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MASS TRANSFER TO NEWTONIAN AND NON-NEWTONIAN SYSTEMS IN STIRRED TANK GAS-FILLED CONTACTORS

William C. Wernau* and Charles R. Wilke

July 26, 1972

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MASS TRANSFER TO NEWTONIAN AND NON-NEWTONIAN SYSTEMS
IN STIRRED TANK GAS-LIQUID CONTACTORS

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MASS TRANSFER TO NEWTONIAN AND NON-NEWTONIAN SYSTEMS IN STIRRED TANK GAS-LIQUID CONTACTORS

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Berkeley, California

July 26, 1972

ABSTRACT

An experimental method for the simultaneous determination of the interfacial areas and mass transfer coefficients in gas-liquid stirred tank contactors, such as those used for aerobic fermentation, was used to determine the effects of power input and the presence of Newtonian and non-Newtonian solid additives on these parameters. Measurements of the gas holdup in these systems were coupled with the interfacial area measurements to yield the values of the average bubble diameters in a 12" diameter stirred tank contactor.

The results of these experiments indicate that the power range common to industrial operations corresponds to the transition region between "large" and "small" bubbles in this scale equipment. A significant decrease in mass transfer coefficient and bubble diameter with increasing power input was shown to take place in this power region. The Newtonian additive was shown to affect this transition region drastically, resulting in a larger bubble diameter at any power input and a decreased mass transfer coefficient at any bubble diameter. A logarithmic dependence of mass transfer...
coefficient on bubble diameter was found for both the Newtonian and the non-Newtonian systems in the transition region.

The overall volumetric mass transfer coefficients \( (K_La \text{ or } K^*_{L}) \) were determined using both the sodium sulphite oxidation system and the dissolved oxygen probe transient response method. The sodium sulphite method used a copper sulphate catalyst and systems investigated by this method were found to be in the "small" bubble regime because of the high ionic strength of the solutions. A definite effect of ionic strength on \( K_La \) was determined with the dissolved oxygen probe.

In those systems in which interfacial areas were determined, the \( K_La \) values were found using the dissolved oxygen probe response to a step change in oxygen feed composition. Simultaneously, the interfacial areas per unit volume \( (a) \) were determined by the steady state absorption of \( CO_2 \) into dilute alkali-salt solutions in the pseudo-first order reaction regime. Weak alkali-salt mixtures of 0.1M ionic strength, with and without the addition of additives, were investigated.

In addition, \( K_La \) determinations were made with the dissolved oxygen probe in distilled water with and without additives, and in sodium sulphate solution. The latter measurements determined the enhancement effect of chemical reaction on the sodium sulphite \( K^*_{L} \) values. The effects of gas flow on \( K_La \) and \( K^*_{L} \) were also determined for several of the systems investigated.

The application of these results for scale-up and design is discussed and recommendations for future rational investigation of mass transfer in these systems are presented. Several innovations in technique and analysis are also reported.
I. INTRODUCTION

1. General Discussion of Mass Transfer in Gas-Liquid Stirred Tank Contactors

The process of gas absorption into liquids finds many applications in the chemical process, petroleum and fermentation industries. Stirred tank gas-liquid contactors are, in many instances, preferred to packed tower absorbers, crossflow scrubbers and other gas-liquid contactors. This is particularly true in some heterogeneous catalysis systems and in the fermentation industry. In the latter case, agitation of the liquid insures uniform dispersion of the absorbed gas throughout the liquid phase and is useful for dispersion of microbial mass, nutrients and toxic metabolic end-products.

It is well-known that the transfer of oxygen to growing microbial cells can become a limiting process in many aerobic fermentation processes. Previous studies in this area have firmly established that in non-clump forming fermentations, the transfer of oxygen from the gas bubbles to the liquid phase is often controlled by the high liquid phase resistance to mass transfer of the oxygen (1). In clump forming fermentations, such as some fungal ones, transfer of nutrients, including oxygen, into the interior of the pellet may be the most important mass transfer process in terms of its restraints on cell growth and production of products.

Oxygen transfer in fermentation systems becomes particularly important in the case of high microbial population density and large microbial respiration rate. When the rate of supply of oxygen from the gas bubbles to the liquid exceeds the rate of oxygen demand by the organisms, the dissolved oxygen concentration in the liquid broth increases until a dynamic
equilibrium is reached. In this case, no oxygen supply problems exist (excepting those fermentations where a low dissolved oxygen concentration is desirable) and the rate of growth of the organisms is not decreased by the oxygen concentration. On the other hand, when the rate of supply of the oxygen to the broth is less than the microbial oxygen demand, the concentration of oxygen in the liquid decreases until it reaches what is called the critical oxygen concentration \( C_{\text{crit}} \). When this happens, microbial growth rate decreases and production of the desired fermentation product may be adversely affected. Many examples of fermentations affected by oxygen requirements can be found in the literature \( (2-21) \). Particularly bad in this respect are some of the fungal-type fermentations in which the presence of long, intertwined filamentous organisms considerably reduces the degree of turbulence in the liquid and thus reduces the breakup of bubbles and mixing of the dissolved gas. The non-Newtonian character of these broths poses a challenging problem for the engineer faced with design and scale-up of systems of this type.

A partial listing of products produced by fungi and the Actinomycetes (a fungi-like class of bacteria) is given in Table 1.1. Despite numerous publications on oxygen transfer in some of these systems, no reliable method of scale-up for these fermentations is generally known. The problem is compounded by the diverse geometries used by different investigators and the lack of a fundamental approach to the problem. Numerous empirical correlations have been proposed using different geometries of equipment, different liquid systems and different amounts of surface-active, organic and ionic additives. Various polymeric and solid additives
Table 1.1. Partial Listing of Fermentation Products Produced by Fungi and Actinomycetes

### Fungi

<table>
<thead>
<tr>
<th>Organism</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aspergillus niger</td>
<td>citric acid</td>
</tr>
<tr>
<td></td>
<td>glucose oxidase</td>
</tr>
<tr>
<td></td>
<td>amylase</td>
</tr>
<tr>
<td>Penicillium sp.</td>
<td>penicillin</td>
</tr>
<tr>
<td>Rhizopus sp.</td>
<td>fumaric acid</td>
</tr>
<tr>
<td>Trichoderma viride</td>
<td>cellulase</td>
</tr>
</tbody>
</table>

### Actinomycetes

<table>
<thead>
<tr>
<th>Organism</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Streptomyces aureofaciens</td>
<td>chlortetracycline</td>
</tr>
<tr>
<td>Streptomyces griseus</td>
<td>streptomycin</td>
</tr>
<tr>
<td></td>
<td>vitamin B₁₂</td>
</tr>
<tr>
<td>Streptomyces orchidaceus</td>
<td>cycloserine</td>
</tr>
<tr>
<td>Streptomyces fradiae</td>
<td>neomycin</td>
</tr>
<tr>
<td>Streptomyces erythreus</td>
<td>erythromycin</td>
</tr>
<tr>
<td>Streptomyces noursei</td>
<td>nystatin</td>
</tr>
<tr>
<td>Streptomyces nodosus</td>
<td>amphotericin B</td>
</tr>
</tbody>
</table>
have been added in an attempt to simulate non-Newtonian broths and studies on the living systems have also been attempted. In almost all cases (the exceptions will be cited later) the mass transfer parameter which was measured is the overall volumetric mass transfer coefficient \( (K_L a) \) or the overall volumetric mass transfer coefficient in the presence of chemical reaction \( (K_{L}^{R} a) \). As will be shown later, these quantities are really the products of two more fundamental parameters, the mass transfer coefficient \( (K_L) \) and the interfacial area per unit volume of liquid \( (a) \). In addition, when chemical reaction is present, \( K_{L}^{R} \) is distinctly different from \( K_L \) and can be understood using the theory of mass transfer with accompanying chemical reaction.

The first successful attempt at a better understanding of these more fundamental parameters, \( K_L \) and \( a \), was made by Calderbank and Moo-Young (22) in 1961. Using a light transmission probe technique, they were able to study the variation of interfacial area in gas-liquid dispersions. In addition, they correlated their and other mass transfer coefficient data to bubble diameter and were able to demonstrate the existence of two types of bubbles, "large" and "small" bubbles. It was postulated that "large" bubbles acted in such a manner as to be freely circulating and that "small" bubbles behaved as if they were rigid and could not circulate. "Small" bubble mass transfer coefficient results correlated well with the results for rigid particles. No attempt was made, however, to establish which regime—the "large" bubble or the "small" bubble regime—was predominant in power ranges of industrial importance.

Other work using sodium sulphite oxidation and absorption into alkali solutions with accompanying chemical reaction, was also carried out
to determine interfacial areas in stirred tanks (1, 23-35). However, comparison of these interfacial area results with overall volumetric mass transfer coefficient results was not possible because the data for $K_La$ and $a$ were not available in the same systems.

Most recently, the development of fast, reliable dissolved oxygen polarographic and galvanometric membrane probes, has allowed Robinson and Wilke (36) to carry out the first simultaneous measurements of $K_La$ and $a$. The advantage of this system over other methods lay in the fact that $K_La$ and $a$ were determined in the same tank, in the same system and in the same bubbles, i.e., simultaneously. The system used consisted of dilute alkali-salt mixtures into which carbon dioxide was absorbed. The CO$_2$ absorption took place under pseudo-first-order reaction conditions in the liquid and the rate of CO$_2$ absorption was directly proportional to the interfacial area per unit volume of liquid. Simultaneously, dissolved oxygen present in the liquid was desorbed through the same bubbles and entered the gas phase. The partial pressure of the dissolved oxygen in the liquid was continuously monitored with a dissolved oxygen probe of the Borkowski type (37, 38). From the transient response of the probe and a diffusion model for the probe response, the value of $K_La$ could be calculated. Additional information on the gas holdup of the systems could then be combined with this information to yield the values of $K_La$, $a$, $K_L$ and bubble diameter ($d_B$). This method yielded valuable information on the properties of salt solutions and helped to clarify some of the discrepancies among the results of other investigators.

In the present work, the method of Robinson and Wilke is extended to other systems and some improvements and refinements in the method are
reported. Specifically, this method was used to study $K_L a$, $K_L$, $a$ and $d_B$ in a larger sized tank than that used by Robinson and Wilke (36) and, because of the importance of non-Newtonian systems in fermentation, these parameters were investigated in the presence of a non-Newtonian solid additive, paper pulp. "Solka Floc" (T.M. of Brown Company Berlin, New Hampshire), a highly purified form of wood cellulose was also used. This study has shed new light on the Newtonian systems studied and has yielded valuable insight into the effects brought about by the presence of solid phase non-Newtonian additives. Improvements in technique include a new method for control of the alkali concentration in the liquid phase, a new and faster method for interpretation of $K_L a$ data and improvements in gas phase $CO_2$ concentration measurements by continuous monitoring. A new holdup measurement technique was also devised which was found to work adequately even in the presence of fibrous suspensions.

"Solka Floc" was chosen as one of the additives in the non-Newtonian experiments in the hope that it would serve as a model for fungal mass. An ideal additive for this purpose should not react to any extent during the period of the experiments, should be usable at pH levels greater than 12, and should simulate the properties of fungal mass by its fibrous structure and pseudoplastic non-Newtonian character. Equally important, it should offer reproducible results because of its standardized size and purity. "Solka Floc" is presently being used in our laboratory as a convenient source of cellulose for experiments on the microbial saccharification of cellulose. Unfortunately, experiments performed on the filtrate prepared from washed "Solka Floc" indicated that the presence of very small quantities of water soluble materials in "Solka Floc" had very dramatic effects on the mass transfer properties being investigated. The short, stubby fibers of "Solka Floc" did not behave in as non-Newtonian a manner as was hoped.
Because of undesirable effects of water soluble materials and the shortness of fibers in "Solka Floc", studies were carried out in paper pulp suspensions prepared from Whatman #40 filter paper (15.0 cm. circles, hydrochloric and hydrofluoric acid extracted, W. and R. Balston, Ltd., England). Studies on the filtrate prepared from these suspensions indicated that there was no effect on the mass transfer properties caused by any material that may have been extracted from the paper pulp.

A disadvantage of the use of water-insoluble pulps for the simulation of non-Newtonian mycelial suspensions is the fact that the viscosity of these pulps is not measureable under the shear field conditions existing in a stirred-tank contactor. This problem exists because of the non-Newtonian character of the material. Viscosity measurements under laminar flow conditions are also virtually impossible using standard methods because of the large size and rapid settling of the cellulose fibers. A pseudo-Newtonian viscosity could be defined for the system however and will be discussed later.

Dissolved polymeric material was not used for fungal simulation because it was not felt that it simulated the presence of a third phase as adequately as suspended solid material could.
II. THEORY AND PREVIOUS WORK

1. General Review of Mass Transfer Theory

The transfer of matter across the interface between two distinct phases has been of interest to chemical engineers for some time. Transfer occurs under the influence of a driving force, usually concentration, and proceeds in such a manner as to approach an equilibrium condition. In certain cases this transfer occurs under steady-state conditions and could be described as a dynamic equilibrium process.

Several models have been proposed to describe the mass transfer process. Those models which are applicable to gas-liquid systems will be described here. The "Film Theory" of Whitman (39) is perhaps the simplest. In this theory, transfer of mass across the gas-liquid interface is assumed to occur by diffusion through a hypothetical film of stagnant liquid of thickness L. In the steady state, the mass transfer flux is given by

\[ N_A = \frac{D_A}{L'} (C^* - C_L) \]  \hspace{1cm} (2.1)

\[ = K_L (C^* - C_L) \]  \hspace{1cm} (2.2)

Here, \( N_A \) describes the flux of component A between the two phases and \( C^* \) represents the concentration of component A at the gas-liquid interface. \( C_L \) represents the concentration of component A in the bulk liquid outside of the liquid film. \( D_A \) represents the diffusivity of component A in the liquid film. It is clear from Eq. (2.1) that the "Film Theory" predicts a direct proportionality between \( K_L \) and \( D_A \). Experimental evidence (23, 40-46) indicates, however, that

\[ K_L \propto D_A^{0.5-0.7} \]  \hspace{1cm} (2.3)
Therefore, the film theory is inadequate for describing mass transfer across gas-liquid interfaces.

Higbie (47) proposed a penetration model to describe mass transfer at gas-liquid interfaces. In this model it is assumed that elements of liquid travel from the bulk liquid to the interface, remain at the interface for a set amount of time (equal life for all surface elements) and then return to the bulk of the liquid. During the residence of these elements at the surface they are assumed to absorb or desorb component A from or to the gas phase. This is an unsteady-state process and transfer follows Fick's Second Law

\[
\frac{\partial C_A}{\partial t} = D_A \frac{\partial^2 C_A}{\partial x^2}
\]

where \(t\) is the time of residence of the surface element and \(x\) is the linear dimension perpendicular to the interface. This equation can then be solved by Laplace Transformation under the appropriate boundary conditions to give

\[
N_A(\text{aver.}) = 2 \sqrt{D_A/\pi t'} (C^* - C_L)
\]

where \(N_A(\text{aver.})\) is the average rate of absorption of component A during the life of the surface element, \(t'\). It is clear from Eq. (2.5) that

\[
K_L = 2 \sqrt{D_A/\pi t'}
\]

It should be noted that only in the simplest systems is \(t'\) known. The dependence of \(K_L\) (the mass transfer coefficient) on \(D_A^{0.5}\) agrees with results found for freely circulating bubbles.

A modification of the penetration theory of Higbie was proposed by Danckwerts (48). In this model, the assumption made by Higbie that all surface elements experience an equal lifetime was replaced by the assumption that the lifetime of a surface element is independent of its age. In this case, the
The rate of disappearance of surface elements of age between \( t \) and \( (t + dt) \) is proportional to the number of elements in that age interval. If \( \psi(t)dt \) represents all elements with ages between \( t \) and \( (t + dt) \), then

\[
-\frac{d\psi}{dt} = s\psi \quad .
\]

The constant \( s \) is a proportionality constant. Integrating this equation and substituting into Fick's Second Law gives

\[
N_A = \sqrt{D_A/s} (C^* - C_L) \quad .
\]

It should be noted that all surface age distributions which are independent of diffusivity will yield a direct proportionality between \( K_L \) and \( D_A^{0.5} \), when substituted into the penetration model. Clearly

\[
K_L = \sqrt{D_A s} \quad (2.9)
\]

for this model. An equivalent diffusion time may be substituted for \( s \). In this case

\[
t_D = 1/s \quad .
\]

This equivalent diffusion time, \( t_D \), was proposed by Astarita (49) and effectively eliminates the distinction between the Higbie and the Danckwerts models in those cases where \( t' \) or \( t_D \) cannot be measured.

2. General Review of Mass Transfer with Chemical Reaction

In the presence of a liquid phase chemical reaction, the governing equation describing gas-liquid mass transfer from the gas phase to the liquid phase is

\[
\frac{\partial C_A}{\partial t} = D_A \frac{\partial^2 C_A}{\partial x^2} + r_A \quad (2.11)
\]

in a one-dimensional system. Here \( r_A \) represents the rate of disappearance of component \( A \) by chemical reaction in the liquid phase. At steady-state we can write

\[
\frac{\partial C_A}{\partial t} = 0 \quad (2.12)
\]
and Eq. (2.11) reduces to

\[-r_A = D_A \frac{\partial^2 C_A}{\partial x^2} \quad (2.13)\]

Here we have assumed that the penetration model for mass transfer is applicable and that appreciable chemical reaction can take place during the lifetime of the average surface element. This regime is called the "fast reaction regime" and, as we shall see, is the basis for interfacial area measurements in reactive systems. As long as the term \( r_A > > \frac{\partial C_A}{\partial t} \), we can solve Eq. (2.13) with boundary conditions:

- at \( x = 0 \) (interface), \( C_A = C_A^* \)
- at \( C_A = C_{AL} \), \( \frac{\partial C_A}{\partial x} = 0 \)

The solution of this problem yields

\[ N_A = \sqrt{2D_A \int_{C_{AL}}^{C_A^*} r_A(c) dc} \quad (2.14) \]

In the case where the rate of chemical reaction is first order in component A, i.e., \( r_A = kC_A \), integration of Eq. (2.14) gives

\[ N_A = \sqrt{D_A k \left(C_A^* - C_{AL}\right)} \quad (2.15) \]

In the case of chemical absorption of CO\(_2\) into KOH solution, under conditions where the concentration of OH\(^-\) ion does not change with time

\[ k = k_2 B \quad (2.16) \]

where \( k \) is the pseudo-first order reaction rate constant, \( k_2 \) is the second order rate constant for the reaction between OH\(^-\) ions and CO\(_2\) and \( B \) is the bulk liquid phase concentration of OH\(^-\) ions. In addition, the concentration of CO\(_2\) in the liquid phase under the conditions of fast reaction, is essentially zero,
so we can write:

\[ N_A = C_A^* \sqrt{K_2 B D_A} \quad (2.17) \]

By measuring the total rate of absorption of CO2 into the liquid phase, it is possible to measure the interfacial area per unit volume of liquid, a, as follows. By definition,

\[ N_A = \frac{R_A}{A} \quad (2.18) \]

where \( R_A \) equals the total molar rate of CO2 absorption (moles/sec) and \( A \) equals the total interfacial area of the system. If we divide both sides of the equation by the liquid volume, \( V_L \), we obtain

\[ \frac{\overline{R_A}}{\overline{V_L}} = \frac{N_A}{V_L} a \quad (2.19) \]

where \( \overline{R_A} \) is the specific molar absorption rate per unit volume (moles/cm³·sec). Therefore:

\[ \overline{R_A} = a C_A^* \sqrt{K_2 B D_A} \quad (2.20) \]

It can be seen then, that under pseudo-first order chemical absorption conditions, the rate of absorption of gas per unit volume of liquid is directly proportional to the interfacial area per unit volume of liquid. Under conditions in which physical mass transfer is significant in comparison with chemical absorption, Eq. (2.20) becomes

\[ \overline{R_A} = a C_A^* \sqrt{k_L^2 + k_2 B D_A} \quad (2.21) \]

The requirements for a fast reaction (under pseudo-first order conditions are given by Danckwerts (48) as

\[ \sqrt{D_A k_2} < 1/2 k_L \left( 1 + \frac{D_B}{zD_A} \right) C_A^* \quad (2.22) \]
where \( D_B \) is the molecular diffusivity of component B in the liquid phase, \( z \) is the stoichiometric ratio of component B to component A (\( z = 2 \) for the reaction of \( \text{OH}^- \) and \( \text{CO}_2 \)). For the \( \text{CO}_2\text{-KOH} \) system, these two conditions are satisfied in the range of concentrations of \( \text{CO}_2 \) and KOH used in the interfacial area experiments reported here.

3. Definition of Driving Force for Mass Transfer

The proper definition of the driving force for mass transfer in gas-liquid stirred tank absorbers has been the subject of some controversy. It is clear that the values for the mass transfer coefficient and the interfacial area are very much dependent on the value of the interfacial concentration of the absorbing species, \( C_A^* \). Under conditions of adequate mixing in the liquid phase (high Reynolds Number) experiments performed by Reith and Beek (50) indicated that the concentration of component A in the gas bubbles was equal for all bubbles and was the same as the exit concentration of component A. The effect of ionic strength on the minimum stirring speed required to achieve this complete mixing in the gas phase was significant and much higher stirring rates were required in ionic solutions. In experiments performed in the present study, well-mixed gas phase conditions exist in water at 240 RPM and in salt solutions of \( \Gamma > 0.4 \)M at 390 RPM, based on equivalence of Reynolds Numbers in the study of Reith and Beek and the present study.

Assuming that the gas phase "film" inside the bubbles is not influencing the mass transfer, then the concentration of component A at the gas-liquid interface is the same as the bulk concentration inside the bubble. This condition of liquid-side mass transfer control has been assumed in all calculations.
reported here and is supported by the work of several authors (1, 36, 132). The assumption of a well-mixed gas phase has also been made based on the work of several authors (36, 50, 116). Clearly, the degree of mixing of the gas phase is a function of the rate of coalescence vs. the rate of breakup of bubbles in the tank, the stirring speed and factors such as ionic strength and the presence of viscosity modifiers. In any event, the degree of mixing will not present serious errors as long as the time required for mixing is short in comparison with the relevant time constants of the systems investigated. As will be shown later, at high rates of chemical absorption, where large changes in gas phase concentration occur between inlet and outlet, the mixing time becomes a significant variable. This concept will be taken up in greater detail later. Mixing in the liquid phase was assumed to be complete in all cases and deviations from this assumption were noted at low stirring speeds in Newtonian and non-Newtonian systems.

4. Chemical Absorption Method—Assumptions and Kinetics

As shown earlier, during the absorption of carbon dioxide under pseudo-first order fast reaction conditions, the rate of absorption per unit volume of liquid is proportional to the interfacial area per unit volume of liquid. The two criteria to be satisfied are listed in Eqs. (2.22) and (2.23).

Eq. (2.20) requires a knowledge of $D_A$, $B$, $k_2$, $R_A$ and $c_A^*$ for calculation of the value of the interfacial area per unit volume, $a$.

a. Diffusivity of CO$_2$. The diffusivity of CO$_2$, i.e., $D_A$, in 0.1M ionic strength solution can be calculated based on diffusivity data presented by Danckwerts and Sharma (23). By plotting values of diffusivity vs. ionic strength for water, sodium chloride, sodium sulphate and magnesium sulphate we obtain by interpolation...
a diffusivity for CO₂ at 0.01M ionic strength of $2.13 \times 10^{-5}$ cm²/sec at 30 °C. Based on results presented by Danckwerts for the diffusivity ratio of hydroxide ion to CO₂ at low ionic strengths, $D_B/D_A$ was chosen to be 1.7.

b. Hydroxide Concentration. The concentration range chosen for hydroxide ion was 0.004-0.06M for the absorption experiments. The total ionic strength was made up to 0.06M at the start of the experiments with KCl and the average ionic strength during the experiments was 0.1M.

c. Second-Order Reaction Rate Constant.

The relevant reaction rate constant for the reaction of CO₂ and OH⁻ in solution is for the reaction

$$\text{OH}^- + \text{CO}_2 \rightarrow \text{HCO}_3^- .$$

A further reaction involving HCO₃⁻ and OH⁻ takes place with extreme rapidity and is not rate limiting (23). Taking the analysis of the effect of ionic strength on the value of $k_2$ given by Hsu (51), we find that at 0.1M ionic strength $k_2 = 12,198$ liters/g-mole sec. at 30 °C.

d. Concentration of CO₂ at Gas-Liquid Interface. In the absence of any gas phase resistance the concentration of CO₂ at the gas-liquid interface during chemical absorption is equal to its solubility at the exit concentration of CO₂ in the gas stream. Using the method of van Krevelen and Hoftijzer (52), the Henry's Constant, $H'$, for the 0.1M ionic strength system is estimated to be 35.2 liters-atm/mole. The solubility is therefore given by the equation

$$c_{CO_2}^w = (y_{CO_2} P_f/RT)(V_{ML}/H) .$$ (2.23a)
e. **Rate of Absorption per Unit Volume of Liquid.** By combining the equations for a mass balance on the gas stream containing the CO\(_2\) to be absorbed and the rate of absorption (Eq. [2.21]), an equation for the interfacial area per unit volume can be obtained based upon the concentration of CO\(_2\) leaving the tank in the gas phase. This procedure yields (36):

\[
a = \frac{(F^0/V_L)(H/V_{ML})(C_{CO2_i} - \frac{y_{CO2f}P_T}{RT})}{y_{CO2f} \sqrt{D_Ak_2B + K_L^2}}
\]  

(2.24)

where 

- \(F^0\) = gas flow rate (cm\(^3\)/sec)
- \(V_L\) = liquid volume (cm\(^3\))
- \(C_{CO2_i}\) = inlet gas concentration (moles/cm\(^3\))
- \(H\) = Henry's Constant (\(H = y/x'\))
- \(y\) = mole fraction of CO\(_2\) in gas phase
- \(x'\) = mole fraction of CO\(_2\) in liquid phase
- \(V_{ML}\) = molar concentration of water (moles/cm\(^3\))
- \(D_A\) = diffusivity of CO\(_2\) (cm\(^2\)/sec)
- \(k_2\) = reaction rate constant (cm\(^3\)/mole sec)
- \(B\) = concentration of OH\(^-\) (moles/cm\(^3\))
- \(P_T\) = total system pressure (atmos.)
- \(R\) = universal gas constant (cm\(^3\)-atmos/mole °K)
- \(T\) = temperature (°K)
- \(K_L\) = liquid film mass transfer coefficient (cm/sec)
- \(y_{CO2f}\) = exit gas CO\(_2\) mole fraction, dimensionless
f. **Hydroxide Ion Concentration.** The hydroxide ion concentration was determined by titration of the liquid phase before and after a run. A method for maintaining a constant liquid phase hydroxide concentration is described later.

g. **Exit CO₂ Concentration.** The exit concentration of CO₂ in the gas phase was measured by Infrared Analysis on a flow-through analyzer and is described later.

5. **Sulphite Oxidation Method—Assumptions and Kinetics**

The reaction of sodium sulphite with oxygen in the presence of a catalyst has been used for both the determination of $K_L^r$ and $a$ (24, 31, 32, 33, 36, 53-58). The basic reaction is

$$0_2 + SO_3^{-2} \rightarrow Cu^{+2} \rightarrow SO_4^{-2}$$

In the presence of Cu⁺² ion, the reaction has been shown to be independent of $SO_3^{-2}$ in the range 0.05-1.0M $SO_3^{-2}$ with a catalyst concentration in the range $10^{-3}$ to $10^{-4}$ Cu⁺². The assumption is made that the concentration of oxygen in the liquid phase is zero and that the rate of mass transfer to the liquid can be described by the equation

$$\bar{R}_A^r = K_L^r a c_A^*$$

(2.25)

where

- $\bar{R}_A^r$ = specific molar absorption rate of oxygen per unit volume (moles/cm³·sec)
- $K_L^r$ = mass transfer coefficient in the presence of chemical reaction (cm/sec)
- $a$ = interfacial area per unit volume (cm⁻¹)
- $c_A^*$ = interfacial concentration of oxygen in sulphite solution.
In the presence of Co$^{2+}$ ion, the sulphite oxidation system can be used to determine interfacial area per unit volume. The kinetics of this reaction are very poorly understood and much confusion still exists in the literature. The presence of trace quantities of organic material and changes in pH have been shown to markedly affect the kinetics of this system (53). In addition the high ionic strengths required for measurements of interfacial areas with this system, drastically alter the characteristics of the liquid phase with respect to bubble coalescence and, as we shall show, mass transfer. For these reasons, the CO$_2$ absorption method described earlier was the preferred method for measuring interfacial area.

Other problems associated with the use of the sodium sulphite oxidation method for the determination of $K^{r}_{La}$ (Cu$^{2+}$ catalyzed) are described in the Experimental Section.

6. Theory of Dissolved Oxygen Probe

a. Description of Probe. The dissolved oxygen probes used in this work were constructed according to the design of Borkowski and Johnson (37, 38). These probes are galvanometric probes, generating their own current based upon the reduction of oxygen at the probe cathode according to the following chemical reactions:

1. $O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^-$

2. $4OH^- + 4H^+ \rightarrow 4H_2O$

The anode reaction is

3. $4Pb^0 + 4Ac^{-} \rightarrow 4PbAc + 4e^{-}$
The $H^{+1}$ for reaction 2 and the $Ac^{-1}$ for reaction 3 are both supplied by an acetic acid buffer solution used as an electrolyte.

A diagram describing the probes used is shown in Fig. (2.1). Oxygen in the bulk solution diffuses from the solution, through a liquid film at the surface of the probe, then through the probe membrane (teflon of 2 mil thickness in this case) until it reaches the cathode. Here the oxygen is instantaneously reduced as shown in equation 1. Under conditions of agitation usually present in fermentation tanks, the liquid film is usually negligible. Aiba and Huang (59) have studied the conditions necessary for achieving negligible film resistance for oxygen probes.

b. Probe Performance Under Steady State Conditions. Under steady state conditions (constant activity of oxygen in the liquid phase) and in the absence of appreciable liquid film resistance at the probe membrane surface, the output of the dissolved oxygen probes is proportional to the partial pressure of oxygen in the liquid. This can be shown by solving Fick's Second Law for the probe membrane

$$\frac{\partial C}{\partial t} = D_M \frac{\partial^2 C}{\partial x^2} \quad (2.26)$$

where $C =$ concentration of oxygen in the membrane,

$x =$ distance through the membrane,

$D_M =$ membrane diffusivity.

If steady state conditions prevail, then

$$\frac{\partial C}{\partial t} = 0 \quad (2.27)$$

and Eq. (2.26) can be solved under the following boundary conditions:

$C = 0$ at $x = 0$,

$C = C_M$ at $x = L$
Dissolved oxygen probe

Cathode reaction

\[ \text{O}_2 + 2\text{H}_2\text{O} + 4e^\text{-} \rightarrow 4\text{OH}^- \rightarrow 4\text{H}_2\text{O} \]

Anode reaction

\[ 4\text{Pb} + 4\text{Ac}^- \rightarrow 4\text{Pb Ac} + 4e^- \]
where $L$ is the thickness of the membrane and $x = 0$ corresponds to the membrane-cathode interface. Solution of this equation yields:

$$C = C_M \cdot \frac{x}{L} \quad (2.28)$$

It should be noted here that $C_M$, the concentration of oxygen in the probe membrane at the membrane-liquid interface is not equal to the concentration of oxygen in the bulk liquid phase. The assumption is made though that a dynamic equilibrium exists between the liquid and the membrane at $x = L$ such that the fugacities of oxygen in the liquid and in the membrane are equal. Under conditions used in this work, the fugacity of oxygen is equal to its partial pressure (Robinson and Wilke [36]). Under these conditions, it can be shown that

$$p = p_M \cdot \frac{x}{L} \quad (2.29)$$

where $p$ is the partial pressure of oxygen in the membrane. Since $p_M$ (the interfacial pressure of oxygen) is the same in both the liquid and the membrane, it is clear that the oxygen probe measures partial pressure (or more strictly, activity) of oxygen in the liquid phase.

The flux of oxygen to the cathode is given by Fick's First Law as

$$N = D_M \frac{dC}{dx} \bigg|_{x=0} \quad (2.30)$$

where $N$ is the flux of oxygen and $\frac{dC}{dx}$ is the gradient of oxygen concentration in the probe membrane. As was shown in cathode reaction 1, for every molecule of oxygen reduced at the cathode, four electrons are used. Therefore, the flux of oxygen to the cathode gives a current which is directly proportional to the gradient of oxygen concentration in the probe membrane. This gradient of oxygen concentration in the membrane is related to conditions in the liquid phase through the partial pressure of oxygen,
and the probe current is therefore proportional to the partial pressure of oxygen in the liquid. This can be expressed as

$$I = K_2 \frac{p_M}{c_M}$$  \hspace{1cm} (2.31)

where $I$ is the probe current, $K_2$ is a constant, and $p_M$ is the bulk liquid partial pressure of oxygen (equal to the partial pressure of oxygen at the probe-liquid interface). In practice, this current is usually passed through a resistor and the voltage generated is read on a recorder.

c. **Probe Performance Under Unsteady State Conditions.** Oxygen probes have found much use recently for the measurement of $K_L$ in various liquid systems under conditions of either unsteady state absorption or unsteady state desorption of oxygen from the liquid phase in stirred tanks (31, 60-68). The use of dissolved oxygen probes for this purpose represents a major advance in measurement technology and allows for greater speed of measurement than older, chemical sampling techniques.

The problem to be solved consists of finding the solution to Fick's Second Law for the probe membrane subject to the boundary conditions

for absorption

I.C. \hspace{0.5cm} t = 0, \hspace{0.5cm} C = 0

B.C. \hspace{0.5cm} x = L, \hspace{0.5cm} C_M = f(t)

B.C. \hspace{0.5cm} x = 0, \hspace{0.5cm} C = 0

for desorption

I.C. \hspace{0.5cm} t = 0, \hspace{0.5cm} C = SHC_0 \left(\frac{x}{L}\right)

B.C. \hspace{0.5cm} x = 0, \hspace{0.5cm} C = 0

B.C. \hspace{0.5cm} x = L, \hspace{0.5cm} C_M = g(t)

The functions, $f(t)$ and $g(t)$ are properties of the specific form of the liquid phase response to changes in boundary condition. $SH$ is a group describing the effect of absorption of oxygen on the membrane (36) and relates membrane concentration to liquid phase concentration.
During oxygen desorption or absorption from the liquid phase in response to step changes in the gas phase composition of gas entering the tank below the impeller, Eq. (2.26) has been solved (36, 69, 70). The specific forms of \( f(t) \) and \( g(t) \) are given below:

\[
f(t) = SP_T \gamma_1 (1 - \exp [-\beta t])
\]

and

\[
g(t) = SP_T \gamma_0 \exp [-\beta t]
\]

where \( \beta \) is given by:

\[
\beta = \frac{P^0_H'K_L a}{(P^0_H' + K_L aV_L RT)}
\]

Here it is assumed that during absorption, a step change from zero concentration of oxygen in the gas phase is made. The new concentration of oxygen in the gas phase fed to the reactor after the step change is \( \frac{P_T \gamma_1}{RT} \).

During desorption, it is assumed that the liquid is initially equilibrated with a gas phase of concentration \( \frac{P_T \gamma_0}{RT} \). A step change in the concentration of gas fed to the reactor is then made to a stream totally deficient in oxygen (concentration of oxygen is zero).

A very important assumption made in the derivation of these equations can be seen by writing the material balance equation for the system:

\[
\frac{P_T}{RT} P^0 (y_i - y_f) - K_L aV_L \frac{P_T}{H} (y_f - \frac{H'C_L}{P_T}) = \frac{P_T}{RT} [d(V_o y_f)/dt]
\]

In order to arrive at Eq. (2.34) it is assumed that the term \( \frac{P_T}{RT} [d(V_o y_f)/dt] \) is very small in comparison with the other terms in Eq. (2.35) and can be ignored (set equal to zero). This assumption is justified in the case of small holdup of gas and after the period of initial establishment of gas holdup in the tank.
With the above assumption, the solution of Fick's Second Law for the probe membrane is given by Heineken (69) as well as by Robinson and Wilke (36) as
\[
E_t = E_o \left[ \tau^{1/2} \exp(-\beta t) \sin \tau^{1/2} \right. \\
- 2 \sum_{n=1}^{\infty} (-1)^n \exp(-n^2 \pi^2 D_M t/L^2)/(1 - n^2 \pi^2/\tau) \left. \right]
\] (2.36)
for the case of oxygen desorption from the liquid. Here \(E_t\) is the probe voltage generated by passing its current through a resistor. Also,
\[
\tau = \beta L^2/D_M
\] (2.37)
In the case of oxygen absorption into the liquid, the corresponding solution for the probe response is given by
\[
E_t = E_\infty \left[ 1 - \tau^{1/2} \sin \tau^{1/2}(\exp[-\beta t]) \right. \\
+ 2 \sum_{n=0}^{\infty} \frac{(-1)^n}{1 - n^2 \pi^2/\tau} \exp \left( - \frac{n^2 \pi^2 D_M t}{L^2} \right) \left. \right]
\] (2.38)
In order to utilize this solution for the purpose of finding \(K_L a\), most past workers have fit their experimental data to the best value of \(\beta\) and have calculated \(K_L a\) values as
\[
K_L a = F^O_H' \beta / (F^O_H' - \beta V_{LRT})
\] (2.39)
The best value for \(\beta\) can be found by use of a nonlinear least squares fitting program which minimizes the function
\[
\text{CHISQ}(X) = \sum_{i=1}^{n} \frac{[YDATA(i) - F(\beta, D_M/L^2, t)]^2}{\text{WEIGHT}(i)}
\] (2.40)
as described by Robinson and Wilke (36). This procedure has been found to
have several disadvantages. The first problem is the proper definition of the time when the step change has taken place. Robinson and Wilke defined this time as ten seconds prior to the first movement of their recorder pen. No significant difference in the best value of $B$ was found if time lags up to 3 seconds different were used. A comparison of the theoretical transient response curves ($E_t/E_0$ vs. $t$) shows that this lag in recorder pen movement depends upon the value of $B$, being longer in duration for small values of $B$ than for large values of $B$. A second disadvantage of the method was noted in runs performed in non-Newtonian suspensions and in some salt solutions reported in this work. At low stirring speeds, the response of the dissolved oxygen probe was found to be influenced by poor mixing in the liquid phase. This mixing problem resulted in a wavy response. Using the least squares fitting routine, it is possible to obtain a value of $B$ for this kind of response. It is apparent, however, that $K_{La}$ is varying throughout the tank and this method of fitting the data can be quite deceptive. Finally, the least squares method is a tedious one, requiring the use of considerable time for key punching of data. Results of experiments are not immediately available and the method would be of little use during actual fermentation runs unless appropriate interfacing equipment and immediate computer facilities were available.

In order to alleviate these problems, a new method for finding $K_{La}$ based on the transient response of dissolved oxygen probes was devised. The principle involved here is an old one. The slope of the dissolved oxygen probe response at some characteristic point is read and the value of $K_{La}$ correlated to the value of the slope. Since the origin of time
(time of the step change) is so poorly defined in actual experimental situations, measurement of the slope would appear to be dependent on the estimation of the time of the step change. This problem is alleviated by taking the slope at the inflection point of the probe response curve. This procedure is illustrated diagrammatically in Fig. (2.2). The use of a high speed recorder with a fast chart speed (1800 in/hr) enabled reading of the slope to three significant figures. The occurrence of multiple inflection points was indication of inadequate mixing. This method proved to be extremely useful and gave results which compared favorably with those obtained for the same data using the least squares fitting method. Values of the inflection point slope vs. $K_La$ are given in the Appendix Section (II.1) for various operating conditions. These curves were generated by taking the first and second derivatives of the transient response equations and finding the first derivative when

$$\frac{d^2}{d\tau^2} \left( \frac{E_t}{E_o} \right) = 0 \quad (2.41)$$

and

$$\frac{d}{d\tau} \left( \frac{E_t}{E_o} \right) = \text{maximum} \quad (2.42)$$

The values of these derivatives are listed in Appendix Section (II.1). The values of time at which the inflection occurred were also found and compared with the estimated time of inflection for actual experiments. In most cases, agreement was excellent (within a few seconds). Where the predicted and actual times of inflection did not agree, multiple inflections due to poor mixing were often found.

d. Generalized Method for Determination of $K_La$. Fig. (2.3) is presented as a generalized method for the determination of $K_La$ using the slope of the
Fig. 2.2. Inflection point slope method for determination of $k_{fA}$ (illustrated for oxygen desorption from stirred tank liquid).
Fig. 2.3. Determination of value of $\beta$ from slope of oxygen probe response curve at inflection point.

$D_M/L^2 = 21.8$ hr$^{-1}$
dissolved oxygen probe response curve at its inflection point. This figure allows the experimental determination of $K_L a$ from Eq. (2.39) regardless of the values of Henry's Constant, gas flow-rate and liquid volume.

A series of curves can be drawn for different values of $D_M/L^2$. For the probe used in this work, the value of $D_M/L^2$ was 21.8 hr$^{-1}$.

Recently, Linek (63) presented a method for the determination of $K_L a$ which eliminates the need to fit data by regression analysis. His method, however, is only useful for very small $K_L a$ values when used for slow response probes such as that used in this work. When the value of $K_L a$ becomes significant, his method fails because it depends upon an accurate determination of the time elapsed since the step change in gas composition. Inaccuracies of several seconds in the determination of this time are possible and could lead to significant errors. It should be noted that the table of examples given by Linek indicates that a teflon membrane probe of the type used in the present investigation allows accurate determination of $K_L a$ by his method for $K_L a = 30$ hr$^{-1}$. This is a very small $K_L a$ value. For $K_L a$ values of 250 hr$^{-1}$, he found it necessary to use very thin, high diffusivity membranes in order to get good accuracy by his method.

The method proposed in this work is independent of an accurate determination of the time of the step change and is applicable for slow probes at $K_L a$ values in excess of 500 hr$^{-1}$.

7. **Holdup Measurement**

Holdup is defined as the fractional volume of dispersed phase (gas) present in the system being studied (gas plus liquid). Thus a holdup of 0.1 would correspond to a system containing 10% gas and 90% liquid.
Many methods have been proposed for the measurement of holdup, and if used properly, most of these methods can give fairly accurate results. Holdup measurements are necessary for the calculation of the average bubble diameter present in stirred tanks (unless photographic measurements of bubble size distribution are made) and a method that could be used in the experimental equipment used in this work was sought. Various workers have suggested methods employing floating discs (60), level takers (72, 74), conductivity tips (25), dispersion sampling (71), electrical conductivity (75), and manometric devices (35, 36). A thorough review of the advantages and disadvantages of each of these methods as well as experiments employing the sampling method and the electrical conductivity method were carried out. None of the methods seemed satisfactory without some modification. Due to the lack of observation ports in the equipment used for these experiments, the floating disc and level taker methods were excluded. The electrical conductivity method proved impractical because of the metal present in the tank which gave distorted conductivity measurements. Dispersion sampling indicated that degassing of the liquid phase during sampling under vacuum was a serious problem. The conductivity tip method (and the level taker method) required measurements at several places on the surface of the tank and was deemed impractical for the acquiring of holdup data over a wide range of conditions with different systems.

A new manometric method was therefore devised. This method enabled measurements to be made in a matter of minutes and gave very reproducible results. The method is described in detail in the Experimental Section and in the Appendix, Section (II.2) and will not be discussed here. Comparison
of results obtained by this method with those of other investigators will be found in the Discussion Section.

8. **Average Bubble Diameter**

Once the interfacial area per unit volume of liquid and the gas holdup of the systems being investigated are known, the average bubble diameter in these systems can be calculated. The total volume of gas present in the system is given by

\[ V_g = \frac{1}{6} \bar{N} \pi \bar{d}_B^3 \]  
(2.43)

where \( \bar{N} \) is the total number of bubbles present in the system and \( \bar{d}_B \) is the average bubble diameter (by definition). The holdup is then given by

\[ \bar{H}_o = \frac{\bar{N} \pi \bar{d}_B^3}{6V_L + \bar{N} \pi \bar{d}_B^3} \]  
(2.44)

Since \( \bar{N} \) is unknown, the interfacial area per unit volume is employed to give

\[ a = \frac{\bar{N} \pi \bar{d}_B^2}{V_L} \]  
(2.45)

Combining Eqs. (2.44) and (2.45),

\[ \frac{\bar{H}_o}{a} = \frac{\bar{d}_B/6}{V_L + V_g} \]  
(2.46)

But this is the same as

\[ \frac{\bar{H}_o}{a} = \frac{\bar{d}_B/6}{1 - \bar{H}_o} \]  
(2.47)

Rearranging Eq. (2.47) gives finally

\[ \bar{d}_B = 6\bar{H}_o/a \left( \frac{1}{1 - \bar{H}_o} \right) \]  
(2.48)

It is to be emphasized that the value of \( \bar{d}_B \) reported here is an average bubble diameter. The average bubble diameter will be used later in explaining the results obtained in this work for \( K_La \) and \( a \) in various systems.
9. Mass Transfer Coefficient

From the values of the volumetric mass transfer coefficient \(K_La\) and the interfacial area \(a\) measured simultaneously by the dissolved oxygen probe and the rate of chemical absorption as described above, it is possible to find the value of the mass transfer coefficient \(K_L\).

\[
K_L = \frac{K_L a}{a} 
\]

The fact that the bubbles being used for the volumetric mass transfer studies are the same as those used for the area studies (simultaneous measurement), allows the use of Eq. (2.49).

Strictly speaking, the \(K_L\) determination is made within the first 30 seconds of a run, whereas the interfacial area measurement is made at 2.5 minutes into a 5-minute run. The changes in composition of the liquid during this period (ionic strength increases from 0.06M to 0.1M) were probably not significant enough to introduce significant errors in the calculations. It can be shown that none of the relevant liquid properties (chemical reaction rate constant, Henry's constant, diffusivity) change significantly with this small change in ionic strength. The interfacial area per unit volume as measured by the outlet \(\text{CO}_2\) composition did not change more than 5%. Experimental observation indicated that an almost steady outlet \(\text{CO}_2\) concentration was obtained indicating a nearly constant value of

\[
aC_A^* \sqrt{D_A k_2B} 
\]

Since \(C_A^*, D_A\) and \(k_2\) only change slightly in this ionic strength range (0.06 - 0.14M), this indicates that

\[
aB^{1/2} \approx \text{constant}
\]
during the runs (after an initial transient as discussed earlier). Slight changes in $B$ (hydroxide concentration) would be compensated for by even slighter changes in area per unit volume due to the square root dependence. Other studies (36) also indicated that area per unit volume did not change appreciably with ionic strength for small ionic strength changes.

10. Non-Newtonian Character

In the context of this discussion, non-Newtonian viscosity can be defined as a shear rate dependent viscosity. Thus in the typical description of viscosity

$$\tau_{ij} = -\mu \dot{\gamma}_{ij}$$

(2.50)

where $\tau_{ij} =$ shear stress (g/cm-$\text{sec}^2$),

$\mu =$ viscosity (g/cm-$\text{sec}$),

$\dot{\gamma}_{ij} =$ shear rate (sec$^{-1}$)

the value of $\mu$ depends upon the value of the shear rate $\dot{\gamma}_{ij}$. It is well-known that in a stirred tank the values of the shear rate is a function of position in the tank and varies with the stirring speed. Under turbulent conditions it has been shown that the power input to an ungassed system is independent of viscosity. For this reason, viscosity measurements are usually made by defining an apparent viscosity, $\mu_a$, which is measured by operating the tank in the laminar regime and measuring the power input under these conditions. This apparent viscosity is defined as the viscosity of a Newtonian solution giving the same power input as the non-Newtonian solution being measured. This method suffers from several deficiencies. First of all, the viscosity is not measured under the conditions existing in the turbulent regime, where mass transfer experiments are
carried out. Secondly, the method will not work for readily settling suspensions. For this reason, a new type of apparent viscosity was defined in this work.

Measurements were carried out by Calderbank and Moo-Young (22) on the mass transfer coefficients in Newtonian solutions of varying viscosities as a function of bubble diameter in these systems. They obtained a series of straight lines on log-log paper when plotting $K_L$ vs. $d_B$. The experiments performed in the present study also yielded similar plots for non-Newtonian pulps and "Solka Floc" suspensions and an apparent viscosity was defined, $\mu_a'$, as the Newtonian viscosity giving the same $K_L$ and $d_B$ curve as that found for the system being studied.

The non-Newtonian character of pulp suspensions is due to the interaction of the fibers of the pulp imparting a certain rigidity to the suspension. As the shear rate increases, the pulp becomes less rigid and exhibits a lower viscosity. The non-Newtonian character of these pulps is generally described as pseudoplastic, i.e., the viscosity decreases as the shear rate increases. At very high shear rates, the viscosity does not change as rapidly as it does at low shear rates and the suspensions become more nearly Newtonian (constant viscosity). This fact again points to the need to measure viscosity under the conditions of agitation to be encountered in the stirred tank. It is felt that the apparent viscosity, $\mu_a'$, satisfies this criterion to a greater extent than does the apparent viscosity, $\mu_a$, used by other workers.
III. EXPERIMENTAL

1. Design of Experimental Equipment

   The basic equipment used in this study is shown schematically in Fig. (3.1). The stirred tank was cylindrical in shape, with a flat bottom and was constructed of 316 stainless steel. The internal tank diameter was 12 inches and the total internal height was 24 inches. Four baffles of 316 stainless steel, 1.2 inches wide and 1/8 inch thick, extending from the bottom to the top of the tank were inserted and held in place by adjustable stainless steel bands. These bands held the baffles at a distance of 1/16 inch from the tank walls and thus helped to alleviate problems of "dead space" behind the baffles.

   The geometrical ratios used in tank construction were those recommended by Aiba, et al. (76) and correspond to so-called "standard geometry". Previous studies in our laboratory (36) also employed these standard geometrical ratios and it was felt that this larger sized tank could yield useful information on scale-up if the same geometrical ratios used in that work were used in the present studies. Fig. (3.2) shows these ratios as used in this system. The impeller was a six blade turbine with a central disk. A sparger with an orifice of 4 mm was placed below the impeller and provided an entrance for the gases used in the experiments. When in operation, the tank was filled to a depth of 12" and held a volume of 21.90 liters of liquid.

   The fermenter headplate contained many ports for the insertion of probes and other devices. An exit port for escaping gas was fitted with a gate valve which allowed the channeling of some of the exit gas through
Fig. 3.1. Diagram of the gas-liquid stirred tank contactor and gas supply system.
Fig. 3.2. Geometrical ratios used in tank construction.

Number of turbine blades = 6
Number of baffles = 4
Sparger hole size = 4 mm
Shaft diameter = 1-1/4 inches
a \text{CO}_2\text{ analyzer} (Beckman Instruments, Infrared Analyzer, Model 315A). The flow rate through the analyzer was monitored on a rotameter and could be adjusted using a needle valve. A thermowell containing a thermistor was inserted in the headplate and connected to a proportional temperature controller (Yellowsprings Instruments, Model 72), which in turn regulated the flow of heat through a heating tape wrapped around the tank. A cooling coil of 316 stainless steel was inserted through two other ports and gave positive control of temperature. A dissolved oxygen probe, wrapped in a metal sheath, was inserted in the liquid approximately 4" below the liquid level and screwed into the headplate. Two pH probes (New Brunswick Scientific Company) were also mounted in the headplate and dipped approximately 2 inches below the liquid surface. Other ports were provided for the addition of chemicals.

Agitation was provided by a variable speed mixing motor (Lightning Mixer Company) adjustable between 213 and 1120 RPM. This motor was coupled to the tank through two universal joints between which was mounted a torque meter (The Bex Company) which allowed measurement of the torque delivered to the liquid in the tank plus that delivered to the bearings in the headplate. Torque readings and mixer speed were read simultaneously using a strobe light (General Radio Company).

The gas feed system is shown in Fig. (3.1). The system was designed in such a way as to allow either a single gas or a mixture of gases to be fed to the tank. During normal operation, either air or a \text{CO}_2-N_2 mixture was used. Compressed air was first filtered to remove any suspended oil aerosol and then metered through a rotameter at 15 psig. This air was then humidified in a 6" diameter x 3' long Pyrex glass column packed with
stainless steel wool. During runs involving the use of alkali in the tank, this column contained concentrated KOH solution. This removed the CO₂ present in the air and humidified the gas at 25°C. The gas was then filtered again through 2' of packed glass wool contained in another glass column of 6" diameter. The gas then entered a manifold where it could be exhausted to the atmosphere or directed into the sparger at the base of the tank. CO₂-N₂ mixtures or pure N₂ gas on the other hand were obtained from gas cylinders and were metered and passed directly into the manifold without humidification or filtration. Mixing of the gases was possible either in the manifold or directly after the rotameters.

Other equipment was at times attached to the tank and will be described later when describing the appropriate experiments.

2. Calibration of Equipment

The two rotameters used for gas metering to the tank were calibrated at 15 psig using a wet test meter. Standard curves were drawn and checked occasionally against rotameter performance. No change in rotameter calibration was observed during the period of the experiments. The rotameter calibration curves are included in the Appendix in Section (III.1).

The pH meter was calibrated by removing a sample of the tank liquid and finding its pH on an already calibrated meter and then adjusting the tank meter to read this pH.

The proportional temperature controller was calibrated using a thermometer and was operated using a proportional band width of 0.5°C. This allowed use of full power for tank heatup to within a fraction of a degree of operating temperature and proportional control in the vicinity of the set
point. Due to the use of proportional rather than integral control, there was necessarily a slight offset of the actual temperature from the set point temperature. This offset never exceeded 0.2°C except during some sodium sulphite oxidation runs where the heat generated by the reaction exceeded the capacity of the cooling coil to remove it. The average temperatures achieved in these runs are noted in the Appendix, Sections (IV.8)-(IV.10).

3. Power Measurements

The amount of power transmitted to the tank contents through the stirrer was calculated from the torque measured on the torque meter and from the stirring speed. This power was actually the sum of two terms, i.e., the power delivered to the liquid and the power dissipated in the bearings mounted in the tank headplate. The bearing friction was found to vary from run to run depending upon the stirring speed, the degree of lubrication and the shaft alignment. The temperature of the bearing housing also increased during the runs and had some effect on the bearing friction. After a run was completed, the tank was drained and the torque meter was read. This value was taken to be the bearing friction and was subtracted from the total torque reading to give the torque delivered to the liquid. This latter torque was the one then used to calculate the power dissipated in the tank contents.

In the ungassed systems, the power dissipated at speeds below 600 RPM was found to agree very well with values calculated assuming a power number of 6. Above this speed, due to the relatively large surface area of the liquid, some entrainment of gas from the headspace was found to occur.
and the power number was found to decrease. Thus, below 600 RPM, the friction could also be calculated from the discrepancy between the power delivered by the shaft and the power calculated to be delivered to the liquid. This was necessary in some runs where the tank contents were not drained between runs.

When gas was added to the liquid through the sparger, the power dissipated was reduced. A general discussion of this is available in reference (76). In most runs the power dissipated in the ungassed system was measured first and the friction of the bearings was calculated. Then the total power dissipated in the gassed system was measured and the friction of the bearings was subtracted to find the actual power dissipated in the gassed liquid. Above 600 RPM's it was often necessary to use past measurements of the power dissipation in runs where the friction was actually measured in order to find the actual power dissipated in the liquid. Since these runs necessarily involved higher power inputs, the error in using this method was less than a few percent.

Fig. (3.3) indicates the effect of entrainment of gas from the headspace into the liquid by vortexing upon the torque delivered by the impeller. At approximately 13 in-lb of torque, the amount of power delivered by the impeller decreases as shown. The value of the calculated torque (the abscissa in Fig. [3.3]) is found from the Power Number, defined as

$$N_p = \frac{P_g c}{N D_i^5 \rho} \quad (3.1)$$

At high values of the Reynolds Number, the Power Number for the impeller used in this work was 6.0. This result is in excellent agreement with the work of Rushton, et al. (77).
Basis for calculation
Power number = 6.0
$D_i = 4.0''$
$T = 12''$
$h_L = 12''$

Fig. 3.3. Effect of entrained headspace gas on measured torque in the absence of forced aeration. Temp. = 30°C.
The reduction in shaft power brought about by the introduction of gas below the impeller through the sparger is illustrated for several systems in Fig. (3.4). The results are plotted against the Aeration Number, defined by Ohyama, et al. (78) as

$$ N_a = \frac{Q}{ND_i^3} \quad (3.2) $$

Data at high aeration numbers scatter considerably. This scatter is due to the low values of stirrer speed at high aeration numbers. At these low stirrer speeds, the difference between the frictional torque delivered to the bearings of the tank and the total torque delivered by the shaft is a very small number and subject to considerable experimental error. The range of Aeration Numbers from $2 \times 10^{-2}$ to $9 \times 10^{-2}$ was subject to the least error in torque meter reading and the data in this region appear to fit the correlation very well.

It should be pointed out that the value of $P$ in the dimensionless ratio $P_{g}/P$ was calculated on the basis of a Power Number of 6. This was necessary in order to get valid results at low Aeration Numbers (high stirrer speeds) where vortexing occurred.

It is clear from Fig. (3.4) that in all systems shown, the data can be correlated to a single curve. It is also clear that the Power Number is independent of viscosity of the solution in an ungassed system as long as the system is turbulent. Therefore very little difference should be expected between the power inputs of all systems studied at equal stirring speeds for the low viscosity systems studied. The effects of non-Newtonian viscosity on agitator power requirements have been investigated by several workers (79-87).
Fig. 3.4. Correlation of mechanical power input in the presence of gassing as a function of the aeration number. Temp. = 30°C.

- □ = Distilled water (0.0106 ft/sec)
- ○ = Distilled water (0.0212 ft/sec)
- △ = Distilled water (0.0318 ft/sec)
- ♦ = 0.1M ionic strength soln. (0.0212 ft/sec)
- ▲ = 0.1M ionic strength soln. + 0.33% paper pulp (0.0212 ft/sec)
- □□ = 0.1M ionic strength soln. + 1% "Solka Floc" wash water (0.0212 ft/sec)
4. **Design and Calibration of Oxygen Probe**

The dissolved oxygen probe used in this work was built in our laboratory according to the design of Borkowski (37, 38). It was mounted in the tank by placing it inside a piece of stainless steel pipe provided with a vent for pressure equilibration between the inside and the outside of the teflon membrane.

The performance of the probe was checked in several ways. Since theory predicts a linear relationship between oxygen partial pressure in the liquid and probe reading, experiments were performed in which various gas mixtures of oxygen and nitrogen were fed to the tank liquid. The steady state reading of the probe was recorded at each concentration. Temperature was controlled at 30°C. In other experiments, the value of the membrane diffusivity was determined by measuring the unsteady state response of the oxygen probe to a step change in oxygen concentration.

The step change experiments with the oxygen probe were performed in the following way. Two solutions were prepared. The first solution contained distilled water at 30°C and was agitated with a teflon coated stirring bar in order to eliminate any liquid film resistance effects on the surface of the probe membrane. Air was sparged into this vessel in order to achieve oxygen saturation at 0.209 atmospheres of oxygen partial pressure. After equilibration of the probe at these conditions, the second solution of 0.5M Na₂SO₃ + 10⁻³M CuSO₄ at 30°C was rapidly substituted for the original solution. The second solution had a dissolved oxygen concentration of zero and was also agitated by a teflon coated stirring bar.

The value of the slope of the oxygen response curve at its inflection point was then compared with the slope vs. membrane diffusivity curve.
found in Appendix (III.2). This curve was generated by assuming a $K_L\alpha$ value of 144,000 hr$^{-1}$ and is indistinguishable from the analytical result one can derive for a step change (infinite $K_L\alpha$).

5. Solution Preparations

All solutions were prepared using distilled water. Comparative experiments using tap water were indistinguishable from those in distilled water but are not reported because of the inherent variability of the ionic and organic components of tap water. Also, since $K_L\alpha$ measurements are known to be extremely sensitive to the presence of surface active materials, it was felt that distilled water would give more reliable results than tap water (60, 88, 89).

The solutions were prepared by first measuring out 21.9 liters of distilled water into two 5-gallon Pyrex glass jars which were carefully cleaned initially and scrupulously protected from contamination. Ionic additives were weighed out on a pan balance and added to the water. The jars were then shaken until the ionic additives dissolved. In those cases where KOH was to be added to the solution, a concentrated (2 molar) solution from a stainless steel storage tank was added. In these cases, the amount of distilled water plus KOH solution was 21.9 liters.

Sodium sulphite solution makeup presented some interesting problems. Dissolution of the sodium sulphite was followed by the addition of CuSO$_4$$_6$. It was found that the addition of CuSO$_4$$_6$ either in the pentahydrate or the anhydrous form presented difficult dissolution problems when added in solid form at basic pH. To alleviate this problem, the CuSO$_4$$_6$ was prepared as a standard solution and then a carefully measured amount (30 ml) was pipetted
into the jars containing the sodium sulphite solution. A temporary precipitate then formed, which, after several minutes of shaking, redissolved into the liquid. Several color changes occurred during this time and it appears likely that the state of the copper ion in the solution was much more complex than cupric ion.

All reagents used were of analytical grade and met ACS specifications on the maximum limits of allowable impurities.

In those experiments calling for the addition of "Solka Floc", grade SW-40 as supplied by The Brown Company was used. The material was measured out on a pan balance in approximately 80-gram batches and added to the jars through a paper funnel. Care was taken to avoid inhalation of the fibers. Any large clumps of "Solka Floc" were broken up before addition to the jars. The jars were then covered and shaken to suspend the material. This procedure was repeated every few minutes until all the fiber clumps were broken apart and the material was thoroughly wetted by the solution.

In all cases, the material was then transferred to the stirred tank by carefully pouring it through a funnel which fitted securely into the headplate of the fermenter. Where "Solka Floc" was present, the jars were shaken several times during the transfer operation in order to keep the material suspended. Better than 95% of the "Solka Floc" could be transferred in this way. The solutions and suspensions were then allowed to remain in the tank under agitated conditions in order to achieve operating temperature (usually 30°C) and in order to keep any solid material suspended.

After each run, the tank was thoroughly cleaned by rinsing with tap water and then distilled water. A minimum of four tap water rinses was usually required. The tank was filled with distilled water and left
overnight. Before filling the tank with the experimental solutions for
the next day, the tank was drained and then vacuumed out with a tube con-
ected to a flask under vacuum. This insured that almost all of the dis-
tilled water was removed. No attempt was made to dry the tank.

After the completion of the final sodium sulphite oxidation run,
the green precipitate which clung to the wall of the tank was removed by
a wash of the tank with dilute H₂SO₄ followed by thorough rinsing. More
will be said about this precipitate later.

In those runs requiring the use of paper pulp suspensions, What-
man #40 filter paper discs (15.0 cm diameter) were weighed out on a pan
balance. They were then shredded by hand, 6 discs at a time, into 3/8 to
1/2 inch squares. The shredded paper was then placed in a "Waring Blender"
with approximately 450 ml. of distilled water and agitated at high speed
for 10 minutes. The pulp was then poured into a 5-gallon pyrex glass jar.
This procedure was repeated until all the filter paper had been pulped.
In most runs, a 0.33% paper pulp was prepared by weighing out 73 grams of
filter paper for pulping. The pulp was then stored for at least 2 days
in order to further break apart the fibers.

Wash water runs were performed using the filtrate prepared from
either "Solka Floc" suspensions or paper pulp suspensions. "Solka Floc"
wash water was prepared by weighing out 219 grams of "Solka Floc" in two
109.5 gram batches. The first batch was suspended in 1.5 liters of dis-
tilled water and mixed. It was then filtered in a Buchner funnel using
Whatman #40 filter paper (of high purity). The pulp was then resuspended
for a total of 6 washings and filtrations. The second batch of 109.5 grams
was then treated in an identical manner and all the washings were combined
in a 5-gallon glass jar. The first washings of the "Solka Floc" had a yellowish tinge, indicating the presence of soluble impurities. The filtrate also had a number of bubbles on the liquid surface which gave it the appearance of detergent. Surface tension measurements, however, were similar to those for water. Paper pulp prepared from Whatman #40 filter paper was treated in three aliquots because of the greater difficulty of filtration with this material. The first washing from this material was colorless and clear and did not show any visual difference when compared to distilled water. The pulp was prepared in an identical manner to that used in all mass transfer runs using paper pulp before filtration in order to simulate actual conditions as closely as possible.

6. $K_L a$ Measurement Techniques and Procedures

Several different methods were used for the determination of the overall volumetric mass transfer coefficient ($K_L a$) in the experimental equipment.

a. The Sampling Method. The first method to be described is the sampling method. This method takes advantage of the accuracy of the dissolved oxygen probe when operated at steady state. The diagram for the experimental apparatus is shown in Fig. (3.5).

The sampling method is based upon the unsteady state response of the tank liquid to a step change in oxygen concentration. A set period of time after the step change, the sample was allowed to flow into the sampling chamber. The steady state reading of the oxygen probe in the sampling chamber then indicated the concentration of oxygen in the tank at the time of sampling. From the known effect of $K_L a$ on the change in liquid composition with time, $K_L a$ could be calculated.
Fig. 3.5. Experimental apparatus for $K_a$ determination by sampling method.
In practice a 100 cm$^3$ capacity sampling chamber, into which was inserted an oxygen probe built in our laboratory was used. This probe did not have a metal protective casing. A Millipore syringe capable of pumping air into the sampling line was connected to a glass tee at the sample port in the tank and the sampling line was connected to the third leg of the tee. The sample chamber was provided with a glass stirring bar which eliminated any significant liquid film resistance to mass transfer at the surface of the probe membrane. This stirring bar was turned by a magnetic mixer. An asbestos board was placed between the sampling chamber and the magnetic stirring motor in order to eliminate temperature changes in the sampling chamber due to heat generated by the mixing motor. The top of the chamber was sealed with a rubber stopper into which was inserted the oxygen probe and a small bore capillary glass tube. This tube allowed air to escape during the sampling and filled with liquid when the chamber was full. The liquid in the capillary acted as a diffusion barrier to the transfer of oxygen from outside of the chamber. A digital clock, capable of measuring time to 0.1 seconds was provided to record the time of sampling and the length of time elapsed during the sampling. Oxygen activity was recorded on a 0-10 mv. recorder.

The experiments were performed as follows. A sample of liquid saturated with oxygen from the air was drawn into the sample chamber from the tank at room temperature and the steady state reading of the oxygen probe in the sample chamber was recorded. The sample chamber and sample line were then drained and flushed with the Millipore syringe by blowing air through them. No more than 0.5 cm$^3$ of liquid remained in the sampling system after this procedure. A step change in the feed gas composition to
the tank was then made and after a predetermined length of time (calculated so as to make the experiment most sensitive to $K_L a$), the sample line pinch clamp was opened and liquid flowed into the sample chamber. The time at this point was noted. When the sample chamber was filled and liquid began to come out of the glass capillary at the top of the chamber, the pinch clamp was closed and the time was again noted. After 5 minutes, when steady state was achieved, the oxygen probe reading was recorded. The temperature of the sample did not change significantly during this period. The sample chamber was then drained and prepared for succeeding experiments.

It was assumed that the oxygen concentration being measured in these experiments was the mean concentration. That is, the time of sampling was chosen as the arithmetic mean of the time sampling began and the time sampling ended. This assumption seemed justified in light of the uncertainties inherent in the sampling procedure. For example, the flow rate of the sample varied with time, being very large initially as it flowed through the empty channel and then tapering off as the liquid head decreased and the friction in the channel increased.

b. The Unsteady State Oxygen Probe Response Method. Another method of determining $K_L a$ is the unsteady state oxygen probe response method. The bulk of the $K_L a$ values obtained in the reported experiments were obtained in this way. This method, as described in Section (2.6), depends upon the response of the oxygen probe in the tank to an unsteady state change in liquid partial pressure of oxygen. The experiments involved a step change in feed gas oxygen partial pressure which brought about a transient change in liquid activity of oxygen. This change in oxygen activity was sensed by the probe and was transformed into a new transient response after being modified by the probe membrane.
The experimental setup was the same as that shown in Fig. (3.1). The tank was initially equilibrated with either air or nitrogen-carbon dioxide mixtures (including pure nitrogen) and allowed to achieve saturation and operating temperature (30°C usually). Because of the extreme sensitivity of the oxygen probe to temperature variations, this initial equilibration period was of utmost importance. During this period the stirrer was in operation in order to give adequate mixing and in order to reduce the liquid film at the oxygen probe membrane to insignificant size. Gas was fed continuously into the tank through the sparger in order to achieve saturation.

After equilibration of the equipment, a step change in feed gas composition was achieved as follows. First the initial gas was turned off and the bubbles in the liquid allowed to leave the liquid phase. Then the new gas was turned on and exited to the exhaust pipe. Once this gas flow was steady and the original gas purged from the manifold, the recorder was turned on (1800 in/hr chart speed) and recorded the oxygen activity. The manifold valves were then turned simultaneously in order to direct the new feed gas into the sparger. Power input data was taken as described previously, during the period of manifold purging (ungassed power) and during the experimental period (gassed power). The oxygen activity was monitored continuously and the chart readings at the beginning and the end of the experiment recorded. The experiment was allowed to continue until the probe reached equilibrium at the composition of the new feed gas. Continuous monitoring was usually maintained but the chart paper was stopped after approximately 70% response had been achieved in order to conserve paper.
The slope of the oxygen response curve at the inflection point of the curve was then read and the value of $K_L$ calculated as described in Section (2.6). It appears likely that at stirring speeds in excess of 600 RPM the step change was not as sharp as desired due to the presence of entrained gas bubbles which mixed with the new feed gas.

c. **Other Oxygen Probe Methods.** Other methods were also used but either proved too tedious or impractical under the restraints of our system. One of these, the flow reactor experiment (as described by Robinson and Wilke, [36]), required the use of unusually high flow rates in the present scale equipment. These flows were unachievable. One experiment performed at lower flow rates gave such a low oxygen activity in the liquid at steady state that the result was no more accurate than ± 20%. The value obtained in this way agreed with the results of the other methods but because of its inaccuracy was not reported.

d. **The Sulphite Oxidation Method.** The final method used for the determination of the overall volumetric mass transfer coefficient was the sulphite oxidation method of Cooper, Fernstrom and Miller (56). In the present experiments a 0.5M Na$_2$SO$_3$ + 10$^{-3}$M CuSO$_4$ solution was used. In experiments calling for the addition of "Solka Floc", either 1% or 3% by weight of this material was added to the solution. The makeup procedure was as described previously. The pH of the solutions before the runs was usually 9.5-9.7 pH units. This pH was found to change slightly during the runs.

The experiments were performed as follows. After the sulphite solution was added to the tank and the system had achieved equilibrium with respect to temperature under a nitrogen atmosphere, the air was turned on and directed into the tank through a sparger. The time at this point was
noted. After about 6 minutes, a sample of the tank liquid was withdrawn and analyzed as described below. Samples were taken at various times after this and analyzed. The number of samples taken during the run ranged in number from 3-5.

Sample analysis was carried out using an iodometric titration. 0.1N iodine reagent in KCl and standardized Na$_2$S$_2$O$_3$·5H$_2$O (24.819 g/liter) were prepared. Just before use, 40.0 ml of the I$_2$ solution was measured out by pipette into a 250 ml flask. A 2 ml pipette was then flushed with purified N$_2$ for a few seconds. After covering the end of the pipette, a 2 ml sample of Na$_2$SO$_3$ solution (the sample) was discharged into the I$_2$ solution. The tip of the pipette was held within 1 cm of the I$_2$ surface during this procedure. The I$_2$ was then mixed well and 4 drops of starch indicator solution were added. The I$_2$ was then titrated with thiosulfate until all the residual I$_2$ was consumed. The titration reactions are listed below.

$$\text{SO}_3^{2-} + \text{H}_2\text{O} + \text{I}_2 \rightarrow \text{SO}_4^{2-} + 2\text{HI}$$

$$2\text{S}_2\text{O}_3^{2-} + \text{I}_2 \rightarrow \text{S}_4\text{O}_6^{2-} + 2\text{I}^{-1}$$

The sulphite concentration in the sample could be calculated as

$$N' = 1.00 - 0.025 (V) \quad (3.3)$$

where $N'$ = normality of SO$_3^{2-}$ (equivalents/liter)

and $V$ = volume of thiosulfate added (ml).

At all stages of the experiments, precautions were taken to eliminate the presence of oxygen. The original solutions for testing were prepared in glass jars as described previously but nitrogen gas was substituted for air in the gas space above the solutions.
During the runs, a precipitate formed in the solutions after a certain stage in the experiments. The slope of the concentration of \( \text{SO}_3^- \) vs. time curve was not affected by the presence of this precipitate. Preliminary experiments indicated that the time of appearance of this precipitate was related to the initial concentration of \( \text{CuSO}_4 \) catalyst. Since the kinetics of the reaction are independent of catalyst concentration between \( 10^{-4} \) and \( 10^{-3} \) M \( \text{CuSO}_4 \) concentration, apparently enough catalyst remained in solution during the runs to remain above \( 10^{-4} \) M concentration.

7. Interfacial Area Measurement Technique and Procedure

Interfacial area experiments were performed using the absorption of \( \text{CO}_2 \) into \( \text{KOH} \) solutions. The concentrations of \( \text{KOH} \) used ranged from less than 0.01 M to 0.06 M. In all experiments the value of \( K_L^2 \) was negligible in comparison with the value of \( D_{\text{CO}_2} k_2 B \) in Eq. (2.24) and could be ignored. The gas phase composition was constant at 10\% \( \text{CO}_2 \)-90\% \( \text{N}_2 \) and was checked on the infrared \( \text{CO}_2 \) analyzer by mixing the 10\% \( \text{CO}_2 \) stream with a known quantity of air and then passing the mixture through the analyzer. Once the composition of the \( \text{CO}_2-N_2 \) mixture was known, it was not checked again until a new gas cylinder was needed.

The infrared analyzer used had three ranges: 0-4.5\% \( \text{CO}_2 \), 0-2.5\% \( \text{CO}_2 \), and 0-0.7\% \( \text{CO}_2 \). Depending upon the composition of the gas leaving the tank, one of these ranges was selected. The instrument was calibrated on all scales before every run and had an accuracy of 1\% of full scale. The gas rate through the analyzer sample cell was kept below a level where it could cause distortion of the analyzer reading. The position of the infrared analyzer is shown in Fig. (3.1).
The composition of the KOH in the tank liquid was checked by titration with HCl before and after the run. The concentration of CO$_3^{2-}$ was also determined. Titration after the run was carried out on a Beckman pH meter using either a 5 or a 10 ml sample. The first endpoint indicated the concentration of the OH$^{-1}$ ion plus one half the normality of the CO$_3^{2-}$. The second endpoint represented the titration of the rest of the CO$_3^{2-}$.

A graph of pH vs. volume of HCl titrant added was constructed for each run and the concentrations of OH$^{-1}$ and CO$_3^{2-}$ were determined. The HCl titrant was standardized against a standard NaOH solution which in turn was standardized against a weighed sample of potassium biphthalate.

In order for the experimental results to be meaningful, it was necessary to maintain the concentration of KOH constant during the period of the run. A method of doing this was devised based upon Fig. (3.6). Here it can be seen that as the percentage of incoming CO$_2$ gas absorbed by the liquid exceeds 90%, the concentration of the exiting CO$_2$ gas approaches zero asymptotically. Taking advantage of this fact it was possible simply to add KOH as a concentrated solution at precisely the rate at which it was being consumed by chemical reaction. It can be shown that if 98% of the CO$_2$ is absorbed instead of 97%, for example, that only 1% more KOH is consumed whereas the exit concentration of CO$_2$ changes dramatically. This indicates two things. Firstly, the exit CO$_2$ concentration is the most sensitive parameter for measuring the interfacial area. Secondly, the addition of KOH at a molar rate in the vicinity of the asymptotic usage rate will allow the system to reach a steady state in which the rate of chemical reaction between the CO$_2$ and the KOH will equal the rate of addition of the KOH. The
Fig. 3.6. Rate of reaction of KOH at different interfacial areas.
experimental apparatus used to perform the required addition of KOH is shown in Fig. (3.7).

The addition funnel works on the principle of the constant head addition devices developed for other applications. The difference in pressure between the bubbling tube tip in the funnel and the exit end of the addition tubing is a constant. The teflon valve allows control of the addition rate. The device was calibrated before each run and added 2M KOH during the entire period of each run. The flow rate of the KOH was approximately 104-113 cm$^3$/min.

The experimental procedure was as follows. After the appropriate KOH solution was added to the tank, the tank and its contents were allowed to equilibrate to the operating temperature. During this period, the oxygen probe and infrared analyzer were in operational condition (warmed up and calibrated) and the alkali addition funnel was calibrated by collection of the concentrated KOH solution in a graduated funnel under identical head conditions as would exist during a run. The slight elevation of the pressure in the tank due to the presence of the gate valve on the exit gas outlet was not significant in comparison with the total head under which the addition funnel operated and was ignored. A sample of the KOH in the tank was then analyzed before the run began. The oxygen probe reading and the infrared analyzer reading were recorded on a double pen recorder. The chart paper was then started. Following this, 10% CO$_2$-90% N$_2$ was passed into the tank through the sparger as described for other experiments and the oxygen tension and CO$_2$ concentration were recorded. After about 1 minute the chart paper was stopped and the recorder allowed to monitor the two compositions every minute for 5 minutes. After 5 minutes the addition funnel
Fig. 3.7. Constant rate KOH makeup device.
was shut off and the gas feed was shut off. As rapidly as possible, a sample of the tank liquid was withdrawn for analysis and analyzed immediately.

In those runs reaching a steady state, the CO₂ concentration in the exit gas was taken to be the steady state reading. In those runs not reaching a steady state due to experimental difficulties, either the results were discarded or the average exit CO₂ concentration was used. This choice depended upon the infrared analyzer readings.

The average concentration of OH⁻ was chosen to be the final OH⁻ concentration in those runs reaching steady state and as the average of the initial and final OH⁻ concentration in those runs not achieving steady state. The average CO₃⁻² concentration was taken to be one-half the final CO₃⁻² in all runs. Spot checks of the concentration of CO₃⁻² in the original pre-experimental KOH solutions did not reveal the presence of any detectable CO₃⁻². The ionic strength of the solution was calculated using the average values of KOH, KCl, K₂CO₃ concentration. In all runs the ionic strength of the initial solution was adjusted to 0.06M using KCl. The ionic strength is given as

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

where \( \Gamma \) = the ionic strength (moles/liter)
\[ z_i \] = the ionic charge of species \( i \)
\[ c_i \] = the concentration of species \( i \) (moles/liter).

8. Holdup Measurements Technique and Procedure

A new holdup measurement technique was devised for the purpose of measuring the volume of the dispersed gas phase in the experimental solutions.
investigated. A diagram of the holdup apparatus is shown in Appendix (II.2). Essentially, the method is a manometric one, where the difference in hydrostatic pressure between the ends of two hollow tube probes is sensed on a manometer. A derivation of the relevant equation describing the holdup in terms of the pressure difference between the two probe tips is also given in Appendix (II.2).

The probes were filled with liquid at all times. The liquid levels in the large flasks were maintained at the same levels as the tips of the probes to which they were attached. The surface area of the liquid (water) in these flasks was large enough so that any liquid in the lines, which flowed into or out of the flask in response to changes in pressure, did not change the height of liquid in the flasks to a measurable extent. If this were not so then some correction for this effect would have been necessary when making the manometer readings.

100 cm$^3$ syringes were attached to the manometer lines. These syringes were used to flush out any bubbles or solid material (paper pulp or "Solka Floc") which entered the lines during and after the adjustment of pressure between the pressure probes and the manometer. These syringes were filled with distilled water and were operated by clamping shut the manometer lines following the syringes and flushing the liquid from the syringes into the tank. The quantity of liquid flushed depended upon the amount of manometer adjustment taking place and was usually about 10 cm$^3$. The presence of gas in the manometer lines would destroy the very delicate pressure balance of the system and thusly, this back-flushing eliminated errors from this source.
The position of the probes was adjusted in order to minimize the
effects of velocity upon the manometer reading. By trial and error, a
suitable position was found in which the variation of manometer reading
(below 600 RPM) with stirring speed was kept below a few percent of the
manometer reading. The assumption was made that in the presence of gas
holdup, this position still eliminated velocity effects. The entire sys-
tem would then respond linearly to pressure changes between the probe tips.

In order to further minimize problems of gas bubbles entering the
probe tips during the run and after flushing (bubbles could enter vertical
tubes by flowing upward under the influence of gravity) the probes were
designed with the openings on the side of the tubes. Each tube contained
a single opening of 1/8 inch diameter located 0.3 inches from the probe
bottom. The probes themselves were 1/4 inch tubes of stainless steel and
were square in cross-section in the vicinity of the holes but round in
cross-section everywhere else. The tube position was adjustable due to
the use of teflon ferrules in stainless steel Swagelok fittings. The loca-
tion of the probes was equal in terms of radial distance from the center
of the tank.

It was further assumed that the reading of the probes was represen-
tative of the holdup for the entire tank and not just of the space between
the probes. The one probe was located very close (0.4 in) to the bottom of
the tank and the other probe was located about 8 inches from the tank bot-
tom. This region covered the region of greatest vertical variation in
holdup as determined by other investigators (71) and was considered satis-
factory.
The experiments were performed as follows. The tank was filled with 21.9 liters of liquid to be tested. The contents were then heated to 30°C with agitation. During this period the manometer tubes were clamped. After attainment of temperature, the stirrer was shut off and the manometer lines flushed. The zero reading (i.e., the reading in the absence of agitation) was then taken. The stirrer was then turned on and the reading in the presence of stirring but the absence of gassing was then taken as a check on velocity effects. If the stirring speed was very high (greater than 600 RPM) the manometer was flushed for this reading in order to eliminate the presence of gas bubbles which entered the manometer lines due to entrainment from the tank headspace. The manometer lines were then clamped shut and the gassing begun. After about 15 seconds, the manometer lines were again opened and after about 30 seconds they were clamped shut again and then flushed. This eliminated the presence of gas bubbles. The clamps were removed and the manometer again readjusted. During this readjustment some more gas bubbles often entered the manometer lines. The flushing procedure was repeated until two successive readings gave the same value for the manometer deflection. The holdup was then calculated according to the method outlined in Appendix (II.2). Power readings were taken throughout this period as outlined previously.

It was observed that the holdup reached a steady state very rapidly after the commencement of gassing (about 8 sec. required). Manometer readings varied during any particular measurement due to fluctuations in the tank and the average reading of the manometer was used in each case to determine the holdup.
IV. RESULTS OF EXPERIMENTS

1. Oxygen Probe Diffusivity

The computer generated curve of oxygen probe membrane diffusivity as a function of the slope of the oxygen probe response curve at its inflection point is shown in Fig. (4.1) for a liquid step change experiment performed at 30°C as described in Section (3.4). Two experiments were performed and yielded membrane diffusivities of $1.56 \times 10^{-7}$ cm$^2$/sec and $1.58 \times 10^{-7}$ cm$^2$/sec assuming a membrane thickness of 2 mils.

Fitting mass transfer data by the Least Squares Varmit Program to two parameters, $K_a$ and $D_M^*$, gave values of membrane diffusivity of $1.562 \times 10^{-7}$ cm$^2$/sec. Since this value lay in the range of the step change experiments, it was used in all subsequent calculations at 30°C.

The effect of temperature on oxygen probe output current was quite dramatic and was assumed to be a reflection of the effect of temperature on membrane diffusivity. The value of membrane diffusivity at temperatures other than 30°C was calculated as

$$D_M (at \ T) = D_M (at \ 30^\circ C) \times \frac{E_{sat.}(at \ T)}{E_{sat.}(at \ 30^\circ C)} \quad (4.1)$$

The linearity of probe output with partial pressure of oxygen was also checked and the experimental results are shown in Fig. (4.2). As can be seen from the figure, the probe responded linearly to oxygen partial pressure.

The effect of temperature on oxygen diffusivity in the teflon membrane of the dissolved oxygen probe is shown graphically in Fig. (4.3). Comparison of the diffusivity values with those of Robinson and Wilke (36) and Heineken (70) appears quite reasonable. The value of diffusivity
Fig. 4.1. Effect of membrane diffusivity on slope of oxygen probe response curve at inflection point for a step change experiment at 30°C.

K_La = \infty \quad \text{Henry's constant} = 834.5 \text{ liter-atm/mole}
Fig. 4.2. Oxygen probe linearity check at 30°C using various metered gas mixtures.
Fig. 4.3. Diffusivity of oxygen in teflon membrane.
(20°C to 37°C)
reported by Heineken was based upon an assumption that the thickness of the membrane used on his probe was 0.001 inches. It appears likely, however, that his membrane was actually 0.002 inches in thickness, in which case the diffusivity value is four times larger than that which he reports. This corrected diffusivity value is plotted in the figure.

2. \( K_{L}a \) Experiments Using Dissolved Oxygen Probe

a. The Sampling Method. Experiments were performed using the sampling method as described in Section (3.6). Results for \( K_{L}a \) were then corrected for temperature to 30°C using the method recommended by Aiba, et al. (76) which corrects the \( K_{L} \) term of \( K_{L}a \) for temperature assuming \( K_{L} \propto D_{O_{2}}^{1/2} \). Two readings were obtained in this way at \( F = 0.0106 \) ft/sec by desorption with nitrogen. The results are shown in Table (4.1). Distilled water was used in both runs.

<table>
<thead>
<tr>
<th>N (RPM)</th>
<th>Temp. (°C)</th>
<th>Start to fill chamber (sec)</th>
<th>Stop filling chamber (sec)</th>
<th>( \beta ) (min(^{-1} ))</th>
<th>( K_{L}a ) (hr(^{-1} )) at 30°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>418</td>
<td>20.7</td>
<td>20</td>
<td>27</td>
<td>1.48</td>
<td>110</td>
</tr>
<tr>
<td>418</td>
<td>21.6</td>
<td>20</td>
<td>28</td>
<td>1.52</td>
<td>113</td>
</tr>
</tbody>
</table>

Here \( \beta \) is defined by Eq. (2.34) and takes into account the liquid phase mass balance during desorption of oxygen.

b. Unsteady State Oxygen Probe Response Method--Distilled Water. Computer generated curves showing the slope of the oxygen probe response curves at the inflection point vs. the value of \( K_{L}a \) during unsteady state oxygen desorption experiments are shown in Fig. (4.4) for low \( K_{L}a \) values and in Fig. (4.5) for high \( K_{L}a \) values. The effect of gas velocity on the probe response is shown for three different gas velocities in distilled water.
Fig. 4.4. Slope of oxygen probe response curve at inflection point in distilled water at 30°C.

\[ D_M = 1.562 \times 10^{-7} \text{ cm}^2/\text{sec} \]

Henry's constant = 834.5 liter-atm/mole
Fig. 4.5. Slope of oxygen probe response curve at inflection point in distilled water at 30°C.

\[ D_M = 1.562 \times 10^{-7} \text{ cm}^2/\text{sec} \]

Henry's constant = 834.5 liter-atm/mole
Experimentally, the value of the inflection point slope was taken to be

\[
\frac{(\Delta E/\Delta t)}{3600} = \frac{3600}{(E_\infty - E_0)} = \text{Slope (hr}^{-1}\text{)}
\]  

(4.2)

where \(\Delta E\) = chart reading change (mv)

\(\Delta t\) = time change (sec)

\(E_\infty\) = steady state reading (mv)

\(E_0\) = initial reading (mv)

The results of many experiments performed at 30°C with distilled water are shown in Fig. (4.6). The corresponding data are reported in the Appendix, Section (IV.1). The effect of gas rate was determined for three different superficial velocities and \(K_L a\) was correlated to \(P^{0.56}\) for power inputs ranging from 0.26 to 50 HP/1000 gal. It can be seen that for power inputs below approximately 2 HP/1000 gal the effect of power input on \(K_L a\) is much greater than at power inputs in excess of this value. This break in the curve corresponds quite closely with the value of the "minimum stirring speed" of 400 RPM found by Westerterp, et al. (33).

Comparison of the \(K_L a\) results obtained by this method with those of the sampling method indicate agreement within 10% which is all that could be expected considering the crudeness of the sampling measurements. Most of the data reported were fit by the Least Squares Varmit Program and found to be in agreement with values obtained by the inflection point slope technique.

c. Unsteady State Oxygen Probe Method—Distilled Water + 1% "Solka Floc".

Since the addition of "Solka Floc" as a solid additive to the liquid phase did not significantly affect the bulk properties of the liquid phase other than its "apparent viscosity", the same computer generated curves used for
Fig. 4.6. $K_a L$ data for distilled water at 30°C.

$K_a = \text{hr}^{-1}$

$F = \text{ft/sec}$
the distilled water system could also be used for those systems containing only distilled water and "Solka Floc". All data for the 1% "Solka Floc"-distilled water system were fit by the Least Squares Varmit Program and spot checked by the inflection point slope technique.

The results of experiments with this system are shown in Fig. (4.7). The relevant data is given in the Appendix, Section (IV.2). The effect of superficial velocity was determined using two different gas rates and $K_L a$ was found to vary with $F^{0.38}$ over the power range 0.29 to 40 HP/1000 gal. Over most of the power range investigated, $K_L a$ was found to vary with the power input as $(P_g/V_L)^{0.65}$; however, at low power inputs, a break in the curve occurs similar to that occurring in the distilled water system, but at lower stirring speeds (around 300 RPM). It should be noted that the superficial velocity effect here is not well-defined because only two gas rates were used for the determination of gas rate dependence.

d. Unsteady State Oxygen Probe Method--Distilled Water + 3% "Solka Floc". $K_L a$ values for the system, distilled water and 3% "Solka Floc", are shown in Fig. (4.8). The relevant data are given in the Appendix, Section (IV.3). The data were fit by the Least Squares Varmit Program and confirmed by the inflection point slope technique.

The effect of superficial velocity on $K_L a$ was determined using two different gas rates and it was found that $K_L a$ was proportional to $F^{0.38}$ in this system. All of the $K_L a$ data were found to correlate with the power input as $(P_g/V_L)^{0.61}$. The dashed lines indicate the standard deviation as determined by least squares analysis of the data. The power range investigated ranged from 0.38 to 48 HP/1000 gal.
Fig. 4.7. \( K_La \) data for distilled water + 1% "Solka Floc" at 30°C.

\[
K_La = hr^{-1}
\]

\[
F = \text{ft/sec}
\]

\[
K_La = 259.3 \left( \frac{P_o}{V_L} \right)^{0.65} (F)^{0.38}
\]
Fig. 4.8. $K_L a$ data for distilled water + 3% "Solka Floc" at 30°C.

$K_L a = hr^{-1}$

$F = ft/sec$  

$K_L a = 140.1 \left( \frac{P}{V_L} \right)^{0.61}(P)^{0.38}$
e. Unsteady State Oxygen Probe Method—0.1M KOH-KCl-K$_2$CO$_3$ Solutions.

Computer generated curves for the effect of 0.1M ionic strength solutions on the unsteady state oxygen probe response to step change experiments were found to be not much different than those for distilled water. Comparison of the computer results can be seen by looking at the results given in the Appendix, Section (II.1) for $F = 0.0106$ ft/sec.

Determinations of $K_L a$ in these systems were carried out simultaneously with interfacial area determinations and are given in Fig. (4.9).

The data are reported in the Appendix, Section (IV.4). The power range investigated was 0.9-40 HP/1000 gallons at a superficial velocity of 0.0212 ft/sec. Since $K_L a$ determinations were made at the beginning of the experiments on interfacial area, the concentration of K$_2$CO$_3$ could be ignored. Note the linearity of the log-log plot of $K_L a$ vs. $P_g/V_L$ in the power range 0.9-10 HP/1000 gallons. Here $K_L a$ is found to be proportional to $(P_g/V_L)^{0.65}$. Beyond this power range, the effect of power input begins to decrease and eventually to reach saturation above 40 HP/1000 gallons. The inflection point slope method was used for all $K_L a$ determinations in this system.

f. Unsteady State Oxygen Probe Method—0.1M KOH-KCl-K$_2$CO$_3$ + 1% "Solka Floc".

It was observed that ionic strength has no effect on the curve of $\beta$ vs. inflection point slope (Fig. [2.3]). Also, since variations in Henry's constant were small going from distilled water to 0.1M ionic strength solutions, the $K_L a$ vs. inflection point slope curves for distilled water (Figs. [4.4] and [4.5]) were used with little error to determine $K_L a$ in the 0.1M ionic strength solutions.

Determinations of $K_L a$ in these systems were carried out simultaneously with interfacial area determinations and are given in Fig. (4.10).
Fig. 4.9. Mass transfer properties of 0.1M ionic strength KOH-KCl-K₂CO₃ solutions at 30°C, F = 0.0212 ft/sec.
Fig. 4.10. Mass transfer properties of 0.1M ionic strength KOH-KCl-K₂CO₃ solutions with 1% "Solka Floc" at 30°C, F = 0.0212 ft/sec.
The data are reported in the Appendix, Section (IV.5). The power range investigated was 1.1-40 HP/1000 gallons at a superficial velocity of 0.0212 ft/sec. Again, the $K_L a$ measurements were carried out at the beginning of the interfacial area experiments when the concentration of $K_2 CO_3$ in the solution was negligible.

In addition, some runs were carried out using 0.06M KCl solution in a manner analogous to that used for distilled water. Here no simultaneous absorption of CO$_2$ took place and the results are given in the Appendix, Section (IV.5) and are plotted in Fig. (4.10) along with the simultaneous determinations.

The $K_L a$ curve with 1% "Solka Floc" present is seen to parallel the curve in the absence of "Solka Floc" and to give lower $K_L a$ values at any power input.

g. Unsteady State Oxygen Probe Method--0.1M KOH-KCl-K$_2 CO_3$ + 0.33% Paper Pulp.

Determinations of $K_L a$ and $a$ were carried out simultaneously in this system and the results are given in Fig. (4.11) and again in Appendix, Section (IV.6). The power range investigated was 2-41 HP/1000 gallons at a superficial velocity of 0.0212 ft/sec.

The results indicate a reduction of $K_L a$ at all power inputs when paper pulp is added to the salt solution. $K_L a$ is found to be proportional to $P g / V L ^{0.65}$ as was found for the 0.1M ionic strength salt solutions.

h. Unsteady State Oxygen Probe Method--0.5M Na$_2$SO$_4$ + 10$^{-3}$ M CuSO$_4$. $K_L a$ data taken in the presence of concentrated sodium sulphate solution containing 10$^{-3}$ M CuSO$_4$ are given in the Appendix, Section (IV.7). The data were analyzed using the Least Squares Varmit Program with Henry's constant adjusted for ionic strength according to the method of van Krevelen and
Fig. 4.11. Mass transfer properties of 0.1M ionic strength KOH-KCl-K$_2$CO$_3$ solutions with 0.33% paper pulp at 30°C, $F = 0.0212$ ft/sec.
Hoftijzer (52). The results are shown in Fig. (4.12). Over the power range 0.29-4.5 HP/1000 gallons, the data were fit to a straight line vs. power input with a slope of 0.93. As will be shown later, this slope corresponds closely to the slope of the sodium sulphite oxidation runs in distilled water.

3. \( K_L^{\text{r}} \)a Experiments Using Sulphite Oxidation

a. Distilled Water + 0.5M \( \text{Na}_2\text{SO}_3 \) + 10^{-3}M \( \text{CuSO}_4 \) System. \( K_L^{\text{r}} \)a data for the sodium sulphite system was obtained for three different gas rates and over the power range 2.0-26 HP/1000 gallons. The data correlated very well against power input on a log-log plot with a slope of 0.95 as shown in Fig. (4.13). The data are reported in the Appendix, Section (IV.8). The effect of gas rate was determined and \( K_L^{\text{r}} \)a was found to be proportional to \( P^{0.28} \).

Comparison of the slope of the sodium sulphite oxidation runs \( K_L^{\text{r}} \)a vs. \( \frac{P}{V_L} \) curve with the sodium sulphate \( K_L \)a vs. \( \frac{P}{V_L} \) curve indicates a slight enhancement of absorption due to chemical reaction, but no change in slope. Thus the effect of chemical reaction is uniform at different power levels. Note that the two power ranges do not agree but do overlap in the vicinity of 2-5 HP/1000 gallons.

b. Distilled Water + 0.5M \( \text{Na}_2\text{SO}_3 \) + 10^{-3}M \( \text{CuSO}_4 \) + 1\% "Solka Floc". \( K_L^{\text{r}} \)a data for the sodium sulphite oxidation system with 1\% "Solka Floc" added were obtained over the power range 2.0-34 HP/1000 gallons, for three different gas rates. The \( K_L^{\text{r}} \)a results were found to depend linearly on gas rate and for convenience were correlated to a factor, \( \phi \), defined as

\[
\phi = 62.8 \left(10^{7.79P}\right)
\]

(4.3)
Fig. 4.12. $K_L a$ data for distilled water + 0.5M $\text{Na}_2\text{SO}_4$
+ $10^{-3}\text{M} \text{CuSO}_4$.

$$K_L a = 118.1 \left( \frac{P_g}{V_L} \right)^{0.932}$$

$T = 30^\circ\text{C}$

$F = 0.0106 \text{ ft/s}$
Fig. 4.13. $K_{La}$ data for sulphite oxidation in 0.5M Na$_2$SO$_3$ + 10$^{-3}$ M CuSO$_4$.

$$K_{La} = \text{hr}^{-1}$$

$$K_{La} = 472 \left( \frac{P_g}{V_L} \right)^{0.952} (F)^{0.276}$$

$F = \text{ft/sec}$
No fundamental significance should be ascribed to this functional dependence, however. The results are given in Appendix, Section (IV.9) and plotted in Fig. (4.14).

It can be seen that the results plot as a curved line on log-log paper. They start off parallel to the system without "Solka Floc" and then curve over at high power inputs.

c. Distilled Water + 0.5M Na₂SO₃ + 10⁻³ M CuSO₄ + 3% "Solka Floc". The results found in the sodium sulphite oxidation system with 3% "Solka Floc" present are shown in Fig. (4.15) and the data are listed in the Appendix, Section (IV.10). In this system, the effect of superficial gas velocity seems to decrease with increasing power level and no attempt was made to correlate the effects of the three different gas rates used.

Here it can be seen that at low power inputs, the $K_R^L$ results parallel those for the 1% "Solka Floc" and the "Solka Floc" free system. However, at even lower power levels than in the 1% "Solka Floc" system, the curves start to bend over.

Note that the values of $K_R^L$ are lowered by the presence of "Solka Floc" and that the shape of the $K_R^L$ vs. $P_g/V_L$ curve is modified.

The enhancement effect due to chemical reaction was assumed to be the same in the absence of "Solka Floc" and in systems with "Solka Floc" present. For this reason, no determinations of this effect using the dissolved oxygen probe were made in the presence of "Solka Floc".

4. **Interfacial Area Determinations**

a. **0.1M Average Ionic Strength KOH-KCl-K₂CO₃ Solutions.** The results of interfacial area measurements on the system, KOH-KCl-K₂CO₃, are reported
Fig. 4.14. $K_L a$ data for sulphite oxidation in $0.5M \text{Na}_2\text{SO}_3$
$+ 10^{-3} \text{M CuSO}_4 + 1\% "\text{Solka Floc}"$

$K_L a = \text{hr}^{-1}$

$\phi = 62.8 (107.79F)$

$F = \text{ft/sec}$
Fig. 4.15. $K_{La}$ data for sulphite oxidation in 0.5M $\text{Na}_2\text{SO}_3 + 10^{-3}\text{M CuSO}_4 + 3\% "\text{Solka Floc}"$. 
in the Appendix, Section (IV.4) and are plotted in Fig. (4.16). The gas rate was 0.0212 ft/sec in all cases.

Here two effects can be seen. The bottom curve represents the true interfacial area in the systems and the other curves which connect with the true curve and then rise rapidly to impossible values of the interfacial area represent an anomalous effect probably due to mixing. This effect will be discussed later. In order to avoid the anomalous effect it was necessary to maintain the exit concentration of CO₂ above 0.002 atmos. This was done by using lower concentrations of KOH at higher interfacial areas.

b. 0.1M Average Ionic Strength KOH-KCl-K₂CO₃ + 1% "Solka Floc". The results of interfacial area measurements on the system, KOH-KCl-K₂CO₃ containing 1% "Solka Floc", are reported in the Appendix, Section (IV.5) and are plotted in Fig. (4.10). The gas rate was 0.0212 ft/sec in all cases.

Here note that the interfacial area results plot as a straight line on log-log scale as a function of the power input. The area measurements are in all cases lower than those found in the identical systems but without the presence of "Solka Floc".

Area measurements were also attempted in systems containing 3% "Solka Floc" but mixing effects predominated and made such measurements unsatisfactory.

c. 0.1M Average Ionic Strength KOH-KCl-K₂CO₃ + 0.33% Paper Pulp. The results of interfacial area measurements on the system, KOH-KCl-K₂CO₃ + 0.33% paper pulp are reported in the Appendix, Section (IV.6) and are plotted in Fig. (4.11). The gas rate was 0.0212 ft/sec in all cases.
Fig. 4.16. Interfacial area measurements in 0.1M ionic strength KOH-KCl-K$_2$CO$_3$ solutions at 30°C, $F = 0.0212$ ft/sec.
The interfacial area results plot as a straight line at low power inputs and curve over at high power inputs. The results are significantly lower than those obtained in the salt system without paper pulp. Anomalous results, similar to those obtained in the pure salt solutions, were also found in this system at high power inputs. Here, mixing was extremely poor and mixing effects were observed at higher exit CO₂ concentrations than those characteristic of salt solutions without paper pulp.

5. Holdup Measurements

Holdup measurements were made on several systems to determine the effects of salt (ionic strength) and insoluble additives ("Solka Floc" and paper pulp) on the value of the gas holdup. The results of these measurements are found in the Appendix, Section (IV.11) and are plotted in Figs. (4.17-4.22).

The presence of salt is seen to decrease the effect of superficial velocity from \( F^{0.56} \) in distilled water to \( F^{0.50} \) in 0.19M ionic strength solution. The exponent of the power term is also decreased with increasing salt concentration. A further effect of the presence of salt is seen in the introduction of curvature in the holdup vs. power plot.

The presence of "Solka Floc" in 0.06M KOH solution is seen to introduce considerable curvature into the holdup vs. power plots. The effect of superficial velocity is seen to decrease with increasing concentration of "Solka Floc" and to practically disappear at very high power inputs (greater than 20 HP/1000 gal).

Holdup results in the system, 0.1M KCl-0.33% paper pulp, were considerably lower at all power inputs than those for the analogous system.
Fig. 4.17. Holdup for distilled water at 30°C.

\[ H_o = \frac{ft}{ft} \]

\[ H_o = 0.1878 \left( \frac{P}{V_L} \right)^{0.59} (F)^{0.56} \]

\[ F = \frac{ft}{sec} \]
Fig. 4.18. Holdup for 0.06M KOH solution at 30°C.

\[ H_0 = \frac{1}{F^{0.54}} \]

- \( T = 12" \)
- \( h_L = 12" \)
- \( \Gamma = 0.06 \text{M} \)
- \( \circ = 0.0106 \text{ ft/s} \)
- \( \square = 0.0318 \text{ ft/s} \)
- \( \triangle = 0.0212 \text{ ft/s} \)

\[ H_0 = 0.1962 \left( \frac{P}{V_L} \right)^{0.54}(F)^{0.54} \]

\[ F = \text{ft/sec} \]
Fig. 4.19. Holdup for 0.19M ionic strength solution at 30°C.

\[ H_0 = \text{ft/ft} \]

\[ F = \text{ft/sec} \]
Fig. 4.20. Holdup for 0.06M KOH solution with 1% "Solka Floc" at 30°C.

\[ H_0 = \text{ft/ft} \]

\[ F = \text{ft/sec} \]
Fig. 4.21. Holdup for 0.06M KOH solution with 3% "Solka Floc" at 30°C.

\[ T = 12'' \quad h_L = 12'' \quad T = 0.06 \text{ M} \]
\[ o = 0.0106 \text{ ft/s} \quad \square = 0.0318 \text{ ft/s} \]
\[ \triangle = 0.0212 \text{ ft/s} \]

\[ H_0 \text{ (ft/ft)} \]

\[ \text{hp per 1000 gallons} \]

\[ H_0 = \text{ft/ft} \]

\[ F = \text{ft/sec} \]
Fig. 4.22. Holdup for 0.1M ionic strength solution with 0.33% paper pulp at 30°C.

T = 30°C
F = 0.0212 ft/sec
with "Solka Floc". Visual inspection of this material in a glass jar fermenter indicated that the fibrous nature of the paper pulp caused a marked decrease in holdup by causing less uniform distribution of the gas bubbles. The fibers of paper pulp were found to average around 1.5 mm in length and to be surrounded by microscopic fibrils. The range of size distribution was approximately 0.3-2.0 mm. In addition, at low degrees of agitation, the fibers tended to flocculate into clumps with diameters averaging around 5 mm. "Solka Floc" on the other hand consisted of more rigid, stubby fibers with a length to diameter ratio around 5-10 and an overall length of only 0.2 mm on the average. Fibers of "Solka Floc" would therefore be expected to be nearly Newtonian and fibers of paper pulp would be expected to be non-Newtonian. Later results will bear out these expected results.

The holdup curves for 0.06M KOH, for 0.06M KOH + 1% "Solka Floc" and for 0.10M KCl + 0.33% paper pulp were used in later calculations for determination of the average bubble diameter in the tank during interfacial area determinations at identical conditions.

6. Mass Transfer Coefficient Calculations

The calculated values of the mass transfer coefficient in 0.1M (aver.) ionic strength solutions with and without "Solka Floc" or paper pulp are reported here in order to facilitate discussion of the experimental results later. Values of the coefficients were calculated and are reported in the Appendix, Sections (IV.4)-(IV.6) and are plotted in Figs. (4.9), (4.10), and (4.11).
The curves drawn in the figures are based on the best values of \((K_L a)\) and \((a)\) and are drawn by dividing the values for the line drawn through the \((K_L a)\) data by the values for the line drawn through the \((a)\) data in each case. Note the decrease in \(K_L\) values with increasing power input. In the case of "Solka Floc" note also the difference in curvature for the two systems, concave upward in the absence of "Solka Floc" and concave downward in the presence of "Solka Floc". Note too that at high power inputs the curve in the absence of "Solka Floc" approaches a limiting value whereas with "Solka Floc" present, the value of the mass transfer coefficient drops precipitously at high power inputs. A discussion of these effects will take place later and depends upon the results obtained for the average bubble diameters in the two systems.

In the case of paper pulp, the mass transfer coefficients obtained at different levels of power input to the liquid in the tank are shown in Fig. (4.11) and are obtained by dividing the \(K_L a\) curve shown by the interfacial area curve. It can be seen that the limiting value of the mass transfer coefficient (at high power inputs) is the same as in the system without paper pulp and that the value of \(K_L\) rises more rapidly with decreasing power input at low power levels than it does in the system without paper pulp.

7. Average Bubble Diameters

The values of the average bubble diameters calculated by Eq. (2.48) from the interfacial area and holdup measurements are given in the Appendix, Sections (IV.4), (IV.5) and (IV.6). The results are also plotted in Figs. (4.9), (4.10) and (4.11) based upon division of the best curves for the interfacial area and holdup measurements in the three systems.
Note first that in the salt system the average bubble diameter decreases with increasing power input and then levels off at high power inputs. Note also that the curves for the mass transfer coefficient and for the average bubble diameter are parallel.

In the presence of "Solka Floc" the average bubble diameter again decreases with increasing power input but does not level off but instead parallels in behavior the mass transfer coefficient for this system.

This parallel nature of the mass transfer coefficient and of the average bubble diameter is extremely important and will be discussed later.

In the presence of paper pulp, the average bubble diameter decreases with increasing power input and then levels off at a value which is essentially identical to that for the salt system without paper pulp. In this system it should be noted that whereas the curves for $K_L$ and $d_B$ are parallel at high power inputs, the mass transfer coefficient rises more rapidly than the bubble diameter at low power inputs. This behavior is completely explainable in terms of the non-Newtonian nature of the paper pulp and will be discussed later.
V. DISCUSSION OF RESULTS

1. $K_La$ Using Probe
   
   a. Effect of Salt Concentration. A comparison of the values of $K_La$ determined by oxygen probe transient response measurements in solutions of various ionic strengths is given in Fig. (5.1). The data points have been omitted in this and subsequent figures for purposes of clarity. The figures are redrawn from those found in Section IV. Values for $K_La$ in sodium sulphate solution were obtained by taking the values obtained at a gas flow of $F = 0.0106$ ft/sec and correcting them for the effect of superficial velocity. This correction was based upon the exponent of the gas flow rate found in Section (4.3) for sodium sulphite oxidation systems. $K_La$ values for the sulphite oxidation system and for the sulphate system were identical except for a 14% enhancement of $K_La$ in the sulphite oxidation system due to chemical reaction (see Section [4.3]). Since sulphite data were taken at several different gas rates and sulphate data were taken at only one gas rate (in order to find the enhancement factor), in order to compare results at different ionic strengths it was necessary to use the gas flow correction.

   The first thing to notice about the curves in Fig. (5.1) is that the effect of adding salt to the system is to increase $K_La$. Furthermore, addition of salt is shown to increase the slope of the $K_La$ vs. $P_g/V_L$ curves in Fig. (5.1). Note also that the addition of 0.1M ionic strength caused a substantial increase in $K_La$, whereas the addition of 15 times as much ionic strength served to increase $K_La$ an amount equivalent to the addition of the first 0.1M of ionic strength. This implies that increases in $K_La$
Fig. 5.1. Effect of ionic strength on $K_La$ at constant gas rate, $F = 0.0212$ ft/sec.
due to the addition of ionic strength are the greatest at low ionic strengths and that the effect saturates at fairly low ionic strengths.

These conclusions confirm the work of Robinson and Wilke (36) using a smaller fermenter (2.5 liters working volume). They investigated the effects of ionic strength on $K_1a$ in a great number of salt systems in a fermenter having identical geometrical ratios to that used in this work. The values of the exponent in the equation

$$K_1a = K_1 (P_g/V_L)^n$$  \hspace{1cm} (5.1)

found by Robinson and Wilke are plotted in Fig. (5.2) along with the values found in the present work. The agreement here is excellent. It appears likely then that in scaling up results from 2.5 liter vessels to 21.9 liter vessels of identical geometrical ratios, that the effects of ionic strength on the power per unit volume exponent in Eq. (5.1) are the same in both sized vessels.

The values of the exponents chosen for plotting in Fig. (5.2) are those for the straight portions of the curves in Fig. (5.1). Notice that the curves show some curvature at the extremes of power input. Distilled water has a slope almost equal to that for sodium sulphate at low power inputs and then tapers off to a slope of 0.38. The 0.1M (KOH-KCl-K_2CO_3) data have a slope of 0.65 at power inputs typical of industrial fermentation processes and then taper off in slope at high power inputs to a slope almost equivalent to that for distilled water. Over the range of power inputs investigated for sodium sulphate of 1.5M ionic strength, no change in slope is apparent. It appears likely, however, that at very high power inputs some saturation of the power input effect should take place and the
Fig. 5.2. Effect of ionic strength on the power per unit volume exponent for $K_{L,a}$ at 30°C.

$$K_{L,a} = K_1 \left( \frac{P_g}{V_L} \right)^n$$

- $H_2O$
- KOH + $K_2CO_3$
- KCl
- $Na_2SO_3$
- $Na_2SO_4$

- Medium A-1
- $Na_2SO_4$
- $Na_2SO_3$
- H$_2O$
- KOH-KCl-$K_2CO_3$

Data of Robinson and Wilke

This work
The slope of this curve is therefore expected to decrease. Overall, it appears that the point at which the $K_L a$ vs. $P_g/V_L$ begins to decrease in slope moves to higher power per unit volume values as the ionic strength increases.

The fact that not only the slope but also the value of $K_L a$ obtained in salt solutions increases with ionic strength was observed by Robinson and Wilke (36). A comparison of their results with the present results is possible for distilled water and for sodium sulphate using Figs. (4.6) and (4.12) to calculate $K_L a$ at a superficial gas velocity of 0.0150 ft/sec (see Figure 4.18 of Robinson and Wilke). This comparison is shown in Fig. (5.3) where the solid lines represent the results of Robinson and Wilke (36) and the dashed lines represent the results of the present work. It is apparent that the results obtained in the present work are considerably higher (a factor of ~2) than those obtained by Robinson and Wilke in the smaller tank. This discrepancy can be examined by a close look at the exponents found for the effect of superficial gas velocity in the two investigations.

Robinson and Wilke found that the velocity exponent in the equation

$$K_L a = K'_1 \left( \frac{P_g}{V_L} \right)^n v_s^m + K_2$$

was 0.35 for distilled water and 0.39 for sodium sulphate solutions of high ionic strength. The present investigation revealed exponents for velocity of 0.56 for distilled water and 0.28 for sodium sulphate solution of high ionic strength (the assumption is made that $m$ for sodium sulphite is the same as $m$ for sodium sulphate). $K_2$ is negligible in the power ranges of interest in the present study.
Fig. 5.3. Comparison of $K_{La}$ for distilled water and for sodium sulphate solutions for two different size tanks at the same gas velocity.
The value of the velocity exponent may be a function of the scale of the equipment. It may also vary with the manner in which gas is delivered to the impeller and the distance between the gas sparger and the impeller. A larger impeller would be expected to capture more of the gas (less bypassing) and thus to be more effective. Tip velocity of the larger impeller \((ND_i/2)\) is not equal to tip velocity of the smaller impeller at equal lower input per unit volume and this may play an important role in the gas velocity exponent. There is widespread disagreement concerning the effects of gas velocity on \(K_a\) in stirred tank absorbers. Values ranging from zero to one for the velocity exponent have been reported and it is not yet clear what effect gas velocity has. Certainly the properties of the liquid phase as well as the equipment scale and magnitude of gas rate and power input all need to be considered before a clear picture of velocity effects can be obtained. Further discussion of gas velocity effects will be presented in subsequent sections.

Comparison of the results of the present work with those of other investigators is complicated by the use of different scale equipment and other types of absorption devices (particularly bubble columns) with similar salt systems. Benedek and Heideger (60), using a stirred tank of standard geometry only slightly larger than that used in this work, found with sodium chloride solutions between 0 and 0.7M in ionic strength, that \(K_{a,L}/K_{a,L\text{water}}\) increased rapidly with ionic strength up to a value of \(\Gamma = 0.2M\), at which point the \(K_{a,L}\) ratio was 2.40. NaCl in excess of 0.2M ionic strength did not increase \(K_{a,L}/K_{a,L\text{water}}\) to any level larger than that achieved in 0.2M NaCl. Comparing their results with those of Robinson and Wilke (36), Figure 4.8, it is clear that \(K_{a,L}/K_{a,L\text{water}}\) did not increase in
that work when \( \Gamma \) exceeded 0.25M, at which point the \( K_{La} \) ratio was 1.7. Similarly, Zieminski and Whittemore (90) correlated \( K_{La} \) for bubbles columns for many different salts to ionic strength. They showed that \( K_{La}/K_{La\text{water}} \) increased with ionic strength at least up to \( \Gamma = 0.35M \), at which point the \( K_{La} \) ratio was 2.25.

Clearly then, the results of these investigators indicate that ionic strength has a profound effect on \( K_{La} \) at low ionic strength and that this effect saturates at ionic strengths in the vicinity of 0.2-0.4M ionic strength. Results obtained in the present investigation at 0.0, 0.1 and 1.5M ionic strength are in good agreement with results of these investigators as shown in Figs. (5.1) and (5.2).

The cause for the increase in \( K_{La} \) with increasing ionic strength at low ionic strengths has been attributed to the inhibitory effect of salt on bubble coalescence (36, 50, 72, 90-93). In pure water, studies by Foulk and Miller (91) and Lessard and Zieminski (92) indicate virtually 100% frequency of coalescence when two bubbles are brought into contact. Studies by these same workers in salt solutions show a marked decrease in frequency of coalescence with increasing ionic strength. Foulk and Miller find a coalescence frequency of less than 10% in solutions of \( Na_2SO_4 \), \( NaCl \) and \( NaSCN \) when the ionic strength of the solutions is between 0.2 and 0.4M. Lessard and Zieminski found that for ionic strengths between 0.1 and 0.3M for solutions of many different salts, the coalescence frequency drops from 100% to less than 10%. The net effect of a decrease in coalescence frequency in a stirred tank would be to decrease the bubble size in the tank and thus to increase the interfacial area per unit volume. As shall be shown later, the mass transfer coefficient for smaller sized bubbles
decreases as the bubble size decreases under conditions present during the present investigations. This decrease in mass transfer coefficient is smaller than the increase in interfacial area per unit volume and the net effect of added salt is an increase in $K_L a$.

Further evidence for the inhibitory effects of salt on bubble coalescence was found by Reith and Beek (50) in their studies with water and high ionic strength Na$_2$SO$_3$ solutions. They measured the coalescence frequency of bubbles in a stirred tank of nonstandard geometry and found that the stirring speed necessary to achieve an equal degree of coalescence in the salt solution was greater than in water. An average of one bubble coalescence took place during the residence time of the gas in the tank at a stirring speed of 480 RPM in water and at 780 RPM in the salt solution. The change in curvature of $K_L a$ curves in Fig. (5.1) may well be an indication of the effect of coalescence on $K_L a$. Since these curves were drawn on the assumption that the driving force for mass transfer in a stirred tank is determined by the exit concentration of gas (well-mixed gas phase assumption), the change in curvature of the $K_L a$ curves in Fig. (5.1) may be due to the fact that the tank contents were not well-mixed previous to the change in slope. Qualitatively speaking, more concentrated salt solutions (up to 0.4M) should show a change in slope at higher power inputs (characteristic of high stirring speeds). This is precisely the effect which is observed in Fig. (5.1). The well-mixed gas phase assumption therefore appears valid for water above 200 RPM, for KCl-KOH-K$_2$CO$_3$ (ionic strength 1.5M) above 1200 RPM. This effect for different ionic strengths may therefore explain the correspondence of slopes of the curves and the similarity of $K_L a$ values evidenced at low power inputs (less than...
1 HP/1000 gallons) for all solutions tested. In any event, the values of \(K_L a\) reported are those based on the exit concentration of the gas.

In summary, it appears that the effect of salt on \(K_L a\) is reflected in a change in coalescence frequency of the bubbles. Since the size of the bubbles in a stirred tank is determined by the equilibrium between the rate of bubble breakup and the rate of bubble coalescence, a decreased coalescence frequency results in smaller bubbles, lower mass transfer coefficient (in the proper bubble size regime—to be discussed later) and an increase in interfacial area per unit volume.

At low power inputs all curves for \(K_L a\) vs. \(P_g/V_L\) tend to converge. This convergence is probably a reflection of the fact that at very low power inputs, the majority of bubbles pass through the tank without coalescing. This is due to the small number of bubbles present and the low turbulence levels which reduce the probability of successful coalescence collisions. At various power levels, which increase with increasing ionic strength up to a limit of ~ 0.4M ionic strength, relatively complete mixing takes place and the curves of \(K_L a\) vs. \(P_g/V_L\) for the various solutions diverge.

Values of the exponent of power per unit volume in Eq. (5.2) are applicable to the curves of Fig. (5.1) only when the gas phase is well-mixed. A lack of understanding of this fact can lead to values of the exponent varying from 0.4 to 0.95 in the water system. The literature is filled with correlations of \(K_L a\) vs. \(P_g/V_L\) for water but few investigators have covered a sufficiently wide range of power inputs to detect changes in the slope of \(K_L a\) vs. \(P_g/V_L\) curves.
Mehta and Sharma (28) investigated $K_La$ in salt solutions in stirred tanks but a surface active agent, tricresyl phosphate, was added in all their runs and no valid comparison with the results of the present investigation is possible. A comparison of $K_La$ results obtained in the present investigation with those of other workers, aside from Robinson and Wilke (36) is not presently possible because of differences in geometry, variable ranges and aqueous systems. In addition many investigators have not reported power input levels used in their studies. Many review articles on $K_La$ measurements in stirred gas-liquid contactors are available (36, 57, 76, 94-104) for further reference.

b. Effect of "Solka Floc". The dissolved oxygen probe transient method was used for the determination of $K_La$ in distilled water and in 0.1M ionic strength solutions, both containing suspended "Solka Floc". $K_La$ in more concentrated salt solutions (0.5M Na$_2$SO$_3$ of 1.5M ionic strength) will be dealt with later.

The effect on $K_La$ of adding "Solka Floc" to distilled water is shown in Fig. (5.4) for a gas rate of 0.0212 ft/sec superficial velocity. At low power inputs, it is clear that the effect of "Solka Floc" is to decrease $K_La$. This decrease in $K_La$ was further investigated by performing simultaneous $K_La$ and a runs in wash water prepared as discussed earlier. $K_La$ results obtained in this way were identical to those obtained with the "Solka Floc" system. The interfacial area results, however, were higher in the wash water than they were in the "Solka Floc" system. These results can be explained as follows. It is clear that some water soluble material present in the "Solka Floc" is chiefly responsible for the decrease in $K_La$. An experiment was performed in which the quantity of water soluble material...
Fig. 5.4. Effect of "Solka Floc" on $K_{La}$ in distilled water at 30°C, $F = 0.0212$ ft/sec.
present in "Solka Floc" was determined. This experiment revealed a 2% water soluble fraction which is believed to consist mainly of short chain polysaccharides of glucose (γ-cellulose) and sugars of low degree of polymerization. Some water soluble ash resulting from the manufacturing process is also present and is responsible for approximately 10% of the water soluble fraction (105).

Dealing first with the effect of the water soluble materials in the wash water, it can be observed from Figs. (4.9) and (4.10) that these materials are responsible for an increase in average bubble diameter when compared to salt solution, a decrease in mass transfer coefficient and interfacial area and a decrease in $K_L a$. Upon addition of the solids present in "Solka Floc", it can be observed from Fig. (4.10) that they are responsible for a further decrease in interfacial area and also for an increase in $K_L$ and bubble diameter. No effect on $K_L a$ was observed when comparing wash water and "Solka Floc" results.

Thus it appears that the decrease in $K_L a$ found in distilled water and in salt solutions is due to two causes. The first of these is the presence of water soluble impurities in "Solka Floc" which are responsible for a decrease in interfacial area and mass transfer coefficient. The second effect is due to water insoluble cellulose present in "Solka Floc" which is responsible for a further decrease in interfacial area and for an increase in $K_L$. The combined net effect of the water insoluble material and the water soluble material is a decrease in $K_L a$. Further discussion of these results will appear later when the relationship between mass transfer coefficient and bubble diameter is examined.
In both wash water and "Solka Floc", an increase in bubble diameter at any power input is observed in salt solutions. This increase in bubble diameter is ascribable to two causes. In the wash water, the presence of water soluble materials brings about an increase in coalescence of bubbles, partially cancelling the coalescence inhibiting effects of the salt. In water solution (no salt) any soluble material would probably cause an inhibition of bubble coalescence, resulting in smaller bubbles. With the water insoluble cellulose present, the initial breakup of bubbles will be inhibited and the coalescence of bubbles will be promoted, resulting in even larger bubbles.

Results obtained for the effect of "Solka Floc" in salt solution are shown in Fig. (5.5). Notice first of all that the curves obtained for 0.1M ionic strength salt solutions with and without "Solka Floc" are more or less parallel. Thus inhibition of coalescence in this system is not accompanied by an increase in slope when plotting $K_{L,a}$ vs. $P_g/V_L$. In other words, the "Solka Floc" system behaves differently than the salt systems investigated. The "Solka Floc" system is quite complex and further explanation of the $K_{L,a}$ behavior will take place later when bubble diameter and mass transfer coefficient effects are discussed more fully.

c. **Effect of Paper Pulp.** The effect of adding paper pulp to 0.1M ionic strength salt solutions is shown in Fig. (5.6). It is clear that the addition of small quantities of the pulp to the salt solutions brought about significant reductions in $K_{L,a}$. Wash water was also prepared from the pulp suspensions and $K_{L,a}$ was measured in this system. The result for the wash water was essentially identical to that found in pure salt solution and is reported in Appendix, Section (V.1). It was thus established
Fig. 5.5. Effect of "Solka Floc" on $K_La$ in 0.1M ionic strength KOH-KCl-K$_2$CO$_3$ solutions at 30°C, $F = 0.0212$ ft/sec.
Fig. 5.6. Effect of paper pulp on mass transfer parameters at 735 RPM, 30°C, $F = 0.0212$ ft/sec, $\Gamma = 0.1M$. 

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that the solids alone were responsible for the decrease in $K_L a$ in paper pulp suspension.

The decrease in $K_L a$ brought about in paper pulp suspensions can be ascribed to two possible causes. First of all, the presence of the pulp promotes the coalescence of bubbles present in the liquid, resulting in larger sized bubbles and decreased interfacial areas. As shall be shown later, these larger bubbles have higher mass transfer coefficients in the transition range of bubble sizes than do smaller bubbles. The net effect of larger mass transfer coefficients and smaller interfacial areas is a decrease in $K_L a$. Secondly, the presence of paper pulp decreases the ability of the impeller to break up bubbles due to damping of turbulence caused by the non-Newtonian character of the suspension. This again will result in larger sized bubbles and decreased $K_L a$. It appears likely that the decrease in $K_L a$ caused by paper pulp can be ascribed to a combination of the two effects just mentioned.

Comparison of the results of the present work, where $K_L a$ has been measured in "Solka Floc" suspension and in paper pulp suspension, with the results of other workers who have measured $K_L a$ in either paper pulp or mycelial suspension, is possible only on a qualitative basis. The use of different geometries of equipment, the lack of reported power data, the use of different measurement systems and differences in suspension properties, including presence of impurities, all conspire to prevent a quantitative comparison with the results shown in Figs. (4.10) and (4.11).

The effects of mold on the transfer of oxygen into fermentation broths were first dealt with by Bartholomew, Karow, Sfat and Wilhelm (4). Later work by Deindoerfer and Gaden (6) demonstrated a marked dependence
of $K_{L,a}$ for *Penicillium chrysogenum* Q-176 broth on the concentration of mold. The oxygen absorption coefficient in their system was shown to decrease to approximately one-fourth its value in the absence of mycelium when the concentration of mycelium was increased to approximately 1.4%. Solomons and Perkins (14) using a polarographic method were able to demonstrate marked decreases in oxygen transfer rate in the presence of *Aspergillus sp.* Viscosities of 1, 100, 1000 and 10000 cp. were investigated and oxygen transfer rates were plotted against stirrer speed. The effect of the mold was most pronounced at low impeller speed and at high mold concentration (high viscosity). Steel and Maxon (16) performed some measurements on oxygen availability rate in Novobiocin fermentations and found that the oxygen availability rate decreases with increase in the apparent viscosity of the broth (increase in mold concentration). The effect of the mycelia was most pronounced at low speeds and tended to level off at viscosities above 80 cp. This region was termed the viscosity independent region and measurements of oxygen availability rate in this region were correlated to power input.

In an attempt to simulate the effects of mycelia on the viscosity characteristics of fermentation broths, Aiba, Okamoto and Satoh (106) added Carboxymethylcellulose in varying concentration to the liquid phase of a jar-type fermenter. Using the gas analysis technique they were able to show a very dramatic decrease in $K_{L,a}$ with increasing viscosity of the solutions. Aiba and Okamoto (2), using the citric acid fermentation of *Aspergillus niger* as a model system, were able to show a decrease in oxygen transfer capacity coefficient ($K_{L,a}$) with increasing mycelial mass after 10 hrs of fermentation. Up until that time, the $K_{L,a}$ value was found to
increase. No explanation for this behavior could be found. Tuffile and Pinho (21), using the oxygen balance method for determination of $K_L \alpha$ in *Streptomyces aureofaciens* fermentation, found that oxygen transfer was best when the broth viscosity was the lowest and that the $K_L \alpha$ value reached a constant value after 70 hrs. This time also corresponded to a plateau in broth viscosity.

Other studies have been performed using paper pulp and mycelia for the simulation of fermentation broth. However, most of these studies have employed the sodium sulphite oxidation method for the determination of $K_L \alpha$. For this reason, these methods will be discussed later during the analysis of the sulphite oxidation data.

Overall it is apparent that the presence of non-Newtonian solids can cause a very dramatic decrease in $K_L \alpha$ values obtained in stirred, gas-liquid absorbers. The results obtained in the present study are in complete qualitative agreement with the results of other investigators. It should be made clear at this point that paper pulp is not nearly as non-Newtonian and viscous as some fermentation broths and that the results obtained in the present study can only serve as guides for a better understanding of the effects of solid non-Newtonian additives on $K_L \alpha$, $a$, $K_L$ and bubble diameter.

d. Net Effects. It is clear from the present studies on the effects of salt and solid non-Newtonian additive on $K_L \alpha$ in stirred tank contactors, that salt tends to decrease the coalescence rates of gas bubbles and that non-Newtonian solid additive tends to promote coalescence of gas bubbles.

One recommendation that can be made based on this conclusion is that fermentations that are limited by oxygen availability should be
carried out at as high an ionic strength as is tolerable in order to increase mass transfer. In those cases where salts exhibit toxic effects, it may be preferable to add salts slowly during the fermentation in order to make up for decreases in ionic strength brought about by cell growth. The added salts need not be necessary for growth but should be good coalescence inhibitors. Fig. (5.1) then indicates that operation of the fermenter at high power inputs will allow the operator to take advantage of the increased slope of the $K_L a$ vs. power input curves in the presence of salt.

Dilution of the fermentation broth as suggested by Taguchi (107) may also serve to increase $K_L a$ in oxygen limited cultures. This is clear from Fig. (5.6) where the effect of concentration of pulp on $K_L a$ is quite dramatic. Mold causes an even sharper decrease in $K_L a$ with concentration than does paper pulp (108).

2. $K_L a$ Using Sulphite Oxidation
a. Studies in the Absence of Additives. Results obtained for the sodium sulphite oxidation system are shown in Fig. (4.13). A direct logarithmic relationship between $K_L a$ and power input per unit volume was found. The slope of $K_L a$ vs. $P_g/V_L$ on log-log scales was found to be 0.95. This value is in excellent agreement with that found by other investigators. The data were correlated to

$$K_L a = 472 \left( \frac{P_g}{V_L} \right)^{0.952} (F)^{0.276}$$

Comparison of these results with those of other investigators will now be attempted. Papers dealing with the effects of agitation, scale and geometrical design on mass transfer in sodium sulphite solutions are to be
found in great proliferation in the literature. The classic paper in
this field was that of Cooper, Fernstrom and Miller (56). These authors
correlated their data for $K_{L}^{r}a$ to the power input per unit volume of liquid
in their contactors. Their calculations of $K_{L}^{r}a$ were based on a log-mean
driving force for oxygen in the gas phase and the data correlated well to
a power exponent of 0.95 and to a velocity exponent of 0.67 for a vaned
disk impeller. The gas rates investigated ranged from 0 to 600 ft/hr,
which is approximately four times the range covered in the present study.
It should be noted, however, that a vaned disk is probably better at col-
lecting sparged gas than is an impeller at high gas rates.

Because of differences noted between $K_{L}^{r}a$ values found in sodium
sulphite solutions and $K_{L}^{r}a$ values found polarographically by other inves-
tigators, Steel and Brierly (31) did a comparative study of the two dif-
ferent methods. Using equipment comparable in geometrical ratio to that
used in the present investigation but of half the internal diameter, they
found for the sulphite system a dependence of $K_{L}^{r}a$ on gas rate to the 0.4-0.7
power and on stirring speed to the exponent of 3.0. Since power (ungassed)
input in the turbulent regime is given by

$$P = k\rho N^3 D_1^5$$  \hspace{1cm} (5.3)

and gassed power is some proportion of ungassed power, it is reasonable
to assume that a dependence of $K_{L}^{r}a$ on $N^{3.0}$ indicates a dependence on power
input to the 1.0 power. This agrees very well with a dependence on power
input to the 0.95 power found in the present work.

Yoshida, et al. (58) used the sulphite oxidation system to study
$K_{L}^{r}a$ in three different size tanks with turbine and vaned disk impellers.
They found values for the exponents of power input and velocity of 2/3. They did not measure power input, however, and actually correlated their data to $N_1^3D_1^2$. Richards (58) lists results of several workers giving power exponents ranging from 0.42 to 1.0 and velocity exponents ranging from 0 to 0.7. Westerterp, et al. (33) perform a similar compilation. Robinson and Wilke (36) have made a detailed analysis of sulphite oxidation results. Their experimental results at 30°C are compared with the results of the present investigation in Fig. (5.7) at a superficial gas velocity of 0.0150 ft/sec. As will be shown in Section (V.2d), the chemical reaction enhancement factor for the work of Robinson and Wilke was larger than that for the present work. A comparison of the two sets of results after correction for the reaction enhancement factor can be found in Section (V.7).

It is clear from Fig. (5.7) that the results of Robinson and Wilke (36) agree quite well with those of the present investigation at this gas rate. Some greater disagreement at higher gas rates should be expected, however, because of the differences in the exponents for gas velocity found in the separate investigations.

b. Effect of Chemical Reaction on $K_{L}^{n}a$. It is interesting at this point to investigate the effect of chemical reaction of oxygen in the liquid phase on the rate of mass transfer of oxygen from the gas phase to the liquid phase. This comparison can be made by comparing the rate of absorption for sodium sulphate solution with that for sodium sulphite solution of identical ionic strength. The assumption is made that the mass transfer properties of the system are insensitive to the change in ionic species. Any enhancement of absorption rate due to chemical reaction would be noticed as an increase in $K_{L}^{n}a$ over $K_{L}a$. This comparison is made in
Fig. 5.7. Comparison of sodium sulphite oxidation results with Robinson and Wilke.
Fig. (5.8) at a gas rate of 0.0106 ft/sec. It is clear from the figure that chemical reaction enhances the rate of oxygen absorption by 14% over that in sodium sulphate solution. Then, for all intents and purposes, identical slopes for the sulphite and sulphate results is indicative of the agreement of the oxygen probe and chemical methods for determination of $K_L a$ and $K^* L a$ at high ionic strengths (1.5M).

c. **Studies with "Solka Floc" Present.** Comparison of sulphite oxidation studies in the pure system with those in the same system but with the addition of 1% and 3% respectively of "Solka Floc" is made in Fig. (5.9) at a superficial gas velocity of 0.0106 ft/sec. It is clear that the addition of "Solka Floc" to the sodium sulphite solutions results in a marked reduction in $K^* L a$ at all power levels investigated. This reduction is in line with results obtained using the dissolved oxygen probe method. Note also that all the curves in Fig. (5.9) have essentially the same slope at low power levels and that the slopes level off to lower values more rapidly with increasing "Solka Floc" concentration. The reason for this behavior is most likely the increase in coalescence brought about by the "Solka Floc". The fact that the curves slope over to lower power per unit volume dependence compares quite well with the trends for the water system, where coalescence frequency is high. Apparently, increases in power bring about an increase in collision frequency and effectiveness of collisions for bubbles present in the salt solutions. As was indicated earlier, the sodium sulphite oxidation runs in the absence of "Solka Floc" are also expected to curve over at high power levels. This trend was noted in the work of Robinson and Wilke (36).
Fig. 5.8. Comparison of Na₂SO₄ and Na₂SO₃ overall volumetric mass transfer coefficients.
Fig. 5.9. Effect of "Solka Floc" on $K_a \alpha$ for sodium sulphite oxidation studies at $30^\circ C$, $F = 0.0106$ ft/sec.
In contrast to the paucity of data for pulp and mycelial suspensions in water, a considerable amount of work has been done in this area using the sodium sulphite oxidation system. Bowers (109) added 2% paper pulp to sodium sulphite solution and measured its effect on oxygen transfer rate in three different systems. Using a ceramic plate in a bubble column he found a twenty-fold decrease in mass transfer rate. Using a paddle and sparge ring, this reduction was decreased to a factor of seven. Finally, using a vaned disk and open tube sparger, the reduction in mass transfer rate was about a factor of two. From his studies it is obvious that the effect of paper pulp on $K_La$ depends upon the geometry of the system being investigated. Mechanical agitation was shown to reduce the effects of the pulp.

Brierly and Steel (108) studied the effect of mycelium, sago pellets and paper pulp on the oxygen transfer rates in a 2.5 liter fermenter. They used a polarographic method of $K_La$ measurement but their results are treated here since they used a high ionic strength salt solution (0.5M KCl) in their fermenter. The present study indicates that this ionic strength solution should act analogously to sodium sulphite solution except for the chemical reaction enhancement, which was found to be small. Their study indicates quite clearly that $K_La$ is significantly reduced by the addition of paper pulp. $K_La$ was reduced by a factor of six in going from a system without paper pulp to a 3.0% paper pulp system at 800 RPM and a volumetric gas rate of 2.5 liters/minute in their fermenter. The addition of a filamentous mold (*Aspergillus niger* N1E) produced even more dramatic results under the same conditions. Mold concentrations less than 0.1% caused very rapid decrease in $K_La$. This decrease in $K_La$ continued at a lower rate.
until 2.5% mold (the highest concentration tested) at which point an overall decrease of a factor of 12 had been effected. Sago pellets showed no significant effect on mass transfer. They plotted their results vs. stirrer speed and their results for the mold system appear in qualitative agreement with those of the present investigation. The slopes of their lines cannot be compared directly with those of Fig. (5.9) but it is interesting to note that their high speed results all parallel each other as do those in Fig. (5.9) and that a change in slope occurs in their results at lower speeds as the mycelial concentration is increased.

Blakebrough and Sambamurthy (54) investigated the effect of a paper pulp suspension in a 5-liter turbine agitated fermentor and found a marked decrease in oxygen uptake rate using the sulphite oxidation method. This decrease in oxygen uptake rate became more significant at higher power levels (higher agitation speeds) which is also in qualitative agreement with the results of the present investigation.

Blakebrough and Sambamurthy (55) then studied mass transfer and mixing rates in laboratory fermenters with and without a 1.6% w/v suspension of paper pulp. Whereas their oxygen absorption rates could be correlated directly with power input using the sulphite oxidation method without paper pulp, impeller geometry became important when the pulp was present. They concluded from their studies of system geometry that small impellers were more effective in transferring oxygen in paper pulp than were large impellers. Their oxygen uptake rates in the presence of the paper pulp were significantly lower than those without pulp.

In conclusion, it appears that the effects of "Solka Floc" on $K_a$ in sodium sulphite solution are in qualitative agreement with the
results of other workers with paper pulp and mycelial suspensions. The effects of the high ionic strength of the sodium sulphite solution are reflected in the high slope of the $K_{L}a$ vs. $P_g/V_L$ curves in Fig. (5.9). The sulphite solution then acts as a coalescence inhibitor. The effects of the "Solka Floc" are reflected in the decrease in magnitude of $K_{L}a$ under equal power input conditions. An additional effect of the "Solka Floc" is to decrease the slope of the $K_{L}a$ vs. $P_g/V_L$ curves to values indicative of coalescing systems at power levels which decrease with increasing "Solka Floc" concentration.

It should be clear that at least some of the effect of "Solka Floc" in the sulphite oxidation system is due to the presence of water solubles. As shall be shown later, these soluble materials are responsible for a decrease in mass transfer coefficient at any bubble diameter.

Aside from the difference in slope and in magnitude of the $K_{L}a$ curves in sodium sulphite solution with "Solka Floc", trends evident in these systems are analogous to those found in nonionic solutions investigated.

d. Chemical Reaction Enhancement. A comparison of Figs. (5.7) and (5.8) indicates clearly that the chemical reaction enhancement effect for sodium sulphite oxidation was greater in the studies of Robinson and Wilke (36) than it was in the present investigation. Even though the sulphite oxidation results at 0.0150 ft/sec agree, the enhancement difference is most likely due to catalyst concentration. The differences between the exponents of superficial velocity for the two investigations makes any further analysis of these differences very speculative.
3. **Interfacial Area**

a. **0.1M Ionic Strength KOH-KCl-K₂CO₃**. The results of interfacial area determinations in 0.1M ionic strength salt solutions were presented earlier in Fig. (4.16). The bottom curve of this figure will be discussed first followed by a discussion of the anomalous curves which break off from the true interfacial area curve.

It is clear from the figure that the interfacial area per unit volume increases steadily with increasing power input per unit volume. The concave nature of the curve indicates that power is less efficient at producing interfacial area at high power inputs. Fig. (4.9) indicates that the average bubble diameter becomes fairly constant at power inputs above 10 HP/1000 gal and therefore increases in interfacial area above this power level are due mostly to increases in gas holdup.

The anomalous curves shown in Fig. (4.16) indicate values of interfacial area far in excess of acceptable values. The analysis of this behavior will now be attempted. First of all, it is important to note that these fictitious curves are generated when the concentration of KOH in the liquid phase is high and the power input to the liquid phase is high. Both of these conditions lead to very low levels of CO₂ in the exit gas stream. The two anomalous curves shown were determined with KOH concentrations of 0.06M and 0.02M respectively. Clearly, higher power inputs were required before deviations from the true area curve became evident with the lower KOH concentration.

One possible explanation of this behavior is as follows. Assume that the large change in concentration of the CO₂ stream is important in determining the behavior being analyzed. In that case, when the rate of
CO₂ absorption is the same for two runs at different KOH concentrations, the exit concentration of CO₂ in the exit gas should be the same. This follows directly from the material balance on the gas stream which indicates that

\[ \bar{R}_A = \frac{F^0}{V_L} (c_{CO_2} - c_{CO_2_f}) \quad \ldots (5.4) \]

Since the assumption has been made that the driving force for mass transfer is the exit concentration of CO₂ gas (after correction for solubility in the liquid), it follows that under conditions of equal absorption rate (and thus equal exit CO₂ concentration)

\[ \bar{R}_A = a_1 c^* A_1 \sqrt{k_e D_p} = a_2 c^* A_2 \sqrt{k_e D_p} \quad \ldots (5.5) \]

In this case \( c^*_A = c^*_A \), and therefore

\[ a_1 \sqrt{B_1} = a_2 \sqrt{B_2} \quad \ldots (5.6) \]

Extrapolating the anomalous curves to the true area curve in Fig. (4.16), it is possible to calculate the quantities in Eq. (5.6). This calculation yields

\[ \frac{a_1 B_1^{1/2}}{a_2 B_2^{1/2}} = \frac{(15)}{(6)} \left( \frac{1}{\sqrt{3}} \right) = 1.44 \quad \ldots (5.7) \]

This value for the ratio of 1.44 is fairly close to the predicted value of 1.0 and indeed the difference, as will be shown, is probably in the right direction.

Proceeding on the assumption that the rate of absorption and thus the exit concentration is important in causing the anomalous behavior observed, it is now possible to postulate a model to explain the observed deviations. The principle error in the calculation of interfacial area...
when exit CO₂ concentration is low is probably in assuming that the exit concentration of CO₂ is the proper driving force for mass transfer in the tank. Let us assume that a finite period of time (a gas phase mixing time) is required before gas entering the stirred tank at 10% concentration can mix completely with the gas already present as holdup in the tank. A simplistic, and not too accurate, model for this behavior would be to assume that the gas phase history can be broken up into two distinct regions. In the premix region the driving force for mass transfer is assumed to be a log-mean concentration driving force of value

$$\Delta C^*_A = \frac{C^*_{A_{inlet}} - C^*_{A_{outlet}}}{\ln(C^*_{A_{inlet}}/C^*_{A_{outlet}})}$$

In the mixed region, the driving force is assumed to be the exit concentration of CO₂

$$\Delta C^*_A = C^*_{A_{outlet}}$$

Clearly this model overestimates the driving force for mass transfer in the premix region, since mixing takes place continually and not during a discreet time period. However, if we define a mixing time for the gas in such a way that it weights the two distinct driving forces for mass transfer

$$\Delta C^*_A = \Delta C^*_A (t^*_{mix}) + \Delta C^*_A (1 - t^*_{mix})$$

where

$$t^*_{mix} = t^*_{mix} / t^*_{res}$$

and $$t^*_{res}$$ is the residence time of gas in the reactor, then it is possible to calculate the relative effect of concentration of the exit CO₂ gas on the proper driving force for mass transfer. This comparison is only qualitative, however, and is intended to indicate the effects of mixing on mass transfer.
The calculation of interfacial area per unit volume is given by Eq. (2.24) if $y_{CO_2}^f$ is assumed to be the driving force. At low CO$_2$ concentrations and with the generalized driving force of Eq. (5.10), it is possible to write

$$a = \frac{(P^o/V_L)(H/V_ML)(C_{CO_2}^i)}{\Delta C_A^* \sqrt{D_A k_B}}$$

(5.11)

All other terms in the equation become insignificant. Therefore, any change in driving force will bring about a comparable change in the calculated interfacial area. An example showing the relative effect of driving force on interfacial area with a mixing time of 0.1 seconds and an assumed constant gas residence time of 5 seconds in the tank is given in Fig. (5.10). The curve corresponding to a mixing time of 0.1 seconds deviates dramatically from the curve where no mixing effects are assumed, when the exit concentration of CO$_2$ decreases.

Fig. (5.10) actually overcorrects for the effects of mixing and the true curve will lie somewhere in between the two curves shown here. At high power inputs the mixing time should decrease and the residence time of the gas should increase (with increasing holdup). Therefore the effects of mixing at high powers (low CO$_2$ concentrations in the exit gas) will not be quite as dramatic as those shown here. In addition, as was mentioned earlier, a log mean driving force during the premix period is also an overcorrection.

In any event the trend is clear and even a very short mixing time can lead to significant errors in the calculation of interfacial area. In order to overcome this effect, it is necessary to keep the concentration
Fig. 5.10. Effect of mixing time on the calculation of interfacial area at constant gas residence time.

$F = 0.0212 \text{ ft/sec}, T = 30^\circ\text{C}, t_{res} = 5 \text{ sec},$

$t_{mix} = 0.1 \text{ sec}, B = 0.06\text{M KOH}, V_L = 21.9 \text{ liters}$
of CO₂ in the exit gas above a certain critical level. This is accomplished by reducing the concentration of hydroxide ion in the liquid phase. Fig. (4.16) is clearly in qualitative agreement with the proposed model. The true interfacial area curve was generated by lowering the hydroxide concentration until the interfacial area values were independent of hydroxide concentration. Then and only then, was it possible to get a true measure of interfacial area.

Several other investigators have made determinations of interfacial area in gas-liquid agitated systems. Calderbank (71) developed the light probe technique for the measurement of interfacial area. With this technique it is possible to measure interfacial area by measuring the attenuation of light transmission through the dispersion being studied. This technique is inherently limited experimentally by the necessity for integrating measurements made in different regions of the tank in order to determine the total interfacial area of the dispersion. One chief advantage of the technique is that ionic species are not needed in solution for making the measurements. Therefore all manner of transparent solutions can be employed for interfacial area measurements. Calderbank's measurements covered the range 1.6-32 HP/1000 gallons and gas rates of 0.01-0.06 ft/sec. Variation of surface tension, viscosity and density were brought about by change in liquid phase. He was able to correlate his interfacial area measurements for both 5 and 100 liter tanks to the equation

\[ a_o = 230 \left[ \frac{(P_L/V_L)^{0.4} \rho_c^{0.2}}{S^{0.6}} \right] V_s^{0.5} \]  \hspace{1cm} (5.12)

with a maximum deviation of ± 8% for all fluids tested. It should be noted that no salt solutions were employed in this work.
Using Calderbank's equation, it should be possible to calculate the mass transfer coefficients for distilled water from $K_{L}$ measurements made in this work. This calculation will be made later but it should be clear at this point that above 1.6 HP/1000 gallons, the lower limit of Calderbank's work, the values of $K_{L}$ found from this investigation in distilled water fall on a straight line when plotted against power per unit volume on log-log scales. The slope of this line is almost exactly 0.4. From this we can conclude that the mass transfer coefficient above 1.6 HP/1000 gallons is a constant. That is, gas bubbles in distilled water have a constant mass transfer coefficient regardless of agitation conditions, above 1.6 HP/1000 gallons. Since bubble diameter decreases with increasing power input, it is also possible to state that gas bubbles in distilled water have a constant mass transfer coefficient regardless of bubble size, below a critical bubble size.

Calderbank and Moo-Young (21) measured interfacial areas and mass transfer coefficients in several different systems and were able to deduce the existence of two distinct regions of mass transfer for bubbles dispersed in a liquid. In the "large" bubble regime, bubbles were assumed to behave as circulating spheres in the manner of Higbie (47) and in the "small" bubble regime, bubbles behaved as rigid spheres. Mass transfer data for "small" bubbles was indistinguishable from that for rigid solid particles. The mass transfer coefficients obtained in this investigation for distilled water are characteristic of those for "large" bubbles and will be discussed later.

Westerterp, et al. (33) measured interfacial areas in gas-liquid contactors using two chemical methods. The first of these involved the
use of the sulphite oxidation system in the presence of cobalt ion catalyst. Unfortunately, the conditions used for their study have been shown to be inadequate by other workers (25) due to confusion about the rate of the chemical reaction between oxygen and sulphite. The second chemical method involved the reaction of CO$_2$ with NaOH solution, a method analogous with that used in the present investigation. They do not report power input data, however, and comparison of their results with those of our study are not possible. They did, however, find that interfacial area increased with the addition of glycerol (to increase liquid phase viscosity).

Yoshida and Miura (35) using the absorption of CO$_2$ into NaOH solutions attempted to measure interfacial area, gas holdup, mass transfer coefficient and reaction enhancement factor in three different size gas-liquid stirred tanks ranging from 25 to 58.5 cm in diameter. They varied NaOH concentration from 0.005 to 1.0N and total alkali concentration from 0.1 to 1.0N. Their agitation speeds were very low, however, ranging from 60 to 400 RPM. Their Figure 2 indicates that interfacial area in these systems is independent of electrolyte concentration at low agitator speeds. At high agitator speeds (232-325 RPM) interfacial area increased with increasing ionic strength. It should be pointed out that their agitator speeds correspond to the lowest speeds used in the present investigation. At the very low agitator speeds they used, bubble collisions are infrequent and ions in solution should have little effect on coalescence rate. At higher speeds, the collision frequency increases and coalescence of bubbles should be more important. Comparison of their results with those of the present investigation is hindered by the absence of power data in
their paper and by the different ranges of variables employed. Their conclusion that interfacial area in 0.1N solutions is the same as in water, dilute electrolytic solutions and nonelectrolytic solutions of similar physical properties appears applicable only to the very limited range of power inputs they studied and is not valid at higher power ranges employed in the present study.

Linek and Mayrhoferova (25), using sulphite oxidation with cobalt catalyst, studied the effects of absorption rate on interfacial area in a stirred tank gas-liquid contactor. Their paper dealt with the problems of excess conversion of gas phase that we have dealt with earlier. Their conclusion, that diluted gases should not be used to measure interfacial area when the conversion of the gas phase is greater than 40% seems quite conservative when compared with the results of the present study where it is clearly shown that there is a limit to conversion of the gas phase but that this limit is considerably higher than 40%.

Lee and Meyrick (72) measured interfacial areas and gas holdup in a 12" tank of standard geometry over a stirring speed range of 300 to 600 RPM, with gas rates from 0.012-0.030 ft/sec in salt solutions of NaCl and Na₂SO₄. Using a light probe, they found interfacial area values significantly lower than those found in the present study. The problem with their technique is that the interfacial area measurements are only point measurements taken at a single position in their tank. Since the holdup of gas is greater in the vicinity of the impeller, and they took their measurements at a mid-height, mid-radial position, significant differences are to be expected. They obtained holdup measurements with a level-taker device but again did not vary the position of the level-taker in order to
obtain the integrated holdup over the whole tank. Their holdup measurements in water are almost insensitive to stirrer speed. The presence of salt was shown to increase interfacial area and holdup significantly. The marked differences between their results and those of the present study are likely due to the techniques used by Lee and Meyrick, which gave only point measurements. It also appears likely that mixing was inadequate in their study. This is supported by the fact that they employed a poor sparger arrangement (because the sparger was located at the tank bottom) and found very little effect of stirring speed on interfacial area or holdup in distilled water. The correlation of their data to a stretched film model for bubble coalescence was not particularly successful, especially at low ionic strengths. Significant differences between the trends indicated by their data and the drawn curves occur at large ionic strengths. Whereas their curves indicate a continuation of increase in interfacial area with increasing ionic strength, their data seem to indicate a saturation of the ionic strength effect in the vicinity of 0.4-0.5M ionic strength.

Robinson and Wilke (36) obtained interfacial area measurements in ionic solutions at a superficial gas velocity of 0.0150 ft/sec using a geometrically similar but smaller tank in their study. The present study employed a gas velocity of 0.0212 ft/sec. Neither study dealt with the dependence of interfacial area on gas velocity. The results of Robinson and Wilke at an average ionic strength of 0.0965M are compared with results of the present investigation at an ionic strength of 0.1020M in Fig. (5.11). (Comparison at equal gas rates is made in Fig. [5.19].) Note that the results of the present study, when compared at equal power input, are higher. There appears to be considerably more scatter in the data of
Fig. 5.11. Effect of mixing on interfacial area results of Robinson and Wilke.

Corrected curve

Robinson and Wilke F = 0.0150 ft/s
Wernau and Wilke F = 0.0212 ft/s
Robinson and Wilke than in the present study. Part of this scatter is due to a difference in experimental technique. Robinson and Wilke used a sampling method with gas chromatographic analysis of exit CO$_2$ concentration. The present study employed continuous monitoring of exit CO$_2$ concentration using an infrared analyzer.

However, a definite pattern in the scatter of Robinson and Wilke's data has been uncovered. A detailed study of their experimental conditions indicates that mixing effects similar to those found in the present study are most likely the cause of their experimental scatter. For example, their data for power inputs up to 21.5 HP/1000 gallons were taken using hydroxide ion concentrations ranging from 0.065 to 0.083M. The trend of this data is similar to that for our study at approximately 0.06M hydroxide concentration. That is, the data indicate a trend toward rapidly increasing interfacial area. Their next data point was obtained at 0.0189M hydroxide concentration and shows a markedly reduced tendency toward increasing interfacial area. Their next point was obtained at an even lower hydroxide concentration of 0.0136M and the interfacial area found was even lower than the previous point, even though the power input was greater. A very steep rise in interfacial area then occurred at the next higher power input, where the hydroxide concentration was raised to 0.0211M. These trends are in complete agreement with those found for the mixing model presented earlier. Clearly then, the interfacial area data of Robinson and Wilke are not independent of hydroxide concentration. The dashed line in Fig. (5.11) is drawn through those data which could be considered most accurate. This line is parallel to the line for the present results. The break in the curve for Robinson and Wilke's data may be due to flooding of their impeller at low power inputs.
In conclusion, the interfacial area results obtained in the present study for ionic systems seem to be in agreement with the corrected results of Robinson and Wilke. Mixing effects in the gas phase may be responsible for significant errors in interfacial area measurement by the chemical method. A model for this effect indicates that even very small mixing times can lead to large errors in calculated driving force for mass transfer if the concentration of transferred species is allowed to fall below certain levels in the gas bubbles. Detailed studies in the present investigation and reexamination of the data of Robinson and Wilke indicate that the model is in qualitative agreement with experimental findings.

b. 0.1M Ionic Strength KOH-K₂CO₃-KCL + 1% "Solka Floc". The results of interfacial area determinations in 0.1M ionic strength salt solution containing 1% "Solka Floc" were presented earlier in Fig. (4.10). In order to avoid mixing effects and thus anomalous results, the concentrations of KOH used in these studies were reduced to 0.01-0.03M depending upon the anticipated value of interfacial area.

It is clear from Fig. (4.10) that the interfacial area of the suspension increases fairly steadily with increasing power input. This is in contrast to the results found in the ionic solutions where the interfacial area vs. power input curve was concave. The reason for this reduction in curvature, can be deduced from the bubble diameter curve in Fig. (4.10). Whereas the ionic solutions showed a minimum bubble diameter, the "Solka Floc" suspensions did not. The bubble diameters in the "Solka Floc" suspensions were also larger at equal power inputs. What this means is that the interfacial area in the "Solka Floc" suspensions continues to increase as the bubble diameter decreases whereas the interfacial area begins to
saturate in the ionic solutions as the holdup and bubble size approach their respective limiting values.

Fig. (5.12) demonstrates the effects of "Solka Floc" on interfacial area in salt solutions of identical ionic strength. It is clear that "Solka Floc" brings about a significant reduction in interfacial area when added to salt solutions. This reduction is particularly acute at low power inputs and becomes less significant at higher power levels. These high power levels are outside of the range normally employed in industrial fermentation, however. Over the power range of industrial interest, the reduction in interfacial area brought about by the addition of "Solka Floc" is on the order of 50%.

The reduction of interfacial area brought about by the addition of "Solka Floc" is probably due to three mechanisms which operate simultaneously in these systems. The first of these is the promotion of coalescence brought about by the increased contact time of colliding bubbles as discussed earlier. The second effect is the decrease in shear rates outside of the immediate vicinity of the impeller due to the damping effect of the solids in "Solka Floc". The third is a promotion of coalescence by impurities in the "Solka Floc". Thus the net effect of the added "Solka Floc" is to decrease bubble breakup and to increase bubble coalescence. This results in significant increases in bubble size and reduced interfacial area.

c. 0.1M Ionic Strength KOH-KCl-K₂CO₃ + 1% "Solka Floc" Wash Water. The relative contributions of the soluble and the insoluble components of "Solka Floc" can be assessed from the results of interfacial area runs in "Solka Floc" and in "Solka Floc" wash water. The results for the wash
Fig. 5.12. Interfacial area effects of "Solka Floc", "Solka Floc" wash water, and paper pulp at 30°C, F = 0.0212 ft/sec.
water are presented in Fig. (5.12) along with the results for "Solka Floc" and the basic salt solutions used. Clearly, most of the reduction in area is brought about by the solid cellulose present in "Solka Floc" although at low power levels the contribution of the solubles is quite significant.

The mechanism by which these solubles act appears to be by increase in coalescence frequency. It has been shown earlier that salt inhibits coalescence. The solubles in the "Solka Floc" appear to partially counteract this effect.

d. 0.1M Ionic Strength KOH-KCl-K₂CO₃ + 0.33% Paper Pulp. The results of interfacial area determinations in 0.1M ionic strength salt solution containing 0.33% paper pulp were presented earlier in Fig. (4.11). Mixing effects were reduced in this investigation by keeping hydroxide concentrations below 0.02M. Even so, at high power inputs, mixing effects predominated and are represented by the dashed line in Fig. (4.11).

The interfacial area increases fairly steadily at low power levels and then curves over at high power levels. The concave nature of the curve can be explained in the same manner in which the concave curve for salt solutions was explained. That is, the bubble diameter reaches a lower limiting value resulting in a saturation effect on interfacial area.

Fig. (5.12) demonstrates the effects of paper pulp on interfacial area in salt solutions of identical ionic strength. It is clear that paper pulp brings about a significant reduction in interfacial area when added to salt solution.

The reduction of interfacial area brought about by the addition of paper pulp is probably caused by the same two mechanisms discussed earlier: a reduction in bubble breakup around the impeller and an increase in bubble coalescence in the bulk of the suspension.
Previous Work. Studies of the effect of non-Newtonian suspensions on interfacial area are conspicuously absent from the literature. The opaque nature of paper pulp and mycelial suspensions makes the light probe technique impractical for measurements in these systems. The high pH levels in the chemical method rule out the use of mycelia as a suspended agent. The poorly understood nature of the sulphite system in the presence of cobalt catalyst and the sensitivity of this system to impurities makes it a poor choice. For these reasons it appears that the chemical method with solid, nondegradable, non-Newtonian additive is the preferred method for interfacial area measurement in non-Newtonian systems.

The addition of clear non-Newtonian polymeric water soluble additives such as carboxymethylcellulose could also be used to measure interfacial area in non-Newtonian systems. These systems could be measured by the light probe or chemical method. The disadvantage, from the standpoint of fermentation studies, with these systems is that they do not truly model the effect of a three phase system. It can easily be shown, for example, that bubbles below a critical size in a non-Newtonian solution of pseudo-plastic character have a very small slip velocity. If a yield stress is also present, bubbles below a certain size are unable to escape from the system. Some non-Newtonian polymer additives, e.g., polyvinyl alcohol, exhibit foaming characteristics that make them unsuitable.

The main argument against the use of soluble non-Newtonian polymers for measurements of interfacial area effects of mycelial suspensions is that these solutions have bulk viscosities that are considerably higher than that of water. In a true mycelial suspension, the liquid phase has a very low viscosity characteristic of water or dilute salt solutions,
whereas the solid phase (mycelium) gives a certain rigidity to the mixture of the two phases. Thus, low viscosity liquid flows among the branches of the mycelium. Bubbles introduced into the system are in contact with this low viscosity liquid and should have considerably different liquid films than bubbles in contact with high viscosity liquid such as that found in polymer solutions.

Mehta and Sharma (28) did investigate the effects of solids on interfacial area in stirred tanks. The suspensions they employed were not non-Newtonian in character, however. They found that interfacial area was increased by the addition of finely divided solids (BaCO$_3$ and CaCO$_3$). They attributed the increase in interfacial area (determined by the chemical method) to a decrease in bubble diameter. $K_La$ values were found to decrease with solids concentration and then to increase. They conclude that the mass transfer coefficient was decreased by the addition of solids. Contrasting these results for a finely divided particulate solid additive with those for our system, it appears that the character of the solid additives used in the present study is extremely important not only in determining the magnitude but also the direction of effect. Area results are compared to those of other investigators in Appendix, Section (V.9).

4. **Holdup**

a. **Effect of Salt.** As discussed earlier, the introduction of salt to distilled water was shown to have a slight effect on holdup. This effect was reflected in a decreased dependence of holdup on gas velocity and on power input. A further effect of the presence of salt was the introduction of a concave curvature into the holdup vs. power input curves.
As discussed earlier, salt is known to inhibit the coalescence of bubbles. At low stirring speeds where collision frequency and turbulence are lowest, coalescence will also be lowest. At high stirring speeds, where collision frequency and turbulence are highest, the coalescence will be greatest and therefore the effect of salt less pronounced when compared to lower stirring speeds. This effect of agitation should be reflected in a saturation of the size of bubbles at high power levels. Assuming that holdup is related to the velocity of rise of bubbles through the liquid in the tank, small bubbles will rise more slowly and will therefore stay in the tank longer, while large bubbles will rise quickly and exhibit low holdups. The effect of additional agitation should then be greatest at low agitation rates where significant reductions in bubble size are possible and lowest at high agitation rates where the bubble size changes very little. This explains the introduction of curvature in the holdup curves caused by the addition of salt.

Lee and Meyrick (72) measured the effects of salt on holdup and found that salt increased gas holdup. Again their data indicate a saturation effect at about 0.4-0.5M ionic strength but their drawn curves do not. The results of the present investigation all agree within 12% for an ionic strength range of 0-0.19M. The experimental technique of Lee and Meyrick with respect to holdup measurement was discussed earlier and was found to give a point value rather than an integrated measurement. Their method could be particularly poor if any froth is carried toward the tank wall during measurement.

It is concluded from our study that salt has some effect on the nature of holdup dependence on power input and gas rate and that some error
is associated with using holdup measurements in water for calculation of holdup in salt solutions.

Many investigators have made holdup measurements in water. Foust, Mack and Rushton (73) measured holdup in a variety of tanks from 12-96 inches in diameter, covering air flows from 1-5 ft/min, varying liquid depths, baffles and impeller positions. They correlated all their data to an equation of the form

$$\frac{H_o}{F} = c(HP)^n/V_L F$$

(5.13)

where $V$ = volume of water (ft$^3$), $F$ = air velocity (ft/sec), $n = 0.47$, $c = 1.65$ for the geometry used in the present study. Their results are shown in Fig. (5.13) and have a lower power exponent.

Calderbank (71) measured holdup by a sampling method. Attempts in our laboratory to duplicate his method have failed because of degassing of the tank liquid upon vacuum sampling. His holdup correlation shows no effect of agitation at 5 HP/1000 gallons where other investigations have found important agitation effects. His holdup results are considerably lower than those found in the present study.

Richards (57) measured holdup in several different sized tanks and correlated all his results as

$$H_o \propto \left( \frac{P_g}{V_L} \right)^{0.4} F^{0.5}$$

(5.14)

The data, however, do not extend to the tank size used in the present study unless holdup is less than 9%. His holdup results are lower than those found in the present study.

Westerterp (110) measured holdup at high gas rates and used a ruler for the measurements. The results are shown in Fig. (5.13) after
Fig. 5.13. Comparison of holdup results in distilled water with those of previous investigators, $F = 0.0212$ ft/sec.

1. Yoshida and Miura  
2. This study  
3. Foust, Mack and Rushton  
4. Westerterp  
5. Richards  
6. Robinson and Wilke  
7. Rushton and Bimbinet  
8. Calderbank
Yoshida and Miura (35) measured holdup in three different sized tanks ranging from 25-58.5 cm in diameter. The agitation range used in their work was much lower than normal (60-400 RPM). These workers used a manometric method in which it appears quite probable that lack of precautions to remove entrapped gas bubbles from their manometer lines caused their readings to be highly inflated. A comparison of their holdup results with those of the present study indicates that their results are considerably higher. In addition, a break in their holdup curves may be an indication of the presence of trapped bubbles in their manometer lines. Power data are again estimated.

Rushton and Bimbine (74) measured holdup using a level-taker device over a considerable range of tank size, and gas velocity. Their results are lower than those of the present study. In addition their correlation indicates a power dependence with an exponent of 0.39 as compared to 0.59 found in the present study.

Linek and Mayrhoferova (25) used a conductivity tip method to measure holdup. Their results are not shown since they were obtained in sulphite solutions of high ionic strength.

As previously mentioned, Lee and Meyrick (72) investigated holdup in water and salt solutions. Their results are considerably lower for water than those of the present study and inadequate mixing may be implicated in their results.

Robinson and Wilke (36), using a manometric method in which gas was continuously bubbled out of the tip of the manometric probes, found
a proportionality of holdup to \((P_g/V_L)^{0.4}\) as compared to \((P_g/V_L)^{0.59}\) in the present study.

Although holdup results found in the present study for distilled water are higher than those found by other investigators, it should also be recalled that \(K_{La}\) values were also higher. For example, if the results of Robinson and Wilke (36) are compared with those of the present study at equal values of \(K_{La}\) in distilled water, holdup values become more comparable as shown in Fig. (5.14) at a gas velocity of 0.0150 ft/sec. It appears then that the tank used in the present investigation was more efficient at producing holdup than tanks used by other investigators. This increase in holdup seems to be responsible for the increase in \(K_{La}\) found for this system when compared to other systems at equal power input.

The cause of the increased holdup in the tank used in this investigation is most probably the method of introduction of the gas below the impeller. In the tank, a sparger nozzle with a 4.0 mm diameter hole was placed below the impeller for gas introduction. Other investigators have used various methods for gas introduction including nozzles, sparger rings and open pipes. The nozzle used in the present study served to prevent bypassing of the tank impeller by the sparge gas. The power input to the liquid caused by the kinetic energy of the incoming gas was calculated to be on the order of 0.1 HP/1000 gallons. When an open-ended tube is used for gas introduction, the flow of gas is less steady and bypassing of the impeller can occur during gas surges. Ring spargers do not introduce the gas immediately below the impeller plate and may also be less efficient for gas dispersion.
This study

Robinson & Wilke

Fig. 5.14. Effect of holdup on $K_{La}$ for two different tanks at $30^\circ C$, $F = 0.0150$ ft/sec.
Considerable confusion concerning the role of gas velocity on holdup now exists due to the use of different methods of sparge gas introduction and different types of stirring devices in past investigations.

b. **Effect of "Solka Floc".** The effect of adding "Solka Floc" to salt solutions was to decrease holdup at low power levels and to increase holdup at high power levels. This change was accompanied by an increase in slope of the holdup vs. power input curves. The effects of "Solka Floc" on holdup were relatively small for both 1% and 3% "Solka Floc" suspensions. Curvature of the holdup curves and a decrease in gas velocity effect were also evident, especially at high power levels.

The reasons for these changes are probably as follows. At low power inputs, the coalescence promoting soluble materials in the "Solka Floc" cause larger bubbles to be formed than in pure alkali-salt solutions. These larger bubbles channel through a region in the vicinity of the impeller due to poor mixing, giving reduced holdup. At high power inputs, bubbles in the "Solka Floc" system are well-mixed throughout the liquid but the "Solka Floc" reduces their escape velocity. This causes the "Solka Floc" to saturate with holdup at lower and lower power levels as more "Solka Floc" is added. This saturation effect is reflected in the concave curvature of the holdup curves in the presence of "Solka Floc" and in the saturation of the gas velocity effect at high power levels.

c. **Effect of Paper Pulp.** The presence of paper pulp at 0.33% concentration in 0.1M ionic strength salt solution causes a marked decrease in holdup, especially at high power inputs. Poor mixing of the liquid phase is responsible for the reduction of holdup. Interfacial area runs in an analogous system revealed anomalous results due to poor mixing of the gas
phase. Since holdup depends upon efficient dispersion of the gas in the liquid phase, it is clear that the non-Newtonian nature of paper pulp is responsible for reductions in shear rate and mixing throughout the liquid phase. This reduced mixing causes more of the bubbles to pass out of the fermenter in the region of the impeller than would normally do this in a pure salt solution. This reduces the effective volume of the fermenter and thus the holdup.

5. Bubble Diameters

The average bubble diameters found in 0.1M KOH-KCl-K₂CO₃ ionic strength solutions are given in Figs. (4.9), (4.10) and (4.11), for the case of the pure salt solution, for the case of the pure salt solution containing 1% suspended "Solka Floc", and for the case of salt solutions containing 0.33% paper pulp. It is clear that in the pure salt solution the bubble diameter is large at low power inputs, decreases with increasing power and then approaches a constant size at high power inputs. It is important to note that the transition between a large and a small bubble size takes place in the range of power inputs most commonly used industrially in the fermentation industry. In the presence of "Solka Floc", however, the bubbles remain large at considerably higher powers and then decrease to smaller size at larger power inputs. It is apparent that the ultimate size of bubbles in this system is smaller than that in the pure salt system. In the presence of paper pulp, the bubble diameters observed behave in an analogous manner to those for pure alkali-salt solutions. Clearly then, the presence of solid additives alone is not responsible for the behavior of the "Solka Floc" system. Experiments were performed
in wash water prepared from "Solka Floc" suspensions. Comparing these results with those for alkali-salt solutions reveals that the water soluble components of "Solka Floc" are responsible for an increase in bubble diameter at any particular power input. Comparison with the results in the "Solka Floc" system then reveals that the solid materials in "Solka Floc" are responsible for a further increase in bubble diameter. This means that both the soluble and the insoluble materials in "Solka Floc" are responsible for increases in bubble diameter. This increased bubble size is probably caused by promotion of coalescence and damping of fluid turbulence by the materials present in "Solka Floc".

In the paper pulp suspension, the minimum bubble diameter achieved is about the same as it is in alkali-salt solutions although slightly larger. It appears that the bubble size is not severely affected by the presence of the pulp and that the reduction in interfacial area is truly a reflection of the reduction of holdup.

The transition of bubbles from large to small diameters is to be expected as power dissipation is increased. The effects of "Solka Floc" on the transition can be explained as follows. With the addition of "Solka Floc", power normally used for bubble breakup is dissipated in mixing the suspension. The increased suspension viscosity causes increased shear stress which in turn causes a rapid decrease in shear rate with distance from the impeller. If the impeller is thought of as delivering a shear rate proportional to its speed, then the more rapid dissipation of this shear rate in the presence of "Solka Floc" causes a decreased breakup of bubbles as the distance from the impeller increases.
Examination of Figs. (4.9) and (4.10) reveals that pure salt solutions are already in the transition zone of bubble sizes at the lowest power levels studied. "Solka Floc" suspensions are near a plateau of "large" bubble size at low power and enter the transition zone at a higher power level. In other words, the effect of "Solka Floc" appears to be that of shifting the transition zone between "large" and "small" bubbles from lower to higher power levels.

Comparison of the data of Robinson and Wilke (36) with that of the present study at equal power dissipation per unit volume in pure salt solutions of 0.1M ionic strength is made in Fig. (5.15) after correction of Robinson and Wilke's interfacial area data.

Fig. (5.15) reveals that bubble diameters found at equal power dissipation in the smaller tank of Robinson and Wilke are larger than those found in the tank used in the present study. The effect of gas rate differences between the two studies makes the graphical comparison of Fig. (5.15) even less dramatic. At higher gas rates, the data of Robinson and Wilke would be expected to give even larger bubbles.

Note that correction of Robinson and Wilke's data for mixing effects reveals that the bubble diameters are actually approaching a constant value as opposed to the dashed line which they drew indicating a decreasing diameter trend. Note also that the smaller impeller of Robinson and Wilke is apparently flooded at power levels below 6 HP/1000 gallons, causing a break in their bubble diameter curve.

Apparently, size of the fermenter has an effect on the transition range for bubble sizes. A larger fermenter with a larger impeller seems to be more effective in causing bubble breakup than a smaller fermenter.
This study $F = 0.0212$ ft/ sec

Robinson and Wilke $F = 0.0150$ ft/ sec

Corrected

Uncorrected

Fig. 5.15. Effect of mixing on bubble diameter results of Robinson and Wilke at 30°C, $\Gamma = 0.1$ mol.
with a correspondingly smaller impeller at the same power input per unit volume. If this is the case, it would explain the discrepancies between the $K_{L,a}$ results under identical power input conditions in large and small tanks. It appears likely that power per unit volume may not be the best variable for use in scale-up correlations at low ionic strengths. This possibility will be explored in more detail later.

Marrucci and Nicodemo (93) measured bubble diameters in a bubble column using a photographic method. They varied salt concentration and found that the bubbles all approached a minimum bubble diameter of 0.05 cm regardless of gas rate used when the ionic strength exceeded 0.2M. For ionic strengths less than 0.2M, the bubble diameter vs. ionic strength curves depended upon gas flowrate. They also found that holdup became independent of ionic strength for KCl solutions if ionic strength was greater than 0.2-0.3M. The bubble size distribution was also narrowed as KCl concentration was increased.

Their results agree quite well with those of the present study in which a minimum bubble diameter of 0.045 cm was found at high power inputs (corresponding to high gas rates in the bubble column study). The sharpening of the bubble distribution curve in their study is indicative of the saturation effect of salt between 0.2 and 0.4M ionic strengths. The independence of holdup of ionic strength in the vicinity of 0.2-0.3M is also indicative of this effect.

Calderbank's data for water (71) indicates that bubble sizes are considerably higher than they are in the 0.1M ionic strength solutions tested in this study. Mean bubble diameters found by Calderbank ranged from 0.2 to 0.5 cm over a considerable power range. Thus, the present
study shows conclusively that bubbles in dilute salt solutions are smaller than those in water. Whereas Calderbank found no minimum bubble size with bubbles in water, our study reveals that the addition of salt results in a minimum bubble size at high power inputs. The work of Marrucci and Nicodemo in bubble columns confirms this.

6. Mass Transfer Coefficients

As shown in Figs. (4.9) and (4.10), the behavior of mass transfer coefficients found in salt solutions and in salt solutions containing "Solka Floc" or paper pulp closely parallels that of the bubble diameters determined in these systems. The singularly most important feature to be noted in these figures is that the mass transfer coefficient of the systems decreases with increasing power input. Note also that the curvature of the mass transfer vs. power input curves is different in the two types of systems, with the pure salt solution or paper pulp solution appearing to approach a constant limiting value and the "Solka Floc" system decreasing throughout the entire power range investigated.

More insight into this behavior can be obtained by plotting the mass transfer coefficient vs. bubble diameter curves in Figs. (5.16a-5.16c). These figures reveal that at any particular bubble diameter, the mass transfer coefficient is significantly lowered by the addition of "Solka Floc" or paper pulp. A direct relationship between mass transfer coefficient and bubble diameter is clearly shown.

A further investigation of the effects of "Solka Floc" on mass transfer coefficient was carried out by performing simultaneous $K_L a$ and a runs in wash water prepared from 1.0% "Solka Floc". The results of these
Fig. 5.16a. Mass transfer coefficients vs. bubble diameters for alkali-salt and salt solutions.

- This work
- Hammerton and Garner (89)
- Robinson and Wilke (36)
- Linek, et al. (44)
- Benedek and Heideger (60)
- Li, et al. (111)
- Coppock, et al. (112)
Fig. 5.16b. Mass transfer coefficients vs. bubble diameters for alkali-salt solutions with 1% "Solka Floc".

- Purity check
- Wash water of 1% "Solka Floc"
- 1% "Solka Floc"

A = Glycerol-H$_2$O (1.3 cp)
B = Glycerol-H$_2$O (1.9 cp)
Fig. 5.16c. Mass transfer coefficients vs. bubble diameters for alkali-salt solutions with 0.33% paper pulp.

- ○ Wash water of paper pulp
- △ Paper pulp
runs are plotted in Fig. (5.16b). It can be seen that the reduction in mass transfer coefficient at any bubble diameter for "Solka Floc" is due entirely to the presence of the soluble materials in "Solka Floc" and is not caused by the solid materials present.

The mass transfer coefficient vs. bubble diameter results are parallel to those found for alkali-salt solutions, indicating that \( K_L a \) is proportional to holdup for this system. This can be shown as follows.

\[ K_L = \frac{K_L a}{a} \]  
\[ d_B = \frac{6H_o}{a(1 - H_o)} \]  
\[ K_L = d_B \left( \frac{K_L a}{6} \right)(1 - H_o)/(H_o) \]  

If \( K_L \) vs. \( d_B \) plots as a straight line on log-log paper with a slope of 1.0, then \( K_L a = (H_o/[1 - H_o]) \) where the latter term is the system holdup based on liquid rather than liquid plus gas height.

This relationship between \( K_L \) and \( d_B \) is therefore independent of interfacial area and all results, even those where anomalous mixing effects were found, should still fall on the same straight line. This conclusion is confirmed in Fig. (5.16a) where the dashed extension of the alkali-salt results fits the anomalous results very well.

Fig. (5.16a) reveals that in systems containing pure salt solutions, a limiting mass transfer coefficient of 0.01 cm/sec is approached at high power input levels. It is important to note that the transition in mass transfer coefficient from high values to low values occurs in the
range of power inputs of industrial importance, i.e., 1-10 HP/1000 gallons. This means that the mass transfer coefficient is not constant and independent of power input in this range. Only at power input levels in excess of 10 HP/1000 gallons is the assumption of a constant mass transfer coefficient valid.

Fig. (4.10) reveals that when "Solka Floc" is added to the salt solutions, the mass transfer coefficient continues to decrease even when the power levels reach 40 HP/1000 gallons. The increased steepness of the curve indicates that smaller mass transfer coefficients will be reached before any constancy of value is reached.

The appearance of the curves in Figs. (4.9) and (4.10) suggests that when "Solka Floc" is added to a salt system, the transition of mass transfer coefficient from large values to small values is shifted and altered in magnitude. That is, "Solka Floc" causes the mass transfer coefficient to remain large at higher power input levels and then causes a very steep decline in mass transfer coefficient value at very high power levels.

Studies on the paper pulp system proceeded in two steps. In the first series of experiments, 0.33% paper pulp in alkali-salt solution was characterized by simultaneous $K_L a$ and $a$ determinations. These results indicated behavior shown in Fig. (5.16c). It can be seen that for this system $K_L$ is not proportional to bubble diameter. This behavior is caused by the non-Newtonian character of the paper pulp suspension. Curves (A) and (B) for Newtonian glycerol-water solutions of different viscosities (22) indicate that as viscosity increases the mass transfer coefficient at any bubble diameter decreases. For the non-Newtonian paper pulp,
at low power inputs the viscosity will be highest (pseudoplastic) and the bubble diameter largest. At high power inputs the viscosity will approach a limiting lower value and the bubble diameter will be smallest. This is precisely the behavior observed. In addition a pseudo-viscosity can be defined as discussed earlier simply by noting which Newtonian viscosity will give the same mass transfer coefficient as the non-Newtonian suspension at a particular bubble diameter. Thus for 0.15 cm bubbles in the paper pulp suspension the pseudo-viscosity is close to 1.3 cp and the power input is approximately 2 HP/1000 gallons.

Because of the difficulty of defining viscosity in a stirred tank with non-Newtonian material present, this method may be useful in defining a viscosity which is relevant to mass transfer processes in the tank.

It can be seen that the paper pulp suspension reaches a limiting viscosity which is larger than that of the alkali-salt solution due to the presence of the cellulose fibers in the pulp.

The second step in the paper pulp characterization involved simultaneous $K_a$ and $a$ experiments on filtrate prepared from the paper pulp. These results were identical to those found for alkali-salt solutions and proved conclusively that the behavior found in Fig. (5.16c) was due to the solid cellulose present and not, as in "Solka Floc", to the presence of dissolved impurities.

An explanation for the behavior of Fig. (5.16a) was first presented by Calderbank and Moo-Young (22) in their studies of the absorption of CO$_2$ into aqueous-glycerol solutions of varying viscosity. They discovered two distinct bubble size regimes which they labeled the "large" and the "small" bubble regimes. The mass transfer coefficients found for "large" and "small"
bubbles were different. All "large" bubbles had large mass transfer coefficients. All "small" bubbles had small mass transfer coefficients. In addition, in solutions of constant physical properties, the mass transfer coefficients of either "small" or "large" bubbles were independent of power input to the system. They also discovered a transition range of bubble sizes in which the mass transfer coefficients changed from those for "large" bubbles to those for "small" bubbles. A plot of \( K_L \) vs. \( d_B \) similar to Fig. (5.16) was made by Calderbank and Moo-Young. They found that the transition range of bubble sizes covered the range 0.05-0.25 cm. Although no bubbles in our system were larger than 0.12 cm, the transition range appears to approach higher levels. The lower limit of the range, 0.05 cm is in excellent agreement with that found in the present study.

The data of Calderbank and Moo-Young also reveal a decrease of \( K_L \) at any particular bubble diameter with increasing liquid viscosity. This is the same tendency revealed in the present study, where the viscosity was increased by the addition of an insoluble third phase, paper pulp.

It should be noted at this time that despite the warning of Calderbank and Moo-Young that \( K_L \) is only independent of \( d_B \) in the "small" and "large" bubble regimes, mass transfer equations used for aeration correlation in the fermentation industry are often based on a constant value of \( K_L \). This type of correlation can lead to significant errors in calculation of mass transfer coefficient. Clearly the mass transfer coefficient decreases with increasing power level if the bubble diameters are in the transition range of 0.05-0.25 cm.

Benedek and Heideger (61) also present data on the transition of mass transfer coefficient from that for "large" bubbles to that for "small"
bubbles. Their data suggests that "large" bubbles may not be approached in salt solutions or in water until a bubble diameter in excess of 0.3 cm is reached. They also found that the mass transfer coefficient for "large" bubbles may be larger than the generally accepted value. Their data indicate that the effects of salt on mass transfer coefficient at any bubble diameter are negligible. This conclusion is also supported by the work of Lessard and Zieminski (92) and Zieminski and Whittemore (90), using non-agitated systems.

Fig. (5.16a) compares the results of these other investigators with those found in the present study for salt solutions. Data for distilled water studies made by Calderbank (71) were used to calculate the value of \( K_L \) in distilled water based upon \( K_{La} \) data obtained in the present investigation. These \( K_L \) results indicate excellent agreement with results of the present study. The difficulty of translating studies done in one tank to those done in another is indicative of the value of the simultaneous determination method used in the present study. Results of Robinson and Wilke (36) in 0.1M ionic strength salt solutions were corrected for the effects of hydroxide concentration during interfacial area determinations and are presented also.

It is clear from Fig. (5.16a) that the results of the present study give mass transfer coefficients which agree quite well with those already published. It is also clear from the curve that simultaneous determination of parameters is a reliable method. Differences between the conditions of Calderbank's study and the present study make direct comparison of the magnitude of \( K_L \) in water impossible. The trend of constant \( K_L \) value for both works is the same, however.
A suitable explanation for transition of mass transfer coefficients from the value for "large" bubbles to the value for "small" bubbles still remains in the realm of speculation. One explanation, advanced by Calderbank and Moo-Young (22), is based on the fact that "small" bubble mass transfer coefficients are indistinguishable from those for rigid spheres. This led the authors to postulate that "small" bubbles behave as rigid spheres and do not undergo the expected internal circulation of "Higbie" bubbles. "Large" bubbles then would be freely circulating bubbles and "small" bubbles would be rigid, noncirculating bubbles. A transition from the case of free circulation to no circulation would then be accompanied by a reduction in mass transfer coefficient. The reduction of mass transfer coefficient would result from the fact that circulating bubbles have better surface renewal characteristics than do noncirculating bubbles.

The cause of the reduction in circulation has been postulated to be the presence of trace quantities of surface active material which accumulate at the rear of the moving bubbles and increase the rigidity of the gas-liquid interface. As the bubbles are reduced in size (due to greater agitation of the system, for example) the proportion of surface covered by the surface active agent increases. Thus these agents are postulated to be more effective on small bubbles.

This concept is supported by studies of other workers (e.g., that of Hammerton and Garner [89]) where mass transfer coefficients determined for ethylene in water are shown under normal conditions to rise from low values at small bubble diameters to larger values at higher bubble diameters. Deliberate contamination of the bubble interfaces was shown to give \( K_L \) values which agree with the Frossling equation for mass transfer.
from rigid spheres. The mass transfer coefficients for "large" bubbles were found to agree with those calculated from the Higbie equation for circulating bubbles. A very close relationship between \( K_L \) and velocity of rise in their studies was observed. This additional fact reveals that the concept of circulating vs. noncirculating bubbles is in agreement with bubble rise velocity equations for circulating and noncirculating bubbles (See Levich [113]) where circulating bubbles can be shown to rise faster than rigid bubbles. Hammerton and Garner's study points out the fact that the transition from "large" bubbles to "small" bubbles is very sensitive to the presence of surface active agents. Calderbank and Moo-Young's (22) study points out the transition's sensitivity to viscosity in Newtonian two phase systems and the present study points out the transition's sensitivity to the presence of a third phase with non-Newtonian character and/or to the presence of small quantities of water soluble impurities.

7. Robinson's Correlation and Comparison

Comparing the results of distilled water, sodium sulphate and sodium sulphite \( K_L \) runs with the generalized correlation proposed by Robinson and Wilke (36), Fig. (5.17) is obtained. Here

\[
\epsilon = K_L a \text{ or } K_L a/\phi' \quad (\text{sec}^{-1})
\]  

(5.19)

where \( \phi' \) is the enhancement factor in the presence of chemical reaction. According to Robinson and Wilke

\[
\epsilon = \lambda (p_g/v_L)^n (v_S)^m \epsilon
\]  

(5.20)

where \( \lambda \) is a proportionality constant which is assumed to be a function of ionic strength,
Fig. 5.17. Comparison with generalized correlation of Robinson and Wilke at 30°C.

- Distilled water
- 0.5M Na₂SO₄ + 10⁻³M CuSO₄
- 0.5M Na₂SO₃ + 10⁻³M CuSO₄
\[
\varepsilon = (\rho_D)^{0.533}(D_L)^{2/3}/(\sigma^{0.6}[\mu_L]^{1/3})
\]
based on the correlations of Calderbank and Moo-Young (22).

The values plotted in Fig. (5.17) were calculated from the data taken in the present work based upon values of the exponents "n" and "m" found in this work. It should be noted that the values of "m" were different in this work than in that of Robinson and Wilke. The values of "n" were very similar except that for the high ionic strength systems a value of 0.95 as opposed to 0.90 has been used. The values of \(\lambda\) used were those found by Robinson and Wilke.

Clearly there is good agreement between the results of the present study and those of Robinson and Wilke for the 0.5M sodium sulphate and sodium sulphite solutions using the values of "m" and "n" for the larger tank used in this study. Thus the value of \(\lambda\) found by Robinson and Wilke seems to be useful for scale-up at high ionic strengths.

The results found for distilled water, however, show a distinct lack of agreement with those of Robinson and Wilke. The differences between the two sets of data are correctable by assuming a lower value of \(\lambda\) than that found by Robinson and Wilke. Thus the two sets of results would correspond if the value of \(\lambda\) were equal to 11.1 (grams\(^{0.4}\)
\(\text{cm}^{0.647}\sec^{0.534}\)[ft-lb/min-ft\(^3\)]\(^{-n}\)[ft/sec]\(^{-m}\)) for distilled water.

Therefore it appears that \(\lambda\) is not only a function of ionic strength but also of scale of the mass transfer equipment. This dependency on scale disappears at high ionic strengths and is most prevalent at low ionic strengths. For this reason, scale-up based upon sodium sulphite oxidation studies is an unreliable method for fermentation work, where low ionic strength solutions are used.
In addition, the gas velocity exponent "m" has been shown to be a function of sparger design or equipment scale and must be better characterized for any ionic strength solution before reliable scale-up is possible. The power per unit volume exponent "n" does not appear to be a function of tank scale but does depend upon ionic strength in a known manner.

8. Comparison with Other Previous Investigations

The results of the present investigation are presented along with those of Calderbank and Moo-Young (22) and Cooper, Fernstrom and Miller (56) in Fig. (5.18). The new results tend to form bands between these two previous studies (the sulphate results are slightly higher than the predictions of Cooper, et al.). Calderbank's equation underestimates the values of $K_{La}/V_s^{1/2}$ for distilled water found in this study by approximately 40% and appears to be useful in predicting a conservative value of power input for design purposes. The equation of Cooper, et al., presented as a band covering the range of gas velocities used in the present study, overestimates the values of $K_{La}/V_s^{1/2}$ for distilled water and low ionic strength salt solutions. The differences become particularly great at high power inputs due to differences in the slopes, as discussed earlier. In high ionic strength salt solutions, the equation of Cooper, et al., agrees reasonably well with the results of the present study and could be used with some confidence for design purposes. The values of $K_{La}$ estimated with this equation are based on log mean concentration driving force rather than exit concentration driving force.

9. Interfacial Area Correlation and Comparison

Fig. (5.19) illustrates the results of several interfacial area
Fig. 5.18. Comparison with $K_La$ results of previous investigators.

- Distilled water
- $0.1M$ ionic strength alkali-salt
- $1.5M$ ionic strength $Na_2SO_4$

$$K_La = hr^{-1}, V_s = ft/sec$$
Fig. 5.19. Comparison with interfacial area results of previous investigators.  
1. This study, $\Gamma = 0.1M$
2. Robinson and Wilke, $\Gamma = 0.1M$
3. Linek, et al., $\Gamma = 0.75$ and $1.5M$
4. Benedek and Heideger, $\Gamma = 0.0M$
5. Lee and Meyrick, $\Gamma = 0.1M$
6. Calderbank, $\Gamma = 0.0M$
investigations. Clearly, wide variations in the value of \( \frac{a}{\gamma_{s}^{1/2}} \) are possible even at the same ionic strength (see curves 1, 2, and 5). All of the results illustrated fall between those of Calderbank in pure water and those of the present study in 0.1M ionic strength alkali-salt solutions. The reasons for this variation are quite complex but appear to be related to the ability to form bubbles which fall within three distinct bubble size ranges, "small" bubbles, transition size bubbles, and "large" bubbles, corresponding to the size ranges \(< 0.5 \text{ mm}, 0.5-2.5 \text{ mm}, \text{ and } > 2.5 \text{ mm}\) respectively. The low area results found by Calderbank, Benedek and Heideger, and Lee and Meyrick were analyzed for bubble diameters and it was found that the average bubble diameters corresponded either to those for "large" bubbles or to large transition range bubbles. The very high interfacial area results found by Robinson and Wilke, and the present study corresponded either to the "small" bubble or transition bubble ranges. Thus the bottom part of Fig. (5.19) represents interfacial area results for "large" bubbles, the top part represents interfacial area results for small bubbles and the middle of the figure represents results for transition range bubbles.

Since several of the vessels used in the studies presented in Fig. (5.19) were geometrically similar, the wide variations found require suitable explanation. The causes for these variations will be discussed in Section (V.10).

10. General Conclusions and Recommendations for Design

On the basis of the present work and results of previous investigators, the following general conclusions have been reached concerning the
variables which influence the volumetric mass transfer coefficient, $K_a$, in agitated gas-liquid reactors. These factors should be considered in the design and scale-up of mass transfer equipment.

a. Power Per Unit Volume. The power input per unit volume of liquid has been used to correlate $K_a$ values in this study. This variable is of fundamental significance to mass transfer in that it determines the gas holdup and bubble diameter in the contactor. Dissipation of energy as small eddys is assumed to be independent of previous history of the large eddys generated by the impeller. The majority of energy dissipation takes place in these small eddys and is responsible for shear forces which determine bubble sizes.

Many investigators have used stirring speed as a correlating variable. Difficulties arise here due to variations in impeller diameter and geometry. The effectiveness of the stirrer is not accounted for in these correlations, particularly in the presence of gas bubbles.

Scale-up at equal power input per unit volume of liquid has been used successfully in several Newtonian fermentations. The correspondence between $K_a$ and $P_g/V_L$ found for sodium sulphite systems indicates that $P_g/V_L$ can also be used successfully for scale-up of mass transfer in high ionic strength ($\Gamma > 0.4M$) salt solutions. The success of this correlating parameter in high ionic strength solutions is probably due to the relatively slow coalescence rates in these solutions. The small eddys generated then determine the ultimate size of the bubbles generated and excess power is manifested as an increase in holdup. Since bubbles in identical solutions will be of the same scale at identical power dissipation per unit volume regardless of tank scale at high ionic strengths, scale-up
will be successful if holdup is independent of tank scale also. This has been shown to be the case provided \( P_g/V_L \) is the same in all systems.

b. Fluid Properties.

1. Ionic Strength. Ionic strength effects on mass transfer are now well documented. This study has confirmed the results of Robinson and Wilke but in a larger scale of equipment. Ionic strength appears to be responsible for differences in dependence of \( K_{La} \) on \( P_g/V_L \). In water (\( \Gamma = 0.0M \)) \( K_{La} \propto (P_g/V_L)^{0.4} \). The power per unit volume exponent increases as ionic strength increases until a limiting dependence of \( K_{La} \propto (P_g/V_L)^{0.95} \) takes place near \( \Gamma = 0.4M \). Not only the power per unit volume exponent but also the superficial velocity exponent is affected. No general conclusion can be reached concerning the latter exponent, however, without further studies on the role of sparger configuration and tank scale. Therefore, correlations presented in the range 0.01-0.03 ft/sec cannot be safely extrapolated to superficial velocities outside this range.

The differences caused by ionic strength among \( K_{La} \) values in different systems are believed to be attributable to coalescence inhibition caused by the presence of salt. Fundamental studies have shown significant variation in coalescence rates and bubble sizes in stirred tanks and bubble columns with varying ionic strength.

In batch fermentation systems, variations in ionic strength during the course of a fermentation are quite common due to microbial requirements for mineral nutrients. Since \( K_{La} \) will decrease if salt is removed during the fermentation, a medium giving adequate \( K_{La} \) values at the beginning of a fermentation may be inadequate in this respect when population densities (and thus oxygen demands) are higher and salt concentration are lower later.
in the fermentation. Equipment should therefore be designed which gives adequate $K_L a$ values in a fermentation broth having properties similar to those found during the stage of microbial growth where oxygen demands are highest.

The effects of ionic strength on the driving force for mass transfer should also be considered in industrial scale equipment. Since salt inhibits bubble coalescence, the assumption that the gas phase is well-mixed should be tested before $K_L a$ values are calculated. Adequate aeration rates should be provided in order to avoid situations in which this driving force is reduced to very low levels by backmixing from the fermenter headspace.

2. **Interfacial Tension.** Calderbank has investigated the effects of surface tension on $K_L a$ in pure liquids. He found that $K_L a \propto \sigma^{-0.6}$. Separating the effects of surface tension on $K_L a$ into its effects on the more fundamental parameters, $K_L$ and $a$, Calderbank showed that the interfacial area is affected as $a \propto \sigma^{-0.6}$ but that $K_L$ is unaffected.

In salt solution studies, variations in surface tension have been quite small and Calderbank's results on pure solvents cannot adequately explain the observed effects. Fundamental studies in this area are still being carried out and no explanation yet advanced appears adequate for explaining all the observed effects in a quantitative manner.

Studies by Benedek and Heideger (60) on the effects of surface active agents (see also Aiba, et al. [76]) have demonstrated a decrease in mass transfer coefficient at any particular bubble diameter when surface active agents are present. The present study indicates that soluble material present as impurities in "Solka Floc" can also reduce mass transfer
coefficients with negligible effects on surface tension. Excessive amounts of surface active agent can lead to a situation in which only noncircular- ing bubbles exist. They also affect the amount of interfacial area generated, either decreasing interfacial area by promoting bubble coalescence (antifoam agents) or increasing interfacial area by inhibiting bubble coalescence.

Since fermentation systems often contain surface active agents, design for adequate $K_L a$ values should take into account the presence of antifoam agents, proteins and other surface active materials present in the broth. Engineering studies in this area are sorely lacking and design of mass transfer equipment for fermentation work is often plagued with much uncertainty.

3. Liquid Phase Density. Calderbank's studies also included the effects of liquid phase density on variations in $K_L a$. Generally speaking, $K_L a \propto \rho_c^{0.466}$. Variations in $K_L$ and $a$ were found to be such that $K_L \propto \rho_c^{0.266}$ and $a \propto \rho_c^{0.2}$.

In most mass transfer situations involving aqueous systems, $\rho_c$ will not vary significantly. Therefore design of mass transfer equipment for aqueous systems requires very little correction for liquid density.

4. Viscosity. Studies on the effects of liquid phase Newtonian viscosity on $K_L a$ were carried out by Calderbank and Moo-Young using aqueous glycol and glycerol solutions. These studies indicate that $K_L a \propto \mu_L^{-0.266}$. Variations in $K_L$ accounted for the entire effect and no effects on $a$ were noted. This situation may be a consequence of the method of correlation, however, and there is some evidence to indicate that $a$ is also affected by viscosity.
In non-Newtonian systems studied here, variations in viscosity with shear rate in the tank were responsible for changes in $K_La$. Both $K_L$ and $a$ were affected. $K_L$ was found to decrease at constant bubble diameter as paper pulp was added to salt solutions. $a$ was found to decrease at constant $P_g/V_L$ as paper pulp was added. The variation of $K_L$ with bubble diameter indicated that $K_La$ is not proportional to holdup in the non-Newtonian system. In addition, holdup was dramatically reduced when pulp was added. All of these changes brought about by the addition of non-Newtonian character to the liquid phase are a function of the properties of the additive causing non-Newtonian characteristics. Knowledge of the "average viscosity" of a non-Newtonian system under conditions of varying shear field is essential for fundamental design of stirred tank contactors used in non-Newtonian fermentation systems. The method presented here allows definition of an "average viscosity" which has significance to mass transfer studies.

The effects of viscosity on $K_La$ in salt solutions have not been studied. It appears that small changes in interfacial tension and viscosity are accompanied by large changes in coalescence rates and $K_La$ for salt solutions. Much work must be done in this area. Since all fermentation broths contain some ionic components, caution must be exercised in using Calderbank's results for nonionic systems to predict physical property effects in fermentation systems. Nevertheless, the correlation of Robinson and Wilke has been used with some success for salt solutions of varying ionic strength. It should be noted, however, that variations in the value of the physical property parameter were quite small in their work.
5. **Liquid Phase Diffusivity.** The effects of diffusivity of the absorbing gas in the liquid phase was studied by Calderbank. Separating the effects of viscosity and diffusivity on $K_L$, they conclude that

$$K_L \propto \sqrt{D/L/ \mu} 0.266$$

$D_L$ is not expected to have any effect on the interfacial area generated, therefore no studies have been carried out in order to investigate effects of $D_L$ on $a$. Thus in general $K_L a \propto D_L^{1/2}$.

In fermentation systems of Newtonian character, variations in the value of $D_L$ can be expected to be small. If temperature changes are made during the course of a fermentation, variations in the value of $D_L$ can be estimated using the relationship

$$D_L \mu_c / T \approx \text{constant}.$$ 

In non-Newtonian fermentation systems, where polymeric soluble materials are present, measurements of the value of $D_L$ should be made since some polymers are known to affect $D_L$.

c. **Sparger.** There is increasing evidence that the method of gas introduction in a gas liquid contactor can have significant effect upon the value of $K_L a$. Lack of agreement between studies supposedly carried out in otherwise identical equipment may be ascribable to sparger configuration differences.

The criteria for sparger configuration are not now understood. In small vessels, a single nozzle appears to give higher $K_L a$ values than either a ring sparger or an open pipe. Initial breakup of the bubbles upon passage from the nozzle and more direct impingement on the impeller disk may be responsible for the higher $K_L a$ values obtained with nozzle spargers.
In larger equipment, ring spargers which break up the gas into many fine bubbles before the gas reaches the stirrer are probably superior to the use of a single open pipe.

Fundamental studies in this area are needed in order to prescribe adequate scale-up criteria for mass transfer. Obviously, if sparger configuration is poor in industrial scale equipment, an otherwise well calculated scale-up design may fail to achieve adequate $K_La$ values.

d. **Vessel Size.** Tank scale was found to have no effect on the mass transfer coefficient vs. bubble diameter transition. Thus different sized tanks gave equal values of $K_L$ at equal average bubble diameters. Differences in bubble diameter were noted, however, at equal power dissipation in the liquid. Differences in interfacial area values at equal power dissipation were also noted, with the larger tank used in this study appearing to be more effective in bubble breakup.

The effect of scale may be misleading, however, since the sparger configuration may be responsible for some or all of the observed effects. Thus the conclusion that $K_La$ increased at low ionic strengths as the vessel size increased cannot be made at this time. The results of other investigators appear to support the conclusion that vessel size is not as significant a variable as $P_g/V_L$ or superficial velocity.

At high ionic strengths, $K_La$ was found to be independent of the tank scale at equal gas rates and power inputs to the liquid. Here the physical properties of the liquid control the bubble size and thus $K_L$. The value of $a$ depends on the gas holdup, which in turn depends on power input to the liquid and gas rate.
e. **General Recommendations for Design.** In view of the foregoing discussion, the following procedure is recommended for reactor design.

1. **Low Ionic Strength Systems.** For low ionic strength systems with ionic character, the generalized correlation of Robinson and Wilke appears to give values for $K_a$ which are reasonable. A more conservative design for salt solutions would be based on the correlation of Calderbank, using the properties for distilled water. This latter correlation can lead to considerable overdesign in salt solutions, however, and an estimation of the uncertainties involved in the system being treated should be made to avoid excessive overdesign. Variations in $\mu_L$, $\rho_c$, $\sigma$, $(P_{g/L})^n$ and $(V_s)^m$ are treated in the former recommended correlation, but effects of surface active agents, non-Newtonian character, microbes and sparger configuration are not considered. In addition, Calderbank's equation does not deal with ionic strength effects.

2. **High Ionic Strength Systems.** For high ionic strength systems with Newtonian character, either the generalized correlation of Robinson and Wilke or the equation of Cooper, et al. (56) can be used with considerable confidence. Neither equation can be used confidently if the physical properties of the solution vary much from those for aqueous salt solutions since neither study involved experiments where physical properties of the solutions were varied over wide ranges.

   Again, if surface active agents, non-Newtonian character or microbes are present, estimation of some safety factor should be made to avoid under-design. Sparger and impeller configuration appear to have no effect on $K_a$ for high ionic strength salt solutions, whereas $P_{g/L}$ and gas rate appear...
quite significant. The value of m in the gas rate dependence appears somewhat controversial but little error is associated with using an average value.

If experimental facilities are available, values of $K_L a$ should be determined in pilot scale equipment in order to make scale-up more reliable. This is especially true if surface active agents, non-Newtonian character or unusual materials are present in the liquid. In fermentation work, experiments should be carried out on the broth as described earlier in order to be assured that adequate $K_L a$ values are achieved. Scale-up on the basis of equal values of $P_g/V_L$ and $V_s$ cannot yet be assured since there is some evidence that the values of n and m are dependent on scale for very large vessels. Past experience is then necessary in order to determine adequate scale-up criteria. Since industrial scale equipment is often of different geometry than pilot scale equipment, $K_L a$ values determined in both scales of equipment would allow adequate cross-correlation of pilot scale experiments and plant scale operations.

It should also be recognized that employment of $K_L a$ for design and scale-up is not as fundamental an approach as the use of $K_L$ and a separately. Unfortunately, generalized correlations for the separate prediction of these factors have not yet been developed.

For nonionic systems, Calderbank has developed a general expression for the area term

$$a_o = 230 \frac{(P_g/V_L)^{0.4} \rho_L^{0.2} \sigma^{0.6}}{V_s^{1/2}} \rho_C^{0.2}$$

However, in high ionic strength systems in which bubble coalescence is inhibited, this equation is not applicable.
Although $K_L$ is found to be a unique function of bubble diameter for nonionic and ionic aqueous systems, prediction of bubble diameter is not yet possible due to variations in the position of transition range bubbles on the power dissipation continuum. These variations, likely due to the presence of minute quantities of surface active agents in water, are at present in need of greater study. In the "small" bubble regime and the "large" bubble regime, the equations of Calderbank and Moo-Young appear applicable

\[
K_L(N_{Sc})^{2/3} = 0.31 \left[ \frac{\Delta \rho \mu \epsilon g}{\rho_c^2} \right]^{1/3} \quad \text{"small" bubbles,}
\]

\[
K_L(N_{Sc})^{1/2} = 0.42 \left[ \frac{\Delta \rho \mu \epsilon g}{\rho_c^2} \right]^{1/3} \quad \text{"large" bubbles.}
\]
VI. SUMMARY AND CONCLUSIONS

1. Systems Investigated

The following systems were investigated for the purpose of understanding the effects of ionic strength and solid additives resulting in both Newtonian and non-Newtonian behavior on the mass transfer coefficient and interfacial area in agitated gas-liquid contactors.

<table>
<thead>
<tr>
<th>System</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distilled Water</td>
<td>( H_0, K_L a )</td>
</tr>
<tr>
<td>Distilled Water + 1% &quot;Solka Floc&quot;</td>
<td>( K_L a )</td>
</tr>
<tr>
<td>Distilled Water + 3% &quot;Solka Floc&quot;</td>
<td>( K_L a )</td>
</tr>
<tr>
<td>0.5M Na(_2)SO(_4) + 10^{-3}M CuSO(_4)</td>
<td>( K_L a )</td>
</tr>
<tr>
<td>0.5M Na(_2)SO(_3) + 10^{-3}M CuSO(_4)</td>
<td>( K_L a )</td>
</tr>
<tr>
<td>0.5M Na(_2)SO(_3) + 10^{-3}M CuSO(_4) + 1% &quot;Solka Floc&quot;</td>
<td>( K_L a )</td>
</tr>
<tr>
<td>0.5M Na(_2)SO(_3) + 10^{-3}M CuSO(_4) + 3% &quot;Solka Floc&quot;</td>
<td>( K_L a )</td>
</tr>
<tr>
<td>0.19M Ionic Strength (KOH + Na(_2)SO(_4))</td>
<td>( H_0 )</td>
</tr>
<tr>
<td>0.10M KOH-KCl-K(_2)CO(_3)</td>
<td>( H_0, K_L a, a, d_B, K_L )</td>
</tr>
<tr>
<td>0.10M KOH-KCl-K(_2)CO(_3) + 1% &quot;Solka Floc&quot;</td>
<td>( H_0, K_L a, a, d_B, K_L )</td>
</tr>
<tr>
<td>0.10M KOH + 3% &quot;Solka Floc&quot;</td>
<td>( H_0 )</td>
</tr>
<tr>
<td>0.10M KOH-KCl-K(_2)CO(_3) + &quot;Solka Floc&quot; Wash Water</td>
<td>( K_L a, a, d_B, K_L )</td>
</tr>
<tr>
<td>0.10M KOH-KCl-K(_2)CO(_3) + 0.33% Paper Pulp</td>
<td>( H_0, K_L a, a, d_B, K_L )</td>
</tr>
</tbody>
</table>

2. New Points in this Study

This study has resulted in several new contributions in the area of mass transfer in gas-liquid stirred tank contactors. A new method for rapid and reliable determination of the value of \( K_L a \) using dissolved oxygen probes has been developed. This method, based upon the value of the slope
of the dissolved oxygen probe transient response at its inflection point, has been used in the present study for the determination of $K_L a$ values in several different systems. In addition, a new method for determination of the gas holdup in an agitated tank has been developed. This method allows manometric determination of holdup in liquid-gas and solid-liquid-gas systems and gives rapid and reproducible results. Another contribution has been a recognition of what appears to be a mixing problem associated with excessive conversion of gas phase reactant during area measurements. Although this problem has been previously described, it had been ignored in the previous study of Robinson and Wilke and re-examination of their results has led to different conclusions regarding the values of mass transfer variables at high power inputs. Velocity effects on mass transfer variables have been examined in this study and it appears that the method of gas introduction to the tank requires more study and indeed may be responsible for wide variations in bubble size found by different investigators in otherwise geometrically similar systems. Finally, the effects of solid additives, resulting in both Newtonian and non-Newtonian behavior, have been studied. Results appear consistent with those for single phase Newtonian systems studied by Calderbank (71). The pseudoplastic character of the paper pulp used was evident in the dependence of mass transfer coefficient on bubble diameter, where the mass transfer coefficient was shown to depend upon viscosity in a manner consistent with pseudoplastic character. Solid additive which did not impart non-Newtonian character to the liquid was shown to have an effect on interfacial area and bubble diameter, but after correction for soluble materials present in the additive, no effect on mass transfer coefficient was found. A new average viscosity has been defined.
for non-Newtonian systems and should be a useful tool for further characteriza-
tion of mass transfer in non-Newtonian systems.

In conclusion, this work demonstrates the necessity of performing scale-up experiments in gas-liquid contactors (stirred tank and other types) using the actual systems to be scaled-up. It has been clearly shown that ionic strength, impurities and non-Newtonian additive can cause dramatic changes in the mass transfer properties of these systems. Furthermore, it has been demonstrated that mass transfer models describing oxygen transfer in fungal fermentations are highly inadequate because they do not properly describe the effect of power input on the mass transfer coefficient or the interfacial area. They also do not adequately describe the effects of non-Newtonian additive on these parameters.

It is interesting to note that in non-Newtonian fermentation systems, the presence of the fungus in the liquid can have one of two effects. It can decrease or it can increase the overall mass transfer. Its physical presence in the liquid has been shown to decrease the physical mass transfer of gas into the liquid phase. On the other hand, this same presence can increase the mass transfer by "chemical reaction". In other words, the respiring fungus, depending upon its $Q_{O_2}$ and its concentration in the liquid film around the bubbles behaves as a large reactant molecule and can increase the flux of gas into the film by increasing the slope of the concentration gradient in the film. Models describing this effect, developed by Tsao, et al. (125-128), however, do not adequately take into account the decrease in physical mass transfer coefficient caused by microbial presence in the gas-liquid film (129-131).
3. **Suggestions for Further Research**

Additional experimental data are needed to provide an adequate basis for a more fundamental and quantitative interpretation of the variables which influence mass transfer in gas-liquid systems. Systems for additional study should include those containing salt, suspended solids, organics, and surface active agents. The effects of scale, geometry, method of agitation, sparger configuration and baffling on the bubble size transition range should be investigated. In addition, these results should then be extended to systems incorporating respiring organisms for use in fermentation studies.
ACKNOWLEDGEMENTS

The assistance of numerous people contributed to the success of this study. Professor Charles R. Wilke, my research director, is to be thanked for his guidance and suggestions. In addition, Dr. Joseph Dabes, Mr. Lynn Williams and Mr. Thomas Murphy are to be thanked for many stimulating discussions touching on all aspects of this work. The patient assembly of the dissolved oxygen probe used in this study was the work of Mrs. Moira Ralls and her contribution is gratefully acknowledged here. The pioneering work of Dr. Campbell Robinson, upon which much of this study is based, is also acknowledged.

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NOMENCLATURE

a interfacial area per unit volume of liquid, cm$^{-1}$

$a_o$ interfacial area per unit volume of water, cm$^{-1}$

A total interfacial area, cm$^2$

B bulk liquid concentration of hydroxide ions, moles/cm$^3$

c constant

c_i concentration of species i, moles/liter

C concentration, moles/cm$^3$

C* concentration of component A at gas-liquid interface, moles/cm$^3$

C_A concentration of component A, moles/cm$^3$

C*$_{A_{inlet}}$ concentration of component A at gas-liquid interface based on inlet gas concentration, moles/cm$^3$

C*$_{A_{outlet}}$ concentration of component A at gas-liquid interface based on outlet gas concentration, moles/cm$^3$

$\Delta C^*_A$$_m$ concentration driving force in mixed region, moles/cm$^3$

$\Delta C^*_A$$_p$ concentration driving force in premix region, moles/cm$^3$

$\Delta C^*_A$$_{overall}$ overall concentration driving force, moles/cm$^3$

$C_{CO_2i}$ inlet gas carbon dioxide concentration, moles/cm$^3$

$C_{CO_2f}$ outlet gas carbon dioxide concentration, moles/cm$^3$

C$_{crit}$ critical concentration of oxygen in liquid, moles/cm$^3$

C$_L$ bulk liquid concentration of component A, moles/cm$^3$

C$_M$ concentration at membrane-liquid interface, moles/cm$^3$

d$_B$ average bubble diameter, cm

d$_i$ impeller diameter, cm

d$_t$ tank diameter, cm
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_A$</td>
<td>liquid phase diffusivity of component A</td>
<td>cm$^2$/sec</td>
</tr>
<tr>
<td>$D_B$</td>
<td>liquid phase diffusivity of component B</td>
<td>cm$^2$/sec</td>
</tr>
<tr>
<td>$D_{CO_2}$</td>
<td>liquid phase diffusivity of carbon dioxide</td>
<td>cm$^2$/sec</td>
</tr>
<tr>
<td>$D_i$</td>
<td>impeller diameter</td>
<td>cm</td>
</tr>
<tr>
<td>$D_M$</td>
<td>membrane diffusivity for oxygen</td>
<td>cm$^2$/sec</td>
</tr>
<tr>
<td>$D_{O_2}$</td>
<td>diffusivity of oxygen in liquid</td>
<td>cm$^2$/sec</td>
</tr>
<tr>
<td>$\Delta E$</td>
<td>change in recorder chart reading</td>
<td>mv</td>
</tr>
<tr>
<td>$E_{sat}$</td>
<td>voltage of oxygen probe when in equilibrium with air saturated water</td>
<td>mv</td>
</tr>
<tr>
<td>$E_t$</td>
<td>probe voltage at time t</td>
<td>mv</td>
</tr>
<tr>
<td>$E_o$</td>
<td>probe voltage at time zero</td>
<td>mv</td>
</tr>
<tr>
<td>$E_\infty$</td>
<td>probe voltage at long times</td>
<td>mv</td>
</tr>
<tr>
<td>$f(t)$</td>
<td>liquid phase concentration function</td>
<td>moles/cm$^3$</td>
</tr>
<tr>
<td>$F^o$</td>
<td>gas flow rate</td>
<td>cm$^3$/sec</td>
</tr>
<tr>
<td>$F'$</td>
<td>gas flow rate, SCFM</td>
<td></td>
</tr>
<tr>
<td>$F$</td>
<td>gas velocity based on tank cross-sectional area</td>
<td>ft/sec</td>
</tr>
<tr>
<td>$g(t)$</td>
<td>liquid phase concentration function</td>
<td>moles/cm$^3$</td>
</tr>
<tr>
<td>$\varepsilon_c$</td>
<td>dimensional conversion factor, various units</td>
<td></td>
</tr>
<tr>
<td>$h_i$</td>
<td>distance from bottom of tank to bottom of impeller</td>
<td>cm</td>
</tr>
<tr>
<td>$h_L$</td>
<td>height of liquid in tank</td>
<td>cm</td>
</tr>
<tr>
<td>$H$</td>
<td>Henry's constant, dimensionless</td>
<td></td>
</tr>
<tr>
<td>$H'$</td>
<td>Henry's constant</td>
<td>cm$^3$-atmos/mole</td>
</tr>
<tr>
<td>$H_o$</td>
<td>holdup, dimensionless</td>
<td></td>
</tr>
<tr>
<td>$I$</td>
<td>current, amperes</td>
<td></td>
</tr>
<tr>
<td>$k$</td>
<td>first order chemical reaction rate constant</td>
<td>sec$^{-1}$</td>
</tr>
<tr>
<td>$k_2$</td>
<td>second order reaction rate constant</td>
<td>cm$^3$/mole-sec</td>
</tr>
</tbody>
</table>
constant defined in Equation (5.3)

liquid phase mass transfer coefficient, cm/sec

liquid phase mass transfer coefficient in the presence of chemical reaction, cm/sec

overall volumetric mass transfer coefficient, hr\(^{-1}\)

overall volumetric mass transfer coefficient in the presence of chemical reaction, hr\(^{-1}\)

constant defined in Equation (5.1)

constant defined in Equation (5.2)

constant defined in Equation (5.2)

constant defined in Equation (2.31)

thickness of liquid film, cm

thickness of membrane, cm

impeller blade width, cm

running index, \(n = 1,2,3,\ldots\)

impeller speed, RPM

normality of sulphite ion, equiv./liter

total number of bubbles in tank

molar flux rate per unit area, moles/cm\(^2\)-sec

flux of component A per unit area, moles/cm\(^2\)-sec

aeration number, dimensionless

power number, dimensionless

Schmidt number, dimensionless

partial pressure, atmos

membrane-liquid interfacial partial pressure, atmos

ungassed power input to liquid, hp

pressure difference between manometer taps, dynes/cm\(^2\)
\[ \Delta P_G \] pressure difference between manometer taps in gassed system, dynes/cm²

\[ P_g \] gassed power input to system in tank, hp

\[ P_{sat} \] saturated partial pressure, atmos

\[ P_T \] total system pressure, atmos

\[ Q \] gas flow rate, cm³/sec

\[ r_A \] chemical reaction rate for component A, moles/cm³·sec

\[ R \] universal gas constant, cm³·atmos/mole·°K

\[ R_A \] total molar rate of absorption of component A, moles/sec

\[ R_A^{sp} \] specific molar absorption rate of component A, moles/cm³·sec

\[ R_A^{r} \] specific molar absorption rate of component A in the presence of chemical reaction, moles/cm³·sec

\[ s \] inverse surface element lifetime, sec⁻¹

\[ S \] oxygen solubility in probe membrane, moles/cm³·atmos

\[ t \] time, sec

\[ dt \] incremental time, sec

\[ t' \] lifetime of surface element, sec

\[ t_D \] equivalent diffusion time, sec

\[ t_{mix} \] mixing time, sec

\[ t_{mix}^* \] dimensionless mixing time, dimensionless

\[ t_{res} \] gas residence time, sec

\[ T \] temperature, °K

\[ v_s \] superficial gas velocity based on tank cross-sectional area, ft/sec

\[ V \] volume of titrant, ml

\[ V_g \] total volume of gas bubbles in tank, cm³

\[ V_L \] liquid volume, cm³
\( V_{ML} \) molar concentration of water, moles/cm³

\( V_s \) superficial gas velocity based on tank cross-sectional area, ft/sec

\( V_o \) volume of gas in tank holdup, cm³

\( v_1 \) velocity past holdup probe 1, cm/sec

\( v_2 \) velocity past holdup probe 2, cm/sec

\( v_{1G} \) velocity past holdup probe 1 with gas present, cm/sec

\( v_{2G} \) velocity past holdup probe 2 with gas present, cm/sec

\( w_b \) baffle width, cm

\( w_1 \) impeller blade height, cm

\( x \) distance, cm

\( x' \) mole fraction of \( CO_2 \) in liquid phase

\( y \) mole fraction of \( CO_2 \) in gas phase

\( y_{CO2f} \) mole fraction carbon dioxide in exit gas, dimensionless

\( y_i \) mole fraction oxygen in inlet gas, dimensionless

\( y_f \) mole fraction oxygen in outlet gas, dimensionless

\( y_o \) initial mole fraction oxygen in gas phase, dimensionless

\( YDATA(i) \) dimensionless voltage at time \( t \), dimensionless

\( z \) stoichiometric ratio of component B to component A, dimensionless

\( \Delta Z \) manometer deflection in ungassed system, cm

\( \Delta Z_g \) manometer deflection in gassed system, cm

\( z_i \) ionic charge of species i, dimensionless

**GREEK SYMBOLS**

\( \beta \) time constant, sec⁻¹

\( \gamma_{ij} \) shear rate, sec⁻¹

\( \Gamma \) ionic strength, moles/liter
\[ \epsilon = K_{L} a \text{ or } K_{L}^{2} a/\phi', \text{ sec}^{-1} \]

\[ \lambda = \text{proportionality constant, } g^{0.4} \text{cm}^{0.6} \text{sec}^{0.5} (\text{ft-lb/ min-ft}^{3})^{-n} \times (\text{ft/sec})^{-m} \]

\[ \mu = \text{viscosity, g/cm-sec} \]

\[ \mu_{a} = \text{apparent viscosity, g/cm-sec} \]

\[ \mu'_{a} = \text{apparent viscosity, g/cm-sec} \]

\[ \mu_{L} = \text{viscosity of liquid, g/cm-sec} \]

\[ \xi = \text{physical property group, sec}^{0.26} g^{0.4} \text{cm}^{-0.5} \lambda^{4} \]

\[ \Delta \rho = \text{density difference between two phases, g/cm}^{3} \]

\[ \rho = \text{density, g/cm}^{3} \]

\[ \rho_{c} = \text{density of continuous phase, g/cm}^{3} \]

\[ \rho_{g} = \text{density of gas, g/cm}^{3} \]

\[ \rho_{L} = \text{density of liquid, g/cm}^{3} \]

\[ \sigma = \text{surface tension} \]

\[ \tau = \text{dimensionless group} \]

\[ \tau_{ij} = \text{shear stress, g/cm-sec}^{2} \]

\[ \phi = \text{gas velocity correction factor} \]

\[ \phi' = \text{chemical reaction enhancement factor, dimensionless} \]

\[ \psi(t) = \text{probability function for surface element lifetime, dimensionless} \]
### Physical Properties of Experimental Systems at 30°C

<table>
<thead>
<tr>
<th>System</th>
<th>Density g/cm³</th>
<th>Surface Tension dyne/cm</th>
<th>Viscosity cp</th>
<th>Diffusivity O₂ cm²/sec</th>
<th>Diffusivity CO₂ cm²/sec</th>
<th>H' for O₂ 1-atm/mole</th>
<th>H' for CO₂ 1-atm/mole</th>
</tr>
</thead>
<tbody>
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<td>0.9957</td>
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<td>2.15 x 10⁻⁵</td>
<td>834.5</td>
<td>34.7</td>
</tr>
<tr>
<td>H₂O + 1% &quot;Solka Floc&quot;</td>
<td>1.006</td>
<td>71.7</td>
<td>---</td>
<td>3.1 x 10⁻⁵</td>
<td>2.15 x 10⁻⁵</td>
<td>853.1</td>
<td>35.2</td>
</tr>
<tr>
<td>0.1M Ionic Strength KCl-KOH-K₂CO₃</td>
<td>1.003 (36)</td>
<td>71.3</td>
<td>---</td>
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<td>35.2</td>
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<td>70.6</td>
<td>---</td>
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<td>35.2</td>
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<td>35.2</td>
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<tr>
<td>0.5M Na₂SO₄ + 10⁻³M CuSO₄</td>
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<td>72.6 (36)</td>
<td>1.098</td>
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<td>---</td>
<td>1288.1</td>
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<tr>
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<td>72.6 (36)</td>
<td>1.031</td>
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<td>1288.1</td>
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APPENDIX

SECTION (II.1)
Values of the Derivatives for the Oxygen Probe Response

The derivatives of Eq. (2.38) that are necessary for evaluation of the slope of the oxygen probe response curve at its inflection point are listed below.

First Derivative

\[
\frac{\partial(E/E_\infty)}{\partial t} = \beta \tau^{1/2} \frac{\exp(-\beta t)}{\sin(\tau^{1/2})} - \sum_{n=1}^{\infty} \left[ \frac{2(-1)^n}{1 - n^2 \pi^2 / \tau} \cdot \left( \frac{n^2 \pi^2 D_M}{L^2} \right) \right] \cdot \exp \left(-\frac{n^2 \pi^2 D_M \tau}{L^2} \right)
\]

Second Derivative

\[
\frac{\partial^2(E/E_\infty)}{\partial t^2} = -\beta \tau^{1/2} \frac{\exp(-\beta t)}{\sin(\tau^{1/2})} + \sum_{n=1}^{\infty} \left[ \frac{2(-1)^n}{1 - n^2 \pi^2 / \tau} \cdot \left( \frac{n^2 \pi^2 D_M}{L^2} \right)^2 \right] \cdot \exp \left(-\frac{n^2 \pi^2 D_M \tau}{L^2} \right)
\]
Slope of Oxygen Probe Response Curve at Inflection Point in Distilled Water at 20°C

21.90 liters water
0.0106 ft/sec gas velocity
Henry's constant of 700.0 l-atm/mole
1.213 x 10^{-7} cm^2/sec membrane diffusivity

<table>
<thead>
<tr>
<th>Slope at inflection (hr^{-1})</th>
<th>Time of inflection (sec)</th>
<th>K_{l,a} (hr^{-1})</th>
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</thead>
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<tr>
<td>14.69</td>
<td>67</td>
<td>20</td>
</tr>
<tr>
<td>24.59</td>
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<td>40</td>
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<td>32.10</td>
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<td>150</td>
</tr>
<tr>
<td>56.56</td>
<td>38</td>
<td>180</td>
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</table>
Fig. II.1.1. Slope of oxygen probe response curve at inflection point in distilled water at 20°C.

\[ F = 0.0106 \text{ ft/sec} \]

Henry's const. = 700

Liter-atmos./mole

\[ D_M = 1.213 \text{ cm}^2/\text{sec} \]
Slope of Oxygen Probe Response Curve at Inflection

Point in Distilled Water

21.90 liters water

Henry's constant of 834.5 1-atm/mole

0.0106 ft/sec gas velocity

1.562 x 10^-7 cm^2/sec membrane diffusivity

<table>
<thead>
<tr>
<th>Slope at Inflection (hr^-1)</th>
<th>Time of Inflection (sec)</th>
<th>K_a L/hr^-1</th>
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<td>105.65</td>
<td>22</td>
<td>1000</td>
</tr>
</tbody>
</table>
Slope at Inflection | Time of Inflection | $K_a$ (hr$^{-1}$)
--- | --- | ---
15.50 | 55 | 20
26.67 | 46 | 40
35.54 | 42 | 60
42.86 | 39 | 80
49.07 | 36 | 100
54.43 | 34 | 120
59.13 | 33 | 140
61.25 | 32 | 150
66.97 | 31 | 180
70.29 | 30 | 200
77.26 | 28 | 250
82.87 | 27 | 300
91.22 | 25 | 400
97.18 | 24 | 500
111.6 | 21 | 1000
Slope of Oxygen Probe Response Curve at Inflection

Point in Distilled Water

21.90 liters water

Henry's constant of 834.5 l-atm/mole

0.0318 ft/sec gas velocity

30°C

1.562 × 10⁻⁷ cm²/sec membrane diffusivity

<table>
<thead>
<tr>
<th>Slope at Inflection (hr⁻¹)</th>
<th>Time of Inflection (sec)</th>
<th>KₐL⁻¹ (hr⁻¹)</th>
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<td>49.45</td>
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<td>54.90</td>
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<td>113.6</td>
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<td>1000</td>
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</table>
Slope of Oxygen Probe Response Curve at Inflection Point in 0.06M KOH

21.90 liters solution

Henry's constant of 852 l-atm/mole

0.0106 ft/sec gas velocity

$1.562 \times 10^{-7}$ cm$^2$/sec membrane diffusivity

<table>
<thead>
<tr>
<th>Slope at Inflection (hr$^{-1}$)</th>
<th>Time of Inflection (sec)</th>
<th>$K_{La}$ (hr$^{-1}$)</th>
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<td>74.58</td>
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<td>93.00</td>
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<tr>
<td>106.27</td>
<td>22</td>
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</tbody>
</table>
APPENDIX

SECTION (II.2)
Operating Principle for New Manometric Holdup Measurement Device

The apparatus used for measurements of the gas-liquid dispersed phase holdup is shown in Fig. (II.2.1). Assuming that the liquid and gas phases have densities $\rho_L$ and $\rho_G$ respectively and that the agitated liquid in the tank moves past probe tips 1 and 2 at velocities $v_1$ and $v_2$ in the absence of gas and $v_{1G}$ and $v_{2G}$ in the presence of a gas phase, we can write

$$\Delta P = \rho_L gh - \rho_L v_1^2/2 + \rho_L v_2^2/2$$

without gas

and

$$\Delta P_G = \rho gh - \rho v_{1G}^2/2 + \rho v_{2G}^2/2$$

with gas.

Here $\Delta P$ and $\Delta P_G$ are the pressure differences between the probe tips 1 and 2 without and with gas phase present, $h$ is the vertical separation of the two probe tips, $\rho$ is the average density of the gas-liquid dispersion between the probe tips and $g$ is the gravitational constant.

We can write for the density of the gas-liquid dispersion

$$\rho = \rho_L + H_o (\rho_G - \rho_L) ,$$

where $H_o$ is the fractional dispersed phase (gas) holdup. If $\rho_G \ll \rho_L$ we can write

$$\rho = \rho_L (1 - H_o) .$$

Thus, in the absence of a gas phase we can write, after substitution into the pressure difference equations

$$\Delta P = \rho_L [gh - v_1^2/2 + v_2^2/2]$$

and, in the presence of a gas phase

$$\Delta P_G = \rho_L (1 - H_o) [gh - v_{1G}^2/2 + v_{2G}^2/2] .$$
Fig. II.2.1. Experimental setup for manometric holdup measurement.
Since the manometer deflection is proportional to the pressure difference being measured, we can write

\[ \Delta Z = k \Delta P \]

and

\[ \Delta Z_G = k \Delta P_G \]

where \( k \) is a constant depending on the density of the manometer fluid, the angle of inclination of the manometer and the gravitational constant, and \( \Delta Z \) is the manometer deflection.

If the probes are located in the tank in such positions as to make the values of the fluid velocities at the probe tips equal, i.e., \( v_1 = v_2 \) and \( v_{1G} = v_{2G} \), then we can write

\[ \Delta Z = k \rho_L gh \]

and

\[ \Delta Z_G = k \rho_L (1 - H_o) gh \]

Solving these two equations simultaneously, we find

\[ H_o = \frac{\Delta Z - \Delta Z_G}{\Delta Z} \].
APPENDIX

SECTION (III.1)
Fig. III.1.1. Rotameter calibration curves for gas feed system.

\[ F \text{ (ft/sec)} = 0.0212 \times \text{gas flow (SCFM)} \]
APPENDIX

SECTION (III.2)
Slope of Oxygen Probe Response Curve at Inflection Point in Distilled Water at 30°C for Step Change Experiment

21.90 liters water

<table>
<thead>
<tr>
<th>Slope at Inflection (hr⁻¹)</th>
<th>Time of Inflection (sec)</th>
<th>Diffusivity (cm²/sec)</th>
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</thead>
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<td>1.0 × 10⁻⁷</td>
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<td>95.63</td>
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<td>110.2</td>
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<td>137.9</td>
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APPENDIX

SECTION (IV.1)
Overall Volumetric Mass Transfer Coefficient

Using Oxygen Probe Response at 30°C

(Distilled Water)

<table>
<thead>
<tr>
<th>N (RPM)</th>
<th>Power Input (HP/1000 gal)</th>
<th>Gas Velocity (ft/sec)</th>
<th>$K_a L$ (hr⁻¹)</th>
<th>$K_{a/L}^{0.56}$</th>
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APPENDIX

SECTION (IV.2)
Overall Volumetric Mass Transfer Coefficient

Using Oxygen Probe Response at 30°C

(Distilled Water + 1% "Solka Floc")

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$$K_La = 259.3 \left(\frac{P}{V}\right)^{0.67} \left(F\right)^{0.38}$$

$$\log \text{(Standard Dev.)} = 0.0269$$
APPENDIX

SECTION (IV.3)
Overall Volumetric Mass Transfer Coefficient

Using Oxygen Probe Response at 30°C

(Distilled Water + 3% "Solka Floc")

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$$K_La = 140.1 (P_g/V)^{0.613} (F)^{0.38}$$

$$\log \text{ (Standard Dev.)} = 0.0422$$

*Power data for Distilled Water + 3% "Solka Floc" are taken to be the values obtained for Distilled Water + 1% "Solka Floc".
APPENDIX

SECTION (IV.4)
Mass Transfer Properties of 0.1M Ionic Strength KOH-KCl-K$_2$CO$_3$

Mixed Solutions at 30°C and a Gas Velocity of 0.0212 ft/sec

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<td>0.0998*</td>
<td>606</td>
<td>6.96</td>
<td>385</td>
<td>9.4</td>
<td>0.0114</td>
<td>0.070</td>
<td>0.0480</td>
<td>0.00963</td>
<td>0.0134</td>
<td>0.05</td>
</tr>
<tr>
<td>0.0956*</td>
<td>900</td>
<td>23.1</td>
<td>795</td>
<td>20.4</td>
<td>0.0108</td>
<td>0.135</td>
<td>0.0460</td>
<td>0.00386</td>
<td>0.0139</td>
<td>0.05</td>
</tr>
</tbody>
</table>

$\Gamma_{\text{aver.}} = 0.1020$
APPENDIX

SECTION (IV.5)
Mass Transfer Properties of 0.1M Ionic Strength KOH-KCl-K$_2$CO$_3$

Mixed Solutions with 1% "Solka Floc" at 30°C, $F = 0.0212$ ft/s

<table>
<thead>
<tr>
<th>Ion Str. (molar)</th>
<th>N (RPM)</th>
<th>Power Input (HP/1000 Gal)</th>
<th>$K_L a$ (hr$^{-1}$)</th>
<th>$a$ (cm$^{-1}$)</th>
<th>$K_L$ (cm/s)</th>
<th>$H_o$ (ft/ft)</th>
<th>$d_B$ (cm)</th>
<th>KOH conc. aver. (molar)</th>
<th>K$_2$CO$_3$ conc. aver. (molar)</th>
<th>KCl conc. aver. (molar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1052</td>
<td>412</td>
<td>2.36</td>
<td>115</td>
<td>1.44</td>
<td>0.0222</td>
<td>0.0435</td>
<td>0.189</td>
<td>0.0289</td>
<td>0.0121</td>
<td>0.04</td>
</tr>
<tr>
<td>0.1017</td>
<td>502</td>
<td>4.26</td>
<td>---</td>
<td>2.47</td>
<td>---</td>
<td>0.0674</td>
<td>0.1755</td>
<td>0.0237</td>
<td>0.0127</td>
<td>0.04</td>
</tr>
<tr>
<td>0.0980</td>
<td>609</td>
<td>7.16</td>
<td>234</td>
<td>4.23</td>
<td>0.0154</td>
<td>0.0930</td>
<td>0.1453</td>
<td>0.0184</td>
<td>0.0132</td>
<td>0.04</td>
</tr>
<tr>
<td>0.1020</td>
<td>740</td>
<td>12.54</td>
<td>260</td>
<td>8.10</td>
<td>0.0089</td>
<td>0.126</td>
<td>0.1068</td>
<td>0.0188</td>
<td>0.0144</td>
<td>0.04</td>
</tr>
<tr>
<td>0.1007</td>
<td>900</td>
<td>23.9</td>
<td>461</td>
<td>13.55</td>
<td>0.0095</td>
<td>0.164</td>
<td>0.0869</td>
<td>0.00990</td>
<td>0.0136</td>
<td>0.05</td>
</tr>
<tr>
<td>0.1028</td>
<td>1100</td>
<td>40.9</td>
<td>510</td>
<td>24.6</td>
<td>0.0058</td>
<td>0.192</td>
<td>0.0580</td>
<td>0.01018</td>
<td>0.0142</td>
<td>0.05</td>
</tr>
</tbody>
</table>

$\Gamma_{aver.} = 0.1017$
Overall Volumetric Mass Transfer Coefficient

Using Oxygen Probe Response at 30°C

(0.06M KCl + 1% "Solka Floc")

<table>
<thead>
<tr>
<th>N (RPM)</th>
<th>Power Input (HP/1000 Gal)</th>
<th>Gas Velocity (ft/sec)</th>
<th>$K_a$ (hr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>326</td>
<td>1.12</td>
<td>0.0212</td>
<td>65</td>
</tr>
<tr>
<td>412</td>
<td>2.36</td>
<td></td>
<td>126</td>
</tr>
<tr>
<td>501</td>
<td>4.26</td>
<td></td>
<td>188.5</td>
</tr>
<tr>
<td>607</td>
<td>7.16</td>
<td></td>
<td>267</td>
</tr>
<tr>
<td>740</td>
<td>12.54</td>
<td></td>
<td>305</td>
</tr>
<tr>
<td>900</td>
<td>23.9</td>
<td></td>
<td>508</td>
</tr>
<tr>
<td>1106</td>
<td>40.9</td>
<td></td>
<td>550</td>
</tr>
</tbody>
</table>
APPENDIX

SECTION (IV.6)
Mass Transfer Properties of 0.1M Ionic Strength KOH-KCl-K₂CO₃ Mixed Solutions with 0.33% Filter Paper Pulp at 30°C, F = 0.0212 ft/s

<table>
<thead>
<tr>
<th>Ion Str. (molar)</th>
<th>N (RPM)</th>
<th>Power Input (HP/1000 Gal)</th>
<th>$K_a$ (hr⁻¹)</th>
<th>$a$ (cm⁻¹)</th>
<th>$K_L$ (cm/s)</th>
<th>$H_o$ (ft/ft)</th>
<th>$d_B$ (cm)</th>
<th>KOH conc. aver. (molar)</th>
<th>$K_2CO_3$ conc. aver. (molar)</th>
<th>KCl conc. (molar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0985*</td>
<td>411</td>
<td>1.91</td>
<td>88</td>
<td>1.33</td>
<td>0.0184</td>
<td>0.0325</td>
<td>0.1516</td>
<td>0.0177</td>
<td>0.0102</td>
<td>0.05</td>
</tr>
<tr>
<td>0.0912*</td>
<td>502</td>
<td>3.70</td>
<td>136</td>
<td>2.66</td>
<td>0.0142</td>
<td>0.0440</td>
<td>0.1039</td>
<td>0.0161</td>
<td>0.0117</td>
<td>0.05</td>
</tr>
<tr>
<td>0.0997*</td>
<td>607</td>
<td>6.89</td>
<td>204</td>
<td>4.93</td>
<td>0.0115</td>
<td>0.0582</td>
<td>0.0751</td>
<td>0.0128</td>
<td>0.0123</td>
<td>0.05</td>
</tr>
<tr>
<td>0.1020*</td>
<td>735</td>
<td>14.0</td>
<td>312</td>
<td>8.50</td>
<td>0.0102</td>
<td>0.0806</td>
<td>0.0619</td>
<td>0.0139</td>
<td>0.0127</td>
<td>0.05</td>
</tr>
<tr>
<td>0.1002</td>
<td>900</td>
<td>22.9</td>
<td>441</td>
<td>18.05</td>
<td>0.0103</td>
<td>0.101</td>
<td>0.0373</td>
<td>0.0110</td>
<td>0.0131</td>
<td>0.05</td>
</tr>
<tr>
<td>0.1021</td>
<td>1100</td>
<td>40.9</td>
<td>632</td>
<td>40.8</td>
<td>0.0102</td>
<td>0.131</td>
<td>0.0222</td>
<td>0.0125</td>
<td>0.0132</td>
<td>0.05</td>
</tr>
</tbody>
</table>

*Mixing effects negligible
APPENDIX

SECTION (IV.7)
### Overall Volumetric Mass Transfer Coefficient

**Using Oxygen Probe Response at 30°C**

(Distilled Water + 0.5M Na₂SO₄ + 10⁻³ M CuSO₄)

<table>
<thead>
<tr>
<th>N (RPM)</th>
<th>Power Input (HP/1000 Gal)</th>
<th>Gas Velocity (ft/sec)</th>
<th>( K_a ) (hr⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>213</td>
<td>0.292</td>
<td>0.0106</td>
<td>34.3</td>
</tr>
<tr>
<td>331</td>
<td>1.00</td>
<td></td>
<td>134.5</td>
</tr>
<tr>
<td>331</td>
<td>1.09</td>
<td></td>
<td>134.5</td>
</tr>
<tr>
<td>416</td>
<td>2.28</td>
<td></td>
<td>239.9</td>
</tr>
<tr>
<td>508</td>
<td>4.59</td>
<td></td>
<td>463.8</td>
</tr>
</tbody>
</table>

\[
K_a = 118.1 \left( \frac{P}{V} \right)^{0.932}
\]

\[
\log \text{(Standard Dev.)} = 0.0444
\]
APPENDIX

SECTION (IV.8)
Overall Volumetric Mass Transfer Coefficient
by Sulphite Oxidation

(0.5M Na₂SO₃ + 10⁻³M CuSO₄)

<table>
<thead>
<tr>
<th>N (RPM)</th>
<th>Power Input (HP/1000 Gal)</th>
<th>Temp. (°C)</th>
<th>Gas Velocity (ft/sec)</th>
<th>K_L^a</th>
<th>K_L^a/F^0.276</th>
<th>Exit O₂ conc. (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>420</td>
<td>2.525</td>
<td>30</td>
<td>0.0106</td>
<td>338</td>
<td>1184</td>
<td>0.179</td>
</tr>
<tr>
<td>517</td>
<td>5.38</td>
<td>30</td>
<td></td>
<td>667</td>
<td>2338</td>
<td>0.157</td>
</tr>
<tr>
<td>628</td>
<td>9.89</td>
<td>30</td>
<td></td>
<td>1070</td>
<td>3745</td>
<td>0.136</td>
</tr>
<tr>
<td>765</td>
<td>15.8</td>
<td>30</td>
<td></td>
<td>2004</td>
<td>7030</td>
<td>0.104</td>
</tr>
<tr>
<td>935</td>
<td>26.37</td>
<td>31</td>
<td></td>
<td>3058</td>
<td>10700</td>
<td>0.083</td>
</tr>
<tr>
<td>419</td>
<td>2.465</td>
<td>30</td>
<td>0.0212</td>
<td>360</td>
<td>1043</td>
<td>0.192</td>
</tr>
<tr>
<td>519</td>
<td>4.475</td>
<td>30</td>
<td></td>
<td>700</td>
<td>2030</td>
<td>0.178</td>
</tr>
<tr>
<td>626</td>
<td>7.78</td>
<td>30</td>
<td></td>
<td>1173</td>
<td>3400</td>
<td>0.162</td>
</tr>
<tr>
<td>760</td>
<td>13.71</td>
<td>31.5</td>
<td></td>
<td>1980</td>
<td>5730</td>
<td>0.140</td>
</tr>
<tr>
<td>420</td>
<td>2.07</td>
<td>30</td>
<td>0.0318</td>
<td>369</td>
<td>955</td>
<td>0.197</td>
</tr>
<tr>
<td>517</td>
<td>3.96</td>
<td>30</td>
<td></td>
<td>694</td>
<td>1796</td>
<td>0.187</td>
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<tr>
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<td>30</td>
<td></td>
<td>1195</td>
<td>3092</td>
<td>0.174</td>
</tr>
<tr>
<td>759</td>
<td>13.09</td>
<td>31.5</td>
<td></td>
<td>2050</td>
<td>5310</td>
<td>0.157</td>
</tr>
</tbody>
</table>

\[
K_L^a = 472 \left( \frac{P_g}{V} \right)^{0.952} (F)^{0.276}
\]

\[
\log \text{(Standard Dev.)} = 0.0211
\]
APPENDIX

SECTION (IV.9)
Overall Volumetric Mass Transfer Coefficient

by Sulphite Oxidation

\((0.5\text{M Na}_2\text{SO}_3 + 10^{-3}\text{M CuSO}_4 + 1\% "\text{Solka Floc"})\)

<table>
<thead>
<tr>
<th>N (RPM)</th>
<th>Power Input (HP/1000 Gal)</th>
<th>Temp. (°C)</th>
<th>Gas Velocity (ft/sec)</th>
<th>(\frac{r}{L}a) (hr(^{-1}))</th>
<th>(\frac{r}{L}a/\phi)</th>
<th>Exit (\text{O}_2) conc. (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>416</td>
<td>2.618</td>
<td>30</td>
<td>0.0106</td>
<td>266</td>
<td>3.50</td>
<td>0.1845</td>
</tr>
<tr>
<td>519</td>
<td>4.83</td>
<td>30</td>
<td></td>
<td>527</td>
<td>6.95</td>
<td>0.1656</td>
</tr>
<tr>
<td>626</td>
<td>8.27</td>
<td>30</td>
<td></td>
<td>811</td>
<td>10.68</td>
<td>0.1488</td>
</tr>
<tr>
<td>760</td>
<td>14.53</td>
<td>30</td>
<td></td>
<td>1271</td>
<td>16.72</td>
<td>0.128</td>
</tr>
<tr>
<td>925</td>
<td>25.3</td>
<td>30</td>
<td></td>
<td>1722</td>
<td>22.7</td>
<td>0.1124</td>
</tr>
<tr>
<td>1030</td>
<td>34.2</td>
<td>30.3</td>
<td></td>
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<td>0.1018</td>
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<tr>
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<td>0.1938</td>
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<td>4.23</td>
<td>30</td>
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<td>550</td>
<td>6.00</td>
<td>0.1838</td>
</tr>
<tr>
<td>622</td>
<td>7.86</td>
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<td>970</td>
<td>10.56</td>
<td>0.1684</td>
</tr>
<tr>
<td>755</td>
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<td>30.3</td>
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<td>1524</td>
<td>16.6</td>
<td>0.1513</td>
</tr>
<tr>
<td>417</td>
<td>1.95</td>
<td>30</td>
<td>0.0318</td>
<td>315</td>
<td>2.83</td>
<td>0.1986</td>
</tr>
<tr>
<td>514</td>
<td>3.66</td>
<td>30</td>
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<td>596</td>
<td>5.37</td>
<td>0.1902</td>
</tr>
<tr>
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<td>6.80</td>
<td>30</td>
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<td>0.1789</td>
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<td>750</td>
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<td></td>
<td>1530</td>
<td>13.74</td>
<td>0.1673</td>
</tr>
</tbody>
</table>

\[\phi = 62.8 \times (10^{7.79 F})\]
APPENDIX

SECTION (IV.10)
Overall Volumetric Mass Transfer Coefficient

by Sulphite Oxidation

\(0.5\text{M Na}_2\text{SO}_3 + 10^{-3}\text{M CuSO}_4 + 3\% "\text{Solka Floc}"\)

<table>
<thead>
<tr>
<th>N (RPM)</th>
<th>Power Input (HP/1000 Gal)</th>
<th>Temp. (°C)</th>
<th>Gas Velocity (ft/sec)</th>
<th>Kpa \text{Lm}^{-1}\text{hr}^{-1}</th>
<th>Exit O\textsubscript{2} conc. (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>410</td>
<td>2.445</td>
<td>30</td>
<td>0.0106</td>
<td>113</td>
<td>0.1973</td>
</tr>
<tr>
<td>508</td>
<td>4.66</td>
<td>30</td>
<td>0.0188</td>
<td>220</td>
<td>0.1884</td>
</tr>
<tr>
<td>618</td>
<td>8.12</td>
<td>30</td>
<td>0.1884</td>
<td>355</td>
<td>0.1776</td>
</tr>
<tr>
<td>752</td>
<td>15.95</td>
<td>30</td>
<td>0.1642</td>
<td>547</td>
<td>0.1642</td>
</tr>
<tr>
<td>915</td>
<td>26.8</td>
<td>30</td>
<td>0.1507</td>
<td>778</td>
<td>0.1507</td>
</tr>
<tr>
<td>1107</td>
<td>46.0</td>
<td>30</td>
<td>0.1358</td>
<td>1082</td>
<td>0.1358</td>
</tr>
<tr>
<td>415</td>
<td>2.043</td>
<td>30</td>
<td>0.0212</td>
<td>130</td>
<td>0.2024</td>
</tr>
<tr>
<td>617</td>
<td>7.26</td>
<td>30</td>
<td>0.1898</td>
<td>406</td>
<td>0.1898</td>
</tr>
<tr>
<td>747</td>
<td>14.29</td>
<td>30</td>
<td>0.1826</td>
<td>580</td>
<td>0.1826</td>
</tr>
<tr>
<td>911</td>
<td>24.2</td>
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<td>0.1742</td>
<td>803</td>
<td>0.1742</td>
</tr>
<tr>
<td>508</td>
<td>2.78</td>
<td>30</td>
<td>0.0318</td>
<td>234</td>
<td>0.2012</td>
</tr>
<tr>
<td>614</td>
<td>6.04</td>
<td>30</td>
<td>0.1964</td>
<td>386</td>
<td>0.1964</td>
</tr>
<tr>
<td>748</td>
<td>11.86</td>
<td>30</td>
<td>0.1902</td>
<td>595</td>
<td>0.1902</td>
</tr>
</tbody>
</table>
APPENDIX

SECTION (IV.11)
# Gas Holdup in Distilled Water

<table>
<thead>
<tr>
<th>Power Input (HP/1000 Gal)</th>
<th>Holdup (ft/ft)</th>
<th>Gas Velocity (ft/sec)</th>
<th>Holdup/(Gas Velocity)^{0.56}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.777</td>
<td>0.013</td>
<td>0.0106</td>
<td>0.1655</td>
</tr>
<tr>
<td>1.252</td>
<td>0.0173</td>
<td></td>
<td>0.220</td>
</tr>
<tr>
<td>2.23</td>
<td>0.0216</td>
<td></td>
<td>0.275</td>
</tr>
<tr>
<td>3.28</td>
<td>0.0303</td>
<td></td>
<td>0.386</td>
</tr>
<tr>
<td>6.07</td>
<td>0.0477</td>
<td></td>
<td>0.607</td>
</tr>
<tr>
<td>11.7</td>
<td>0.0606</td>
<td></td>
<td>0.772</td>
</tr>
<tr>
<td>21.2</td>
<td>0.0779</td>
<td></td>
<td>0.992</td>
</tr>
<tr>
<td>34.6</td>
<td>0.1082</td>
<td></td>
<td>1.378</td>
</tr>
<tr>
<td>59.1</td>
<td>0.195</td>
<td></td>
<td>2.48</td>
</tr>
<tr>
<td>0.801</td>
<td>-----</td>
<td>0.0212</td>
<td>-----</td>
</tr>
<tr>
<td>1.208</td>
<td>0.0217</td>
<td></td>
<td>0.1874</td>
</tr>
<tr>
<td>2.025</td>
<td>0.0326</td>
<td></td>
<td>0.281</td>
</tr>
<tr>
<td>3.412</td>
<td>0.0457</td>
<td></td>
<td>0.394</td>
</tr>
<tr>
<td>5.94</td>
<td>0.0717</td>
<td></td>
<td>0.619</td>
</tr>
<tr>
<td>9.94</td>
<td>0.0978</td>
<td></td>
<td>0.844</td>
</tr>
<tr>
<td>16.48</td>
<td>0.1216</td>
<td></td>
<td>1.050</td>
</tr>
<tr>
<td>28.55</td>
<td>0.1478</td>
<td></td>
<td>1.275</td>
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<td>Holdup (ft/ft)</td>
<td>Gas Velocity (ft/sec)</td>
<td>Holdup/(Gas Velocity)(^{0.56})</td>
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\[ H_o = 0.1878 \left(\frac{P_g}{V}\right)^{0.591}(P)^{0.56} \]

\[ \log \text{(Standard Dev.)} = 0.03778 \]
Gas Holdup in 0.06M Ionic Strength KOH Solution at 30°C

<table>
<thead>
<tr>
<th>Power Input (HP/1000 Gal)</th>
<th>Holdup (ft/ft)</th>
<th>Gas Velocity (ft/sec)</th>
<th>Holdup/(Gas Velocity)^0.54</th>
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<td>0.2017</td>
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<td>1.386</td>
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<td>0.379</td>
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<tr>
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<td>0.556</td>
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<td>Power Input (HP/1000 Gal)</td>
<td>Holdup (ft/ft)</td>
<td>Gas Velocity (ft/sec)</td>
<td>Holdup/(Gas Velocity)^{0.54}</td>
</tr>
<tr>
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<td>---------------</td>
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<tr>
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\[ H_o = 0.1962 \left( \frac{P_g}{V} \right)^{0.54} (\tau)^{0.54} \]

\[ \log \text{ (Standard Dev.)} = 0.0504 \]
Gas Holdup in 0.19M Ionic Strength Salt Solution at 30°C

\( (0.06\text{M KOH} + 0.045\text{M Na}_2\text{SO}_4) \)

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<th>Power Input (HP/1000 Gal)</th>
<th>Holdup (ft/ft)</th>
<th>Gas Velocity (ft/sec)</th>
<th>Holdup/(Gas Velocity)^0.50</th>
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<td>0.0383</td>
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Gas Holdup in 0.06M KOH + 1.0% "Solka Floc" at 30°C

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<th>Holdup (ft/ft)</th>
<th>Gas Velocity (ft/sec)</th>
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</thead>
<tbody>
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<td>0.0043</td>
<td>0.0106</td>
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<tr>
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<td>0.0087</td>
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</tr>
<tr>
<td>1.137</td>
<td>0.0196</td>
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</tr>
<tr>
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<td>0.0304</td>
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</tr>
<tr>
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<tr>
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<tr>
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<td>Power Input (HP/1000 Gal)</td>
<td>Holdup (ft/ft)</td>
<td>Gas Velocity (ft/sec)</td>
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</table>
**Gas Holdup in 0.06M KOH + 3% "Solka Floe" at 30°C**

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<th>Power Input* (HP/1000 Gal)</th>
<th>Holdup (ft/ft)</th>
<th>Gas Velocity (ft/sec)</th>
</tr>
</thead>
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<td>0.0212</td>
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<td>0.913</td>
<td>—</td>
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<tr>
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<td>0.0324</td>
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<td>0.0367</td>
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<td>Gas Velocity (ft/sec)</td>
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<td>----------------</td>
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*Power data for 0.06M KOH + 3% "Solka Floc" are taken to be the values obtained for 0.06M KOH + 1% "Solka Floc" because of experimental difficulties encountered during the 0.06M KOH + 3% "Solka Floc" runs.*
Gas Holdup in 0.1M KCl + 0.33% Filter Paper Pulp

at 30°C, F = 0.0212 ft/sec

<table>
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<td>40.9</td>
<td>0.1245</td>
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APPENDIX

SECTION (V.1)
Simultaneous Results Obtained for the Mass Transfer Properties of Miscellaneous Solutions at 30°C, \( F = 0.0212 \text{ ft/s} \)

0.33% Filter Paper Pulp Wash Water + KOH-KCl-K\( _2 \)CO\( _3 \) (\( \bar{r}_{\text{aver}} = 0.1\text{M} \))

- Speed = 501 RPM
- \( K_a = 239 \text{ hr}^{-1} \)
- \( P/V_L = 3.56 \text{ HP/1000 Gal} \)
- \( a = 2.98 \text{ cm}^{-1} \)
- \( d_B = 0.103 \text{ cm} \)
- \( K_L = 0.0222 \text{ cm/s} \)

1.0% "Solka Floc" Wash Water + KOH-KCl-K\( _2 \)CO\( _3 \) (\( \bar{r}_{\text{aver}} = 0.1\text{M} \))

- Speed = 409 RPM
- \( K_a = 107 \text{ hr}^{-1} \)
- \( P/V_L = 2.02 \text{ HP/1000 Gal} \)
- \( a = 2.04 \text{ cm}^{-1} \)
- \( d_B = 0.134 \text{ cm} \)
- \( K_L = 0.0145 \text{ cm/s} \)

- Speed = 608 RPM
- \( K_a = 267 \text{ hr}^{-1} \)
- \( P/V_L = 6.90 \text{ HP/1000 Gal} \)
- \( a = 8.77 \text{ cm}^{-1} \)
- \( d_B = 0.0701 \text{ cm} \)
- \( K_L = 0.00847 \text{ cm/s} \)

1.0% Filter Paper Pulp + KOH-KCl-K\( _2 \)CO\( _3 \) (\( \bar{r}_{\text{aver}} = 0.1\text{M} \))

- Speed = 735 RPM
- \( K_a = 196 \text{ hr}^{-1} \)
- \( P/V_L = 14.0 \text{ HP/1000 Gal} \)
- \( a = 1.77 \text{ cm}^{-1} \)
- \( d_B = 0.46 \text{ cm} \)
- \( K_L = 0.0307 \text{ cm/s} \)

Check for Purity of KOH Makeup Solution in KOH-KCl-K\( _2 \)CO\( _3 \) (\( \bar{r}_{\text{aver}} = 0.1\text{M} \))

- Speed = 735 RPM
- \( K_a = 496 \text{ hr}^{-1} \)
- \( P/V_L = 13.5 \text{ HP/1000 Gal} \)
- \( a = 14.9 \text{ cm}^{-1} \)
- \( d_B = 0.0448 \text{ cm} \)
- \( K_L = 0.00924 \text{ cm/s} \)
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