_d = \frac{D}{(K_L^o)^2} \quad (52) $$

The reaction time $t_r = \frac{(c^*-c)}{r(c^*-c)} = \frac{c^*}{r(c^*)} \quad (53)$

where rate of reaction $r$ is a function of the available driving force $= r(c^*-c)$. For first-order reactions with kinetic rate constant $k_1$

$$ t_r = \frac{1}{k_1} \quad (54) $$

The diffusion time $t_d$ is the time available for the unsteady state diffusion process within the surface elements to take place. Whereas the reaction time, is the time
required by the reaction and not available for it.

For the effect of surface reaction to be appreciably realized, the reaction needs to be relatively rapid. The condition to satisfy will be, \( t_r \) should not be much greater than \( t_d \). An estimate \( t_d \) and \( t_r \) values are given in Table 2.

Table 2. Estimates of \( t_d \) and \( t_r \)

<table>
<thead>
<tr>
<th>Cells</th>
<th>( t_d ) secs</th>
<th>( t_r ) sec.s</th>
</tr>
</thead>
<tbody>
<tr>
<td>B65</td>
<td>3.50</td>
<td>34.47</td>
</tr>
<tr>
<td>B72</td>
<td>3.52</td>
<td>91.57</td>
</tr>
<tr>
<td>B42</td>
<td>3.32</td>
<td>74.64</td>
</tr>
</tbody>
</table>

Table 2 for the systems studied. Astarita estimates \( t_d \) values of the order \( 5 \times 10^{-3} < t_d < 4 \times 10^{-2} \) secs. in the homogeneous phase. The presence of suspended particles may well impede the motion of the liquid elements and result in slowing down the motion. It is, therefore possible to obtain \( t_d \) of the order of a few seconds.

Reaction time \( t_r \) can have extremely different values depending on the system.

For the B65 case, \( t_r \) is about ten times \( t_d \) and this range is suitable to show the marked increase in mass-transfer coefficient. In the B72 and B42 case, \( t_r \) is about 26 and 22 times \( t_d \) respectively and although these are more than that in
B65, the range was suitable to enhance the mass-transfer coefficient. The $k_l$ value was determined by applying Equation (40) to the entire liquid bulk where the cell concentration may be much less than that at the interface. On comparing $t_d$ against $t_r$, $k_l$ should be based strictly on the cell concentration at the interface. Therefore, the 'true $k_l$' is larger than $k_l$ used and the true ratios between $t_r$ and $t_d$ given in the table may not be as large as shown.

The most appropriate condition to bring out the 'surface-active' effect of enhancing mass-transfer would be $t_r << t_d$. Under this condition the reaction is fast enough to take place appreciably during the life of surface elements. But the ranges are entirely relative and the time ranges studied were adequate to prove the contention that a sufficiently high concentration of biologically active cellular particles at the gas-liquid interface does increase the mass-transfer coefficient.
PART II. VELOCITY AND GAS ABSORPTION STUDIES FOR SINGLE BUBBLES
One of the important problems related to water pollution is the rapid depletion of dissolved oxygen in lakes and streams due to the high biological oxygen demand (BOD) caused by pollutants. Moreover, water bodies in the northern United States and in Canada are mostly covered with ice during long winters, thereby eliminating oxygen supply by absorption from the atmosphere. Winter fish kill has been reported extensively each spring. Other marine flora and fauna are seriously endangered under these critical conditions. Sufficient ecological concern exists to warrant a closer examination of the problem and to suggest efficient and economical methods of raising dissolved oxygen (DO) to safer levels. A study of the basic engineering aspects will concomitantly yield a better understanding of gas absorption fundamentals (23, 24) and be useful for other chemical engineering applications.

There are two reported techniques for supplying oxygen to water bodies. Mechanical surface aerators have been used (25) with limited success in stagnant water bodies. This process becomes inconvenient and expensive in attempting to oxygenate under an ice cover. A sufficiently large opening in the ice layer has to be maintained through long winter periods. Also, to obtain sufficient mixing high energy requirements will be necessary. The alternative suggestion of employing
air diffusors (25, 26) appears more reasonable, but the use of air severely limits the amount of oxygen that can be supplied to the water body. Because of the high nitrogen content (79%) air provides a diminished driving force for oxygen gas absorption. The accumulation and back pressure of the unabsorbed nitrogen trapped under the ice layer will make further aeration difficult. Vast amounts of air have been used to circulate the warmer bottom water in order to melt the ice cover. The power and quantity of air required makes this process uneconomical.

With these considerations in view Tsao (27) proposed the use of pure oxygen to oxygenate water under ice covers. This approach involves automatically bubbling pure oxygen when required from oxygen diffusors. The presence of the ice cover will virtually act as a lid over the unabsorbed amount of oxygen and thus allow surface absorption. This process will avoid the nitrogen back pressure and prove to be efficient by assuring that most of the oxygen gas supplied will eventually be absorbed by the water. Recent developments in water pollution control have verified that the cost of oxygen is no longer prohibitive. This is further evidenced by the increased industrial usage of pure oxygen gas for artificially raising dissolved oxygen concentrations.

A brief description of limnological conditions will be appropriate. Hutchinson (28) in his excellent treatise
describes and compares properties of important lakes and large water bodies throughout the world. It would be difficult to classify the various lakes in any region under special groups because of the immense diversity in the physical and thermal properties. General classification is made according to geographical latitude, altitude, depth of actual basin and thermal history which depends upon the geographical position. Most of the lakes that are of immediate concern to us are called "Dimictic". These are directly stratified in summer, inversely stratified in winter and are freely circulating in spring and autumn. These are characteristic of most of the cooler parts of the temperate zones and some high mountains in subtropical latitudes.

Most dimictic lakes freeze after the water has circulated for some time below 4°C. The water at the ice contact will be 0°C and a slight inverse thermal stratification will be set up immediately below the ice. For lakes of average depth this process is accentuated by solar radiation and heating from the mud, causing the bottom temperature to be raised slightly above 4°C. Since the temperature of maximum density decreases with increasing pressure, for deeper dimictic lakes (over 100 m) bottom temperatures slightly below 4°C have been observed (28).

Hutchinson (28) gives several examples of temperature profiles in various types of lakes during the winter months
Figure 19. Vertical distribution of temperature and oxygen in center of lake (solid line), and of oxygen at a more peripheral station (broken line), Hutchinson (28)
Most profiles are seen to be linear. Especially for moderately deep lakes (20 to 30 feet) a linear temperature profile would be a fair assumption. Linear temperature profiles were also observed by Fast (25) in his recent artificial aeration studies of Hemlock Lake in northern Michigan.

It is important to consider the existing knowledge of the vertical distribution of dissolved oxygen in lakes during winter stagnation. The oxygen profile is intimately related to the nature of the thermal profile. In dimictic lakes when a definite inverse thermal stratification is established in winter with a persistent ice cover, oxygen absorption from the surface and the consequent mixing of freshly oxygenated water into the depths is certainly restricted if not impossible.

There seems to be substantial evidence (28) of the significance of density currents on the distribution of oxygen in the lake. The two main factors are the speed of the density current and the reductive capacity of the mud over which it flows. A relatively slow current will reduce the oxygen content in deeper sections when passing over highly reductive mud. Hutchinson (28) cites Greenbank's work Green Lake in southern Michigan (1945) in which a profile-bound density current seemed to exist, raising the temperature and lowering the oxygen concentration. On the other hand a rapid current descending towards relatively deoxygenated water
is likely to raise the oxygen content near the mud-water interface. Hutchinson further exhibits the results of work done on Lakes Pereslavskoye, Glubokoye and Beloye which remain frozen from November till April. For the deeper lake Glubokoye the isopleth surface seems to dip slightly at the deepest point where the density current loses oxygen faster. Lake Beloye has one localized deeper section and yields convex isopleths of lower oxygen concentration (Figure 20). This is partly caused due to the production of gases such as methane and hydrogen. These gases are oxidized bacterially, reducing the oxygen concentration and producing such extreme patterns.

It is therefore reasonable to expect density currents to maintain more or less anaerobic conditions or very low dissolved oxygen concentrations in the deeper sections of the lake during winter months. Density currents are completely natural phenomena related to the heat effects from solar radiation through the ice and the heat stored in the mud during the summer. These natural effects cannot be entirely separated from the definite heat effects of the industrial effluents, specially the cooling water from nuclear power plants (e.g. Connecticut Yankee, Lake Michigan, Mahoney River, Duane Arnold Energy Center, Palo, Iowa). In an accurate simulation of the heat effects in water bodies, such contributions from neighboring industrial plants must be accounted for.

In most lakes it is entirely possible that a good deal of
Figure 20. Distribution of oxygen at the end of winter stagnation under ice

A, Lake Glubokoye, March 5, 1931
B, Lake Beloye, March 15, 1928

(methane bubbles collect in the ice formed over the deep depression of Lake Beloye, Hutchinson (28))
oxygen is lost under the ice by respiratory decomposition in the free water. To retain an ecological balance it is necessary to maintain at least an absolute minimum DO concentration. According to Hutchinson and other limnologists a value of 7.0 ppm DO is considered an acceptable value. As evidenced most lakes attain values far below this agreed minimum in winter and as a consequence jeopardize marine life and vegetation. To overcome this problem at an early stage it is essential to determine efficient oxygenating methods. In this regard the practical application of a study on single oxygen bubbles will prove to be helpful.

The importance of the action of gas bubbles has been well recognized and consequently interest in its study has existed for a long time. Because of the diverse applications of gas as a dispersed phase, (e.g. foam fractionation, air lift pump, air agitator, extraction by phase change, ore floatation, gas absorption with reaction etc.) vast amounts of pertinent literature exist. Comprehensive treatments on the action of gas bubbles is given by Levich (23) and Brodkey (24). In order to be able to predict results of work involving gas bubbles, it is necessary to understand the bubble motion, characteristics of mass transfer (also heat transfer) to and from bubbles and the effect of the presence of materials which are likely to change physical properties such as surface tension.
Many chemical engineering operations involve mass transfer between a fluid and systems of fluid and solid spheres. A good start towards the theory of mass transfer for such systems is to study the phenomenon with single bubbles. The results can be generalized for multisphere systems by considering the forced convection produced and the effect each sphere will have on the others. Most of the existing semi-empirical equations for mass transfer from a single isolated sphere usually well approximate the rate for a sphere in a multisphere system (29).

Bubble Velocity

The velocity of rise of gas bubbles or liquid drops in liquids has been studied extensively (30, 31, 32, 33, 34, 35, 36, 37, 38, 39). The most general observation is that the terminal velocity increases rapidly with bubble size, decreases to a minimum and then increases with bubble size. The bubble size for maximum velocity varies in the different investigations, but is of the order of 0.2 cms in equivalent spherical diameter (32).

Stokes' analysis (30) was among the first few to explain partially the motion of spheres in fluids. Stokes derived the equation
\[ u_t = \frac{2}{9} \frac{R^2 (\rho_s - \rho) g}{\mu} \]

as the terminal velocity of a solid sphere falling through water. This equation has limited application in that it is not appropriate to use this equation for \( \text{Re} > 1 \). The assumption involved in the analysis is that there is no slip at the surface of the solid sphere. For the case of gas bubbles through water there will in general be a finite velocity of the liquid immediately adjacent to the boundary envelope. This slip velocity induces internal circulation of the gas in the bubble, which has also been studied extensively (23, 33, 34, 35, 37). Hadamard (33) and Rybczynski (34) have studied this phenomenon theoretically and derived the expression for corrected terminal velocity

\[ u_t = \frac{2}{9} \frac{R^2 (\rho - \rho_l) g}{\mu_l} \left[ \frac{3 \mu_g + 3 \mu}{3 \mu_g + 2 \mu_l} \right] \]

The use of this equation yields higher calculated velocities. For most cases of air or oxygen bubbles in water, \( \text{Re} \) is much larger than one, which makes the use of Stokes' Equation inappropriate. One of the important conclusions arrived at was that the drag coefficient for fluid-fluid systems is not a unique function of the Reynolds number. The slip at the interface reduces the induced drag, which in turn increases the velocity. Also, the internal circulation of gas induces a shift in the point of separation, which causes a reduction
in the induced drag and a consequent increase in velocity.

The narrow applicability of Stokes' theory to the motion of bubbles made Levich's expression (23) for terminal velocity of medium-sized bubbles very useful. Through boundary layer theory and by considering the region of separation, Levich derived the expression

\[ u_t = \frac{1}{9} \frac{R^2 (\rho_l - \rho_g) g}{\mu_l} \]  

which is one-half of Stokes' velocity.

It has been shown that surface active agents present in the liquid are responsible for converting the fluid behavior of gas bubbles into rigid sphere behavior (23, 24, 35, 36, 37, 38). The deviation from fluid behavior was attributed to the distribution of surfactants on the interface and the significant parameter was reported to be the reduction in surface tension (\(\Delta \sigma\)). In his work with carbon tetrachloride drops in unsaturated glycerine, Griffith (37) has demonstrated that for high concentration of surface active material, the distribution at the interface will be sufficient to make the interface behave as a rigid sphere. In such cases "slip" of the fluid at the interface will reduce and may even be nonexistent, satisfying Stokes' assumption. As a result the velocity of rise will be reduced considerably as compared to the fluid behavior of bubbles.

Levich and his co-workers (23) were among the first to
suggest the most likely mechanism of the effect of surfactants. In his book, Levich has developed the theory in a systematic manner. In essence he has examined the change in the hydrodynamic regime due to the presence of surface-active substances. The nature of the effect is determined by the slower of the two processes (1) rate of adsorption or desorption of the surface-active molecules, (2) rate of transfer of molecules of surface-active material from the bulk of the liquid to the surface of the bubble.

An attempt is made to determine quantitatively the deviation in surface density ($\Gamma'$) of surface-active molecules from the equilibrium amount ($\Gamma_0$) that ought to exist at the interface for a given bulk concentration of surface-active substance.

Hence,

$$\Gamma = \Gamma_0 + \Gamma'$$  \hspace{1cm} (58)

This is expressed in terms (usually $\Gamma'\ll\Gamma_0$) of the variation in capillary pressure (normal force acting per/cm$^2$ of surface area)

$$p_n = \frac{2\sigma(\Gamma)}{R}$$  \hspace{1cm} (59)

and the tangential force per unit surface area,

$$p_t = \text{grad} \sigma = \frac{3\sigma}{\partial \Gamma} \text{grad} \Gamma$$  \hspace{1cm} (60)
Using either the Gibb's theory or Langmuir's (isotherm) adsorption kinetics and fairly involved computations, Levich arrived at expression for $\gamma_1$, the retardation coefficient, due to surface-active material. He arrived with expressions for velocity which corroborate the Hadamard-Rybczynski

\[ (\gamma_1<<(\mu_g+\mu_\ell)) \] and Stokes' equations \((\gamma_1>>(\mu_g+\mu_\ell))\)

\[
\begin{align*}
    u_t &= \frac{2}{9} \frac{R^2 (\rho_\ell - \rho_g) g}{\mu_\ell} \frac{3\mu_g + 3\mu_\ell + \gamma_1}{3\mu_g + 2\mu_\ell + \gamma_1}
\end{align*}
\]

(61)

Physically, as the bubble travels upwards the surface-active molecules are adsorbed at the interface. During the travel the molecules are dragged to the rear surface of the bubble by the adjacent liquid. The resulting composition gradient of the surfactant yields a surface tension gradient. A tangential force is created directed from points of lesser to points of greater surface tension. This tangential force opposes the viscous stress at the surface due to the liquid flow past the interface. The equation describing this hindering action is a force balance at the interface. Referring to Figure 21,

\[
\frac{1}{r} \frac{d\sigma}{d\theta} = \tau_{r\theta_2} + \tau_{r\theta_1}
\]

(62)

where $\tau_{r\theta_1}$ is the shear stress in the gas phase acting in $\theta$ direction on a surface perpendicular to $r$ and $\tau_{r\theta_2}$ is the shear stress in the continuous (liquid) phase in $\theta$ direction on a surface perpendicular to $r$. When the external viscous
Figure 21. Diagram of surface flow on a sphere partially hindered by interfacial tension gradient
drag and the interfacial tension gradient are of the same order, surface flow and internal circulation of gas in the bubble can be retarded or stopped altogether. This can occur at sufficiently high surface-active material concentration, at which point the bubble behaves as a rigid sphere.

Levich also documents Boussinesq's hypothesis that a thin layer of higher viscosity exists near a gas-liquid interface. This approach becomes specially pertinent for insoluble films and slow adsorption kinetics. But Boussinesq's theory of the existence of a high surface viscosity has been losing support with increasing evidence that the change in surface tension is the more important parameter (40). Much like the property of elasticity of surface layers, the high surface viscosity concept may only be regarded as a measure of the ability of the interface to resist a permanent deformation. But it does not explain the retardation observed in the velocity of rise of a bubble with increased surface-active contamination.

It has been shown that surfactants produce caps of im-mobile interface on moving drops and bubbles. Savic (39) has derived the streamline functions for flow at small Reynolds number around such drops of zero viscosity. Griffith (37) has extended Savic's work to obtain expressions for terminal velocity in relation to cap size and to the amount and type of surfactant.
Bond and Newton (41) have suggested from dimensional approach a criterion for the departure from solid sphere behavior. The dimensionless number

\[
\frac{(\rho_g - \rho_l)D^2g}{\sigma} = 0.4
\]

(63)

The exact value of this number will depend upon the ratio \(\mu_g/\mu_l\). The smaller this ratio the smaller will be the value for the dimensionless Bond number. But it has since been shown by Garner and Hammerton (35) that this criterion should be associated with the onset of distortion and swerving motion of bubbles rather than the effect of "slip" and internal circulation.

Garner and Hammerton (35) have studied the velocity of rise and circulation inside gas bubbles with respect to temperature, rate of formation, wall effect and contamination by surface-active agents. They proposed that the cessation of internal circulation will increase form drag as well as skin friction. With regard to wall effect they recommend the use of the Ladenberg-Faxen correction

\[
u_{\text{infinite liquid}} = \frac{\nu_{\text{cylindrical}} (1 + 2.1 \frac{D}{D_c})}{\text{column}}
\]

(64)

where, \(D\) is the diameter of the bubble and \(D_c\) is the column diameter.

The effect of temperature on the rise velocity is inclu-
ded in a comprehensive work in the field of velocity of air bubbles by Haberman and Morton (38). They contend that the velocity of the bubble is reduced in a way similar to the action of surface active agents, for bubble diameters from 0.5 mm to 4.0 mm.

Various other empirical relations exist for the rise velocity of bubbles. In each case the relation between the drag coefficient and the Reynolds number was re-evaluated. This was then used to determine the total drag and through a force balance an expression for velocity of rise was obtained.

Mass Transfer from Bubbles

A rigorous mathematical treatment of the problem of mass transfer from a bubble rising in a column of liquid is not easily developed. Some noteworthy theories for more idealized conditions have been forwarded and have been shown to be valid within specific ranges of study.

The differential vector equation governing the behavior is

\[ \frac{\partial c}{\partial t} = \text{div}(\mathbf{J} \text{ grad } c - \mathbf{V} c) \]  \hspace{1cm} (65)

where \( \mathbf{V} \) represents the velocity of the external fluid relative to the bubble due to its own motion.

Various mathematical models of interfacial mass transfer
have been developed starting from Equation (65) by making simplifying assumptions. Foremost among these was the Whitman's Film Theory (42). This was modified by Higbie (43) in the Penetration Theory which asserted that mass transfer across a flowing interface can be represented by ordinary diffusion, provided the surface renewal times were all sufficiently small and of equal duration. Although the physical interpretation involved in the penetration theory was sound, Danckwerts (44) has modified Higbie's Theory to allow for a distribution of the surface renewal time. The chance of a liquid element being replaced is not correlated with the age of the element. Danckwerts and Kennedy (45) have shown that this modification leads essentially to the same results as the Higbie Theory. More detailed review of these and other models are given in Part I of the thesis and will not be repeated here.

The subject that deserves further elaboration is the particular case of turbulent flow of the liquid around the bubble. Due to the lack of a rigorous mathematical understanding of this case, an approach involving dimensional analysis has been usually adopted. Garner, Foord and Tayeban (46) have summarized some specific dimensional analysis correlations. All of these are of the form

\[
\frac{K^D}{(\frac{\nu}{\mu})} = a + b \left( \frac{Du}{\mu} \right)^{1/2} \left( \frac{\nu}{\mu} \right)^m
\]  

\[ (66) \]
where a, b and m are constants to be determined. The value of m lies between 1/2 and 1/3, according to Garner et al. (46). To obtain a complete correlation all the pertinent variables must be accounted for and included in the product of dimensionless numbers. A discussion of the important studies conducted in this regard follows.

The rate of solution of single bubbles in free rise has been studied extensively (40, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56) with a view towards predicting transfer coefficients for swarms of bubbles that are normally used in chemical engineering operations. Datta, Napier and Newitt (32) were among the first to appreciate the involved problem of studying the mass transfer between two moving entities, in their work with the dissolution of carbon dioxide in water. The dissolution of oxygen in water has been studied by Hammerton and Garner (50), Griffith (40, 52) and Deindoerfer and Humphrey (54).

It is well accepted now that the mass transfer from bubbles depends largely upon the state of the interface and its vicinity. The classical theories of mass transfer are partially valid in the moving boundary situation. A substantial effort has been made by Levich (23) to include the velocity profile and expressions for streamlines into the predictive expression for mass transfer. It is important to realize the difference between the concentration boundary layer and the velocity boundary layer, also that one can
affect the other. Mass transfer can retard the rise of bubbles. This is evidenced by Leonard (47, 48, 49), Datta et al. (32) and Handlos and Baron (56). Leonard's expression for mass transfer is

\[ K_L^0 = 0.00153 (u-7) \]  \hspace{1cm} (67)

where \( u \) is the velocity of rise. Leonard (48) also found that the mass transfer coefficient is time-dependent such that its value decreases along the length of the column from bottom to top.

Internal circulation of gas in bubbles, distortion and interface turbulence are important factors that affect mass transfer. Internal circulation of gas enables the fluid at the interface to be continually replenished and this leads to a higher value of mass transfer. For a mobile interface \( K_L^0 \propto (\mathcal{A})^{1/2} \). The mobility of the interface is stopped by the action of surface-active matter, in which case \( K_L^0 \propto (\mathcal{A})^{2/3} \). These results are documented by Griffith (52) in his work with isobutyl acetate drops and ethyl-acetate drops using several types of surfactants. This is particularly true if Sc is high such that the concentration boundary layer is thinner than the velocity boundary layer. In such cases, for the section important for mass transfer, velocity gradient can be considered linear.

Some of the more important semi-empirical expressions for
mass transfer are due to Fröessling (52)

\[ Sh = 2 + 0.55 \frac{\text{Re}^{1/2}}{\text{Sc}^{1/3}} \]  

(68)

due to Garner and Suckling (52)

\[ Sh = 2 + 0.95 \frac{\text{Re}^{1/2}}{\text{Sc}^{1/3}} \]  

(69)

due to Griffith (52)

\[ Sh = 2 + 0.57 \frac{\text{Re}^{1/2}}{\text{Sc}^{0.35}} \]  

(70)

due to Higbie (43)

\[ Sh = 1.13 \frac{\text{Re}^{1/2}}{\text{Sc}^{1/2}} \]  

(71)

due to Calderbank and Moo-Young (57)

for bubbles, \( D > 2.5 \text{ mm} \),

\[ K^o_L (\text{Sc})^{1/2} = 0.42 \frac{\text{Ra}^{1/3}}{\text{Re}} \]  

(72)

for bubbles, \( D < 2.5 \text{ mm} \),

\[ Sh = 2 + 0.31 \frac{\text{Ra}^{1/3}}{\text{Re}} \]  

(73)

Friedlander (58) showed by theoretical consideration of
the boundary layer adjacent to rigid bodies for low Re,

\[ K^o_L \propto \left( \frac{\text{Re}}{\text{Sc}} \right)^{2/3} \].

In general, the mass transfer rate across a
rigid sphere with an immobile interface will be less than that
across a mobile interface. This is not due to the lack of
"slip" at the interface. It is primarily due to the stoppage
of internal circulation of gas.

If the mobility of the interface lies between the rigid
and the completely mobile cases, one would expect the exponent,
to which \( \Phi \) is raised, to lie between 2/3 and 1/2 respectively.
This intermediate situation of slowly moving surface has been
studied by Griffith (40, 52) and theoretically treated by Savic
(39). Using Savic's work, Griffith corrected the forced
convection term in the expression for rigid spheres, allowing for slow interfacial flow. His final expression was

$$\text{Sh} = 2 + (0.57 \, (\text{Re})^{1/2}(\text{Sc})^{0.35})(1 + \frac{22}{13} \, k_v^{1/2}(\xi/\xi_0)^{-1}$$

(74)

where, $k_v$ is the ratio of actual interfacial speed to the potential flow interfacial speed, and $(\xi/\xi_0)$ is the ratio of concentration boundary layer thickness with interfacial flow to that without interfacial flow. The correction factor was taken to be the ratio of mass transfer rates from plane plates with and without mobile surface. Griffith (52) also provided a working expression for the case of unhindered surface flow.

$$\text{Sh} = 2 + 1.13 \, (\text{Pe})^{1/2}(k_v)^{1/2}$$

(75)

The surface could be rapidly moving for cases where the inertial forces are much more than viscous forces, such as in potential flow and where $\frac{\mu_x}{\mu_g} = \infty$. The correction in this case is due to replacing the potential flow interfacial velocity with the actual interfacial velocity. This case would be applicable when the contamination is dilute enough so that the gaseous sphere is not completely covered with surface-active material. There seems to be no handy equation in literature that gives directly a value for the mass transfer coefficient for a given concentration of any particular type of surfactant. Although the two limiting cases of fluid and
rigid sphere behavior are well documented. The Equation (74) approximates an intermediate case, but does not necessarily encompass the complete range of slowly moving surfaces. In this regard it would be advantageous to obtain a predictive expression, though experimentally it may not be simple to work in the range of very dilute surfactant concentrations.

Other factors of importance to mass transfer from bubbles and drops are distortion and local turbulence. Distortion will have a considerable influence on mass transfer as has been pointed out by Calderbank and Lochiel (55) and Calderbank, Johnson and Loudon (59). They included an additional factor called "eccentricity" in their expressions for mass transfer from oblate and prolate spheroids. They also determined that for spherical cap bubbles, $K_L^c \propto \varnothing^{1/2}$. With regard to local turbulence, the penetration theory of mass transfer seems to be applicable. In keeping with the fundamental concept, concentration packets penetrate the interface film and mass transfer occurs by means of an unsteady-state molecular diffusion mechanism. This leads to the prediction $K_L^c \propto \varnothing^{1/2}$. An estimate must be obtained of the Higbie contact time or the distribution of the surface renewal periods under the specific local turbulent conditions.

On the other hand for mass transfer from a sphere suspended in a stagnant fluid, $K_L^c \propto \varnothing$. In the limiting case this would mean an infinite film of extremely small film thickness,
to exhibit the fairly large values of $K_L^0$ that have been observed. The independence from the time element indicates that asymptotic (solutions) values for $K_L^0$ may be possible, corresponding to the steady-state solution of the Whitman film theory. But this direct dependence on diffusivity is not seen for cases where mutual motion exists, either slow or boundary-layer flow.

The system of mass transfer from single bubbles is therefore quite complex. Coppock and Meikeljohn (53) have tied down the inter-related results dealing with single bubbles over a wide range of system parameters in a comprehensive manner. Determining expressions for accurate evaluations of mass-transfer and velocity of rise for a wide range of all the variables involved is still necessary as many of the published results are contradictory.

**Effect of surface-active material**

The studies of surfaces, interfaces between phases and surface-activity of various materials have been subjects of intense interest and vast amounts of publication exist in this area. Excellent comprehensive treatments are obtained in texts by Harkins (60), Adam (61), Gaines (62), and Adamson (63). It is not the purpose here to give a detailed analysis of the physical chemistry of surfaces, but a brief overview of interfaces in general and the effect of surface-activity
The importance of surfaces stem from the tremendously high surface energy contained by interfaces, which forms the foundation of colloidal chemistry. This excess surface energy manifests itself in the form of surface tension at the interface and is a measure of the energy expended to create the extra surface area. As in all other natural systems, in its tendency to acquire the lowest potential, nature attempts to contract the surface to the smallest possible area for the volume of fluid, provided other forces do not act to change the form. Thereby a minimum characteristic free energy is contained by the newly formed surface.

As early as 1912, Hardy suggested the useful idea of systematic molecular orientation at the interface, creating a polarization of the surface and "the surface film must therefore have a characteristic molecular architecture." Subsequent research (60) has amply substantiated Hardy's conjecture. Whether it be a molecular orientation at the surface of a pure liquid or the adsorption of a foreign molecule at the surface of a solution, the alignment of the molecule is always such that requires the least expenditure of work. This leads to the general law (60), "at any surface or interface the change which occurs is such as to make the transition to the adjacent phase less abrupt." In general, the nonpolar, "greasy", less active portion of the molecule will orient
itself out towards the vapor phase and the polar or more active group of the molecule will turn toward the interior of the liquid.

The interest in the study of the effects of surface-active material on mass transfer from rising bubbles or falling drops has been fairly recent. Levich (23) with Frumkin investigated extensively the theoretical implications of this effect and with Gorodetskaya's experimental verification the theory seems to be well established. Several other investigations have been made since (40, 47, 50, 55) to explain the effects of several surfactants such as various alcohols, oleic acids, aerosol, teepol, carbon tetrachloride, various detergents etc.

The general effects and the mechanism seem to be well agreed upon in literature. The surface-active agents absorb on the interface between the fluids, forcing the globule to behave as a rigid sphere. As a result the form drag and the skin friction are increased, lowering the velocity of the bubble. In the case of mass transfer also the change in the nature of the interface decreases the value of the coefficient and therefore the mass transfer rate.

As has been stated previously, the study of mass transfer from a rising bubble essentially becomes a problem of close scrutiny of the interface between the gas and the continuous fluid. The local hydrodynamics and the physical state of the
interface will govern the entire phenomenon. Levich has put forth the most likely mechanism to explain his disagreement with Boussinesq's theory of an intermediate high surface viscosity due to the agglomeration of surface-active particles. The molecules of surfactant are adsorbed on the interface according to the Langmuir adsorption isotherm. The equilibrium adsorption is given by

\[ \Gamma_0 = \frac{k_c^0}{1 + \frac{k_c^0}{\Gamma_\infty}} \]  

(76)

according to Levich's nomenclature (23). During the passage of the bubble, the motion of the adjacent liquid will tend to carry the adsorbed surfactant to the rear or downstream end of the bubble. At the front stagnation point the concentration of the adsorbed molecules will be lower than the equilibrium value, whereas the downstream end will exceed the equilibrium value. The physical property affected by the surfactants is the surface tension at the interface. The relative decrease of surface tension (\(\Delta\sigma\)) and the rate of decrease (\(\frac{d\sigma}{dc}\)) is a property of the particular surfactant. The retarding coefficient \(\gamma\) can be expressed in terms of \(\frac{d\sigma}{dc}\). Due to the uneven distribution of the surfactant a surface tension gradient is created at the interface. The effect is to counteract the viscous shear of the outer fluid and as a result it retards
the surface motion. If the surface tension gradient is high enough it can completely stop all internal circulation and expose a rigid surface to the outer fluid. The motion then becomes that of a solid sphere, the drag increases and the velocity is lowered. While the surface motion still exists, the normal component of the surface velocity is zero, but the tangential component gradually diminishes as the surfactant concentration increases at the interface. Although the bubble assumes a rigid sphere behavior, unless Re ≤ 1 Stokes' law is not applicable and Levich's expression for medium-sized bubbles yields more realistic values for velocity.

The effect of surface-active material on mass flux from the bubble has been discussed previously. Noteworthy investigations have been those of Leonard (48), Hammerton and Garner (50), Griffith (40) and Coppock and Meikeljohn (53). It is generally agreed upon that the diffusional flux will depend upon the concentration boundary layer adjacent to the bubble. The thinnest diffusion layer will be at the upstream end of the bubble (θ=0) and the mass transfer will be maximum at that point. The rate of transfer will decrease as θ increases round the bubble being minimum at θ=π. At the downstream end (θ=π) the diffusion layer is infinite or at least comparable to the size of the bubble. The rapid adsorption of surfactants help achieve this state even quicker. When the concentration of the surfactant is sufficiently high, the concentration
boundary layer is uniformly infinite throughout and mass transfer occurs out of a rigid sphere.

In the initial stages of adsorption and an unsteady state of diffusion, it is entirely possible that the surfactant molecules can cause local turbulence at the interface (23). This in turn will aid the mass transfer of gas from the bubble. The factors of crucial importance seem to be the relative magnitudes of the time required for adsorption of the surfactant molecule and the surface renewal time. The extremely small amounts of surfactant required to produce a rigid surface makes it unlikely that the time required for adsorption will be appreciably greater than the surface renewal time.
EXPERIMENTAL EQUIPMENT
AND PROCEDURE

The apparatus used in the present investigation was designed for two specific purposes. Accurately measure the velocity of rise of single oxygen bubbles in water and estimate average mass transfer rates of oxygen from the gas phase into the liquid. The apparatus also allows a convenient study of the effect of pollutants and surface active agents on the velocity and mass transfer of oxygen.

Basically, the design approach is the same as used by several investigators, notably Leonard and Houghton (47), Hammerton and Garner (50), Redfield and Houghton (51), Coppock and Meikeljohn (53) and Calderbank et al. (59) among others. The fundamental idea was to obtain instantaneous values of the velocity of the bubble and a convenient measurable parameter for mass transfer calculations. Velocity measurements are best obtained by timing the passage of the bubble accurately for known distances. Mass transfer measurements are obtained by monitoring bubble volume or system pressure for a closed system. Literature review indicates that various modifications of the available options have been employed previously. In order to use the available resources the apparatus devised was simple and effective without sacrificing accuracy. Construction details and operating procedures for the entire apparatus follows.
Single Bubble Absorption Column

A schematic diagram (Figure 22) and photograph (Figure 23) illustrate the physical appearance of the process. The main absorption section consisted of a cylindrical plexiglass column 3 inches internal diameter, 6 feet high with a 1/8 inch wall thickness. The two ends of the column were fitted with plexiglass flanges 5-9/16 inches diameter, provided with O-ring seals. The bottom flange was 15/16 inch thick and the top flange 3/4 inch thick. The flanges facilitate easy sealed connection with two useful plexiglass sections. At the bottom a rectangular plexiglass section (3-3/4 inch x 3-1/4 inch x 6-1/8 inches) was attached to the flange and had a plexiglass base plate 1/2 inch thick. At the top a cylindrical plexiglass section (3 inches internal diameter, 4 inches high, 1/8 inch wall thickness) was attached and had a top covering plate 1/4 inch thick. The lower rectangular section housed the sealed Swagelok connection for single bubble release mechanism. One end of a stainless steel rod ended in an inverted cup which held the bubble momentarily before release. The other end of the rod was fitted to a knurled knob, outside the section, to rotate the cup externally. The desired stainless steel nozzle was located centrally in the column through a port in the base plate. Nozzles were interchanged conveniently
Figure 22. Schematic diagram of experimental equipment

A  Elevated 5-gallon pyrex jar
B  Eastern centrifugal pump
C  Series of filters
D  Pyrex 5-gallon storage jar
E  Cole-Palmer centrifugal pump
F  Whitney micrometer valve
G  Inverted stainless steel cup
H  Plexiglas absorption column
I  CdS photoconductor bank
J  Plano-convex condenser lens
K  Light source
L  Humidifier
M  Pure oxygen cylinder
N  Heath electronic timer circuit
P  Whitey 3-way valve
Q  Beckman dissolved oxygen analyzer
Figure 23. Photograph of experimental apparatus, featuring the absorption column and the opto-electronic device
and connected to a stainless steel Whitey micrometer valve for the passage of oxygen gas, by a series of farrelled pipe fittings. The base plate also had provisions for a three-way Whitey valve connection for filling and emptying the column. Details of this section are illustrated in photograph (Figure 24). The purpose of the top cylindrical section was essentially to maintain an inert nitrogen atmosphere during mass transfer runs to avoid surface absorption of oxygen and also helped in flushing away the unabsorbed amount of oxygen. For the velocity runs an oxygen atmosphere was maintained at the surface in order to avoid loss of dissolved oxygen through surface desorption. The inlet port of the top section was connected to the appropriate gas cylinder by tygon tubing. The outlet port was open to the atmosphere, ensuring atmospheric pressure at the surface.

The column was fitted with viewing windows at several locations for recording bubble volume and shape on motion pictures. Details about motion pictures will follow in a later section. The windows were made of plexiglass flat discs, 2-1/4 inches diameter and 1/8 inch thick. These discs were cemented to machined sections to fit the column side.

The column was erected so that the bottom flange connection rested on an aluminum table. The table top was 16
Figure 24. Inverted cup device for releasing single bubbles
inches above the laboratory bench. This allowed the lower rectangular section to be located under the table but well above the lab bench (Figure 24). The arrangement made it easy to reach the micrometer valve, knurled knob attachment and the three-way valve. It was extremely important to make sure the column was vertical. The top flange connection was used to brace the column to the vertical supports of the bench framework. With the aid of a plumb-bob and level absolute verticality was ensured.

Principles of optics and electronics were used to time the passage of single bubbles between known distances along the column. Effectively, an intense collimated beam of light was produced by condenser lenses and a narrow slit board. The light beam passed horizontally through the column and focused directly on a photo-electronic detector on the far side. The light transmission characteristics of the liquid-filled column changed momentarily as the bubble passed through the light beam. This change was reflected in the resistance of the cadmium sulphide (CdS) photoconductive cell. The transient in the D.C. output triggered an electronic clock. The column was divided into six equal vertical divisions using seven photoconductors. The electronic clock times the bubble accurately through the six spans. The electronic circuit was designed to store these readings in memory, which were easily retrieved after the run was
completed. Figure 25 illustrates the physical appearance of the opto-electronics. Some of the details of construction and principles of operation of this part of the apparatus follows.

The light source consisted of eight equally spaced 12 volt high-intensity light bulbs, arranged in a circuit to yield maximum brightness. Groups of two light bulbs were in series. Four such groups were hooked up in parallel. The circuit was individually powered by a well regulated transistorized (Elasto) 38 volts D.C. power supply. A 1 ohm resistor in series with the power supply reduced the voltage to the required value of 24 volts. The choice of power supply was an important consideration. It needed to be well rectified and regulated for the following reasons. Good rectification was necessary because the slow ripple alternated the light intensity enough to actuate the photoconductors without the passage of the bubble. Proper line voltage regulation was found necessary in order to smooth out periodic line transients of sufficient magnitude which actuated the photoconductors automatically. The sensitivity of the system was rather acute which made experimentation cumbersome at times, but aided the general accuracy and reproducibility.

The light bulbs were encased in a rectangular aluminum channel (3-1/2 inches x 4 inches), 6 feet 4 inches high.
Extraneous light was eliminated and the room darkened. Light beam from the source passed through circular ports on the face of the channel towards the column. Provisions were made for a natural draught of air through the channel in case of excessive heat. The channel housing was erected on an aluminum table at a predetermined distance from the plexiglass column. Parabolic reflectors behind the light source helped in intensifying the light beam. The lowest light bulb was located under the table and merely illuminated the bubble release mechanism.

Condensing lenses concentrate light into a projected beam. Use of this fact was made by placing a plano-convex condenser lens at a distance equal to the focal length of the condenser from the light source. Lenses used were 77 mm. diameter and 113 mm. focal length. Seven lenses were mounted in bakelite casings which were clamped to vertical metal rods at appropriate heights directly in line with the seven light sources, with the convex side towards the column. In connection with the sensitivity of the setup it should be mentioned that the vertical metal rods must be firmly braced. Even the slightest draught due to room ventilation was enough to sway the lenses, which tripped the photoconductors and triggered the circuit.

In order that the smallest bubble may actuate the photoconductor and also for purposes of accuracy, the total...
brightness of light was reduced without reducing intensity. This was achieved by allowing the beam to pass through a narrow slit so that a narrow collimated intense beam of light passed through the liquid-filled column. The adjustable slits were made of bakelite plastic strips attached to an oversize wooden board with spring-screws. Seven such slits were arranged on the vertical board, each slit in a horizontal plane with a light source and a condenser lens. The board was painted black to absorb the light that was not transmitted. The slit-board was of the same height as the column and was erected on the same aluminum table. A shallow channel was cut out along the length of the board. This allowed the slits to be immediately adjacent to the column wall, thereby reducing the loss of intensity due to diffusion of light between the board and the column.

The cylindrical wall of the plexiglass column acts virtually as a cylindrical lens. Effectively, the wall refracts the edges of the incoming light beam inwards giving it a triangular appearance (looking from the top) with the apex lying outside the column on the far side (Figure 25). This effect enhances the intensity of the beam travelling through the liquid but narrows the horizontal section the bubble must pass through to successfully trip the circuit. A better estimate of the true vertical velocity of the bubble was obtained. Bubbles that gyrated or veered too far off
Figure 25. Schematic diagram of opto-electronic arrangement
course did not trigger the photoconductor. Data for such bubbles were discarded.

The CdS photoconductor was located in a horizontal plane with the light source, condenser lens and slit. It was positioned such that the apex of the triangular beam transmitted through the liquid-filled column illuminated the photoconductor in a narrow vertical section. The intensity of illumination was adjusted so that even the smallest bubble caused a sufficient change to trigger the circuit. The optimum intensity best suited for these experiments was arrived at through studies made on a scaled down mockup of the system. The photoconductors were mounted on bakelite plastic pieces, which were screwed to a narrow blackened 6 feet long channel-iron at appropriate heights. The seven photoconductors were placed exactly 11-1/2 inches apart, thereby dividing the 6 feet column height into six equal experimental sections, each 11-1/2 inches long. Enough space was left at the top and the bottom to eliminate end-effects.

The transient change in the light transmission characteristics of the liquid-filled column due to the bubble, was reflected in the momentary change in the resistance of the photoconductor. The transient output from the photoconductor was directed to a novel electronic logic design which accomplished a number of functions in split-second timing. The electronic timer was composed of appropriate components
obtained from the Heath-Schlumberger Scientific Instruments Co. Parts description and functions are described in the Heath Analog Digital Designer (64). Useful suggestions by Mahmstadt and Enke (65) were incorporated in designing the logic circuit. Schematic diagram of the detailed logic design and the patchwork is given in Appendix A. It will suffice here to describe the basic functions briefly.

The DC component of the photoconductor output was filtered by the input capacitor and after amplification was conducted to a comparator. The level of the comparator was adjusted externally to increase the sensitivity for runs with very small bubbles. The transient voltage then actuated a series of electronic logic units to perform the following functions with the aid of several monostable multivibrators. The sequence of functions are GATE OFF, MEMORY UPDATE, DELAY 1, RESET, DELAY 2 and GATE ON. Each monostable multivibrator was actuated when the output of the previous monostable had a transition from 1 to 0. A 1 MHz crystal oscillator provided the time base which actually kept account of the time elapsed. The gate sequence allowed the accurate counting of these oscillations between the GATE ON and GATE OFF signals. The MEMORY UPDATE monostable permitted the count to be displayed momentarily and this reading was stored in 64-bit (fully decoded read/write TTL) memory integrated circuits. The DELAY 1 monostable was
introduced in order to have enough time (10 µsecs.) to store the reading before the RESET pulse arrived. A 1 µsec pulse from the RESET monostable reset the gate count on the Decade Counting Unit to zero. The pulse from the RESET monostable was also used to trigger the DELAY 2 monostable. The 10 µsecs. pulse from the DELAY 2 monostable was employed to stretch the entire sequencing period and also to trigger the GATE ON monostable. The Decade Counting Unit began counting the oscillations of the crystal time base on command from the GATE ON pulse. It is pertinent to point out that although the entire sequence of functions occurred at each photoconductor station, the time accumulated from the GATE ON signal at one station till the GATE OFF signal at the next station was the reading that was displayed and recorded in memory (Fairchild TTL Memory 93403 IC). The time readings were later retrieved by conveniently thumbing through push button PBl on the Binary Information Module. An important feature in the design was the inclusion of a binary counter from 0 to 7. The counter indicated which particular span of the column was being traversed at any particular instant and also prompted a particular location in the memory IC at which to store the next reading. Status light 1 on the Decimal Readout Module was lit when the gate was open and counting. Status light 4 blinked when the time elapsed was more than 2 seconds, indicating
the bubble had failed to trip one or more photoconductors. The time was thus accurately recorded correct to four significant figures in seconds. The sequence of functions took 22 μsecs. from start to finish, which is less than the least count of the timer. For a schematic diagram of the logic circuit and the actual card patchwork refer to Appendix A.

The output from the operational amplifier card and the comparator card were monitored on a dual trace storage Tektronix 549 oscilloscope. The travel of the bubble up the column and the successful sequencing of events at all seven photoconductor stations were followed on the oscilloscope display. Channel 1 stored the instant pulse generated by the comparator which began the sequencing function at each station. The output from the operational amplifier indicated the relative size of the transient signal produced by the bubble. This account was stored on channel 2 of the oscilloscope trace. Figure 26 illustrates two typical storage displays of the dual traces for two separate runs. The displays further corroborated the triggering of the circuit, ensuring the time readings recorded in memory were newly generated values and not redundant values recorded previously.

A brief mention could be made here about the output from the operational amplifier. The signal may be of significance in determining the size and shape of the bubble
Figure 26. Typical storage display on oscilloscope of photocell signals
at that particular point, which can be used for mass transfer or hydrodynamic calculations. By strategically employing the delayed sweeping facility on the Tektronix 549 oscilloscope a much more detailed profile of the transient signal was obtained. Various bubble sizes at various sweeping speeds produced interesting results. An example of a profile is given in Appendix B. But after elaborate testing, this approach for size determination was abandoned because of lack of reproducibility. Erratic features of bubble behavior such as rocking, spiralling and pulsations were quite unpredictable, especially in clear water. These variations in turn imparted signals of various sizes for essentially the same bubble volume. A description of this difficulty and suggestions for future improvement are given in Appendix B.

Bubble sizes and shapes were recorded on motion pictures using Eastman Kodak Ciné-Special II 16 mm movie cameras fitted with a 63 mm lens. The films used were Eastman Kodak Plus X Negative, ASA 64. The settings were standardized after repeated trials in order to obtain sharp features of the bubble. The pictures were taken with the camera speed at 64 frames/second, 1/4 open shutter, f stop 5.6 and with the film plane at 24-1/2 inches from the center of the column. Back lighting reflected from a white board placed behind the column yielded adequate illumination. The test sections were viewed through the flat plexiglass windows to minimize
distortion. For velocity runs, the original bubble size was recorded using only the lower window. For mass transfer runs, the original and final bubble sizes were recorded through windows at the bottom and top of the column, 69 inches apart, using two similar movie cameras. Initial plans of recording bubble volume at each photoconductor station had to be abandoned because of the limited number of cameras available.

In order to interpret the bubble dimensions in measurable units, motion pictures were taken of a transparent plastic scale located in the liquid at the center of the column, for the same camera and light settings. Measurements from the bubble frames were related to the standard scale measurements by means of a scale factor described below.

The EAI Variplotter (65) offers a very accurate and convenient method of determining bubble shapes and sizes. A brief description of the operating procedure follows. The particular frame to be studied was projected on the screen of the plotter and focused to get a sharp image of the bubble. An arm carrying a fine cross-wire was moved by two potentiometers (for the x- and y-axes respectively) to the desired point on the edge of the bubble. A remote control switch sent a pulse to the automatic Dymec scanner which located the desired point precisely by scanning the millivolts proportional to the x- and y-axes respectively.
The origin of the coordinates was arbitrarily fixed in the plotter system. The millivolt readings were displayed on a Hewlett Packard Digital Voltmeter and with the aid of a Hewlett Packard Coupler unit was transmitted to a teletype. The readings were typed on paper and also punched out on paper tape.

The bubbles examined in the course of this study were oblate-spheroidal in shape, which was more consistent with increasing contamination. The essential measurements on the plotter were those of the major and minor axes of the ellipse that would generate the oblate spheroidal bubble. In a particular order, four points at each extremity of the bubble were located with the cross-wire piece and the millivolts measured and recorded on paper tape. For every treatment (a combination of nozzle and contamination) 15 to 25 frames were studied. Also for every treatment the scale-factor (cms/millivolt) was evaluated to eliminate possible errors from repositioning the camera and the projector.

The bubble data processing was facilitated by developing a Conversational Programming System (CPS PL/I) program to feed the raw data from paper tape through the teletype reader into the resident disk pack (named RJEPAK) in the computation center. A simple FORTRAN program was developed to determine and also evaluate statistically the relevant dimensions and eccentricity of the ellipse, for each treat-
ment. Volume and surface area of the oblate spheroid, equivalent spherical diameter and surface area were also evaluated and analyzed. The CPS and FORTRAN IV programs are listed and explained in Appendix C.

Water Purification and Flow Process Description

One of the important considerations during experimentation was to avoid inadvertent contamination of the water. Accordingly, extreme precautions were taken to insure the water used was double-distilled, well filtered, stored in and transported through scrupulously clean jars, pumps and pipes.

The double-distilled water was obtained from a Barnstead still and was contained in a clean elevated 5-gallon pyrex jar. A 1/5 H.P. Eastern centrifugal pump was used to pump the water through a series of filters in cascade. The filters used were a 20 µ raw water cartridge, a standard mixed bed ion exchange cartridge, followed by two ultrapure mixed bed cartridges and finally an oxygen removal cartridge. All the Barnstead brand filters were obtained from the Scientific Products Co. The purified water was stored in a stoppered, clean, graduated 5-gallon pyrex jar to desired volumes. Usually the pump was used to create the syphon between the elevated and storage jars. Subsequently the
water syphoned through the filters and greater cleaning action was achieved. The flow was regulated by means of a valve in the line placed immediately after the pump.

According to the specific treatment, predetermined amounts of contamination (Sodium oleate solution) were introduced into the storage jar and mixed thoroughly with known volumes of pure water to obtain the desired contamination concentration. The storage jar was fitted for connection to either an oxygen or nitrogen cylinder. To saturate the liquid with dissolved oxygen, pure oxygen gas was bubbled through the liquid (for the velocity runs). Nitrogen gas was bubbled through the liquid to strip the liquid of dissolved oxygen (for the mass transfer runs), before filling the column. The constant bubbling of gas through the liquid helped in the uniform mixing of the contamination. The liquid was pumped from the jar into the test column using a sealless centrifugal pump, through the 3-way valve located at the bottom. The body, impeller and shaft of the pump was made of 316 stainless steel (Cole-Palmer Model 7004-60). All 1/4 in. dia. pipes, Swagelok fittings and valves were of stainless steel. The flow process is illustrated in Figures 22 and 23.

Brief descriptions will be given of the accessory apparatus used to measure several properties of the system.
Dissolved oxygen concentration

Instantaneous DO values were obtained using the Beckman In Situ Submersible Oxygen sensor (39552) in conjunction with a Beckman Fieldlab Oxygen Analyzer (100800) with rechargeable Nickel-Cadmium batteries (66). The sensor consists of a platinum cathode and a silver anode which are electrochemically connected by a potassium chloride solution. A gas permeable membrane, which selectively allows the passage of oxygen, separates the electrolytic cell from the sample. As oxygen diffuses through the membrane, it is electrochemically reduced at the cathode by 0.55 volt supplied by the Fieldlab. An internal current flow is measured which is proportional to the partial pressure of the oxygen in the sample. Corrections due to hydrostatic pressure compensation and temperature of the sample are provided. Titration accuracy of ± 0.2 ppm was possible by calibrating the instrument using the Winkler titration method.

All dissolved oxygen measurements of samples taken from the column before and after each run were checked by using the Modified Azide-Winkler method with drop count titration. The procedure is explained in detail in the methods manual of the Hach Chemical Co. (67). It is a variation of the standard Winkler process and yields an accuracy of ± 0.2 ppm.
Surface tension determination

Surface tension measurements were made of samples taken directly from the column, using a bubble pressure technique developed by Sugden (69, 70). The principles and application of this method are clearly described by Svec and Peterson (71). The maximum gas pressure required to detach a bubble from two tubes of different radius was determined. The difference between these two pressures was directly related to the surface tension of the sample. The Sugden's tube apparatus was calibrated periodically. Reagent grade benzene was distilled and the middle distillate was used as a reference standard for calibration. Better results were obtained by using spectrophotometric grade benzene. Surface tension values for double distilled water agreed very well with published values (71). For more contaminated systems variations were observed in the readings. 95% ethanol was used as the manometer liquid.

Viscosity determination

Viscosities of samples were determined using the Stormer viscometer manufactured by Arthur H. Thomas Co. The detailed description and operating procedures are outlined in the viscometer manual (72). The instrument was carefully calibrated in terms of absolute units (centipoise) for a specific condition of temperature (24°C) and driving weight, using prepared samples of glycerol solution. Absolute viscosity
values for aqueous solutions of glycerol are tabulated in the manual (72). The calibration graph appears in Appendix D with the parameters of a linear model in the range of interest.

**pH measurement**

The Heath servodigital pH/volt meter (Model EU-302A) was used to determine the pH of arbitrary samples taken from the column. The working principle of the instrument is described in the manual (73). Regular Corning glass and calomel pH electrodes were used. The calomel electrode was kept filled with saturated potassium chloride solution. The DC voltage developed between the electrodes was amplified and served to drive a servo motor. The digital display was geared directly to this voltage, which was forced by the servo to equal the reference voltage. When not in use the electrodes were immersed in a buffer solution of pH 7.0.

**Conductivity measurement**

Conductivity of samples was measured using a Hach Conductivity meter (Model 2510). The operation of the device was quite simple and is described in the manual (74). The instrument accuracy was ± 2% of the full scale value.
Density measurement

Sample density was obtained using 25 ml. pyrex pycnometers. All weighings were done on a Mettler analytical balance.

Experimental Procedure

The experimental procedure was devised to study the effect of surface-active material on the velocity of rise of single oxygen bubbles and the average rate of mass transfer of oxygen from the bubble. The experimental design included making observations for bubbles from each of three nozzles at each of five contamination levels. Altogether there were fifteen treatments for velocity runs and also fifteen treatments for velocity with mass transfer runs.

Velocity runs

At the start of each velocity run the desired nozzle was fitted centrally at the bottom of the column. Fourteen liters of filtered water in the storage pyrex jar was saturated with dissolved oxygen by bubbling pure oxygen for approximately 1-1/2 hours at atmospheric pressure. The Beckman oxygen analyzer indicated a continuous rise in dissolved oxygen concentration till saturation was achieved. This was checked by conducting a Winkler test on a random water sample. For pure water runs the column was filled by
pumping the water through the stainless steel pipes and airtight fittings to a fixed level at the top flange. For runs in contaminated systems a predetermined concentration of sodium oleate solution was mixed thoroughly with the pure water to achieve the desired level of contamination in the storage jar. Usually oxygen was allowed to bubble through till Winkler tests of grab samples indicated complete saturation, in agreement with the oxygen analyzer. The contaminated water was then pumped into the column to the fixed level.

An oxygen atmosphere was created at the liquid surface by allowing pure oxygen gas to flow through the top plexiglass section under atmospheric pressure. This eliminated the possibility of rapid depletion of dissolved oxygen by desorption at the surface.

Oxygen gas from a third cylinder was bubbled through a humidifier column in order to saturate the oxygen with water vapor (Figure 22). The pure humidified oxygen gas was collected over the water surface in the humidifier at approximately 5 psig. Stainless steel pipe and fittings connected this gas space to the micrometer valve at the bottom of the column.

After waiting for a few minutes for the apparatus to stabilize and for all vibrations to cease, the room lights were switched off and the eight high-intensity light bulbs
were switched on. The laboratory was darkened by completely covering the windows and all extraneous light was eliminated. It usually took about a minute for the CdS photoconductor resistance to arrive at the equilibrium value. This is a property of the cadmium sulfide and cadmium selenide photoconductive cells known as the Light Memory Effect (75). At the equilibrium resistance the sensitivity of the photoconductor is highest without automatically tripping the electronic circuit. With the aid of channel 1 trace on the oscilloscope and the external comparator control \( R_1 \) on the Heath Digital Timing module, this equilibrium value was easily reached.

The system was ready to measure bubble velocity. The micrometer valve was operated carefully to allow exactly one oxygen bubble to form at the nozzle and collected momentarily under the inverted cup. The cup was turned slowly, using the knurled knob, to release the bubble. As the bubble travelled up through the liquid in the column it actuated the photoconductors at appropriate levels. In turn, the electronic circuit timed the bubble accurately and stored the readings in memory for each of the six spans. The bubble surfaced at the top of the column and the gas was swept away, with the surface gas flow, through the exit port.

The passage of the bubble was followed on the dual storage traces of the oscilloscope. As described previously
the sweep traces from channels 1 and 2 on the oscilloscope yielded a visual display of the success of a bubble run. If the bubble missed a photoconductor the traces did not record any transient signal nor the pulse from the comparator. Moreover, status light #4 blinked indicating the failure. Time observations were noted for bubble runs where all seven photoconductors were actuated. By thumbing through push-button PB1 on the Binary Information Module, the readings were displayed on the Decimal Readout Module and systematically noted.

Usually ten to fifteen bubbles were timed for each treatment at the start. As more confidence developed on the equipment and reproducibility improved (evidenced by statistical analysis) the number of repetitions were reduced to five bubbles per treatment.

Three samples of the liquid were randomly obtained while filling the column and stored in clean 300 ml ground-glass stoppered bottles. The samples were analyzed for viscosity, surface tension, density, conductivity and pH using equipments described previously. The temperature of the liquid was determined while withdrawing samples from the column before and after each run. The temperature seemed to remain steady at 23.8°C ± 0.3°C.

Original bubble size was determined by taking motion pictures of the bubble as it crossed the first photoconductor.
station. The camera and light settings have been described previously. Five repetitive observations were made. From the motion pictures, twenty-five arbitrary frames were selected to study and analyze statistically the bubble shape and size.

A Winkler dissolved oxygen test was made of the liquid at the end of the run. The oxygen concentration did not change noticeably during the course of a run and remained at saturation level within the limits of accuracy.

**Mass transfer runs**

For mass transfer runs the procedure was similar to the velocity runs with slight modifications. The water in the storage jar was stripped of dissolved oxygen by continuously bubbling nitrogen gas. It was not possible to obtain zero ppm DO within a reasonable time period. In about two hours it was possible to reduce the DO to 0.6 ppm under atmospheric pressure and 23.8°C. The DO level was checked continuously on the expanded scale (1 ppm entire scale) of the oxygen meter and also verified by conducting Winkler tests.

Pure water or sodium oleate contaminated liquid was obtained as before and the DO concentration verified. The liquid was then pumped to the fixed level in the column. For mass transfer runs an inert atmosphere of nitrogen gas was allowed to flow above the liquid surface at atmospheric
pressure. This ensured an uniform low DO concentration at the surface and in the bulk to create the necessary driving force for mass transfer from bubbles.

When the apparatus stabilized, a humidified pure oxygen bubble was collected in the inverted cup and released as before. For these runs, the change in bubble size as it travelled up in the column was recorded first. Two movie cameras (described previously) were used to record the size of the bubble at the first and last photoconductor positions 69 inches apart. Bubble volumes at intermediate locations were not obtained and therefore an overall average mass transfer measurement was made. This is a serious shortcoming in the experimental procedure. Mass transfer behavior for three bubbles were recorded for each treatment. Fifteen arbitrary frames from each, the "bottom" and "top" films were selected to study and analyze the shape, and reduction in volume of the bubble.

Velocity of rise of the oxygen bubble with simultaneous mass transfer was obtained by timing the bubble through the six spans as described previously. These velocity runs could not be conducted while change in bubble volume was being recorded on motion pictures, because the ciné lights were too bright for the photoconductors to operate.

Three samples, 300 ml. each, were obtained at random while draining the column. These samples were analyzed for
viscosity, surface tension, density, conductivity and pH. Temperature of the liquid sample was recorded immediately. A final Winkler test was made to determine if the DO concentration had altered appreciably at the end of the run.

After each run the column and the lines were rinsed thoroughly several times with double distilled water. Also the storage pyrex jar was cleaned by vigorously scrubbing with 0.5M chromic acid and rinsed with double distilled water, after each run.

Fifteen treatments (3 nozzles x 5 contamination levels) were studied in this category. The treatments progressed in order of increasing contamination. At each contamination level the nozzles were changed in an arbitrary manner.

The purified sodium oleate used in this work was obtained from the Fisher Scientific Co.
RESULTS AND DISCUSSION

Experiments performed in this investigation have been described in the previous chapter. The specific purpose of the study was to determine the effect of sodium oleate surfactant on the velocity of rise and on the rate of mass transfer from single oxygen bubbles of varying sizes. The results of these experiments are reported in this chapter. Included are the bubble velocity data with and without simultaneous mass transfer, data on the solution rate of bubbles and a mathematical model simulating the dissolution of oxygen bubbles in a frozen lake system. All experimental data are reported in tabular form in Appendix E.

Velocity of Rise Study

Perhaps the most important qualitative observation of the bubble motion was that the intrinsic hydrodynamics of the motion was extremely complex, especially in relatively uncontaminated systems. Spontaneous rocking, spiralling, pulsating and such irregular movements were observed from the motion pictures studied. It is conceivable that these irregularities actually aid the process of mass transfer of gas and will be discussed in a later section. In general, smaller bubbles travelled with less irregularities than did larger bubbles. Convenient measurements of the superficial
velocity of rise were made as a function of bubble size at various contamination levels. These values may be quite different from the instantaneous true vector velocity accounting for the sideways oscillatory motions.

Figures 21, 28 and 29 illustrate the variation in velocity with increasing span number (or vertical distance travelled) at various contamination levels, for the three nozzles studied respectively. These figures pertain to the system with no simultaneous mass transfer of oxygen. The corresponding results for the system with simultaneous mass transfer are shown in Figures 30, 31 and 32.

Statistical analysis of the repetitive velocity data (Appendix E) indicates that there is a significant difference in the time taken to traverse each span along the column height. Consequently, the velocity of the bubble should be treated as a continuous variable. Exact point values of this variable are difficult to obtain experimentally, but by progressively decreasing the distance between successive photocells a more accurate measure of the variation is possible. It is therefore erroneous to consider the bubble to be rising at a uniform terminal velocity (with no acceleration or retardation) especially in taller columns. Many previous investigators have considered a constant velocity throughout the rise.

Figures 27, 28 and 29 clearly indicate that the velocity
Figure 27. Effect of sodium oleate surfactant on span average velocity.

NO SIMULTANEOUS MASS TRANSFER
(NOZZLE ID = 0.023 in.)

SPAN AVERAGE VELOCITY, cm/sec

SPAN NUMBER

9.0 7.0 5.0 3.0 1.0
Figure 28. Effect of sodium oleate surfactant on span average velocity
Figure 29. Effect of sodium oleate surfactant on span average velocity
Figure 30. Effect of sodium oleate surfactant on span average velocity
Figure 31. Effect of sodium oleate surfactant on span average velocity
Figure 32. Effect of sodium oleate surfactant on span average velocity.
decreases with height. This effect is more pronounced in uncontaminated systems and for smaller bubble size. Without any mass transfer, the effect of reduction of hydrostatic pressure is to enlarge the bubble volume. For the range of bubble size studied (0.20 cm to 0.58 cm diameter) the velocity decreases with increasing diameter, in pure water. This is in agreement with Datta et al. (32) who have found the maximum velocity to exist at 0.12 cm diameter for air-water systems.

The effect of contamination with increasing amounts of sodium oleate is to reduce the span average velocity and the overall average velocity substantially. The initial sharp retardation is dampened out at higher concentrations of surfactant (Figures 27, 28, 29) and the bubble seems to travel at a velocity closer to uniform velocity. The significant effect of surfactant on bubble velocity (without mass transfer) is better perceived from Figures 33 and 34. On the addition of 500 ppm of the surfactant, the velocity decreased about 40% for bubble size 0.31 cm diameter and about 24% for bubble sizes 0.49 cm and 0.58 cm diameter. Figure 34 shows the effect of varying nozzle diameter for the various contaminated systems.

The more prominent effect on smaller bubbles seems to be more reasonable. The distribution of the surfactant at the interface is such as to cover the downstream part of the
Figure 33. Effect of sodium oleate concentration on column average velocity for various nozzle sizes.
Figure 34. Effect of varying nozzle sizes on column average velocity, for contaminated systems.
bubble first and then the upper stagnation point. With a smaller absolute interfacial area it is quite likely that the smaller bubble gets coated with the surfactant film sooner and eventually exposes a rigid surface to the liquid. This in turn increases the drag on the bubble and the internal circulation of the gas ceases. The net effect is the reduction of the bubble velocity. The effect of contamination, though appreciable is less pronounced for larger bubbles. It is conceivable that internal circulation has not ceased completely for larger bubbles, or else a more flattened profile would be obtained for the range studied (Figure 29).

For the case of rise velocity studies with simultaneous mass transfer, the effect of surfactant is shown in Figures 30, 31 and 32. It is clear from comparison with Figures 27, 28 and 29 that the average rise velocity decreases due to the simultaneous mass transfer process. Explanation for the retardation caused by mass transfer will be included in a hypothesized mechanism to be presented later. For the case of pure water, the trend of decreasing velocity with increasing span number is maintained, being most prominent for smaller bubbles. But this trend is rapidly lost on increasing the contamination level - in fact the trend is reversed and the bubbles speed up slightly instead. Although the rate of dissolution of oxygen is slower as compared to other gases such as CO₂, N₂O, C₂H₄, the mass transfer is suf-
ficient to shrink the bubble size. As described earlier, smaller bubbles travel faster in the range studied and hence the increased velocity is observed.

It is interesting then that the velocity should decrease consistently for the case of pure water (0 ppm curve in Figures 30, 31 and 32). This observation can be explained as a result of two competing phenomena - rise velocity decreases as the mass transfer rate increases; and the rise velocity increases due to the physical reduction in the size of the bubble. For the case of pure water, the mass transfer rate is highest for smaller bubbles (Figure 30). Here the retarding effect predominates over the effect caused by physical size reduction. This characteristic is gradually lost with increasing contamination at which instance the mass transfer rates are much lower and then the accelerating effect predominates. These competing phenomena are not observed in Figures 27, 28 and 29.

This illustrates an interesting hypothesis. For a bubble rising through a liquid, a boundary layer flow exists where the inertial and viscous forces are important. The hydrodynamic boundary layer has a finite thickness $\delta_0$. The process of mass transfer and the physical passage of gas molecules into the adjacent liquid goes to increase the thickness of the boundary layer. The net result is a retarding effect on the rise velocity.
The effect of contamination level on rise velocity is better shown in Figures 35 and 36. The effect is again more pronounced on smaller bubbles, but less than in the case without mass transfer. The presence of the surfactant molecules complicates the interacting phenomenon in the boundary layer. A discussion on the orientation of surface-active molecules and their effect at the interface will follow. The effect of varying nozzle sizes is indicated in Figure 36, where increased contamination alters the trend of rise velocity.

Mass Transfer Study

A comprehensive study of mass transfer in a flowing system across a moving interface can be conducted employing several approaches. Two of which are a semi-theoretical (qualitative) approach as opposed to a dimensional analysis type approach. This section includes the analysis of experimental results from a more semi-theoretical standpoint.

It is important to realize that for the case of a bubble rising in a liquid medium, the hydrodynamic effect on mass transfer rate is substantial and by no means negligible. In fact for moving boundary problems the hydrodynamic and mass transfer phenomena are intimately related and cannot be discussed separately. In gaseous systems, $Sc = 1$
Figure 35. Effect of sodium oleate concentration on column average velocity for various nozzle sizes
Figure 36. Effect of varying nozzle sizes on column average velocity, for contaminated systems.
and molecular diffusion becomes the predominating consideration. But in flowing liquid systems (such as clear water) $\text{Sc} \approx 10^3$ which signifies that even at low velocities convective mass transfer will predominate over molecular diffusion. For the oxygen-water system studied, $\text{Sc} = 480$ and $\text{Re}$ varies from 450 to 1200. This accounts for fairly high values of $\text{Pe}$, in which case the oxygen concentration distribution is determined essentially by convective transfer and the contribution due to molecular diffusion is negligible in comparison.

If the molecular diffusion term is neglected, the equation for convective diffusion becomes

$$\frac{\partial c}{\partial t} + u_x \frac{\partial c}{\partial x} + u_y \frac{\partial c}{\partial y} + u_z \frac{\partial c}{\partial z} = 0 \quad (77)$$

at steady state,

$$u_x \frac{\partial c}{\partial x} + u_y \frac{\partial c}{\partial y} + u_z \frac{\partial c}{\partial z} = 0 \quad (78)$$

which is satisfied by the solution

$$c = \text{constant} \quad (79)$$

This solution does not apply at the interface since it does not satisfy the boundary condition at the interface. Some particular systems may have $c = c^*$ or $c = 0$ as a condition at the interface, then Equation (79) becomes invalid.

This argument leads to the contention that there must be
a thin liquid layer adjacent to the interface where the concentration changes rapidly. Because of this large concentration gradient, although diffusivity may be small, the molecular diffusion contribution becomes comparable. Also, a diffusion boundary layer $\delta$ becomes established. This layer in mass transfer is analogous to Prandtl's boundary layer $\delta_0$ for momentum transport. Therefore at high Pe, the system can be divided into two regions - a region of constant concentration far from the interface and a region of a steep concentration profile in a thin film adjacent to the interface. Levich (23) points out that the diffusion boundary layer thickness $\delta$ has certain characteristics: $\delta \propto \sqrt{x}$, where $x$ is the distance from the leading edge, $\delta \propto \frac{1}{\sqrt{u}}$, $\delta \approx (v)^{1/6}$ (where $v$ is the kinematic viscosity) and $\delta \approx (\eta)^{1/3}$. The fact that $\delta$ is dependent on diffusivity indicates that the thickness depends upon the species which is diffusing into the liquid. In essence, therefore, convective diffusion is an important consideration in the transport of solute for moving boundary situations.

The presence of surfactant material which agglomerate at the interface further complicates the problem. The general effect of contamination level on mass transfer coefficients is shown in Figures 37, 38 and 39. A second-order interpolated curve is fitted through the span average values of $K^p_L$. Mass transfer rates are seen to be higher
Figure 37. Effect of sodium oleate surfactant on span average $K_L^o$
Figure 38. Effect of sodium oleate surfactant on span average $K_L^o$
Figure 39. Effect of sodium oleate surfactant on span average $K_{L}^{o}$
for the case of smaller bubbles. For clear water the tendency is to decrease with span number. But for contaminated systems the $K_L^0$ values increase with span number, primarily due to the reduction in size.

The average value of $K_L^0$ does decrease with increasing contamination, this effect being most pronounced for the smallest nozzle diameter. For the larger nozzles the $K_L^0$ values also decrease with increased contamination, but seem to arrive at an asymptotic value much sooner. This is featured in Figure 40. The decrease in $K_L^0$ could be attributed to two reasons. First is the physical barrier of the surfactant molecules crowding at the interface, which manifests itself with a corresponding increase in the diffusion boundary layer thickness. The second reason is the result of two competing shear forces at the interface - the viscous force and the surface tension force. When the surfactant concentration is sufficient, the surface motion stops and the bubble behaves as a rigid sphere. Also internal gas circulation ceases and as a result the constant replenishment at the interface of gas and liquid elements required for a rapid mass transfer vanishes. This latter effect is the dominant feature of contaminated systems and is largely responsible for the decrease in $K_L^0$.

It will be of interest to discuss briefly the inter-relationship of velocity and mass transfer phenomena. The
Figure 40. Effect of sodium oleate concentration on column average $K_L^0$. 

- **NOZZLE ID = 0.173 in.**
- **NOZZLE ID = 0.085 in.**
- **NOZZLE ID = 0.023 in.**
discussion is with specific reference to Figures 30, 31 and 32 for velocity and Figures 37, 38 and 39 for mass transfer. The existence of the hydrodynamic boundary layer $\delta_0$ and the diffusion boundary layer $\delta$ have been established. In the region immediately adjacent to the interface in the liquid phase, $\delta_0$ is several times larger than $\delta$ and the layers overlap. For the pure water system, an estimate of the thickness of the layers are obtained by the relations,

$$\delta_0 = \sqrt{\frac{\nu R}{\rho u}} \quad \text{and} \quad \delta = \sqrt{\frac{\alpha R}{u}}.$$  

Table 3 gives the estimates of $\delta_0$ and $\delta$ in the pure water system for comparative purposes for the three nozzle sizes studied.

Table 3. Comparison of hydrodynamic and diffusion boundary layer thicknesses for pure water-oxygen system

<table>
<thead>
<tr>
<th>Average bubble diameter, cm.</th>
<th>Hydrodynamic boundary layer thickness, $\delta_0$, cm.</th>
<th>Diffusion boundary layer thickness, $\delta$, cm.</th>
<th>$\delta_0$</th>
<th>$\delta$</th>
<th>$\frac{\delta_0}{\delta}$</th>
<th>$\frac{\delta_0}{\delta}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5814</td>
<td>1.095 x $10^{-2}$</td>
<td>5.06 x $10^{-4}$</td>
<td>21.65</td>
<td>0.4138</td>
<td>9.243 x $10^{-3}$</td>
<td>4.22 x $10^{-4}$</td>
</tr>
</tbody>
</table>
For the experimental system studied, the tangential component of the velocity at the outer edge of the diffusion boundary layer is about 21% of its value far from the interface. Also, from the average value of the ratio $\frac{\delta_0}{\delta}$ and the average $Sc$ for the system ($Sc = 483.34$) the empirical relationship

$$\frac{\delta_0}{\delta} = (Sc)^{0.5}$$

is obtained. This relationship contrasts with Levich's theoretical expression at higher $Sc$,

$$\frac{\delta_0}{\delta} = (Sc)^{0.33}.$$

The difference in the exponents is probably due to the difference in the nature of the interface. For the pure water system, the interface is fluid whereas Levich's derivation assumes a solid surface. This difference in exponents of $Sc$ is noticed frequently in literature for mass-transfer correlations reflecting the state of the interface (Table 4).

With simultaneous mass transfer, the physical event of the movement of solute molecules actually increase the hydrodynamic boundary layer thickness. It is conceivable that a hypothetical boundary layer viscosity also increases. This in turn effectively increases the resistance to motion and decreases the rise velocity. This effect is well
observed in pure water systems. In contaminated systems, the reasoning may not be so straightforward. The accelerating effect of reduction in size seems to have more effect than the retarding effect due to mass transfer. Also, the mass transfer coefficient has much lower values in contaminated systems.

Theoretical Treatment

For the case of a stagnant bubble in an infinite liquid, mass transfer rate can be calculated by solving the Fourier-Poisson law of diffusion

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

(80)

Here diffusivity is considered independent of concentration. It will be convenient to work in spherical coordinates since a spherical bubble is assumed. No angular effects exist for a stagnant bubble. The expression for radial effect becomes

$$\frac{\partial^2 c}{\partial \theta^2} + \frac{2}{r} \frac{\partial c}{\partial r} - \frac{1}{D} \frac{\partial^2 c}{\partial t} = 0$$

(81)

The boundary conditions can be written for initially the bulk concentration exists everywhere in the liquid, for all times the concentration remains the same at an infinite extent and at the interface the concentration is at a saturation level,
Carslaw and Jaeger (76) have solutions for analogous heat transfer problems. Using Laplace transformation technique (76) the differential equation becomes,

\[
\frac{d^2c}{dr^2} + \frac{2}{r} \frac{dc}{dr} - \frac{1}{\Delta} (sc - c_b) = 0
\]  

(83)

or,

\[
\frac{d^2(rc)}{dr^2} - \frac{s}{\Delta} (rc) = \frac{-rc_b}{\Delta}
\]  

(84)

Upon Laplace transformation, the boundary condition becomes,

\[
\bar{c}(R,s) = \frac{c^*}{s}, \lim_{r \to \infty} \bar{c}(r,s) = \frac{c_b}{s}
\]  

(85)

A solution satisfying Equations (84) and (85) is

\[
rc = \frac{R(c^*-c_b)}{s} \exp[-\sqrt{\frac{s}{\Delta}}(r-R)] + \frac{rc_b}{s}
\]  

(86)

In order that the solution remain finite as \(r \to \infty\), a term involving a positive exponential is neglected. The inverse Laplace transformation yields

\[
c(r,t) = \frac{R(c^*-c_b)}{r} \operatorname{erfc}\left(\frac{r-R}{2\sqrt{\Delta t}}\right) + c_b
\]  

(87)

where,

\[
\operatorname{erfc}(x) = 1 - \frac{2}{\sqrt{\pi}} \int_0^x \exp(-z^2)dz
\]  

(88)

Instantaneous mass transfer rate per unit area is given by
\[ K_L^o (c^*-c_b) = -\frac{\partial c}{\partial r}\bigg|_{r=R} \] (89)

therefore,

\[ K_L^o = \frac{-\frac{\partial c}{\partial r}\bigg|_R}{(c^*-c_b)} \] (90)

By differentiating Equation (87) and substituting in Equation (90),

\[ K_L^o = \mathcal{D}(\frac{1}{R} + \frac{1}{\sqrt{\pi \Delta t}}) \] (91)

Therefore, the instantaneous mass transfer coefficient \( K_L^o \) depends upon the bubble radius \( R \) as well as on the time of exposure \( t \).

The solution to the simple system can be applied to the case of a rising bubble in the manner of Higbie. Higbie (43) postulated that the element of surface is created at the front of the bubble, passes over the peripheral contact surface in contact time \( t_c \) and is then destroyed at the rear. The contact time \( t_c \) is simply the time for the bubble to rise through its own diameter

\[ t_c = \frac{D}{u} \] (92)

The best measure of the mass transfer coefficient is the integrated-average of the instantaneous value during the period of contact time.
Applying this procedure to Equation (91) gives,

\[ \bar{K}_L^0 = \frac{\int_0^{t_c} K_L^0(r,t)\,dt}{t_c} \quad (93) \]

Substituting the value for \( t_c \) from Equation (92) gives,

\[ \bar{K}_L^0 = \frac{\theta}{R} + 2\sqrt{\frac{\theta}{\pi t_c}} \quad (94) \]

This equation is close to Higbie's original expression and may be obtained by \( R \to \infty \). If the bubble is stationary or is travelling very slowly, the second term is negligible yielding a case of classical molecular diffusion. On the contrary, if the bubble is rising rapidly under sufficiently turbulent conditions, the first term becomes negligible and convective diffusion becomes the controlling factor. This is usually what occurs in the cases of rising bubbles with high Peclet number conditions.

Equation (95) has been used to evaluate the span average \( K_L^0 \) values for Figures 37, 38 and 39 using the reliable velocity of rise data from experimental runs.
Dimensional analysis

An alternate approach to the study of turbulent flow of liquid around a dissolving bubble is through dimensional analysis. Several dimensionless correlations have been developed for mass transfer phenomena by previous investigations. Very few, if any, seem to support the correlations with any statistical analyses - the worth of such correlations are extremely doubtful.

An attempt has been made here to determine the effect of varying surface tension of the system on the mass transfer rate. Figure 41 represents the effect observed on Nusselt number due to the varying dimensionless term γ*. Experimental values averaged over the entire column height were used to evaluate the parameters. No specific trend seems apparent and the discussion will be kept to a minimum. An optimum level of contamination (or corresponding value of surface tension) seems to exist at which the highest mass transfer rate can be expected. It is possible that at a low enough surfactant concentration the interfacial turbulence is enhanced and aids the surface renewal process leading to high mass transfer rates. With increased contamination, the turbulence ceases and the interface gets heavily covered exposing a rigid surface to the surrounding liquid. This can reduce the mass transfer rate substantially. No attempt will be made at this point to modify the Higbie
Figure 41. Effect of $\gamma^*$ on Nusselt number.
or Froësling correlation in order to introduce the effect of surface-active material.

**Bubble size**

Initial bubble size will change with the concentration of the surfactant. This variation is shown in Figure 42. In discussing the effect of surfactant concentration on rise velocity or span average $K^o_L$, it is useful to treat the nozzle size as the parameter and not the equivalent bubble diameter.

**Wall effect**

An important consideration in the study of rise velocity of large bubbles is the wall effect. The Ladenberg correction is given by

$$\frac{u_{\text{infinite liquid}}}{u_{\text{column}}} = 1 + 2.7 \frac{D}{D_c}$$

(96)

where $D_c$ is the column diameter. But the correction is recommended for cases where $Re < 0.2$. For higher $Re$, the ratio $\frac{D}{D_c}$ decreases to low values. Garner and Hammerton (50) further suggest that the error introduced by wall effect will be less than 1% if the column diameter is 100 times the bubble diameter. In the present study the ratio $\frac{D}{D_c}$ varies from 0.02 to 0.07 and no wall effect corrections have been made. Therefore the qualitative discussion remains unaltered.
Figure 42. Effect of sodium oleate concentration on equivalent bubble diameter
Hypothesized Interfacial Mechanism

In attempting to explain the observed bubble phenomena it is necessary to examine closely the possible interfacial mechanism at the molecular scale.

For the case of an oxygen bubble rising and dissolving in pure water the hydrodynamic and convective diffusion boundary layers have been postulated. The existence of the boundary layers suggest the existence of a film at the interface composed mainly of solute molecules packed intensely together with the solvent molecules in a definite manner. The use of the term "film" is debatable. Harkins (60) defines a "film" as a "layer, which has a different composition from the body of the liquid or solid, present at the boundary surface, provided the area and form of this layer are independent of the gravitational forces" and depends largely on the surface forces that are active. In the case of pure water-oxygen interface, because of the high surface tension values, the potential exists for surface active forces to be more influential and the term "film" may be appropriate. The oxygen molecules pack themselves in an oriented manner whereby the concentration of oxygen decreases from saturation level at the interface to the bulk concentration at the outer edge of the film. This oriented layer is not quite stagnat in a flowing system. A dynamic
equilibrium is perceived in which the constituents of the layer are continuously replenished at a rapid rate due to the hydrodynamics of the situation and also because the interface is mobile in pure systems resulting in the internal gas circulation. How rapid the turnover of the gas molecules will be is dependent on the local turbulence and the particular species that is migrating. Consequently the film thickness will vary according to the immediate physical environment. Also, velocity of rise of absorbing bubbles decreases as the symmetry of gas molecules decrease. The cohesive forces of the oriented gas molecules or the tendency of film formation is proportional to the degree of asymmetry of the molecules. Since oxygen molecules are relatively more symmetric, the film formed in less rigid and stagnant, accounting for the higher rise velocities.

In the presence of molecules of surface active material, the interfacial tension decreases fairly rapidly. This is tantamount to a loss of potential energy. In other words the form and area of the interfacial layer now depends upon the surface forces as well as gravitational forces, still maintaining a composition different from the bulk. According to Harkins (60) such a layer is more appropriately termed a "lens" and not a "film". A hypothetical process is envisaged where the sodium oleate molecules are adsorbed in the lens contiguously with the dynamically oriented solute
molecules. Sodium oleate \([\text{CH}_3(\text{CH}_2)_7\text{CH}:\text{CH}(\text{CH}_2)_7\text{COONa}]\) molecules also are oriented in a definite manner. The orientation of the molecule is perpendicular to the interface with the polar carboxyl group turned towards the polar liquid (water) and the nonpolar greasy hydrocarbon end turned toward the gaseous phase. This allows for a condition at the interface at which the transition to the adjacent phase is less abrupt.

For sodium oleate the critical micelle concentration is \(7 \times 10^{-4}\) M to \(9 \times 10^{-4}\) M. Above this concentration, sodium oleate molecules are adsorbed more rapidly and below it only slowly. As discussed earlier the oriented molecules arrange in a monomolecular layer at the interface, but due to the liquid flow is swept to the rear of the bubble where the packing is more intense. With increased concentration of the sodium oleate surfactant the remaining portion of the bubble including the frontal stagnation point is gradually covered up with the oriented surfactant molecules. The interface then becomes rigid, the point of separation is moved, the drag force on the bubble is increased which reduces the velocity. Also the diffusing oxygen molecules now have to penetrate through the lens in which its diffusivity may be less than in pure water and also pass through an increased diffusion boundary layer. The net effect is the reduction of mass transfer coefficient. The concentrations
of sodium oleate used ranged from 0 M to $4 \times 10^{-4}$ M. It is therefore conceivable that the rate of sodium oleate absorption was not too rapid and entirely rigid interfaces were not achieved. Internal gas circulation was probably impeded but not stopped entirely. The substantial effect that can be caused by the presence of minute quantities of surfactant has thus been demonstrated.

Just as in the case of pure water systems it seems unlikely that a monomolecular layer of surface active material will be able to survive the local turbulence and remain as a totally stagnant layer throughout the bubble rise. Although the work of adhesion between the carboxyl group and water will have to be overcome, it is speculated that sufficient attrition of the surfactant molecules will occur. In fact the molecules can be pictured to be "ripped off" the interface by the fluid to be replaced by freshly adsorbed molecules. At sufficiently high concentrations a multimolecular layer of surfactant molecules can be present in a state of dynamic equilibrium. Its effect on velocity and mass transfer phenomena will depend upon how rapidly the adsorption occurs after the interface has been temporarily relieved. Though difficult to demonstrate experimentally, this hypothetical mechanism is capable of explaining the observed events.
In this section a theoretical study is reported related to the oxygenation of water under an ice cover, such as in a frozen lake, using single oxygen bubbles.

The following discussion is with reference to Figure 43. The water in close contact with the ice layer will have a temperature of 0°C. The water temperature will increase with depth. Hutchinson (28) indicates that the temperature profile is linear with depth. An inverse stratification occurs in the winter with bottom temperatures of the order of 4°C. The basic differential equation can be altered to include any temperature profile. For this study a linear temperature profile is assumed with a bottom temperature 10°C, which is slightly exaggerated to identify the effect of temperature, if it is important.

At any depth the temperature of the gas in the bubble may not equal the temperature of the water around it. A consideration of instantaneous heat transfer is involved. Two asymptotic cases are considered - (i) the bubble rises slowly enough so that the bubble is in thermal equilibrium with the water at any time, (ii) the bubble rises fast enough so that the gas is in an isothermal condition during the period of rise. The results of these two asymptotic cases show a negligible difference in the bubble volume. A
Figure 43. Schematic diagram of frozen lake model
thermal equilibrium assumption is appropriate for the study, especially if the lake is deep enough.

**Derivation of the differential equation**

A detail derivation follows of the differential equation which describes the volume change of the bubble as it rises and undergoes simultaneous gas absorption.

Here,

- $V$ represents the instantaneous volume of the bubble
- $T$ represents the temperature of the gas in the bubble
- $P$ represents the total pressure of gas in the bubble
- $n$ represents the number of moles of gas in the bubble
- $x$ represents the distance from the water surface (positive measured downwards)
- $t$ represents the time from bubble release

and

- $u$ represents the instantaneous velocity of the bubble (positive upwards)

The volume of the bubble at any time will depend upon the pressure, temperature and number of moles of gas.

$$V = V(P, T, n)$$ \hspace{1cm} (97)

Here $P$, $T$ and $n$ are not independent variables, since $P = P(x)$, $T = T(x)$ and $n = n(t)$. The fundamental independent variables are vertical distance $x$ and time $t$. These two variables are related through velocity

$$u = - \frac{dx}{dt}$$ \hspace{1cm} (98)
It will be convenient to work with only one of these two variables as the independent variable. Vertical distance \( x \) will be the most convenient, since \( P \) and \( T \) can be easily expressed as functions of \( x \).

Total derivative,

\[
dV = \left( \frac{\partial V}{\partial P} \right)_{T,n} dP + \left( \frac{\partial V}{\partial T} \right)_{P,n} dT + \left( \frac{\partial V}{\partial n} \right)_{T,P} dn
\]

(99)

Derivative with respect to \( x \) gives

\[
\left( \frac{dV}{dx} \right) = \left( \frac{\partial V}{\partial P} \right)_{T,n} \left( \frac{dP}{dx} \right) + \left( \frac{\partial V}{\partial T} \right)_{P,n} \left( \frac{dT}{dx} \right) + \left( \frac{\partial V}{\partial n} \right)_{T,P} \left( \frac{dn}{dx} \right)
\]

(100)

Using Equation (98),

\[
\frac{dt}{dx} = - \frac{1}{u}
\]

(101)

\[
\left( \frac{dV}{dx} \right) = \left( \frac{\partial V}{\partial P} \right)_{T,n} \left( \frac{dP}{dx} \right) + \left( \frac{\partial V}{\partial T} \right)_{P,n} \left( \frac{dT}{dx} \right) + \left( \frac{\partial V}{\partial n} \right)_{T,P} \left( \frac{dn}{dx} \right) \left( - \frac{1}{u} \right)
\]

(102)

To arrive at a workable form of equation, a set of assumptions will be made.

**Assumption 1** Ideal gas law holds for the gas in the bubble

\[
P V = n R T
\]

(103)

or,

\[
V = \frac{n R T}{P}
\]

(104)
Substituting Equations (105, 106 and 107) in Equation (102),

\[
\left( \frac{\partial V}{\partial T} \right)_{T,n} = (nRT) \left( - \frac{1}{p^2} \right) = - \frac{nRT}{p^2} = - \frac{V}{T} \quad (105)
\]

\[
\left( \frac{\partial V}{\partial p} \right)_{P,n} = (\frac{nR}{p}) = \frac{V}{T} \quad (106)
\]

\[
\left( \frac{\partial V}{\partial n} \right)_{T,P} = \frac{RT}{p} \quad (107)
\]

Assumption 2  Density of water \( \rho \) is constant. This assumption is quite reasonable, since Hutchinson (28) records the density of water to be 0.99986 gms/c.c. at 0°C to 0.99972 gms/c.c. at 10°C.

Assumption 3  Pressure equilibrium exists between gas and liquid. The total pressure on the bubble (atmospheric plus hydrostatic) must equal the pressure of the gas inside the bubble. This implies that the pressure variations around the bubble due to surface tension are negligible. This is valid for large bubbles, but for small bubbles the surface tension effects due to surface active particles present in the lake may not be negligible and in fact make the small bubbles behave like rigid spheres. For the present, the
surface tension gradients and the pressure due to the ice layer are neglected.

Total pressure on the bubble at depth $x$, 

$$p = p^0 + \rho \left( \frac{g}{g_c} \right) x \quad (109)$$

$$\frac{dp}{dx} = \rho \left( \frac{g}{g_c} \right) \quad (110)$$

**Assumption 4** Temperature profile is linear. The water is colder on top and warmer at the bottom. The linear temperature profile has been discussed previously. If the lake is not too deep, the linear temperature profile according to Hutchinson (28) is an acceptable assumption. In this connection, natural convection currents including the effect of Grashoff's number should be examined, although there seems to be ample evidence in literature that forced convection effects predominate. As reasoned earlier the bubble is in thermal equilibrium with the water at any depth.

Steady state temperature profile of water in the lake is given by

$$T = T^0 + Bx \quad (111)$$

therefore,

$$\left( \frac{dT}{dx} \right) = B \quad \text{(temperature gradient)} \quad (112)$$

For the second asymptotic case (isothermal process) it is quite simple in the computer program to arrange to have
The instantaneous rate of absorption of gas from the bubble is given by

\[ \frac{dc_b}{dt} = K_L^* a (c^* - c_b) \]  \hspace{1cm} (115)

where \( c^* \) is the saturation concentration of oxygen.

Neglecting the gas film resistance, the interface is considered to have an oxygen concentration \( c^* \) and \( c_b \) is the bulk concentration of oxygen in water at any time.

Denoting this in terms of the number of moles of gas leaving the bubble per unit time,

\[ -\frac{dn}{dt} = K_L^* A (c^* - c_b) \]  \hspace{1cm} (116)

here, \( K_L^* \) is the liquid-film controlled mass transfer coefficient and \( A \) is the total surface area of the bubble.

Now, substituting Equations (110, 112 and 116) into Equation (108) gives,

\[ \left( \frac{dV}{dx} \right) = \left( -\frac{V}{F} \right) \left( \frac{\rho g}{g_c} \right) + \left( \frac{V}{T} \right) (B) + \left( \frac{RT}{F} \right) \left( -K_L^* A (c^* - c_b) \right) \left( -\frac{1}{u} \right) \]  \hspace{1cm} (117)

or,

\[ \left( \frac{dV}{dx} \right) = -\left( \frac{V}{F} \right) \left( \frac{\rho g}{g_c} \right) + \left( \frac{V}{T} \right) (B) + R \left( \frac{T}{F} \right) K_L^* A (c^* - c_b) \left( \frac{1}{u} \right) \]  \hspace{1cm} (118)
\[
\frac{dV}{dx} = -V \left( \rho \frac{g}{g_c} \frac{1}{\bar{P}} \right) + V \left( \frac{K^o A}{T^o + B x} \right) + \left( \frac{L}{\bar{u}} \right) \frac{R(c^*-c_b)}{p} T
\]  

Since \( P \) and \( T \) are simple functions of \( x \), substituting Equations (109) and (111),

\[
\frac{dV}{dx} = -V \left[ \rho \frac{g}{g_c} \left( \frac{1}{p^o + \rho g_x} \right) T^o + B x \right] + \frac{K^o A}{\bar{u}} \frac{R(c^*-c_b)}{(p^o + \rho g_x) g_c} \left( T^o + B x \right)
\]

Equation (120) is the differential equation which was numerically integrated with respect to \( x \), in order to estimate the volume of the bubble at any depth \( x \). The same differential equation can be derived by considering time \( t \) as the fundamental independent variable and obtaining an expression for \( \frac{dV}{dt} \). Then by using the relation, velocity \( u = -\frac{dx}{dt} \), time \( t \) can be eliminated to arrive at Equation (120).

The immediate purpose is to obtain a relation between \( V \) and \( x \) as explicitly as possible before integration. The factors that need to be simplified in terms of measurable quantities are \( K^o_L \), \( A \) and \( u \).

**Assumption 5** The bubble rises vertically upwards at Stokes' terminal velocity (reasonable for very small bubbles with surface active layer).
\[ u = \frac{2}{9} R^2 \frac{\rho_{H_2O} - \rho_{O_2}}{\mu} g \]  

(121)

Here, \( R \) is the radius of the bubble and \( \mu \) is the viscosity of the liquid, which is constant for the analysis.

Velocity,
\[ u = \frac{D^2}{18} \frac{\rho_{H_2O} - \rho_{O_2}}{\mu} g \]  

(122)

Here, \( D \) is the diameter of the bubble. Neglecting the density of oxygen compared to that of water \( (\rho_{O_2} \ll \rho_{H_2O}) \),
\[ u = \frac{D^2 \rho_{H_2O} g}{18 \mu} \]  

(123)

Rearranging,
\[ u = \left( \frac{\rho_{H_2O} g}{18 \mu} \right) D^2 \]  

(124)

The computer program does not assume that the velocity remains constant right through the rise of the bubble. After each round of ten integrations, a new Stokes' velocity is calculated corresponding to the new diameter of the bubble. Constant velocity is assumed only for a distance approximately equal to 1.0 cm. As seen from the results this is an acceptable assumption.

Strictly, velocity \( u \) will change as the bubble rises due to a) change of diameter of the bubble, b) change in viscosity \( \mu \) of water with temperature, c) direct retarding
effect of mass transfer on velocity and d) Stokes' terminal velocity may be an oversimplification, since it is applicable in the region \( \text{Re} \leq 1 \).

With regard to the last point, it has now been well established that Levich's approach (23) from the boundary layer theory leads to a more realistic value for velocity of bubbles. The result is essentially

\[
   u = \left( \frac{\rho_{\text{H}_2\text{O}}g}{36\mu} \right) D^2 = \frac{1}{2} u_{\text{Stokes}}
\]

(125)

Also, the Hadamard-Rybczynski correction (33, 34) for velocity due to internal circulation of the gas in the bubble allows for slip at the boundary

\[
   u_{\text{H-R}} = \left( \frac{u_{\text{Stokes}}}{2} \right) \left( \frac{3\mu + 3\mu'}{2\mu + 3\mu'} \right)
\]

(126)

here, \( \mu \) is the viscosity of water and \( \mu' \) is the viscosity of oxygen.

These two Equations (125) and (126) have been used in particular to account for the extreme cases of the bubble behaving as a rigid sphere (totally covered with surface active particles) and the bubble behaving as a fluid sphere (no surface-active particles, completely developed internal circulation).

Velocity \( u \) is included in the differential equation as a continuous variable by expressing it as a function of
volume V using the Stokes' relation,

\[ u = \left[ \left( \frac{\rho H_2 g}{18 \mu} \right) \left( \frac{6}{\pi} \right)^{2/3} \right] (V)^{2/3}, \text{ due to Stokes'} \]  

(127)

\[ u = \left[ \left( \frac{\rho H_2 g}{36 \mu} \right) \left( \frac{6}{\pi} \right)^{2/3} \right] (V)^{2/3}, \text{ due to Levich} \]  

(128)

\[ u = \left[ \left( \frac{\rho H_2 g}{36 \mu} \right) \left( \frac{6}{\pi} \right)^{2/3} \left( \frac{3 \mu + 3 \mu'}{2 \mu + 3 \mu'} \right) \right] (V)^{2/3}, \]  

(129)

due to Hadamard-Rybczynski

More generally, \( u = [F](V)^{2/3} \)  

(130)

where \( F \) is a function of the properties of the system.

**Mass-transfer coefficient, \( K_L^0 \)**

It is now necessary to substitute an appropriate semi-empirical relationship for mass-transfer coefficient in terms of parameters that can be measured or predicted.

From Calderbank's Chapter (77), for small bubbles behaving as rigid spheres, the mass transfer coefficient has been correlated in terms of hydrodynamic and physical property parameters by Froessling's equation

\[ \text{Sh} = 2.0 + 0.552 \ (\text{Re})^{1/2} (\text{Sc})^{1/3} \]  

(131)

or

\[ \frac{K_L^0 D}{D} = 2.0 + 0.552 \left( \frac{D \mu}{\mu} \right)^{1/2} \left( \frac{\mu}{\rho D} \right)^{1/3} \]  

(132)

therefore,
Mass transfer coefficient $K^c_L$ will change as the bubble rises, since a) velocity $u$ will change, b) diameter $D$ will change and c) $\rho$, $\mu$, $\mathcal{S}$ will change with temperature. 

In the course of the analysis, other semi-empirical relations have been used to determine $K^c_L$. These appear in Table 4 with remarks on appropriate applicability.

Assumption 6 Shape of the bubble is spherical. This assumption is reasonable for small bubbles of the order of 1 mm diameter (23).

Volume of the bubble, $V = \frac{\pi D^3}{6}$

or,

$diameter$ $D = (\frac{6}{\pi} V)^{1/3}$

Surface area of the bubble, $A = \pi D^2$

$A = \pi (\frac{6}{\pi} V)^{2/3}$

rewriting,

$A = (\pi)^{1/3}(6)^{2/3}(V)^{2/3}$

Therefore, $A = \{E\}(V)^{2/3}$

where,

$E = constant = (\pi)^{1/3}(6)^{2/3}$

In order to obtain the explicit relationship required in differential form between $V$ and $x$, expressions for $K^c_L$
(Equation 133), A (Equation 139) and u (Equation 130) are substituted in Equation (120), which yields,

\[
\frac{dV}{dx} = -V \left[ \frac{\rho \frac{1}{g_c}}{(p_0 + \rho \frac{g}{g_c} x)^2} \right] + V \left[ B \right] + K_L^0 \left[ \frac{\rho (c^* - c_d)(T_0 + Bx)}{(p_0 + \rho \frac{g}{g_c} x)^2} \right]
\]

(141)

Equation (141) is the final form of the differential equation. The computer program is designed to numerically integrate Equation (141) after selecting the appropriate expression for \( K_L^0 \) depending upon the physical nature of the system studied.

\textbf{Initial condition} The first order ordinary differential Equation (141) requires one initial condition to be solved numerically. This condition is at time

\[
t = 0, \begin{cases} x = h, \text{ bottom of lake} \\ V = V_0, \text{ initial volume of bubble.} \end{cases}
\]

(142)

\textbf{Computer program} The entire listing of the computer program appears in Appendix F. The main features of the program will be discussed briefly.

Given the initial diameter and hence the volume \( (V_0) \) of the bubble, it advances the bubble up a distance equal to 1 mm and evaluates the new volume by numerically integrating the differential Equation (141). The program is designed
to carry out ten such integration steps before storing the new bubble volume in memory. In the case of 1 mm diameter bubble, it is advanced ten bubble diameters before the new volume is stored.

The mass transfer coefficient $K_L$ is the only major factor that is considered constant in the space of 10 mm, all other variables are expressed as functions of volume. Pressure, temperature and $c^*$ are considered constant in the space of 10 mm. These variables and $K_L$ are updated periodically and stored, ready to be used in the next range of integration steps, taking the bubble up another 10 mm. Quantities that have been treated as constants throughout the program are,

- acceleration due to gravity, $g = 980.665 \text{ cm/sec}^2$
- proportionality constant, $g_c = 1.0 \frac{\text{gm cm}}{\text{dyne sec}^2}$
- gas law constant, $R = 83.151 \times 10^6 \frac{\text{dyne cm}}{\text{gm mole } ^\circ\text{K}}$
- density of water, $\rho_{\text{H}_2\text{O}} = 1.00 \text{ gms/cm}^3$
- viscosity of water at 5°C, $\mu = 1.5188 \text{ cp}$
- diffusivity of oxygen, $D = 2 \times 10^{-5} \text{ cm}^2/\text{sec}$
- bulk dissolved oxygen concentration, $c_b = 0 \text{ ppm}$.

The conditions at the water surface ($x=0$) are,

- atmospheric pressure, $P^0 = 1.0133 \times 10^6 \frac{\text{dyne}}{\text{cm}^2}$
temperature, \( T^\circ = 273^\circ K \)

The variation of \( C^* \) with temperature was accounted for by using the relation,

\[
c^* = \frac{ae^{bT}}{100}
\]

where \( c^* \) is in \( \frac{mgm}{liter} \), \( a = 5.647 \times 10^6 \) and \( b = -0.02455 \)

The results of the theoretical treatment are presented in graphical form in Figures 44 to 52 and will be discussed individually.

The following discussion is an attempt to tie down the possible direct application with regard to water pollution to the theories on bubble behavior. In analyzing the pollution problems of a particular water body, the probable parameters that will be expected to be provided are:

(a) Lake depth
(b) Temperature profile
(c) Biological oxygen demand
(d) Pollutant concentration.

These physical parameters are related to the dimensionless parameters derived below.

Rewriting Equation (141),

\[
\frac{dV}{dx} = -V\left(\frac{\rho g}{g_c}\right) \frac{1}{\left(\frac{\rho}{\rho + \rho g g_c}\right)^2} + V\left(\frac{B}{T^\circ + Bx}\right) + K_L \left(\frac{E}{F}\right) \left(\frac{R(c^* - c_D)(T^\circ + Bx)}{(\rho + \rho g g_c x)}\right)
\]

(141)
To obtain a dimensionless equation, let dimensionless depth of lake,

\[ z = \frac{x}{L} \]  

(144)

and dimensionless volume of bubble, \( \phi = \frac{V}{V_0} \)  

(145)

Then, \( x = Lz \)

and

\[ dx = (L)dz \]  

(146)

also,

\[ V = V_0 \phi \]

and

\[ dV = (V_0)d\phi \]  

(147)

Here, \( z \) is the independent variable and \( \phi \) is the dependent variable.

Therefore, \( \frac{dV}{dx} = \frac{V_0}{L} \frac{d\phi}{dz} \)  

(148)

Substituting the new dimensionless variables in Equation (141) yields,

\[
\frac{V_0}{L} \frac{d\phi}{dz} = -V_0 \phi \left[ \frac{\rho g}{g_c} \frac{1}{(p^0 + \frac{\rho g}{g_c} Lz)} \right] + V_0 \phi \left[ \frac{B}{T_0 + BLz} \right] \\
+ K^r \frac{E}{F} \left[ \frac{R(c^* - c_D)}{(p^0 + \frac{\rho g}{g_c} Lz)} \right] 
\]

(149)

Simplifying,
\[
\frac{d\phi}{dz} = -\phi L \left[ \frac{\rho g}{g_c} \frac{1}{(P^0 + \frac{\rho g}{g_c} Lz)} \right] + \phi L \frac{B}{T^0 + BLz}
\]
\[+ K_L \frac{E}{F} \left( \frac{L}{V_0} \right) \frac{R(c^* - c_d)}{(P^0 + \frac{\rho g}{g_c} Lz)} \]

Equation (150) can be written as

\[
\frac{d\phi}{dz} = -\phi \left[ \frac{1}{P^0 \frac{\rho g}{g_c}} + \frac{1}{L \frac{\rho g}{g_c}} \right] + \phi \left[ \frac{1}{P^0 \frac{\rho g}{g_c}} + \frac{1}{(BL) + z} \right]
\]
\[+ \left[ K_L \frac{E}{F} \left( \frac{L}{V_0} (c^* - c_d) \right) \right] \frac{\left( \frac{T^0}{BL} + z \right)}{\left( \frac{P^0}{BLR} + \frac{\rho g z}{Rg_c B} \right)} \]

Now let four dimensionless parameters be defined.

\[
\frac{P^0}{L \frac{\rho g}{g_c}} = \alpha \quad (152)
\]

\[
\frac{T^0}{BL} = \beta \quad (153)
\]

\[
\frac{P^0}{BLR} \frac{1}{V} = \gamma \quad (154)
\]

and

\[
\frac{\rho g}{Rg_c B} \frac{1}{V} = \delta \quad (155)
\]

In Equations (154) and (155),
\[ \nu = K_L \left( \frac{E}{F} \right) \left( \frac{L}{V_0} \right) (c^*-c_b) \]  

(156)

Substituting these dimensionless parameters into Equation (151) yields

\[ \frac{d\phi}{dz} = -\phi \left[ \frac{1}{\alpha + z} \right] + \phi \left[ \frac{1}{\beta + z} \right] + \left[ \frac{\beta + z}{y + \delta} \right] \]  

(157)

Equation (157) is the final dimensionless equation derived to include the four dimensionless parameters \( \alpha, \beta, \gamma \) and \( \delta \) of practical physical significance.

**Initial condition**. The initial condition which must be satisfied is

\[ z=1, \; \phi=1 \]  

(158)

**Physical significance of parameters**. The physical significance of \( \alpha \) is that it makes the incumbent pressure on the bubble dimensionless and also includes the depth of the lake, which is an important consideration. The parameter \( \beta \) converts the temperature profile into a dimensionless parameter and also encompasses the lake depth. The factor \( \nu \) is not dimensionless. \( \nu \) is a measure of the instantaneous ratio, \( \frac{\text{rate of oxygen supplied}}{\text{volume of gas}} \). This quantity is important in that the numerator should be proportional to the oxygen demand of the lake (BOD). Also, the volume of
oxygen required and hence also the flow rate of oxygen can be evaluated from $v$ once it is known. $v$ also aids in taking into consideration the pollutant concentration. The pollutant, because of its physical and chemical nature, especially its surface activity will affect the mass transfer coefficient $K_L^o$ of oxygen and the velocity of rise $u$ of the bubble. Both of these quantities are included in $v$. It is envisaged that a sample of lake water will be analyzed in the laboratory. Oxygenation experiments will be conducted with the sample water to yield either an empirical relationship or an estimate of the values for $K_L^o$ and velocity. These can then be used to evaluate the value of $v$. Though $v$ is dimensional ($\frac{gm\text{ mole}^2}{cm^3}$) it is an important factor in the present analysis.

For the present theoretical calculations, empirical relationships are used to evaluate $K_L^o$ (Table 4) and velocity (Table 5) as is appropriate to the physical nature of the system. In each case the expression used is clearly identified. The dimensionless parameters $\gamma$ and $\delta$ are useful in that these include the important factor $v$ and also account for the lake depth and temperature profile.

The main objective of the dimensionless approach is to be able to numerically solve Equation (157) and obtain plots for $\phi$ vs $z$ for certain values of $\alpha$, $\beta$, $\gamma$ and $\delta$ which will depend upon the system. Four distinct parameters are difficult to represent in a two-dimensional plot. The
Table 4. Mass transfer correlation used in the analysis

<table>
<thead>
<tr>
<th>Equation</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Froëssling's equation:</strong></td>
<td></td>
</tr>
<tr>
<td>$Sh = 2 + 0.55 \ (Re)^{1/2} (Sc)^{1/3}$</td>
<td>$2 &lt; Re &lt; 1000$, Sc $= 1.0$</td>
</tr>
<tr>
<td>(rigid sphere)</td>
<td></td>
</tr>
<tr>
<td><strong>Leonard's equation:</strong></td>
<td></td>
</tr>
<tr>
<td>$K_L = 0.00153 \ (u-7)$</td>
<td>$u &gt; 22 \text{ cm/sec}$</td>
</tr>
<tr>
<td>(u is velocity of rise)</td>
<td></td>
</tr>
<tr>
<td><strong>Garner and Suckling:</strong></td>
<td></td>
</tr>
<tr>
<td>$Sh = 2 + 0.95 \ (Re)^{1/2} (Sc)^{1/3}$</td>
<td>$60 &lt; Re &lt; 660$, $1100 &lt; Sc &lt; 2200$</td>
</tr>
<tr>
<td>(rigid sphere)</td>
<td></td>
</tr>
<tr>
<td><strong>Griffith's equation:</strong></td>
<td></td>
</tr>
<tr>
<td>$Sh = 2 + 0.53 \ (Re)^{1/2} (Sc)^{0.35}$</td>
<td>$Re &gt; 1$, $Sc &gt; 1$</td>
</tr>
<tr>
<td>(rigid sphere)</td>
<td>Thin concentration boundary layer</td>
</tr>
<tr>
<td><strong>Griffith's equation:</strong></td>
<td></td>
</tr>
<tr>
<td>$Sh = 2 + [(0.57 \ (Re)^{1/2} (Sc)^{0.35}) (1 + \frac{22}{13} \ k_V)^{1/2} \ (\varepsilon/\varepsilon_0)^{-1} ]$</td>
<td>$Re &gt; 1$</td>
</tr>
<tr>
<td></td>
<td>$Sc &gt; 1$</td>
</tr>
<tr>
<td></td>
<td>Slowly moving surface, thin concentration</td>
</tr>
<tr>
<td></td>
<td>boundary layer</td>
</tr>
<tr>
<td><strong>Griffith's equation:</strong></td>
<td></td>
</tr>
<tr>
<td>$Sh = 2 + 1.13 \ (Pe)^{1/2} (k_V)^{1/2}$</td>
<td>$Re &gt; 1$</td>
</tr>
<tr>
<td>where $Pe = (Re)(Sc)$</td>
<td>$Sc &gt; 1$</td>
</tr>
<tr>
<td></td>
<td>Unhindered surface flow</td>
</tr>
</tbody>
</table>
Table 5. Velocity correlations used in the analysis

<table>
<thead>
<tr>
<th>Equation</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Stoke's equation:</strong></td>
<td></td>
</tr>
<tr>
<td>$u_t = \frac{2}{9} \frac{R^2(\rho_s-\rho_l)}{\mu_l} \cdot g$</td>
<td>$Re \leq 1.0$, Zero slip at surface</td>
</tr>
<tr>
<td>(rigid sphere)</td>
<td></td>
</tr>
<tr>
<td><strong>Levich's equation for medium-sized bubbles:</strong></td>
<td>50 &lt; $Re$ &lt; 800</td>
</tr>
<tr>
<td>$u_t = \frac{1}{9} \frac{R^2(\rho_l-\rho_g)}{\mu_l} \cdot g$</td>
<td></td>
</tr>
<tr>
<td>(rigid sphere)</td>
<td></td>
</tr>
<tr>
<td><strong>Hadamard-Rybczynski equation:</strong></td>
<td></td>
</tr>
</tbody>
</table>
| $u_t = \frac{2}{9} \frac{R^2(\rho_l-\rho_g)}{\mu_l} \left[ \frac{3\mu_g+3\mu_l}{3\mu_g+2\mu_l} \right] g$ | For $Re > 1$
|                                                                   | and for very high $Re$, internal circulation
|                                                                   | of gas exists                                  |

representation is therefore restricted to (say) holding the lake depth constant and studying the effect of various $V_0$ by selecting $v$ as a parameter. Alternatively, $V_0$ can be fixed and lake depth ($L$) can be varied, by using $\alpha$ or $\beta$ as the parameter. Under these circumstances, a three-dimensional plot would probably give the best representation.

An alternative form of Equation (157) can be obtained
by redefining the dimensionless variable

\[ \phi = 1 - \frac{V}{V_0} = \frac{V_0 - V}{V_0} \quad \text{(volume decrease ratio)} \quad (159) \]

with \( \alpha, \beta, \gamma, \delta \) and \( \nu \) defined as before, Equation (157) becomes,

\[ \frac{d\phi}{dz} = (1-\phi)\left[\frac{1}{\alpha + z}\right] - (1-\phi)\left[\frac{1}{\beta + z}\right] - \left[\frac{\beta + z}{\gamma + \delta z}\right] \quad (160) \]

with the new initial condition,

\[ z = 1, \phi = 0 \quad (161) \]

Numerical solutions of Equation (161) yield plots of \( \phi \) vs \( z \) that appear different, but gives no more information than solutions of Equation (157).

Results The results of numerical solution of Equations (141) and (157) appear in graphical form in Figures 44 to 52, for various physical and operating conditions. Preliminary checks were made by using the computer program (Appendix F) to simulate unrealistic conditions, such as no pressure variation, no thermal gradient or no mass transfer of oxygen. This was done to check the program logic and was found to be satisfactory.

Figure 44 simulates a condition where the bubble is covered with surface active material such that the bubble behaves as a rigid sphere. Using Levich’s rigid sphere
Figure 44. Effect of strong contamination; bubble behaves as a rigid sphere.
velocity (Table 5) and Froëssling's mass transfer expression have been used. Figure 44 indicates that bubbles below 0.1 cm diameter will dissolve completely before reaching the top of the lake. Bubbles 0.1 cm in diameter will have a 75% reduction in diameter. These are typical curves to be expected in fairly deep lakes, about 28 feet. When the lake is relatively free of surface active material, internal circulation will develop in the bubble. The increased rise velocity is accounted for by employing the Hadamard-Rybczynski equation. Figure 45 indicates that the net amount of gas absorption without surfactants is actually less than with surfactants. This is explained by the substantial effect the surfactants have in retarding the rise velocity, thereby increasing the residence time of the bubble.

Froëssling's correlation for mass transfer from rigid spheres is applicable in the region $2 < Re < 1000$ and $Sc < 1$. For oxygen-water system, $Sc$ is much larger (about 760). For this reason a more applicable semi-empirical correlation due to Garner and Suckling (Table 4) is used which is valid at higher $Sc$. The result appears in Figure 46, which indicates that for all sizes of bubbles the mass transfer of oxygen was more although the simulation was for a heavily contaminated state.

In simulating the effect of various amounts of surface
Figure 45. Effect of less contamination; bubble with moving surface
Figure 46. Effect of heavy contamination; bubble behaves as a rigid sphere
active material, Griffith's (52) semi-empirical equations have been useful. Griffith takes into consideration the state of interfacial flow in deriving the predictive equations for mass transfer. Figure 47 simulates a bubble rising at Re > 1 with a thin concentration boundary layer and an immobile interface. Such a system has high Sc, and Levich's expression for velocity has been used. Figure 46 and 47 may be compared to notice the effect of using different correlations to the same physical situation.

When the gas bubble has adsorbed only small amounts of surface active material, the interface is not totally immobile but moves slowly. To simulate this condition Griffith's equation for slowly-moving interface is used with the Hadamard-Rybczynski expression for velocity to give the results in Figure 48. A comparison of Figures 47 and 48 indicates that the mass transfer of oxygen has been many times more in the relatively less polluted system.

In the absence of surface active material and for fairly high Re (potential flow) a well developed internal circulation pattern exists and the interface presents a mobile, fluid surface. The unhindered surface flow condition is simulated by using Griffith's expression (Table 4) and the Hadamard-Rybczynski equation for velocity. The result appears in Figure 49, emphasizing the marked effect the absence of surfactants have had on gas absorption.
Figure 47. Effect of contamination; immobile interface
Figure 48. Effect of partial contamination; slowly moving interface

L_D = 28 ft

INITIAL DIAMETER = 0.05 cm

0.06
0.07
0.08
0.09
0.10
0.11
0.12 cm
Figure 49. Effect of no contamination; unhindered surface flow
The effect of surfactant on oxygen absorption can also be compared in Figures 50 and 51 in which the lake depth is treated as a parameter. Figure 50 is a simulation of a high level of surfactant contamination, using Griffith's expression for immobile surface and Levich's rigid sphere equation. Figure 51 assumes a total absence of surfactant and Griffith's mobile surface expression is used with the Hadamard-Rybczynski equation. Once again the striking effect of surfactants on gas absorption is noticed.

For bubbles of larger diameter (0.2 cm to 0.6 cm) the ascending velocity is no longer a strong function of the diameter. Levich's expression for velocity of medium-sized bubbles is applicable within the range $50 \leq \text{Re} \leq 800$, corresponding to diameters less than 0.2 cm. Above this range, $\text{Re} > 800$ to 1000, bubbles become erratic in motion and need not necessarily remain spherical. Levich (23) contends "at this stage the velocity of rise of bubbles is not a function of the bubble's dimensions. All sufficiently large bubbles rise at a velocity close to 30 cm/sec." Datta et al. (32) measured the rise velocity of air bubbles in water and for the range of larger bubble size found it to be between 24 to 30 cm/sec. Using an average rise velocity of 27 cm/sec and Froësling's correlation for mass transfer the effect on various bubble sizes was observed. The results in Figure 52 suggest that the
Figure 50. Effect of various lake depth; immobile interface
Figure 51. Effect of various lake depth; unhindered surface flow
Figure 52. Effect of larger bubble sizes; rigid bubble behavior
bubbles will expand slightly as they rise. The clustering of the curves in Figure 52 indicate that the effect of bubble size is less for bigger bubbles, unlike the effect observed for smaller bubbles. Also, for any given condition of the physical environment there must be an optimum bubble size, which will retain a constant diameter, balancing out primarily the effects due to hydrostatic pressure, mass transfer and temperature gradient.

In conclusion, the theoretical treatment on lake oxygenation has helped in identifying and estimating the relative significance of the effects of various parameters. The most important parameter in oxygen absorption from very small bubbles into water seem to be the level of surfactant contamination.
SUMMARY

Part I

The first part of the thesis is a report of an experimental investigation of the effect of surface active material on the rate of mass transfer in a reactive system. Three highly reactive cultures Acetobacter rancens, Acetobacter suboxydans and Acetobacter xylinum were tested for a system of glucose oxidation to gluconic acid at pH 6.1. Automatic titration with sodium hydroxide was employed to follow the rate of oxygen uptake. Values for the kinetics of the oxidation reaction, mass transfer coefficient without reaction and with reaction were obtained. Tsao's theoretical model of direct uptake by small reactive particles was verified by the manifold increase in the value for mass transfer coefficient. A comparison of the experimental values with Danckwerts' theoretical model for mass transfer indicated that existing theories of mass transfer for reactive systems were not adequate. A physical model is perceived in which the high concentration of the surface-active particles at the interface reduces the film thickness, allows spontaneous direct uptake of oxygen and also creates local turbulence, thereby explaining the increased values of mass transfer coefficients.
Part II

The second part of the thesis is a report of an experimental investigation of the effect of surface active material (sodium oleate) on the velocity of rise and the rate of dissolution of single oxygen bubbles in water. Pure, humidified single oxygen bubbles were timed accurately by an optoelectronic device along the rise path to obtain values for velocity. Mass transfer rates were calculated from the reduction in bubble volume observed from motion picture studies of the dissolving bubble. Great precaution was taken to purify the water and keep the experimental system clean.

The rise velocity decreased with height in pure water, but this tendency was diminished in contaminated systems. With simultaneous mass transfer in the presence of surfactants, the rise velocity increased slightly with height. By successively increasing the surfactant concentration, striking changes were observed for the average velocity results from three specific nozzles studied. Rise velocity was reduced from those of fluid sphere to those of rigid spheres. This effect was more pronounced for bubbles from smaller nozzles than larger nozzles. This observation is attributed to the stoppage of internal circulation of gas and increased drag on the rigid bubble surface due to the surfactant molecules agglomerating at the interface in a
particular polar orientation.

The values for mass transfer coefficient was higher for smaller bubbles than larger bubbles. Average mass transfer rates were found to decrease with increased surfactant concentration, the effect being more prominent for smaller bubbles. Especially in pure water, mass transfer rates decreased with height, but this tendency was reversed in contaminated systems. The retarding effect on the velocity due to simultaneous mass transfer of oxygen has been demonstrated. This effect is due to the interaction between the hydrodynamic and convective diffusion boundary layers. The importance of local hydrodynamics on mass transfer rates have been discussed and demonstrated.

A theoretical study of the oxygenation of a frozen lake by single oxygen bubbles has been conducted. Starting from fundamental analysis, a differential equation has been derived to describe the way bubble volume will vary due to hydrostatic pressure, temperature gradient and simultaneous mass transfer in clear and polluted systems. Several appropriate semi-empirical correlations for velocity and mass transfer have been used according to the state of the environment. Numerical solutions in graphical form indicate that the presence of surface active material makes a substantial effect in gas absorption for various bubble sizes and lake depths. As before, the hydrodynamic and mass
transfer phenomena are discussed with emphasis on the internal circulation of gas to explain the results.
RECOMMENDATIONS FOR FURTHER STUDY

Part I

1. Similar experiments may be conducted with reactive systems where \( t_r < t_d \), specifically to obtain experimentally a concentration profile \( s = s(x) \) of the surfactant material at the interface. The use of high-resolution microscopes or other sophisticated techniques may be necessary to examine the composition of the interfacial layer. With known kinetic relationship and \( s(x) \) the mathematical model can be rigorously tested.

Part II

1. The existing apparatus can be profitably used to study the effect of surface active catalysts in reactive systems. For example the formation of carbonic acid by reacting carbon dioxide gas from bubbles in pure water in the presence of varying amounts of carbonic anhydrase enzymes.

2. With slight modifications of the apparatus, better mass transfer measurements can be made by following the change in volume in a closed system due to dissolution of the bubbles. From such observations good estimates can be made of bubble size and interfacial area.
3. The hydrodynamic behavior of rising bubbles in pure and polluted systems would make an interesting study. With the facility of a rising movie camera, the bubble motion can be continuously followed and studied in detail on the EAI Variplotter described in the thesis. With the use of the opto-electronic device velocity of rise can be studied of gas bubbles of varying solubilities. The manner in which the diffusion boundary layer affects the hydrodynamic boundary layer can be observed.

4. It seems worthwhile to obtain a working relationship between the bubble size and the delayed sweep oscilloscope trace described in Appendix B. If a statistically valid correlation can be obtained, this method of estimating bubble size will prove to be most convenient and will also facilitate following the size variation with dissolution and rise of the bubble.


12. Freeman, R. S., III and G. T. Tsao, Submitted for publication in Biotechnology and Bioengineering.


41. Bond, W. N. and D. A. Newton, Philosophical Magazine 5: 794 (1928).

42. Whitman, W. G. Chemical and Metallurgical Engineering 29: 146 (1923).


56. Handlos, A. E. and T. Baron, American Institute of Chemical Engineers Journal 3: 127 (1957)


69. Sugden, S. Journal of the Chemical Society, 121: 858 (1922)

70. Sugden, S. Journal of the Chemical Society, 27 (1924)


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APPENDIX A

The electronic circuit associated with the opto-electronic device to measure the time taken by a rising bubble to cover each span of the column is shown in this section.

Figure 53 illustrates in a schematic form the logic circuit design and explains the sequence of functions performed during gate operation.

Figure 54 shows the actual patchwork made on cards contained in the Heath Analog Digital Designer unit. The lines represent connections between two connector points. All the cards and modules used have been identified.
Figure 53. Schematic diagram of the logic circuit design

Time taken for correct sequence of gate operation from OFF to ON = 22\(\mu\)sec. = 0.000022 sec.
Least count on DRM = 0.0001 sec.
Gate time is less than 1/4 of least count.
Time readings are acceptable.
Figure 54. Patchwork diagram of the electronic circuit associated with the opto-electronic device of time measurement

**Cards Used**

1. Breadboard Patch Card
2. 1-MHz Crystal Time Base Card
3. Comparator/V-F Card
4. Operational Amplifier Card
5. Top Layout of Card #1
6. Nand Gate Card
7. Gate and Overrange Card
8. Quad Monostable Card
9. Nand Gate Card
10. Quad DCU Card
11. Dual In Line IC Card
12. Dual In Line IC Card
13. Dual In Line IC Card
14. Dual In Line IC Card
15. Multiple Connector/Blank PC Card
16. Multiple Connector/Blank PC Card
17. Dual J-K Flip-Flop Card
18. Dual J-K Flip-Flop Card
19. Nand Gate Card
20. Multiple Connector/Blank PC Card

**Modules Used**

I. Digital Power Module
II. Digital Timing Module
III. Digital Readout Module
IV. Binary Information Module
APPENDIX B

In an attempt to design the experimental equipment preliminary studies were made on an improvised mockup. With two successive photocells relatively close together it was necessary to sweep rapidly in order to follow the bubble on the oscilloscope. By using the delayed-sweep option of the Tektronix 549 oscilloscope a much more detailed contour of the signal was noticed. Numerous trials showed that the detailed profile varied in size according to the size of the bubble - larger bubbles exhibited larger humps and smaller bubbles created smaller humps. There seemed to be a general trend developing between the area under the curve and the bubble size.

Figure 55 is an example of this technique applied to the main experimental column. The delay timer was actuated by the signal from the first photoconductor. The delay (1.5 secs) was long enough for the bubble to rise up to the second photoconductor when the rapid sweep (10 msec/cm) occurred, giving the detailed profile shown in the figure. With similar delayed-sweep mechanisms, the bubble size at each station can be stored in an overlapping fashion on the scope screen and the decrease (or increase) measured by the area under each curve.

Though it seemed theoretically sound, it was difficult
Figure 55. Photograph of oscilloscope trace showing the possibility of bubble size determination by "delayed rapid sweep" method
to reproduce experimentally the trace for the same bubble volume. This is mainly because of the general erratic behavior of the bubble in pure systems. Bubbles seem to rock, pulsate and spiral rather irregularly along its ascent. Depending upon the instantaneous configuration the shape of the trace will be different. This method was abandoned because of this difficulty. Although, in fairly contaminated systems, with less erratic bubble behavior, reproducibility of the scope trace was much better and could have been used.

It seems that by making sufficiently large number of observations for particular settings on the oscilloscope, a statistical evaluation can be made and perhaps a relationship can be established. This should be more applicable for rigid regular shaped objects such as glass beads or metal spheres.
APPENDIX C

1. Conversational Programming System (CPS) program to store bubble size data from paper tape to resident disk pack (RJEPAK).

2. FORTRAN IV program to sort raw data and determine bubble size and perform statistical analysis.
CPS PROGRAM

10. DECLARE PLTFLE FILE ENV( SPACE(TRK,20) ) ;
20. DECLARE COEFF(215) DEC(6);
30. PUT LIST('CPS DATA TO TAPE PROGRAM');
40. PUT LIST('ENTER PLOT DATA VIA TAPE READER');
50. NOPLOT=0;
60. NXTPLT: COEFF=0;
70. NOPLOT=N0PL0T+1;
80. ON ERROR GO TO ENDINP;
90. GET LIST(COEFF);
100. ENDINP: ON ERROR SYSTEM;
110. DO I=1 TO 212 WHILE(COEFF(I)]=0);
120. END ;
130. COEFF(213)=I-1;
140. IF COEFF(213)=0 THEN GO TO ENDJOB;
141. GET LIST(COEFF(214),COEFF(215));
142. /*READ TWO NUMBERS, THE FIRST IS THE NOZZLE NUMBER */;
143. /* THE SECOND IS THE CONTAMINATION LEVEL */;
144. /* THUS COEFF(214)=NOZZLE # ,COEFF(215)=CONT.LEVEL */;
150. WRITE FILE(PLTFLE) FROM(COEFF) ;
160. PUT LIST('RUN:',NOPLOT,' POINTS INPUTTED:',COEFF(213)
170. GO TO NXTPLT;
180. ENDJOB: PUT LIST('END OF COEFFICIENT FILE CREATION');
190. CLOSE FILE(PLTFLE) ;
200. PUT LIST('SUBMIT SCHEDULE ORDER');
210. STOP ;
C3100 JOB U3543, MUKERJEE FORTRAN IV PROGRAM

//STEP1 EXEC WATFIV
//GO.FT10F001 DD DSN=CPS14.U3543.PLTFILE,DISP=OLD
//GO.SYSIN DD *

$JOB U3543MUERJEE,TIME=10,PAGES=20

DIMENSION AA(215), XP(106), YP(106), X(106), Y(106)
DIMENSION A(25), B(25), E(25), AOS(25), IFLAG(25), FLAG(2)
DATA FLAG/' *','***'/
READ(10,10,END=100)AA

10 FORMAT(215A4)

C M1 IS THE NUMBER OF DATA ENTRIES IN THE INPUT VECTOR AA.
M1=AA(213)+0.5
C M2 IS THE NOZZLE NUMBER.
M2=AA(214)+0.5
C M3 IS THE CONTAMINATION LEVEL.
M3=AA(215)+0.5
C SEPARATING THE HORIZONTAL AND VERTICAL COMPONENTS OF POINTS.
N1=M1/2
DO 20 I=1,N1
XP(I)=AA(2*I-1)
YP(I)=AA(2*I)
C SUBTRACTING THE TRAILING 5 DUE TO THE VOLTMETER.
X(I)=XP(I)-5.
Y(I)=YP(I)-5.

C EVALUATING THE SCALE FACTOR DUE TO DISTORTION AND PARALLAX.
C ALL MEASUREMENTS ARE FINALLY RELATED TO THE 'BACK'SCALE,WITH THE 'MIDDLE'
C SCALE AS REFERENCE.
SCALE=(2.0/(Y(1)-Y(2)))*((Y(3)-Y(4))/(Y(5)-Y(6)))
C EVALUATING THE SEMI-MAJOR AXIS(A) AND SEMI-MINOR AXIS(B) OF THE
C OBLATE SPHEROID.
K=0
VSUM=0.0
ASUM=0.0
ESUM=0.0
VSQ = 0.0
ASQ = 0.0
FSQ = 0.0
PI = 22. / 7.

DO 30 J = 7, N1, 4
K = K + 1
A(K) = ((X(J) - X(J+1)) / 2.) * SCALE
B(K) = ((Y(J+2) - Y(J+3)) / 2.) * SCALF
IFLAG(K) = 1

C CHECK TO SEE IF THE BUBBLE IS FLIPPED.
C
IF(A(K) .GE. B(K)) GO TO 25
IFLAG(K) = 2
FLIP = B(K)
B(K) = A(K)
A(K) = FLIP

C EVALUATING THE ECCENTRICITY OF THE OBLATE SPHEROID (ELLIPSE)

25 F(K) = SQRT(1.0 - (B(K) / A(K))**2)

C EVALUATING THE VOLUME AND SURFACE AREA OF OBLATE SPHEROID.
VOS(K) = (4. / 3.) * PI * (A(K)**2) * B(K)
AOS(K) = (2. * PI * A(K)**2) + PI * (B(K)**2) / E(K) * ALOG((1. + E(K)) / (1. - E(K)))

C STATISTICAL ANALYSIS OF THE VARIATION IN VOLUME, SURFACE AREA AND
C ECCENTRICITY OF OBLATE SPHEROID, ASSUMING NORMAL DISTRIBUTION.
VSUM = VSUM + VOS(K)
ASUM = ASUM + AOS(K)
ESUM = ESUM + E(K)
VSQ = VSQ + VOS(K)**2
ASQ = ASQ + AOS(K)**2
FSQ = FSQ + E(K)**2

30 ESQ = ESQ + E(K)**2
MEAN, VARIANCE AND STANDARD DEVIATION.

OF VOLUME.
FK=K
VBAR=VSUM/FK
VVAR=V SQ/(FK-1.) - (V SUM**2)/((FK-1.)*FK)
VSTD=SQRT(VVAR)
VHI =VBAR+2.*VSTD
VLO =VBAR-2.*VSTD
IF(VLO.LE.0.0) VLO=0.0

OF SURFACE AREA.
ABAR=ASUM/FK
A VAR=ASQ/(FK-1.) - (ASUM**2)/((FK-1.)*FK)
ASTD=SQRT(AVAR)
AHI =ABAR+2.*ASTD
ALO=ABAR-2.*ASTD

OF ECCENTRICITY OF ELLIPSE.
EBAR=ESUM/FK
EV AR=ESQ/(FK-1.) - (ESUM**2)/((FK-1.)*FK)
ESTD=SQRT(EVAR)
EHI =EBAR+2.*ESTD
ELO =EBAR-2.*ESTD

THAT COMPLETES THE STATISTICAL ANALYSIS.

EVALUATING THE DIAMETER AND SURFACE AREA OF THE EQUIVALENT SPHERE.
DE=(VBAR*6./PI)**(1./3.)
DEP=(VHI*6./PI)**(1./3.)
DEM=(VLO*6./PI)**(1./3.)
ASE=PI*(DE**2)
ASEP=PI*(DEP**2)
ASEM=PI*(DEM**2)

WRITING ALL RELEVANT INFORMATION ABOUT BUBBLE MEASUREMENTS FOR THE PARTICULAR NOZZLE AND CONTAMINATION TREATMENT. ALSO PUNCHING OUT ON CARDS FOR FURTHER STATISTICAL EVALUATION.
WRITE(6,40) M2, M3, M1
40 FORMAT(1*1'I', 10X, 16HNOZZLE NUMBER = ,I4, 10X, 22HCONTAMINATION LEVEL =
  1, 13, 16X, 41HNUMBER OF DATA ENTRIES IN INPUT VECTOR = ,I4///51X, 24
  2HRAW DATA IN MILLIVOLTS/11X, 2H I, 27X, 4H X(I), 36X, 4H Y(I)///)
WRITE(7,200) M2, M3, M1
200 FORMAT(3I5)
WRITE(6,60) M2, SCALE, M3
60 FORMAT(1*, 10X, 16HNOZZLE NUMBER = ,I4, 21X, 17HSCALING FACTOR = ,1PF
  114.7, 17H(CMS./MILLIVOLTS), 3X, 22HCONTAMINATION LEVEL = ,12/)
WRITE(6,91)
91 FORMAT('0',40X,46HTHE EQUIVALENT SPHERE (VOS = VOLUME OF SPHERE)\/
 1/30X,25HEQUIVALENT DIAMETER, CMS.,15X,31HEQUIVALENT SURFACE AREA, S
 2Q.CMS.)
WRITE(6,92)DE,ASE
92 FORMAT('0',20X,4HMEAN,9X,F12.4,33X,F12.4)
WRITE(6,93)DEP,ASEP
93 FORMAT('0',20X,8HHIGH END,5X,F12.4,33X,F12.4)
WRITE(6,94)DEM,ASEM
94 FORMAT('0',20X,8HLOW END,5X,F12.4,33X,F12.4)
WRITE(7,203)DE,DEP,DEM,ASE,ASEP,ASEM
203 FORMAT(6F12.4)
100 STOP
APPENDIX D

Stormer viscometer calibration using standard glycerol solution.

Figure 56 shows the variation in viscosity of standard glycerol solution with specific gravity. The data for this plot are obtained from the Stormer viscometer manual (71).

Figure 57 is the required calibration curve for the viscometer relating time for 100 revolutions to the absolute viscosity.

Linear regression on the data yields the equation,

\[ \mu = (0.022) \theta - 7.4 \times 10^{-4} \]

where, \( \mu \) represents absolute viscosity in cp. and \( \theta \) represents time for 100 revolutions in sec.
Figure 56. Variation of viscosity with specific gravity of standard glycerol solution
Figure 57. Stormer viscometer calibration curve
APPENDIX E

In this section experimental data are arranged in tabular form. All tables are appropriately identified. Also, examples of statistical analysis appear in this appendix.
Table 6a. Experimental data: velocity, $\frac{\text{cms}}{\text{sec}}$ (without mass transfer)

<table>
<thead>
<tr>
<th>Run No. VxClN101</th>
<th>Nozzle I.D. 0.173&quot;</th>
<th>Na Oleate 0 ppm</th>
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<tr>
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<th>Na Oleate 0 ppm</th>
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### Table 6a (Continued)

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<th>Na Oleate 5 ppm conc.</th>
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</thead>
<tbody>
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### Table 6a (Continued)

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Table 6b. Experimental data: velocity, \( \text{cm/s} \) (with mass transfer)

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<th>Run No. MxC1N101</th>
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Table 6b (Continued)

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<th>Na Oleate 15 ppm conc.</th>
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Table 6b (Continued)

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Table 7. Span average $K^o_L$, cm/sec for various nozzles at various contamination levels

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<td>0.0430</td>
<td>0.0431</td>
</tr>
<tr>
<td>Sodium</td>
<td>0.173</td>
<td>0.0313</td>
<td>0.0313</td>
<td>0.0314</td>
<td>0.0314</td>
<td>0.0316</td>
<td>0.0321</td>
</tr>
<tr>
<td>Oleate</td>
<td>0.085</td>
<td>0.0353</td>
<td>0.0357</td>
<td>0.0359</td>
<td>0.0359</td>
<td>0.0359</td>
<td>0.0366</td>
</tr>
<tr>
<td>120 ppm</td>
<td>0.023</td>
<td>0.0425</td>
<td>0.0425</td>
<td>0.0426</td>
<td>0.0429</td>
<td>0.0429</td>
<td>0.0435</td>
</tr>
</tbody>
</table>
Table 8. Effect of sodium oleate concentration on equivalent bubble diameter (spherical)

<table>
<thead>
<tr>
<th>Sodium Oleate conc. M</th>
<th>Sodium Oleate conc. ppm</th>
<th>Equivalent bubble diameter, cms.</th>
<th>Nozzle ID</th>
<th>Nozzle ID</th>
<th>Nozzle ID</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.173 in.</td>
<td>0.085 in.</td>
<td>0.023 in.</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0.5814</td>
<td>0.4881</td>
<td>0.3069</td>
<td></td>
</tr>
<tr>
<td>3.93 x 10^{-6}</td>
<td>1.2</td>
<td>0.5681</td>
<td>0.4515</td>
<td>0.2945</td>
<td></td>
</tr>
<tr>
<td>1.65 x 10^{-5}</td>
<td>5.0</td>
<td>0.5499</td>
<td>0.4175</td>
<td>0.2813</td>
<td></td>
</tr>
<tr>
<td>4.93 x 10^{-5}</td>
<td>15.0</td>
<td>0.5374</td>
<td>0.4205</td>
<td>0.2931</td>
<td></td>
</tr>
<tr>
<td>1.97 x 10^{-4}</td>
<td>60.0</td>
<td>0.4768</td>
<td>0.3984</td>
<td>0.2557</td>
<td></td>
</tr>
<tr>
<td>3.29 x 10^{-4}</td>
<td>100.0</td>
<td>0.4787</td>
<td>0.4036</td>
<td>0.2831</td>
<td></td>
</tr>
<tr>
<td>3.94 x 10^{-4}</td>
<td>120.0</td>
<td>0.4759</td>
<td>0.3662</td>
<td>0.2467</td>
<td></td>
</tr>
<tr>
<td>1.64 x 10^{-3}</td>
<td>500.0</td>
<td>0.4166</td>
<td>0.3199</td>
<td>0.2042</td>
<td></td>
</tr>
</tbody>
</table>
Table 9. Experimental data for velocity runs (no mass transfer)

<table>
<thead>
<tr>
<th>Nozzle ID</th>
<th>Viscosity, µ, cp</th>
<th>Density, ρ, gm/ml</th>
<th>Conductivity, µmhos/cm</th>
<th>Surface tension, γ, dynes/cm</th>
<th>Temp., T, °C</th>
<th>Dissolved oxygen conc., ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na 0.173</td>
<td>0.923</td>
<td>0.982</td>
<td>10.90</td>
<td>72.96</td>
<td>24.09</td>
<td>36 47 42</td>
</tr>
<tr>
<td>Oleate 0.085</td>
<td>0.925</td>
<td>0.984</td>
<td>11.83</td>
<td>73.30</td>
<td>23.94</td>
<td>45 46 46</td>
</tr>
<tr>
<td>0 ppm</td>
<td>0.023</td>
<td>0.934</td>
<td>8.43</td>
<td>72.96</td>
<td>23.77</td>
<td>39 41 38</td>
</tr>
<tr>
<td>Na 0.173</td>
<td>0.927</td>
<td>0.983</td>
<td>7.66</td>
<td>71.62</td>
<td>23.90</td>
<td>37 38 37</td>
</tr>
<tr>
<td>Oleate 0.085</td>
<td>0.927</td>
<td>0.983</td>
<td>4.13</td>
<td>72.33</td>
<td>23.65</td>
<td>36 35 36</td>
</tr>
<tr>
<td>1.2 ppm</td>
<td>0.023</td>
<td>0.942</td>
<td>7.43</td>
<td>71.22</td>
<td>23.80</td>
<td>36 38 36</td>
</tr>
<tr>
<td>Na 0.173</td>
<td>0.921</td>
<td>0.984</td>
<td>4.60</td>
<td>69.31</td>
<td>23.78</td>
<td>37 36 36</td>
</tr>
<tr>
<td>Oleate 0.085</td>
<td>0.933</td>
<td>0.984</td>
<td>5.47</td>
<td>70.64</td>
<td>23.82</td>
<td>35 36 35</td>
</tr>
<tr>
<td>5 ppm</td>
<td>0.023</td>
<td>0.926</td>
<td>4.30</td>
<td>68.61</td>
<td>23.83</td>
<td>36 37.5 35</td>
</tr>
<tr>
<td>Na 0.173</td>
<td>0.954</td>
<td>0.984</td>
<td>21.83</td>
<td>61.89</td>
<td>24.00</td>
<td>30 37 34</td>
</tr>
<tr>
<td>Oleate 0.085</td>
<td>0.950</td>
<td>0.984</td>
<td>21.83</td>
<td>67.52</td>
<td>23.93</td>
<td>34 40 34</td>
</tr>
<tr>
<td>100 ppm</td>
<td>0.023</td>
<td>0.966</td>
<td>22.17</td>
<td>62.19</td>
<td>23.88</td>
<td>33 38 33</td>
</tr>
<tr>
<td>Na 0.173</td>
<td>0.932</td>
<td>0.983</td>
<td>93.00</td>
<td>29.81</td>
<td>24.02</td>
<td>-a 35-a</td>
</tr>
<tr>
<td>Oleate 0.085</td>
<td>0.922</td>
<td>0.984</td>
<td>93.00</td>
<td>31.21</td>
<td>23.83</td>
<td>-a 37-a</td>
</tr>
<tr>
<td>500 ppm</td>
<td>0.023</td>
<td>0.921</td>
<td>93.33</td>
<td>29.16</td>
<td>23.77</td>
<td>37 37.5-a</td>
</tr>
</tbody>
</table>

*aNo reading due to formation of black precipitate.
Table 10. Experimental data for mass transfer runs

<table>
<thead>
<tr>
<th>Nozzle ID</th>
<th>Viscosity, μ, cp</th>
<th>Density, ρ, gm/ml</th>
<th>Conductivity, µhos/cm</th>
<th>Surface tension, γ, dynes/cm</th>
<th>Temp., T, °C</th>
<th>Dissolved oxygen conc., ppm Winkler DO Meter (after run)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na 0.173</td>
<td>0.955</td>
<td>0.984</td>
<td>10.60</td>
<td>69.07</td>
<td>25.1</td>
<td>0.80 0.04 0.60</td>
</tr>
<tr>
<td>Oleate 0.085</td>
<td>0.946</td>
<td>0.984</td>
<td>9.15</td>
<td>69.07</td>
<td>24.8</td>
<td>0.35 0.02 0.45</td>
</tr>
<tr>
<td>0 ppm</td>
<td>0.023</td>
<td>0.952</td>
<td>7.00</td>
<td>69.07</td>
<td>0.70</td>
<td>0.05 0.90 0.10</td>
</tr>
<tr>
<td>Na 0.173</td>
<td>0.933</td>
<td>0.984</td>
<td>4.45</td>
<td>68.08</td>
<td>0.75</td>
<td>0.10 0.02 0.60</td>
</tr>
<tr>
<td>Oleate 0.085</td>
<td>0.933</td>
<td>0.984</td>
<td>4.15</td>
<td>69.39</td>
<td>0.25</td>
<td>0.05 0.02 0.15</td>
</tr>
<tr>
<td>5 ppm</td>
<td>0.023</td>
<td>0.937</td>
<td>4.05</td>
<td>69.06</td>
<td>0.90</td>
<td>0.03 0.25</td>
</tr>
<tr>
<td>Na 0.173</td>
<td>0.955</td>
<td>0.984</td>
<td>6.35</td>
<td>68.74</td>
<td>0.75</td>
<td>0.05 0.04 0.35</td>
</tr>
<tr>
<td>Oleate 0.085</td>
<td>0.950</td>
<td>0.984</td>
<td>6.35</td>
<td>68.41</td>
<td>0.25</td>
<td>0.05 0.02 0.15</td>
</tr>
<tr>
<td>15 ppm</td>
<td>0.023</td>
<td>0.943</td>
<td>6.65</td>
<td>67.43</td>
<td>0.90</td>
<td>0.03 0.25</td>
</tr>
<tr>
<td>Na 0.173</td>
<td>0.952</td>
<td>0.984</td>
<td>14.45</td>
<td>65.79</td>
<td>0.70</td>
<td>0.05 0.05 0.25</td>
</tr>
<tr>
<td>Oleate 0.085</td>
<td>0.946</td>
<td>0.984</td>
<td>14.85</td>
<td>65.79</td>
<td>0.55</td>
<td>0.07 0.35</td>
</tr>
<tr>
<td>60 ppm</td>
<td>0.023</td>
<td>0.947</td>
<td>14.90</td>
<td>63.17</td>
<td>0.60</td>
<td>0.03 0.25</td>
</tr>
<tr>
<td>Na 0.173</td>
<td>0.942</td>
<td>0.984</td>
<td>27.00</td>
<td>52.04</td>
<td>0.55</td>
<td>0.03 0.35</td>
</tr>
<tr>
<td>Oleate 0.085</td>
<td>0.938</td>
<td>0.984</td>
<td>26.00</td>
<td>50.08</td>
<td>0.30</td>
<td>0.02 0.25</td>
</tr>
<tr>
<td>120 ppm</td>
<td>0.023</td>
<td>0.931</td>
<td>26.00</td>
<td>50.41</td>
<td>0.30</td>
<td>0.03 0.30</td>
</tr>
</tbody>
</table>

*a* No reading due to formation of Black precipitate.
Table 11. Summary of experimental data for mass transfer correlation

<table>
<thead>
<tr>
<th>Nozzle</th>
<th>Average diameter</th>
<th>Reduction in volume</th>
<th>Average $K_L$</th>
<th>Nu</th>
<th>Re</th>
<th>Sc</th>
<th>$\gamma^*$ (=\gamma/\mu u)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ID in.</td>
<td>D, cm.</td>
<td>$\Delta V$, cm.$^3$</td>
<td>K$_L^{\circ}$ cm/sec ($\times 10^2$)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>0.173</td>
<td>0.5365</td>
<td>0.0225</td>
<td>14.63</td>
<td>3926</td>
<td>1252</td>
<td>485</td>
</tr>
<tr>
<td>Oleate</td>
<td>0.085</td>
<td>0.4055</td>
<td>0.0043</td>
<td>7.84</td>
<td>1589</td>
<td>982</td>
<td>480</td>
</tr>
<tr>
<td>0 ppm</td>
<td>0.023</td>
<td>0.2786</td>
<td>0.0037</td>
<td>9.52</td>
<td>1327</td>
<td>680</td>
<td>484</td>
</tr>
<tr>
<td>Na</td>
<td>0.173</td>
<td>0.5176</td>
<td>0.0089</td>
<td>9.11</td>
<td>2357</td>
<td>1090</td>
<td>474</td>
</tr>
<tr>
<td>Oleate</td>
<td>0.085</td>
<td>0.4102</td>
<td>0.0054</td>
<td>7.95</td>
<td>1631</td>
<td>854</td>
<td>474</td>
</tr>
<tr>
<td>5 ppm</td>
<td>0.023</td>
<td>0.2761</td>
<td>0.0029</td>
<td>6.96</td>
<td>962</td>
<td>566</td>
<td>476</td>
</tr>
<tr>
<td>Na</td>
<td>0.173</td>
<td>0.5190</td>
<td>0.0156</td>
<td>11.83</td>
<td>3072</td>
<td>1109</td>
<td>485</td>
</tr>
<tr>
<td>Oleate</td>
<td>0.085</td>
<td>0.4049</td>
<td>0.0080</td>
<td>9.67</td>
<td>1959</td>
<td>856</td>
<td>482</td>
</tr>
<tr>
<td>15 ppm</td>
<td>0.023</td>
<td>0.2871</td>
<td>0.0016</td>
<td>4.90</td>
<td>703</td>
<td>584</td>
<td>479</td>
</tr>
<tr>
<td>Na</td>
<td>0.173</td>
<td>0.4691</td>
<td>0.0054</td>
<td>6.58</td>
<td>1544</td>
<td>901</td>
<td>484</td>
</tr>
<tr>
<td>Oleate</td>
<td>0.085</td>
<td>0.3791</td>
<td>0.0087</td>
<td>9.69</td>
<td>1837</td>
<td>726</td>
<td>481</td>
</tr>
<tr>
<td>60 ppm</td>
<td>0.023</td>
<td>0.2542</td>
<td>0.0004</td>
<td>2.87</td>
<td>365</td>
<td>483</td>
<td>481</td>
</tr>
<tr>
<td>Na</td>
<td>0.173</td>
<td>0.4659</td>
<td>0.0069</td>
<td>7.10</td>
<td>1654</td>
<td>876</td>
<td>478</td>
</tr>
<tr>
<td>Oleate</td>
<td>0.085</td>
<td>0.3546</td>
<td>0.0046</td>
<td>10.46</td>
<td>1856</td>
<td>665</td>
<td>477</td>
</tr>
<tr>
<td>120 ppm</td>
<td>0.023</td>
<td>0.2417</td>
<td>0.0010</td>
<td>3.71</td>
<td>448</td>
<td>440</td>
<td>473</td>
</tr>
</tbody>
</table>
Table 12a. Example of T-statistic table for span average velocity of rise (Null hypothesis $H_0: \bar{u}_1 = \bar{u}_2 = \bar{u}_3 = \bar{u}_4 = \bar{u}_5 = \bar{u}_6$) 

<table>
<thead>
<tr>
<th>Nozzle I.D.</th>
<th>$T_{n,0.05}$</th>
<th>$T_n$ (calculated)</th>
<th>Span average velocities compared</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.023 in., n=42</td>
<td>1.684</td>
<td>28.82</td>
<td>1 and 6</td>
</tr>
<tr>
<td></td>
<td>1.684</td>
<td>7.623</td>
<td>1 and 2</td>
</tr>
<tr>
<td></td>
<td>1.684</td>
<td>7.503</td>
<td>2 and 3</td>
</tr>
<tr>
<td></td>
<td>1.684</td>
<td>3.031</td>
<td>3 and 4</td>
</tr>
<tr>
<td></td>
<td>1.684</td>
<td>4.419</td>
<td>5 and 6</td>
</tr>
<tr>
<td>0.085 in., n=50</td>
<td>1.675</td>
<td>14.210</td>
<td>1 and 5</td>
</tr>
<tr>
<td></td>
<td>1.675</td>
<td>4.355</td>
<td>1 and 2</td>
</tr>
<tr>
<td></td>
<td>1.675</td>
<td>3.987</td>
<td>2 and 3</td>
</tr>
<tr>
<td></td>
<td>1.675</td>
<td>3.324</td>
<td>5 and 6</td>
</tr>
<tr>
<td></td>
<td>1.675</td>
<td>2.350</td>
<td>4 and 5</td>
</tr>
<tr>
<td>0.173 in., n=40</td>
<td>1.684</td>
<td>9.952</td>
<td>1 and 6</td>
</tr>
<tr>
<td></td>
<td>1.684</td>
<td>2.862</td>
<td>1 and 2</td>
</tr>
<tr>
<td></td>
<td>1.684</td>
<td>2.358</td>
<td>3 and 4</td>
</tr>
<tr>
<td></td>
<td>1.684</td>
<td>3.022</td>
<td>2 and 4</td>
</tr>
<tr>
<td></td>
<td>1.684</td>
<td>3.172</td>
<td>5 and 6</td>
</tr>
</tbody>
</table>

\(^a\)This table indicates the T-statistic to lie in the critical region, the null hypothesis is therefore rejected.
<table>
<thead>
<tr>
<th>Runs</th>
<th>(Volume) Variance, $S^2$</th>
<th>Standard Error (Individual)</th>
<th>Standard Error (Mean)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Volume cm$^3$</td>
<td>Eq. Dia., cm.</td>
</tr>
<tr>
<td>Velocity</td>
<td>$13.25 \times 10^{-5}$</td>
<td>$11.51 \times 10^{-3}$</td>
<td>$1.43 \times 10^{-2}$</td>
</tr>
<tr>
<td>Mass Transfer</td>
<td>$6.55 \times 10^{-5}$</td>
<td>$8.09 \times 10^{-3}$</td>
<td>$1.01 \times 10^{-3}$</td>
</tr>
</tbody>
</table>
APPENDIX F

1. FORTRAN IV program for numerical solution of Equation (141)

2. FORTRAN IV program for numerical solution of Equation (157) (dimensionless parameter approach).
DOUBLE PRECISION FUNCTION VFUN(UK, PIV, V, TWT)

DOUBLE PRECISION UK, PIV, TWT

REAL DIAM(5) / 0.2, 0.3, 0.4, 0.5, 0.6/, VL(5) / 30.0, 30.0, 27.0, 25.0, 24.0 /

IF(O.GE.0.19) GO TO 10
VFUN = UK*PIV*(V**TWT)
RETURN

10 IF(O.LT.0.6) GO TO 20
VFUN = 24.0
RETURN

20 DO 900 I=1,5
IF(O.GT.DIAM(I)) GO TO 900
VFUN = VL(I)
RETURN

900 CONTINUE
VFUN = VL(5)
RETURN

END

SUBROUTINE BUBBLE

DOUBLE PRECISION UK, VEL

DIMENSION X(1000), D(1000), AR(1000), VR(1000)

DIMENSION PR(1000), TEMP(1000), BR1(1000), BR2(1000), BR3(1000)

DIMENSION VEL(1000), FKL(1000), CSTAR(1000)

LIST ALL THE PHYSICAL CONSTANTS AND PROPERTIES HELD CONSTANT UNDER ONE COMMON STATEMENT

COMMON/CONST/UK, G, GC, R, RO, FMU, DIF, PO, TEMPO, B, CL, RHOG, Sdif, SKL

COMMON/PASS/VEL, N, X, VR, AR, D, PR, TEMP, BR1, BR2, BR3, FKL, CSTAR

EVALUATE TOTAL PRESSURE AT DEPTH X(N)

PR(N) = PO + RHOG*X(N)
C        EVALUATE TEMPERATURE AT DEPTH X(N)
        TEMP(N) = TEMPO+B*X(N)
C        EVALUATE SQUARE BRACKET BR1 AT DEPTH X(N)
        BR1(N) = RHOG/PR(N)
C        EVALUATE SQUARE BRACKET BR2 AT DEPTH X(N)
        BR2(N) = B/TEMP(N)
C        EVALUATE SATURATION CONC. AT NEW TEMPERATURE
        POWER = -0.024545*TEMP(N)
        CSM = 5.647008E+04*(EXP(Power)) 1.E-06/32.0
C        EFFECT OF PRESSURE ON CSTAR.
        CSTAR(N) = CSM*(PR(N)/PO)
C        EVALUATE SQUARE BRACKET BR3 AT DEPTH X(N)
        BR3(N) = R*(CSTAR(N)-CL)*TEMP(N)/PR(N)
C        EVALUATE MASS TRANSFER COEFFICIENT AT DEPTH X(N)
C        FROESSLING'S CORRELATION
        FKL(N) = SDIF/D(N) + SKL*((VEL(N)/D(N))**0.5)
RETURN
END

C        ANALYSIS OF A SINGLE OXYGEN BUBBLE RISING IN LAKE WATER
C        FOR THE PRESENT ASSUME PHYSICAL PROPERTIES TO BE CONSTATE (RO,MU,DIF,CL)
C        PRESSURE, TEMPERATURE, VELOCITY, CSTAR, KL, AREA ARE ASSUMED CONSTANT OVER
C        TEN BUBBLE DIAMETERS.

C        DOUBLE PRECISION V,B1,B2,B3,FKL,A,U,DX,DVDX,AK1,AK2,AK3,AK4,
1        PIA,UK,PIV,VCF,TWT,VEL,VFUN
DIMENSION X(1000),D(1000),AR(1000),VR(1000)
DIMENSION PR(1000),TEMP(1000),BR1(1000),BR2(1000),BR3(1000)
DIMENSION VEL(1000),FKLR(1000),CSTAR(1000)
DIMENSION DELD(50),DEPTH(50)
DIMENSION XLAB(5), YLAB(5), GLAB(5), DATLAB(5)

LIST ALL THE PHYSICAL CONSTANTS AND PROPERTIES HELD CONSTANT UNDER ONE COMMON STATEMENT

COMMON/CONST/UK, G, GC, R, RO, FMU, DIF, PO, TEMPO, B, CL, RHOG, SDIF, SKL

COMMON/PASS/VEL, N, X, VR, AR, D, PR, TEMP, BR1, BR2, BR3, FKL, CSTAR

DEFINE FUNCTION TO BE INTEGRATED LATER IN THE MAIN PROGRAMME

DVDX(V) = (-V*B1) + (V*B2) + (FKL*B3*PIA/U)*(V**TWT)

READ IN THE VALUES OF ALL THE PHYSICAL CONSTANTS AND OTHER PROPERTIES HELD CONSTANT

READ(5,10) G, GC, RO, FMU, CL, FMU0

10 FORMAT(6F10.6)

R=82.06*1.0133E+06

DIF=2.0E-05

READ IN PRESSURE, TEMP. AT X=0

READ(5,15) TEMPO, B

15 FORMAT(2F10.6)

PO=1.0133E+06

EVALUATE CERTAIN LUMPED PARAMETERS WHICH WILL REMAIN CONSTANT

RHOG=(RO*G)/GC

UK =(RO*G)/(36.0*FMU)

PI =3.1415926536

ONT =1.0/3.0

TWT =2.0/3.0

ONS =1.0/6.0

PID =(6.0/PI)**ONT

PIA = (PI**ONT)*(6.0**TWT)

PIV = (6.0/PI)**TWT
SDIF=2.0*DIF
SKL =0.552*(DIF**TWT)*((RO/FMU)**ONS)
C READ IN THE CONSTANT DISTANCE OF ITERATION DELX, IN WHICH PHYSICAL
C PARAMETERS ARE ASSUMED CONSTANT
READ(5,35) DELX
35 FORMAT(F10.6)
C READ IN THE NUMBER OF RUNGE-KUTTA INTEGRATION STEPS TO BE EXECUTED
C WITHIN THE DISTANCE DELX
READ(5,40) NX
40 FORMAT(I4)
C EVALUATE INCREMENT IN X FOR EACH INTEGRATION STEP
C INCREMENT IN X IS NEGATIVE, SINCE THE BUBBLE IS RISING OPPOSITE TO THE
C POSITIVE X-DIRECTION.
C
DX = -(DELX/NX)
C
C READ IN INITIAL DEPTH AND DIAMETER OF BUBBLE
C
READ(5,20) X(I)
20 FORMAT(F10.6)
D(I) = 0.10
C
KS = 6
XSIZE = 10.0
MODE = 20
READ(5,106)XLAB,YLAB,GLAB,DATLAB
106 FORMAT(20A4)
DO 400 M=1,5,1
D(I) = D(I)+0.10
C
C INTEGER N KEEPS COUNT OF THE SEQUENTIAL JUMP OF THE BUBBLE AS IT RISES
C SO N IS A MARKER ON THE DEPTH OR STRATUM
C
N=1
EVALUATE INITIAL SURFACE AREA AND VOLUME OF BUBBLE

\[
AR(N) = \pi \times (D(N)^2) \\
VR(N) = \frac{\pi}{6} \times (D(N)^3) \\
V = VR(N)
\]

EVALUATE INITIAL (RIGID SPHERE) VELOCITY OF BUBBLE.

\[
VEL(N) = VFUNKUK, PI, V, TWT, D(N))
\]

WRITE(6,25)

25 FORMAT('1',32X,55HANALYSIS OF A SINGLE OXYGEN BUBBLE RISING IN LAK
1E WATER//41X,38HHWITH SIMULTANEOUS ABSORPTION OF OXYGEN//)

WRITE(6,26)

26 FORMAT('0',9X,99HNOTE: 1. VOLUME OF BUBBLE IS NUMERICALLY INTEGRA
1TED FOR EACH ADVANCE EQUAL TO ONE BUBBLE DIAMETER.//16X,94H2. PHY
2SICAL PROPERTIES OF THE SYSTEM ARE ASSUMED CONSTANT OVER TEN BUBBL
3E DIAMETERS DISTANCE.///)

WRITE(6,27)

27 FORMAT('0',10X,14HSTRATA COUNTER,5X,16HDEPTH OF STRATUM,5X,18HDIAM
1ETER OF BUBBLE,4X,22HSURFACE AREA OF BUBBLE,10X,16HVOLUME OF BUBBL
2E/17X,1HN,14X,12HXIN CMS.,10X,12HD(N) IN CMS.,10X,16HAR(N) IN
3SQ.CMS.,13X,16HV(R(N) IN CU.CMS.)

WRITE(6,30) N,X(N),0(N),AR(N),VR(N)

30 FORMAT('0',10X,17,13X,F11.4,9X,F14.8,6X,F18.8,12X,F17.8)

NOW EMPLOY SUBROUTINE 'BUBBLE' TO EVALUATE ALL PARAMETERS NECESSARY FOR
INTEGRATION AT EACH ITERATION OF DEPTH 'x'.

5 CONTINUE

CALL BUBBLE

CONVERT THE PERTINENT VECTORS EVALUATED IN 'BUBBLE' INTO SCALARS

\[
V = VR(N) \\
B1 = BR1(N) \\
B2 = BR2(N) \\
B3 = BR3(N) \\
FKL = FKL(N) \\
U = VEL(N)
\]
RUNGE-KUTTA INTEGRATION STEP FOLLOWS, INTEGRATING VOLUME WITH RESPECT TO X

DO 1 I=1,NX
    AK1 = DX*DVDX(V)
    AK2 = DX*DVDX(V+AK1/2.DO)
    AK3 = DX*DVDX(V+AK2/2.DO)
    AK4 = DX*DVDX(V+AK3)
    V = V+(AK1+2.DO*AK2+2.DO*AK3+AK4)/6.DO
    IF(V.LE.0.0) GO TO 32
1 CONTINUE

MOVE MARKER UP TO NEW STRATUM AND STORE NEW DIA., AREA AND VOLUME OF BUBBLE

N = N+1
X(N) = X(N-1)-DELX
VR(N) = V

EVALUATE NEW DIAMETER AND SURFACE AREA OF BUBBLE AT DEPTH X(N).
D(N) = PHI*(V**ONT)
AR(N) = PI*V**TWT

EVALUATE NEW RIGID SPHERE VELOCITY OF BUBBLE AT DEPTH X(N); LEVICH PAGE 446
VEL(N) = VFUN(UK,PIV,V,TWT,D(N))

WRITE(6,31) N,X(N),D(N),AR(N),VR(N)
31 FORMAT(' ',9X,10X,17,13X,F11.4,9X,F14.8,6X,F18.8,12X,F17.8)

CHECK TO SEE IF THE BUBBLE HAS REACHED THE TOP OF THE LAKE

IF(ABS(X(N)) .GT. 0.0) GO TO 5
CALL BUBBLE

WRITE DOWN THE VALUES OF PARAMETERS AT EACH STRATUM.

WRITE(6,50)
50 FORMAT(' ',1X,9X,6X,11HSTRAVA,6X,11HPRESSURE IN,10X,14HTEMPERATURE IN,12X
1,11HVELOCITY IN,12X,8HCSTAR IN,15X,5HKL IN/12X,1HN,9X,12HDYNES/SQ.
2CM.,13X,5HDEG.K,18X,9HCMS./SEC.,11X,13HGM.MOLES/C.C.,10X,9HCMS./SE
3C./)
WRITE(6,55)(K,PR(K),TEMP(K),VEL(K),CSTAR(K),FKLR(K),K=1,N)
55 FORMAT(* ',I12,7X,1PE14.7,12X,0PF8.4,16X,F8.4,10X,1PE15.8,8X,1PE14
1.7)

C
C PLOT PROGRAM FOR PERCENT EXPANSION VS DIMENSIONLESS DEPTH.
C L IS A COUNTER FOR PERCENT EXPANSION POINTS.
L = 1
DEPT(L) = (X(1)/X(1))*100.0
DELD(L) = 0.0
CENT = 1.0
DO 101 J=2,N,1
RD = (D(J)-D(1))/D(1))*100.0
IF(ABS(RD).LT.CENT) GO TO 101
L=L+1
DEPT(L) = (X(J)/X(1))*100.0
DELD(L) = RD
CENT = CENT+1.0
101 CONTINUE
WRITE(6,104)
104 FORMAT(* ',14X,1HK,15X,16HPERCENT.EXPANDED,14X,1HDEPTH RATIO//)
WRITE(6,105)(K,DELD(K),DEPT(K),K=1,L)
105 FORMAT(* '0',10X,15,15X,F10.2,20X,F9.3)
IF(L.LE.1) GO TO 110
IF(L.LT.7) MODE=101
CALL GRAPH(L,DELD,DEPT,KS,MODE,XSIZE,10.0,10.0,0.0,10.0,0.0,XLAB,
1YLAB,GLAB,DATLAB)
C
KS = KS+1
XSIZE = 0.0
MODE = 120
READ(5,106,END=110) DATLAB
400 CONTINUE
110 CONTINUE
STOP
END
ENTRY
$STOP
C310D JOB 'U3543,TTME=4,SIZF=128K',MUKERJFF,TTME=3 1. Numerical solution
//STEP1 EXEC WATFIV,REGION.GO=128K
//GO.SYSTN DD *
$JOB U3543MUKERJFF,TIME=80,PAGES=100
C SINGLE BUBBLE ANALYSIS IN DIMENSIONLESS FORM.
C SYSTEM PARAMETERS TO BE SUPPLIED ARE:
C 1. LAKE DEPTH
C 2. TEMPERATURE PROFILE
C 3. RATE OF BIOLOGICAL OXYGEN DEMAND
C 4. POLLUTANT CONCENTRATION (EFFECT ON MASS TRANSFER AND VELOCITY)
C DOUBLE PRECISION DZ,DPDZ,Z,PHI,AK1,AK2,AK3,AK4,ALPHA, BETA, GAMA,
   DELTA, VR, AR, D, VO, PIA, PID, TWT, ONT
DIMENSION PHIR(150),ZR(150)
DIMENSION D(150),AR(150),VR(150)
DIMENSION FNUC20>,GAMAR(20),DELTAR(20)
DIMENSION XLAB(5),YLAB(5),GLAB(5),DATLAB(5)
C
C DEFINE FUNCTION TO BE INTEGRATED LATER IN THE PROGRAMME
OPPZ(Z,PHI) =-PHI/(ALPHA+Z) + PHI/(BETA+Z) + (BETA+Z)/(GAMA+DELTA+Z)
C
C READ IN THE VALUES OF ALL PHYSICAL CONSTANTS AND OTHER PROPERTIES HELD
C CONSTANT
READ(5,10) G,GC,RO,FMU,CL,FMUO
10 FORMAT(6F10.6)
   R = 82.06*1.0133E+06
   DIF = 2.0E-05
C
C READ IN AMBIENT PRESSURE AND TEMPERATURE AT TOP OF LAKE
READ(5,15) TEMPO
15 FORMAT(F10.6)
   PD = 1.0133E+06
C
C EVALUATE CERTAIN LUMPED PARAMETERS THAT WILL REMAIN CONSTANT
C
PI = 3.1415926536
ONT = 1.0/3.0
ONS= 1.0/6.0
TWT= 2.0/3.0
PID= (6.0/PI)**ONT
PIA= (PI**ONT)*(6.0**TWT)
PIV= (6.0/PI)**TWT
RHOG = (RO*G)/GC

C HADAMARD-RYBCZYNKSI CORRECTION FOR INTERNAL CIRCULATION IN BUBBLE.
C

VCF = (3.0*FMU+3.0*FMU0)/(2.0*FMU+3.0*FMU0)

READ(5,25) XLAB,YLAB,GLAB,DATLAB

25 FORMAT(20A4)
KS = 5
MODE = 20
XSIZ= = 10.0
CALL ORIGIN(0.5,9.5,6)

C
DO 400 I=1,6,1
C
READ IN LAKE DEPTH AND TEMPERATURE GRADIENT
READ(5,20) FL,B

20 FORMAT(2F10.6)
C
EVALUATE SATURATION CONCENTRATION AT AVERAGE TEMP. AND PRESSURE
POWER = -0.024545*(TEMPO+B*FL/2.)
CSM = 5.647008E+04*(EXP(POWER))*1.E-06/32.0
CSTAR = CSM*((PO+RHOG*FL/2.)/PO)

C EVALUATE PARAMETERS ALPHA AND BETA (CONSTANT FOR EACH LAKE DEPTH)
C
ALPHA = PO/(FL*RHOG)
BETA = TEMPO/(FL*B)

C READ IN INITIAL DIAMETER OF BUBBLE AT BOTTOM OF LAKE
D(1) = 0.10
AR(1) = PI*(D(1)**2.0)
VR(1) = PI*(D(1)**3.0)/6.0
VO = VR(1)
EVALUATE EFFECT OF POLLUTANT ON MASS TRANSFER COEFF. AND VELOCITY

THIS RUN: PARTIAL POLLUTION EXISTS; APPLY H-R CORRECTION VELOCITY.

\[ F = \frac{(RO \cdot G \cdot P \cdot IV)}{(360 \cdot FMU)} \times VCF \]

\[ VEL = F \times (VO^2) \times T^W \]

GRiffITH'S EXPRESSION FOR KL FOR 'SLOWLY MOVING SURFACE'.

\[ FKl = 2.0 \times DIF / D(1) + (0.53 \times ((VEL / D(1))^0.5) \times DIF^0.65) \times (RO / FMU)^0.15) \times (1.0 + 22.0 / 13.0) \times (1.0 / 0.525) \]

EVALUATE PARAMETER 'NU', CONSTANT FOR EACH PLOT.

PHYSICAL SIGNIFICANCE OF 'NU' IS GM. MOLES OF OXYGEN SUPPLIED PER UNIT VOLUME OF GAS.

\[ FNU(I) = FKL \times (PIA / F) \times (FL / VO) \times (CSTAR - CL) \]

EVALUATE PARAMETERS GAMA AND DELTA (CONSTANT FOR EACH PLOT).

\[ GAMAR(I) = PO / (R \times B \times FL \times FNU(I)) \]

\[ DELTAR(I) = RHOG / (R \times B \times FNU(I)) \]

READ IN INITIAL CONDITION

\[ N = 1 \]
\[ ZP(N) = 1.0 \]
\[ PHIR(N) = 1.0 \]

CONVERT THE PERTINENT VECTORS INTO SCALARS FOR INTEGRATION

\[ Z = ZR(N) \]
\[ PHI = PHIR(N) \]
\[ GAMA = GAMAR(I) \]
\[ DELTA = DELTAR(I) \]

READ IN INCREMENT IN Z FOR EACH INTEGRATION STEP

INCREMENT IS NEGATIVE SINCE THE BUBBLE RISES IN A DIRECTION OPPOSITE TO THE POSITIVE X DIRECTION

\[ DZ = -0.01 \]
FOURTH-ORDER RUNGE-KUTTA INTEGRATION STEP FOLLOWS
INTEGRATING PHI WITH RESPECT TO Z

DO 100 N=2,101,1
AK1 = DZ*DPDZ(Z,PHI)
AK2 = DZ*DPDZ(Z+DZ/2.DO,PHI+AK1/2.DO)
AK3 = DZ*DPDZ(Z+DZ/2.DO,PHI+AK2/2.DO)
AK4 = DZ*DPDZ(Z+DZ,PHI+AK3)
PHI = PHI + (AK1+2.DO*AK2+2.DO*AK3+AK4)/6.DO
Z = Z +DZ
ZRCN) = Z
PHIR(N) = PHI
IF(PHI.GT.0.0) GO TO 30
VR(N) = 0.0
AR(N) = 0.0
D(N) = 0.0
GO TO 50
30 VR(N) = VO*PHI
AR(N) = PIA*(VR(N)**TWT)
D(N) = PID*(VR(N)**ONT)
100 CONTINUE
N = 101

50 WRITE(6,60)
60 FORMAT('ANALYSIS OF A SINGLE OXYGEN BUBBLE RISING IN LAK','E WATER//WITH SIMULTANEOUS ABSORPTION OF OXYGEN//IN DIMENSIONLESS FORM//')
WRITE(6,61)
61 FORMAT('FOLLOWING ARE THE PARTICULAR SYSTEM PARAMETERS:/','1/1')
WRITE(6,62)FL,B,ALPHA,BETA,GAMA,DELTA,FNU(I),VEL,FKL,CSTAR
62 FORMAT('LAKE DEPTH =,F10.6//TEMPERATURE G','RADIENT =,F10.6//ALPHA =,1PE14.7//BETA =,1PE14.7//GAMA =,1PE14.7//DELTA =,31PE14.7//NU =,1PE14.7//VELOCITY =,0PE1','40.4//KL =,1PE14.7//CSTAR =,1PE14.7')
5///)
WRITE(6,63)
63 FORMAT('0',10X,14HSTRATA COUNTER,5X,19HDIMENSIONLESS DEPTH,2X,20HD
1DIMENSIONLESS VOLUME,1X,16HVOLUME OF BUBBLE,2X,14HAREA OF BUBBLE,6X
2,18HDIAMETER OF BUBBLE/17X,1HN,22X,1HZ,18X,3PHI,10X,16HVR(N) IN C
3U,CMS,,2X,16HAR(N) IN SQ.CMS,,7X,12HD(N) IN CMS./)
WRITE(6,65) (J,ZR(J),PHIR(J),VR(J),AR(J),D(J),J=1,N,1)
65 FORMAT(' ',10X,17,17X,F10.4,1OX,F10.4,6X,F15.8,5X,F12.8,8X,F13.8)
  C
  PLOT PROGRAMME FOR DIMENSIONLESS VOLUME VS DIMENSIONLESS DEPTH
  IF(N.LE.7) MODE=101
  CALL GRAPH(N,ZR,PHIR,KS,MED,SIZE,10.0,0.10,0.0,0.10,0.0,XLAB,YLAB
1B,GLAB,DATLAB)
  KS = KS+1
  MODE = 120
  XSIZE = 0.0
  READ(5,25,END=400) DATLAB
400 CONTINUE
STOP
CONTINUE
END
ENTRY
980.665 1.000 1.000 0.015188 0.0 0.000196
STOP
//G0,FT14F001 DD DSNAME=SM,UNIT=SP00L,DISP=(NEW,PASS),
// SPACE=(800,(120,151),DCB=(RECFM=VS,LRECL=796,3LKSIZ800)
//SMPLTTR EXEC PLOT,PLOTTER=INCRMTL,TIME.PLOT=(,30)