GAS ABSORPTION WITH CHEMICAL REACTION IN AN AGITATED REACTOR

by

Brahm D. Prasher

Thesis submitted to the Graduate Faculty of the Virginia Polytechnic Institute and State University in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

in

CHEMICAL ENGINEERING

APPROVED:

JB Wills, Chairma

Dr. A.L. Fricke

uphy_ Dr. W.F. Murphy

pluistiman Dr. J.P. Wightman

December 1970

Blacksburg, Virginia

þ

LD 5655 V856 1970 P68 c.2

ACKNOWLEDGMENTS

The author wishes to thank the Department of Chemical Engineering at Virginia Polytechnic Institute and State University for the award of a teaching assistantship for the period of study here.

Sincere thanks and appreciation are also expressed to Professor George Bailey Wills for his help and guidance in the preparation of this dissertation. For his sustained interest and suggestions, the author also wishes to express his appreciation to Dr. A.L. Fricke, Assistant Professor of Chemical Engineering. Thanks are also due to Mr. A.A. Lafon and Mr. B.G. Williams, Technicians in the Department of Chemical Engineering for their help in the construction and assembling of the equipment.

Finally, to her who desires to remain anonymous, special thanks and grateful appreciation are tendered for her constant encouragement and help.

-i i -

TABLE OF CONTENTS

			Page
	ACKNOW	LEDGMENT	ii
	LIST O	F TABLES	vii
	LIST O	F FIGURES	/iii
Ι.	INTROD]
II.	LITERA	TURE REVIEW	4
	Mass	Transfer	4
		Film Theory	5
		Penetration Theory	7
		Surface Renewal Theory	9
		Penetration-Film Theory	9
		Other Theories of Mass Transfer	10
	Mass	Transfer in Agitated Systems	11
		Effect of Agitation on Mass Transfer Coefficient.	11
		Effect of Gas Flow Rate on Mass Transfer Coefficient	13
		Effect of Agitation and Gas Rate on Inter- facial Area	13
		Overall Mass Transfer Coefficients	14
	Chem	istry of Reaction and Equations for Diffusion with Reaction	15
		Chemistry of the Reaction	16
		Effect of Temperature on $k_2 \cdot \cdot$	17
		Effect of Ionic Strength on $k_2 \ldots \ldots \ldots$	18
:		Equations for Diffusion with Reaction for the System Chosen	19

Phys	ico-Chemical Parameters Used	22
	Specific Rate Constants	22
	Solubility of Carbon Dioxide	22
	Diffusivity of Carbon Dioxide	23
	Diffusivity of Hydroxyl Ions	23
III. EXPERI	MENTAL	25
Plan	of Investigation	25
Mate	rials	26
Appa	ratus	27
	Assembly of Equipment	27
Proc	edure	27
	Development of Stirred Tank	29
	Calibration of Equipment	31
	Experimental Measurement of Absorption Rates	31
	Measurement of Rates of Absorption in 1.0 M and 1.5 M Caustic Solutions	31
	Measurement of Rates of Absorption in 0.085 M Caustic Solutions	32
	Measurement of Rates of Absorption in Distilled Water	33
Metho	od of Analysis of Data	34
	Analysis Based on Pseudo-First Order Reaction	34
	Analysis Based on Ratio of Rates of Absorption with Reaction to Rate without Reaction	37
	Prediction of Bubble Size Using Time of Contact	39
Data	and Results	40
	Effect of Agitator Speed and Gas Superficial Velocity on Interfacial Areas	40

	Effect of Agitator Speed and Gas Superficial	
	Velocity on Contact Time	46
	Correlation for Interfacial Areas	46
	Correlation for Time of Contact	47
	Predicted Bubble Diameters	48
IV.	DISCUSSION	58
	Discussion of Procedure	58
	Some Comments on the CO ₂ -HaOH System	58
	Experimental Plan	60
	Discussion of Special Techniques for Measuring Rates of Absorption	62
	Use of Subsidiary Data	63
	Discussion of Results	65
	Method of Approach Used by Previous Investigators	65
	nethod of Approach used by frevious investigators	05
,	Evaluation of Interfacial Areas and Contact Times by Chemical Methods	67
	Correlations for Interfacial Areas	69
	Correlation for Time of Contact	74
	Predicted Bubble Diameters	74
	Comparison of Results Obtained on Interfacial	
	Areas	76
	Recommendations	77
	Agitation and Gas Input Rate	77
	Effect of Solute	77
	Effect of the Type of Impellers	77
	Limitations	78

۷.	CONCLUSIONS
VI.	SUMMARY
VII.	BIBLIOGRAPHY
	APPENDICES
Α.	DEVELOPMENT OF CORRELATION FOR THE PREDICTION OF TIME OF CONTACT
Β.	CALIBRATION DATA AND PROCEDURES
с.	EQUIPMENT AND APPARATUS AND MATERIALS
D.	SAMPLE CALCULATIONS
Ε.	PHYSICO-CHEMICAL PROPERTIES OF SOLUTIONS USED 117
	VITA

· ·

.

-vi-

LIST OF TABLES

Page

1.	Data and Results for the Absorption of Carbon Dioxide in Water at 25°C in a Stirred Tank for Different Gas Superficial Velocities and Different Agitator Speeds	41
II.	Data and Results for the Absorption of Carbon Dioxide in 0.085 M Caustic at 25°C in a Stirred Tank for Different Gas Superficial Velocities and Different Agitator Speeds	42
III.	Data and Results for the Absorption of Carbon Dioxide in 1.0 M Caustic at 25°C in a Stirred Tank for Different Gas Superficial Velocities and Different Agitator Speeds	43
IV.	Data and Results for the Absorption of Carbon Dioxide in 1.5 M Caustic at 25°C in a Stirred Tank for Different Gas Superficial Velocities and Different Agitator Speeds	44
۷.	Predicted Bubble Diameters for Different Agitator Speeds and Gas Superficial Velocities	45
VI.	Calibration Data and Results for Orifice- meter with Carbon Dioxide Gas	101
VII.	Calibration of Agitator Gear	105
VIII.	Physico-Chemical Properties of Caustic Used	118

LIST OF FIGURES

		Page
1.	Model for Two-Film Theory	6
2.	Schematic Diagram of Apparatus	28
3.	Agitator and Orifice Design and Dimensions	30
4.	Theoretical Relationship between β and γ	36
5.	Theoretical Relationship between the Ratio of the Rate of Absorption of CO ₂ in 0.085 M Sodium Hydroxide to that in Water and the Time of Contact	. 38
6.	Effect of Impeller Tip Speed and Superficial Gas Velocity on Interfacial Areas in 0.085 M Caustic Solution	49
7.	Effect of Impeller Tip Speed and Superficial Gas Velocity on Interfacial Areas in 1.0 M Caustic Solution	50
8.	Effect of Impeller Tip Speed and Superficial Gas Velocity on Interfacial Areas in 1.5 M Caustic Solution	51
9.	Effect of Impeller Tip Speed and Superficial Gas Velocity on the Time of Contact between Gas-Liquid Particles	52
10.	Correlation of Interfacial Areas in 0.085 M Caustic Solution	53
11.	Correlation of Interfacial Areas in 1.0 M Caustic Solution	54
12.	Correlation of Interfacial Areas in 1.5 M Caustic Solution	55
13.	Correlation of Gas-Liquid Contact Time	56
14.	Log-Log Plot of Predicted Bubble Diameter Versus Impeller Tip Speed for Different Gas Superficial Velocities	57

15.	Average Total Fluid Velocity in Tank Versus $NO^2/(T^2H)^{1/3}$		•	•	•	•	•	93
16.	Flow Rate of Carbon Dioxide through Orifice Versus Manometer Reading		•	•	•	•	•	102
17.	Calibration Chart for Caustic Rotameter	•	•	•	•	•	•	103
18.	Calibration Chart for Agitator Gear Setting		•	•	•	•		106

I. INTRODUCTION

Numerous operations occur in chemical engineering which involve the contact of two phases with simultaneous heat and mass transfer and the additional possibility of chemical reaction. A phenomenon of mass transfer with chemical reaction occurs whenever two phases which are not in chemical equilibrium with one another are brought into contact. Such a phenomenon may consist of a number of elementary steps, which may be put briefly as follows.

(i) Diffusion of one reactant or a number of reactants from the bulk of phase 1 to the interface separating the two phases. (ii) Diffusion of these reactants from the interface towards the main body of phase 2. (iii) Chemical reaction within phase 2. (iv) Diffusion of reactants initially present within bulk 2, together with reaction products, because of concentration gradients set up by the overall chemical reaction.

The occurrence of the last three steps is usually simultaneous, but the overall phenomenon resulting from these three steps is in series with step (i). Thus, if step (i) is controlling, the overall rate is not influenced by chemical reaction. When the overall phenomenon resulting from steps (ii), (iii), and (iv) is rate controlling, the analysis must take into account the rate of chemical reaction.

A considerable amount of work has been done on problems associated with gas absorption with chemical reaction. In general, systems with simple geometry such as wetted-wall columns and laminar liquid jets have been successfully treated by theoretical analysis, but fewer attempts have been made to treat the more complicated systems.

Two sets of factors influencing the rate of absorption of a pure gas into a liquid may be distinguished, those of the physicochemical nature and those of the hydrodynamical nature. In the design of gas absorption contacting equipment, the prediction of mass transfer rates is complicated by the difficulty of describing the complex flow characteristics. It is because of this that the absorption models thus far developed have been applied mainly for devising methods for the correlation of data. Thus, the difficulty in predicting mass transfer rates is due not to a lack of absorption theory or models, but to a lack of knowledge about the dynamic state of the system. From this it is clear that one possible approach to determining the characteristics of a gas absorber could be the application of the theory for predicting absorption rates to actual data in such a way as to force the theory to yield the parameters of the theory chosen consistent with the observed mass transfer rates.

Of all the theories of mass transfer known at the present time, the penetration theory model has a special attraction in the sense that it is a realistic depiction of the transfer phenomenon and yet is quite simple for comprehension. The penetration theory has been shown to be valid for systems of simple geometry [47].* Danckwerts

*Numbers in brackets refer to appended references.

-2-

et al [18] applied the penetration theory to the study of the behavior of the packed column; Eben and Pigford [20], Smith and Wills [61] applied the same theory to the study of the sieve plate column.

Models based on the penetration theory for predicting mass transfer rates generally involve such parameters as interfacial area and effective contact time. The latter refers to that interval of time during which the fluid elements through which transfer takes place are in contact with the soluble gas. In stirred tank reactors these quantities can only be roughly approximated. Thus, further improvement in design procedures depends to a great extent upon better knowledge of these parameters.

The purpose of this investigation was to determine the applicability of the penetration theory for a reacting system in a stirred tank reactor and to obtain meaningful values of interfacial area and contact time by forcing the theory to give results consistent with observed absorption rates.

-3-

II. LITERATURE REVIEW

The literature review pertinent to this investigation is divided into four sections. The first section deals with mass transfer and enumerates the basic theories in mass transfer. The second section deals with work that has been done in connection with absorption in stirred tank reactors. The third section concerns the chemistry of the reactions chosen and the equations that can be applied to describe the absorption reaction. The last section deals with the data collected from literature to be used in this investigation.

Mass Transfer

The differential equations which represent the phenomenon of simultaneous diffusion and chemical reaction in a liquid phase may be written for each of the species, in the form

$$D_i \nabla^2 c_i = u \nabla c_i + \frac{\partial c_i}{\partial t} + r \qquad (1)$$

where the vector notation is the one used by Bird, Stewart, and Lightfoot [6].

Equation (1) simplifies considerably for the hydrodynamic conditions such as those assumed for the film-theory and the penetration models. For both these models u = 0, and in the case of the film theory also, $\partial c_i/\partial t = 0$. The equation is written with reference to a system of coordinates which moves together

-4-

with the surface elements considered. Hence, u = 0 simply means that during its life, the surface element behaves as a rigid body, but does not imply that its position does not change. Another simplification arises from the fact that the gas-liquid interface may be assumed to be plane, or, more exactly, its curvature may be neglected for the surface elements of the liquid.

Film Theory

The two-film theory of Whitman [70] was the first hydrodynamic model which has been proposed for the investigation of transport processes. The theory makes the assumption that, close to any interface there is an immobile film of thickness L through which transport processes take place by simple molecular diffusion. Outside the laminar layer turbulent eddies supplement the action caused by the random movement of the molecules, and the resistance to transfer becomes relatively small. For equimolar counter-diffusion the concentration gradient is linear close to the interface and gradually becomes less at greater distances as shown in Figure 1 by the full lines ABC and DEF. The basis of this theory is the assumption of the existence of two layers, on either side of the interface, in which resistance to molecular diffusion lies. The broken lines in Figure 1 indicate the hypothetical concentration distributions, and L_1 and L_2 the thickness of the two films.

The mass transfer is treated as a steady state process. Since equilibrium is assumed to exist around the interface, the concentration at points C and D are determined by the equilibrium relationships

-5-



FIGURE 1. MODEL FOR TWO-FILM THEORY

-6-

between the two phases. For this case Whitman [70] has shown that for a non-reacting system the flux may be expressed as:

$$N_{A} = \frac{D_{A}}{L} (c_{A}^{*} - c_{o})$$
 (2)

where

- N_{Δ} = molar flux of A, mole/cm. sq./sec.

L = film thickness in phase 1, cm.

$$c_A^*$$
 = saturation concentration of species A in phase 1, mole/cm.³
 c_o = bulk concentration of A in phase 1, mole/cm.³

It is difficult to accept the film theory as an actual description of the physical situation, except in the case of very few processes. The most serious objection is its failure to account for the variation of absorption rates for transient contact times.

Penetration Theory

Higbie [26] proposed a model of the hydrodynamic conditions in the liquid phase close to a gas-liquid interface, which postulates that the gas-liquid interface is made up of a variety of small liquid elements. These are continuously brought up to the surface from the bulk of the liquid and vice-versa by the motion of the liquid phase. Each of the elements may be considered to be stagnant. Absorption takes place by unsteady state molecular diffusion in the various elements of the liquid surface and equilibrium is supposed to take place immediately at the interface.

Considering mass transfer without reaction in one direction and for species A, the unsteady state molecular diffusion process within each element can be written from equation (1) as follows.

$$D_{A} \frac{\partial^{2} c_{A}}{\partial x^{2}} = \frac{\partial c_{A}}{\partial t}$$
(3)

where t is the time elapsed from the moment the surface element is brought to the surface. The boundary conditions are

$$t = 0 \qquad c_{A} = c_{o} \qquad 0 < x < \infty \qquad (4)$$

$$t \ge 0$$
 $c_A = c_A^*$ $x = 0$ (5)

 $t \ge 0$ $c_A = c_o$ $x \to \infty$ (6)

The instantaneous absorption rate for a unit interfacial area obtained by the solution of equation (3) with the boundary conditions given is given by [26]

$$N_{A}^{\star} = (c_{A}^{\star} - c_{o}) \sqrt{\frac{D_{A}}{\pi t}}$$
(7)

and the average absorption rate over the whole "life" t of an element is given by [26]

$$N_{A} = 2(c_{A}^{*} - c_{o}) \sqrt{\frac{D_{A}}{\pi t}}$$
(8)

Thus, it can be seen that the rate of absorption depends on the contact time; the shorter the contact time, the greater the rate of absorption. The contact time would be progressively smaller as the degree of turbulence increases. It should also be noticed that the rate of absorption is proportional to the square root of the diffusivity.

Surface Renewal Theory

Danckwerts suggested that each element of surface would not be exposed for the same time, but that a random distribution of ages would exist. The probability for a surface element to disappear from the surface in a given interval of time is independent of its age, but the rate of disappearance of the surface elements of any given age is simply proportional to the number of elements of that age which are present. For the case of a non-reacting system, the rate of absorption of species A based on this model is [15]

$$N_{A} = (c_{A}^{\star} - c_{o}) \sqrt{D_{A}s}$$
(9)

where s = fractional rate of surface renewal, \sec^{-1} . Here again it is noticed that the mass transfer rate is proportional to the concentration gradient and to the square root of the diffusivity. The numerical value of s is difficult to estimate, but will clearly increase as the fluid becomes more turbulent.

Penetration-Film Theory

Toor and Marchello [63] incorporated some of the principles of

-9-

both the two-film and penetration theories. The whole of the resistance is supposed as lying within the laminar film at the interface as in the two-film theory, but the mass transfer is regarded as an unsteady state process. It is assumed that fresh surface is formed at intervals from fluid brought to the surface from the bulk by the action of eddy currents. Thus, mass transfer takes place as in the penetration theory, with the exception that the resistance is confined to the finite film. For short times of contact, the process is identical to that postulated in the penetration theory. For long periods of exposure, when a steady concentration gradient has developed, conditions are similar to the two-film theory. The rate of absorption for the Toor-Marchello model is:

$$N_{A} = (c_{A}^{*} - c_{0}) \sqrt{\frac{D_{A}}{\pi t}} [1 + 2 \exp(-L^{2}/Dt)]$$
(10)

Note that according to this theory two parameters, i.e., contact time and film thickness are unknown quantities, neither of which is readily known.

Other Theories of Mass Transfer

Kishinevskii's model [33,34] is based on the hypothesis that for mass transfer across an interface molecular diffusion plays no part. He postulates that as a result of turbulence, fresh material is continuously brought to the interface and after exposure to the second phase, this fluid element attains equilibrium with it and then gets mixed again with the bulk of the phase. The model thus suggests no relation with molecular diffusivity since it presupposes surface renewal only through convective effects.

Bakowski [2] postulated that the transfer rate from a turbulent gas stream to an interface is a function of the number of molecules of the diffusing component in the gas layer with the liquid. The absorption of molecules by the liquid is assumed to be rapid so that the rate of replacement of the molecules in the surface layer is the rate determining factor. Hence the velocity of the gas stream over the surface directly influences mass transfer rate.

Fortescue and Pearson [22] proposed a model in which mass transfer across the surface of a turbulent flowing liquid is assumed to be determined by relatively large scale eddies. Their length scale is taken to be the integral scale of the turbulence in the bulk of the fluid, while their intensity is also taken to correspond to that of the bulk turbulent flow field.

Mass Transfer in Agitated Systems

The effect of the variables encountered in agitated systems on mass transfer and interfacial mass transfer areas has been the subject of many studies. In this section literature pertinent to this investigation is summarized.

Effect of Agitation on Mass Transfer Coefficient Calderbank's work [10,11] suggests that the mass transfer

-11-

coefficient k_L is practically independent of agitation intensity. This is substantiated by findings reported by Hyman [29] that the mass transfer coefficient is relatively constant, even at high rates of shear. It is, however, significant to note that theoretical consideration [10,11] for high mixing rates yields

$$k_{L} \propto (P/V)^{0.25} \propto N^{0.75}$$
 (11)

where

P = power input, horse-power

- V = volume of agitated fluid, ft.³
- N = impellar rotation per minute.

Empirical considerations based on mass transfer between a liquid and suspended solids led Vermuelen [65] to suggest that

$$k_{L} \propto N^{0.6} \propto (P/V)^{0.2}$$
 (11-a)

An almost identical relationship was obtained by Davis, Kilmer, and Ratcliff [19] who considered gas absorption rates in exceedingly clean water surfaces in a stirred cell. This is also in fair agreement with the empirical correlations suggested by Yoshida [68] which reduces to

$$k_{L} \propto N^{0.42} \propto (P/V)^{0.14}$$
 (turbine) (12)

$$k_{L} \propto N^{0.54} \propto (P/V)^{0.18}$$
 (vaned disc) (13)

It should be noted too that k_L was found to decrease with increased stirring rates above 100 revolutions per minute when oxygen was absorbed in a sulphite solution [46,55].

Effect of Gas Flow Rate on Mass Transfer Coefficient

For a given gas-liquid system, no effect of gas flow rates on the value of mass transfer coefficient has been detected by Calderbank [9]. This conclusion should be taken with reservations, since the transfer coefficient depends on the bubble diameter which often depends on the gas flow rate [60].

Effect of Agitation and Gas Rate on Interfacial Area

A general correlation suitable for aerated mixing vessels as well as sieve plate columns was suggested by Calderbank [8,11]:

a = (const)
$$\frac{(P/V)^{0.4} \rho_c^{0.2} V_s^{0.5}}{\sigma_c^{0.6}}$$
(14)

where

a = interfacial area, cm⁻¹ ρ_c = continuous phase density, gm/cm³ σ = interfacial tension of liquid, dynes/sec. sq.

 V_s = superficial gas velocity based on tank cross-section, cm/sec. It should, however, be emphasized that equation (14) is limited to relatively low specific power input up to 0.2 horsepower per cubic foot. The dependency of interfacial area on power input and on V_s varies with impeller type. For a 12 blade turbine at low impeller velocities of up to 300 r.p.m. and low holdup Yoshida [68] reports

$$a \propto V_s^{0.75} N^{1.1} \propto V_s^{0.75} (P/V)^{0.37}$$
 (15)

assuming that (P/V) is proportional to N^3 .

The exponents of V_s and N for different impellers vary as reported by different workers. For a 16 blade vane disc impeller the exponent for V_s ranges from 0.33 to 0.66 and for N from 0.9 to 0.7 as reported by Yoshida [15]. For a 5 blade paddle impeller Preen [50,66] reported exponents of 0.60 and 0.35 for V_s and (P/V) respectively. Vermuelen [65] suggested an exponent of 1.50 for N.

Overall Mass Transfer Coefficients

The overall mass transfer coefficients using different gasliquid systems for different agitations have been reported by several investigators. Generally, the correlations for the overall mass transfer coefficient have been expressed in the form:

or

$$k_{L}a \propto V_{s}^{m}(P/V)^{h}$$
 (17)

where m, n, h are constants depending on the type of agitator, geometry of agitator, and the type of system dealt with.

Cooper [12] et al working with 16 bladed vaned disc agitator and a 2 bladed paddle gave the values of 0.67 and 0.95 for the exponents of V_s and P/V respectively. Hixson-Gaden [28] working with vaned disc impellers gave an exponent of 0.68 for V_s .

Yoshida [68] working with 12 bladed turbine impeller, gave values of 0.67 and 2.00, respectively, for V_s and N, while for a 16 blade vaned disc impeller he gave a value ranging from 0.40 to 0.84 and 1.29 to 2.05, respectively. Bartholomew, [3] working with turbine impellers, gave values ranging from 0 to 1 for V_s . Oldshue [42], working with 8 blade turbine impellers, gave values of 0.4 and 0.53 for the exponents of V_s and (P/V), respectively, while Polejes [49] gave values of 1.0 and 3.0 for the exponents of V_s and N, respectively, for the same type of impeller. Rushton [39] gave exponent values of 0.76 and 0.71 to 0.79 for multiple six blade turbine impellers for V_s and (P/V), respectively. Johnson [31] gave values of 0.75 and 1.67, while Westerterp [66] gave values of 0 and 1, respectively, for the exponents of V_s and N for turbine and propeller impellers.

Hyman [30] worked with 6 and 4 blade turbines, 4 blade vaned disc, and 4 and 2 blade paddle impellers and obtained exponents in the range of 0 to 0.21 and 1.26 to 2.04 for V_s and N, respectively. Friedman-Lightfoot, [21] working with 4 blade paddle impellers, obtained values of 0 and 3.00, respectively, for V_s and N. Karwat [32] suggested exponent values ranging from 0.43 to 0.95 for (P/V) while, on the other hand, Maxon [38] obtained values of 0.40 and 1.70 for V_s and N, respectively.

Chemistry of Reaction and Equations for Diffusion with Reaction

In this section, the reactions that occur between carbon dioxide and a hydroxide are first enumerated. Then the effect of the variables on the rate constant is discussed and finally the differential equations describing the diffusion and reaction process are given and discussed.

Chemistry of the Reaction

When carbon dioxide is absorbed in aqueous solutions of strong hydroxides, a number of reactions take place. Payne and Dodge [43] list the following reactions which may be involved in the absorption process:

$$CO_{2(gas)} \stackrel{\neq}{\leftarrow} CO_{2(dissolved)}$$
 (18)

$$CO_{2} + H_{2}O \neq H_{2}CO_{3}$$
(19)
(dissolved)

$$H_2 CO_3 \stackrel{2}{\leftarrow} H^+ + HCO_3^-$$
(20)

$$HCO_{3}^{-} \neq H^{+} + CO_{3}^{-}$$
 (21)

$$CO_2 + OH^- \stackrel{?}{\leftarrow} HCO_3^-$$
 (23)

$$HCO_{3}^{-} + OH^{-} \stackrel{?}{\leftarrow} CO_{3}^{-} + H_{2}O$$
 (24)

The ionic reactions given by equations (18) through (22) are believed to be very rapid [58]. Thus, when a substantial amount of free hydroxide is present, reactions (23) and (24) are the main reactions to be considered. In concentrations above 10^{-2} gram mole

per liter, both reactions may be considered to be irreversible [1,41].

Of the two reactions given by equations (23) and (24), the reaction given by equation (24) can be considered to be instantaneous. According to Pinsent, Pearson and Roughton [48] for concentrations of OH^- less than 0.0018 N the error in assuming that all HCO_3^- is transformed to CO_3^- is less than 5 percent as long as the first 50 percent of the reaction is used for purposes of calculation. Thus, the overall reaction which takes place during the absorption of carbon dioxide in hydroxide solutions may therefore be assumed to be the following:

$$CO_2 + 20H^- \xrightarrow{k_2} CO_3^- + H_2O$$
 (25)

and the overall rate of the second order reaction for the absorption of carbon dioxide may be given by the equation

$$r = k_2 c_A c_B$$
(26)

where

r = rate of reaction of carbon dioxide, gm/sec/l
c_A = concentration of carbon dioxide, gm mol/l
c_B = concentration of hydroxide, gm mol/l
k₂ = second-order rate constant, l/gm mol/sec.

Effect of Temperature on k2

The temperature dependency of k_2 is governed by an activation

energy of 13,250 calories per gram mole and the equations giving the dependency of k_2 on temperature at infinite dilution are given as [48]:

$$\log_{10} k_2 = 13.635 - 2895/T$$
 (27)

or

$$k_2 = A \exp \left(- E_A / RT \right)$$
 (28)

where

$$E_A$$
 = activation energy, cal/gm mol
T = temperature in degrees Kelvin
A = 4.2 x 10¹³.

Effect of Ionic Strength on k2

According to Moelwyn-Hughes [40] for dilute solutions the relationship of the specific rate constant with ionic strength can be expressed as

$$\log k_r = \log k_{ro} + AI_i$$
 (29)

where

 k_r = specific rate constant at an ionic strength of I_i k_{ro} = specific rate constant at infinite dilution A = constant depending on the system.

For sodium hydroxide solutions the data of Nizsing, Hendriksz and Kramers [41] suggests the following relationship for the specific rate constant of the carbon dioxide and sodium hydroxide reaction.

$$\log k_2 = \log k_{20} + 0.13 I_i$$
 (30)

Equations for Diffusion with Reaction for the System Chosen

For the case of one mole of absorbent A reacting with two moles of the reactant B, which is analogous to the system chosen here, the diffusion equations with all the simplifications mentioned before can be written for unidirectional mass transfer as follows [6]

$$\frac{\partial c_A}{\partial t} = D_A \frac{\partial^2 c_A}{\partial x^2} - k_2 c_A c_B$$
(31)

$$\frac{\partial c_{B}}{\partial t} = D_{B} \frac{\partial^{2} c_{B}}{\partial x^{2}} - 2k_{2} c_{A} c_{B}$$
(32)

where in the case of the system chosen

c_A,c_B = concentration of carbon dioxide and hydroxide respectively, gm mol/ml D_A,D_B = diffusivities of carbon dioxide and hydroxide in the medium, respectively, cm²/sec t = time, sec

x = distance, cm.

The following boundary conditions can be written for these equations.

$$t < 0$$
 $0 < x < \infty$ $c_A = 0$ $c_B = c_{Bo}$ (33)
 $t \ge 0$ $x = 0$ $c_A = c_A^*$ $\frac{\partial c_B}{\partial x} = 0$ (34)

$$t \ge 0$$
 $x = \infty$ $c_A = 0$ $c_B = c_{B0}$ (35)

where

 c_A^* = solubility of carbon dioxide, gm mol/ml c_B = bulk concentration of hydroxide, gm mol/ml.

If the concentration of B is much higher than the concentration of A the contact times are not very long, the condition of pseudo-first-order reaction is approached and the set of non-linear partial differential equations represented by equations (31) and (32) can be reduced to one linear partial differential equation as shown below since the concentration of B is assumed to be constant throughout [17,41].

$$\frac{\partial c_A}{\partial t} = D_A \frac{\partial^2 c_A}{\partial x^2} - kc_A$$
(36)

where

$$k = k_2 c_B$$
(37)

and is assumed to be constant in value at a constant temperature.

Danckwerts [14] has given the solution of this equation in terms of concentration, instantaneous rate of absorption and the total absorption for different contact times. The concentration is given as

-20-

$$\frac{c_{A}}{c_{A}^{*}} = \frac{1}{2} \exp\left(-x \sqrt{\frac{k}{D_{A}}}\right) \operatorname{erfc}\left[\frac{x}{2\sqrt{tD_{A}}} - \sqrt{kt}\right] + \frac{1}{2} \exp\left(x \sqrt{\frac{k}{D_{A}}}\right) \operatorname{erfc}\left[\frac{x}{2\sqrt{tD_{A}}} + \sqrt{kt}\right]$$
(38)

where

erfc = error complementary function. The instantaneous rate of absorption is given by

$$N_{A}^{*} = c_{A}^{*} \sqrt{D_{A}k} \left[\text{erf } \sqrt{kt} + \frac{e^{-kt}}{\sqrt{\pi kt}} \right]$$
(39)

and the total amount absorbed for a unit interfacial area for a contact time t is

$$Q = c^* \sqrt{\frac{D_A}{k}} \left[(kt + \frac{1}{2}) \operatorname{erf} \sqrt{kt} + \sqrt{\frac{kt}{\pi}} e^{-kt} \right]$$
(40)

where

Q = amount absorbed per unit interfacial area for contact time t, gm mol/sq cm erf = error function

Numerical solutions by computer for the reversible secondorder reaction using the penetration or surface-renewal theory have been given by a number of workers [7,45,51].

Physico-Chemical Parameters Used

A number of physico-chemical parameters have been used in this investigation. In this section the effects of different factors and the sources where these parameters were obtained are discussed.

Specific Rate Constants

The specific rate constants used and the effect of different factors on them have already been discussed under the previous section.

Solubility of Carbon Dioxide

Values of the physical solubility of carbon dioxide in water are well known. The values in aqueous solutions of electrolytes can be calculated by the method of van Krevelen and Hoftijzer [64]. According to this method

$$\log \frac{c^{\star}}{c_{W}^{\star}} = -k_{s}I$$
 (41)

where

- $\frac{c_{\star}^{\star}}{c_{W}}$ = ratio of solubility of gas in electrolyte solution c_{W} to solubility in water
- I = half the sum of the concentrations of the different ions multiplied by the square of the corresponding charge, gm mol/l

k = constant depending on ions, 1/gm mol.

The values of k_s can easily be obtained for certain electrolytes [64].

Diffusivity of Carbon Dioxide

A number of workers have given values for the diffusivity of carbon dioxide in water [41]. The values given are quite in fair agreement with each other. The most reliable value for the diffusivity of carbon dioxide in water at 25°C seems to be one given by Davidson and Cullen [13].

For the diffusivity of carbon dioxide in electrolyte solutions of varying viscosity the diffusivity is quite reliably estimated by the Nernst-Einstein relationship:

$$\frac{D\mu}{T} = constant$$
 (42)

where

D = diffusivity of gas in medium

 μ = viscosity of medium

T = absolute temperature for the medium.

Diffusivity of Hydroxyl Ions

Direct estimations of the diffusivity of hydroxyl ions in different solutions are difficult to make. Various values of diffusivity have been reported. Roberts and Danckwerts [18] have obtained effective values 2.3 x 10^{-5} and 2.5 x 10^{-5} centimeter square per second at 25°C. Rehm [51] et al used values between 2.0 and 3.0 x 10^{-5} centimeter square per second at 25°C

and found that the calculated rates of absorption were relatively insensitive in this range.

III. EXPERIMENTAL

This section of the dissertation consists of the plan of investigation, a list of materials and main apparatus used, the method of analysis of data, the data and the results obtained, and the sample calculations used in the analysis.

Plan of Investigation

The overall purpose of this investigation is to get meaningful values for contact times and interfacial areas for the range of variables in these experiments. The absorption experiments conducted involved the absorption of carbon dioxide into water, 0.085 M caustic solution, 1.0 M caustic solution, and 1.5 M caustic solution for different sets of gas superficial velocities and stirrer revolutions, respectively.

The approach for this investigation varies for the different dynamic conditions obtained in the stirred tank for solutions of different strengths. In general, other factors remaining equal, according to the penetration model, the rate of absorption of gas is dependent on the interfacial area and the contact time. Thus, if we conduct only one experiment to determine these two parameters, for a given set of conditions, it is not possible to obtain the values of these parameters exclusively without assuming the value of one.

Some previous workers [15,20] have suggested a way to get around this problem by conducting two absorption experiments under the same set of conditions, one absorption being with chemical reaction and the other being absorption without reaction. Then from the ratio of the rate of absorption in the two cases, the contact time and the interfacial area can be evaluated exclusively without assuming the value of any one of them, as will be outlined later in the procedure.

It is, however, implicit in the above method that the condition of dynamic similarity of the two cases be met with. In principle, the condition of dynamic similarity can be assumed to be satisfied between the cases of 0.085 M caustic solution and pure water, for a given set of conditions, since the physical properties of 0.085 M caustic solution are almost the same as that of water.

In the case of absorption with the more concentrated solutions, viz. 1.0 M and 1.5 M sodium hydroxide solutions, dynamic similarity cannot be assumed between them and water for a given set of conditions, since the physical properties of the solutions change quite significantly as compared to those of pure water. It can, however, be proved theoretically that the rate of absorption of carbon dioxide in these solutions for not very large contact times is not sensitive to the time of contact. Thus, the interfacial areas involved are evaluated solely on the basis of experiments with these solutions alone.

Materials

A list of materials used and their respective specifications

-26-
is given in the Appendix.

Apparatus

The apparatus used in this investigation are listed in the Appendix.

Assembly of Equipment

Figure 2 shows a schematic diagram of the apparatus set up used in this investigation. The absorption tank is assembled out of a section of an eleven and a half inch internal diameter cast acrylic glass tube. The baffles and the bottom of the tank are also made of acrylic glass.

The saturation column consists of two three and a half inch diameter flanged glass columns, each three and two feet long respectively. The top and bottom of this column are blanked with one eight inch thick steel plates.

The gas lines running to and from the saturation column and the absorption tank are either made of half inch steel tubing or three-eighths inch copper tubing. The concentrated alkali line from the overhead bottle consists of polyethylene tubing and threeeighths inch copper tubing.

The impeller used, whose details are given later in this chapter, was fabricated completely from stainless steel.

Procedure

The procedure employed in this investigation consists of the



-28-

development of the proper equipment for absorption, development of procedures for the actual experimental runs, calibration of equipment, and the development of mathematical techniques for the analysis of data.

Development of Stirred Tank

The stirred tank consists of an eleven and half inch internal diameter acrylic glass tubing having an acrylic glass bottom as well. A gas sparger consisting of one sharp-edged orifice, having a diameter of one-eighth inch, is led through the center of the tank bottom. The size of the orifice was chosen in such a way that the flow of gas through the orifice for the gas rates used was always turbulent. Since this flow was turbulent for all the gas rates used, the bubble size produced at the orifice was always less than 5 millimeters in diameter, as could be estimated from the work of Leibson et al [36]:

d =
$$0.28(\text{Re}_{0})^{-0.05}$$
 (centimeters) (43)

where Re_{o} is the Reynolds number through the orifice.

A flat six-bladed radial-flow impeller was chosen as the agitator because of its desirable power characteristics. As shown by Rushton, [53] this type of agitator operating in a baffled tank has a constant power number in the region of fully developed turbulence, a state which encompasses most normal operating conditions. In this condition the power needed to operate the impeller at a given speed is independent of the viscosity of fluid being agitated.



The relative dimensions of the impeller used were similar to that used by Rushton [53] and Calderbank [8]. The overall diameter of the impeller as shown by Figure 2 was one-third the diameter of the tank and the liquid height in the tank, respectively. The impeller, placed centrally in the tank at one impeller diameter above the tank bottom, was driven at speeds varying from 150 to 350 revolutions per minute by a stainless steel shaft from a geared motor.

In order to minimize the effect of the gravity forces and consequently prevent the appearance of the vortex, the tank was symmetrically baffled by four radial baffles, whose width corresponded to a tenth of the diameter of the tank.

Calibration of Equipment

The method of calibration, calibration data, and calibration figures for gas orificemeter, gear controlling agitator speed, and caustic rotameter are given in the Appendix.

Experimental Measurement of Absorption Rates

The techniques developed for the measurement of absorption rates in the different strength solutions vary from one another because of the different rates of caustic depletion. In general, experiments with all solutions involved some degree of trial and error procedures.

Measurement of Rates of Absorption in 1.0 M and 1.5 M Caustic Solutions

The constant temperature bath is set at 25°C and the water is

circulated through the saturation column as shown in Figure 2. The requisite strength caustic at a temperature of 25°C is filled up in the tank up to a height of one tank diameter. The carbon dioxide from the gas cylinder is bubbled through the saturation column and the flow is set while the gas is vented into the atmosphere for a few minutes to insure that no air is left in the line. The agitator is then started at the required speed, the flow of gas to the air is cut, and the valve leading the gas to the tank opened. After the gas establishes a uniform pattern of the bubbles in the agitated solution, the initial sample at time 0 seconds is withdrawn. The absorption is conducted for a half minute and the final sample is withdrawn from the tank. The initial concentration of the caustic before the introduction of carbon dioxide is adjusted by trial and error, so that the concentration of alkali at the initial time of O seconds is near either one molar caustic strength or one and a half molar strength, respectively.

The samples at time 0 seconds and time 30 seconds are diluted to forty times their initial strengths and titrated against standard hydrochloric solution to a pH of seven, respectively. The difference in the titration readings is proportional to the amount of carbon dioxide absorbed.

Measurement of Rates of Absorption in 0.085 M Caustic Solution

The handling and introduction of the carbon dioxide is the same as in the absorption experiments in 1 M and 1.5 M concentrated

-32-

solutions. Because of the low bulk concentration of caustic involved, there is a significant relative rate of depletion of sodium hydroxide. Therefore, to maintain the caustic level at 0.085 M strength, 3 M concentrated caustic is fed into the tank at the same equivalent rates as the rates of absorption of carbon dioxide. The procedure involved trial and error until the concentration of sodium hydroxide in the tank both at initial time of 0 seconds and final time of 60 seconds remains at 0.085 M. The rate of absorption of carbon dioxide in this case is simply half of the rate at which the concentrated caustic is added. Again, the concentration is determined by titrating the sodium hydroxide to its end point and the sodium carbonate formed to its half end point by titrating the solution of a pH of seven.

Measurement of the Rates of Absorption in Distilled Water

The trial and error procedure involved here is the same as in absorption of carbon dioxide in 0.085 M sodium hydroxide solution. To keep the concentration of carbon dioxide at 0 strength 1.0 M sodium hydroxide is continuously added to the tank to neutralize the carbon dioxide to give sodium bicarbonate. The pH of the solution in the reactor has to be kept constant at all times at about a pH of 8.5, which is found by actually titrating a sodium carbonate solution to sodium bicarbonate. Then the number of moles of carbon dioxide absorbed is equal to the number of moles of sodium hydroxide added.

-33-

Method of Analysis of Data

Since the hydrodynamic properties involved for the different strength absorption solutions vary widely and the reactant depletion considerations around the gas-liquid interface differ in the different strength solutions, two methods of analysis of data are used.

Analysis Based on Pseudo-First Order Reaction

It has been seen in the literature review that the simultaneous non-linear differential equations (31) and (32) with the appropriate boundary conditions describing the absorption process with simultaneous chemical reaction for a second order nonreversible reaction can be reduced to one linear differential equation under certain simplifying conditions. The amount of gas absorbed in contact time t per unit interfacial area is given as

$$Q = c_{A}^{*} / \frac{D_{A}}{k_{2}c_{B}} \left[(k_{2}c_{B}t + \frac{1}{2}) \operatorname{erf} \sqrt{k_{2}c_{B}t} + / \frac{k_{2}c_{B}t}{\pi} e^{-k_{2}c_{B}t} \right]$$
(44)

This pseudo-first order solution is only valid for small depletion of reactant around the interface and not very large contact times. These conditions are satisfied provided [72]

$$1 < (\frac{\pi}{4} k_2 c_B t)^{1/2} \le (1 + \frac{c_B}{z c_A})$$
 (45)

where z is the number of moles of reactant reacting with one mole

-34-

of absorbed gas. The amount of gas absorbed per unit interfacial area in time t under non-reacting conditions by the Higbie penetration theory is

$$Q = c_A^* \sqrt{\frac{D_A t}{\pi}}$$
(46)

Combining equations (44) with the expression for k_L from the Higbie penetration model one obtains the value of β the so-called reaction factor (which is the ratio of the transfer coefficient with chemical reaction to the transfer coefficient without reaction) as follows [1,69]

$$\beta = (\gamma + \frac{\pi}{8\gamma}) \operatorname{erf} \left(\frac{2\gamma}{\sqrt{\pi}}\right) + \frac{1}{2} \exp\left(-\frac{4\gamma^2}{\pi}\right)$$
(47)

where

$$\gamma = \frac{(k_2 c_B D_A)^{1/2}}{k_L}$$
(48)

The average rate of transfer with chemical reaction is given by

$$N_{A} = k_{L}'c_{A}^{*} = \beta k_{L}c_{A}^{*}$$
(49)

Figure 4 shows a plot of β calculated from equation (47) against γ . It is interesting to note that above a value of $\gamma = 5$, β is practically equal to γ so that equation (49) for the case of pseudo-first order reaction reduces to

$$N_{A} = (k_{2}c_{B}D_{A})^{1/2} c_{A}^{*}$$
(50)



FIGURE 4. THEORETICAL RELATIONSHIP BETWEEN β AND γ

-37-

provided

$$\dot{\gamma} \ge 5$$
 (51)

As will be shown later in the discussion, with the experiments involving the absorption of carbon dioxide in 1.0 M and 1.5 M molar caustic solutions, the constraints represented by equations (45) and (51) are fully met so that equation (50) is used to calculate interfacial areas as shown in Appendix D.

Analysis Based on Ratio of Rates of Absorption with Reaction to Rate Without Reaction

With very dilute solutions the equations making the pseudofirst order assumptions given in the preceding section are not valid since there is a significant amount of depletion of reactant. The approach taken here is that equations (31) and (32) with the appropriate boundary conditions satisfying the penetration model are solved on the computer in terms of rates of absorption for different contact times. Then, from the rates of absorption with and without reaction, the ratio R of the rate of absorption with reaction to that without reaction can be obtained as a function of time of contact as shown in Figure 5. If two absorption experiments one with reaction and the other without reaction are conducted with all the other conditions remaining constant in both, then from the graphical solution of this ratio R against time of contact, the contact time can be evaluated. Once the contact time is known, the interfacial





٠.

area can be calculated.

J.R.A. Pearson [44] and others [7,45] have published solutions to these sets of differential equations that are appropriate for the overall reaction (25). In order to obtain solutions to the differential equations (31) and (32) with the boundary conditions represented by equations (33) through (35), a computer program for their solution was written [5]. The numerical technique used was that given by Pearson [44].

The program was checked by comparing its results to the published results. An additional check on the computer was provided by obtaining a limiting value of the ratio of absorption rate in sodium hydroxide solution to that in water. A limiting value for this ratio is obtained when reaction (25) is considered to be instantaneous. For the instantaneous reaction case the analytical solution of equations (31) and (32) is available. The limiting value for the ratio is approached as time increases.

Prediction of Bubble Size Using Time of Contact

If the assumptions used in the derivation of time of contact for the gas-liquid particles (see Appendix A) are approximately sound, then it should be possible to obtain the average gas particle bubble diameters by the following equation.

$$t = \frac{d}{U}$$
(52)

-39-

Such an equation has been found to be valid in the case of absorption from rising gas bubbles in queiscent liquids [25].

Schwartzberg and Treybal (See Appendix A) have published results on studies of average liquid velocities in stirred tanks for similar relative tank and turbine stirrer dimensions as used in this investigation. If the contact times found in this study are used to calculate bubble sizes on the basis of the hydrodynamic variables used, with the help of Schwartzberg and Treybal's results, then we should have another way of obtaining the size of bubbles in an agitated tank.

Data and Results

In this section the data and results obtained are presented. For almost all the experimental runs the data has been taken when two or more experiments yield reproducible results. Wherever titration readings show fractions up to two decimal places, the reading had been obtained by doubling the titre solution and dividing the titration result by the appropriate factor. Wherever there was a close difference in any trial and error procedure and exact reproducibility could not be obtained, the final experimental result was obtained by averaging the results of three experimental runs.

Effect of Agitator Speed and Gas Superficial Velocity on Interfacial Areas

The effect of gas superficial velocity and the speed of the

-40-

1		•
1	1	I
1		ī
1	Ŷ	ā
	Δ	Ĉ
	-	-

Stirred Tank for Different Gas Superficial Velocities and Different Agitator Speeds

peri- ent mber	Gas Super- ficial Vel. V cm/sec	Agitator Speed N revol/sec	Feed Rate of 1 M Caustic to Tank m1/min	GM. Mol CO ₂ Abs. Per Sec Per Ml Liq. x TO ⁶	kLa sec-1 × 10 3	Time of Contact t sec x 10 ²	Interfacial Area a cm ⁻¹	Impeller Reynolds No. Re _i
-285500860-28592860-285 255500855555555555555555555555555555	0.29845 0.59690 0.74613 0.89535 1.19380 0.29845 0.29845 0.29845 0.29845 0.29845 1.19380 0.29845 0.2984	2.500 2.5000 2.5000 2.5000 2.5000 2.5000 2.5000 2.5000 2.50000 2.50000000000	110.0 160.0 160.0 178.0 178.0 245.0 245.0 245.0 245.0 245.0 245.0 275.00	0.1970 0.1568 0.1568 0.1568 0.1807 0.1568 0.1568 0.1763 0.2513 0.2513 0.2513 0.2513 0.2513 0.2513 0.2513 0.2513 0.2515 0.2513 0.2515 0.2733 0.2821 0.2821 0.3615 0.3615	3.2120 4.6700 5.1943 5.9850 7.1535 4.2921 7.1535 6.2758 8.7596 7.7535 8.7596 9.9287 7.7363 9.0506 9.4883 11.9721 11.9721 11.9721 9.3426 11.9721 9.3426 11.9721 9.3426 11.9721 9.3426 11.9721 9.3426 11.9721 9.3426 11.9721 11.972	1.172 2.345 2.345 2.345 2.665 0.842 1.410 2.665 0.842 1.452 1.161 1.722 0.657 0.657 0.641 1.167 1.167 1.167 1.167 1.167 0.639 0.850 0.850	0.1178 0.1178 0.1178 0.1178 0.1807 0.2117 0.2033 0.1495 0.1333 0.1333 0.1333 0.1333 0.1333 0.1495 0.1333 0.1495 0.1333 0.1495 0.15098 0.15098 0.1573 0.1573 0.1573 0.2533 0.1577 0.2533 0.1577 0.2533 0.1560 0.2573 0.2553 0.1577 0.2553 0.2555 0.2553 0.25555 0.2555 0.2555 0.2555 0.25555 0.25555 0.25555 0.25555 0.25555 0.25555 0.25555 0.255555 0.25555555 0.25555555555	25,983 25,983 25,983 25,983 34,644 43,305 43,305 43,305 43,305 43,305 51,967 51,977 51,977 51,9775555555555555555555555555555555555
25	1.19380	5.833	480.0	0.4232	14.0115	1.074	0.2940	60,628

-41-

	Stirred Tan	< for Differe	ent Gas Supert	Ficial Velo	cities an	d Differe	nt Agitato	or Speeds	
Experi- ment Number	Gas Super- ficial Velocity V _S cm/sec	Agitator Speed N revol/sec	Feed Rate of 3M Caustic to Tank ml/min	Gm Mol Gm Mol CO2 Abs. Per Sec. Per Ml. Lia.6 x 10 ⁶	kla sec-1 x 10 ³	~	Time of Contact t sec. x 10 ²	Interfacial Area a cm ⁻¹	Impeller Reynolds No. Re _i
26	0.29845	2.500	135.0	0.1785	6.0739	1.8400	1.172	0.07036	24.515
27	0.59690	2.500	205.0	0.2711	9.2248	1.9226	1.554	0.1178	24,515
28	0.74613	2.500	240.0	0.3174	10.8003	2.0242	2.345	0.1447	24,515
29	0.89535	2.500	275.0	0.3637	12.3758	2.0127	2.230	0.1807	24,515
30	1.19380	2.500	350.0	0.4431	15.0776	2.0510	2.665	0.2117	24,515
31	0.29845	3.333	170.0	0.2248	7.6494	1.7345	0.842	0.0797	32,686
32	0.59690	3.333	240.0	0.3174	10.8003	1.8949	1.410	0.1333	32,686
33	0.74613	3.333	280.0	0.3703	12.6004	1.9540	1.727	0.1495	32,686
34	0.89535	3.333	320.0	0.4232	14.4004	1.9035	1.452	0.1609	32,686
35	1.19380	3.333	390.0	0.5158	17.5514	1.9500	1.722	0.2083	32,686
36	0.29845	4.167	220.0	0.2910	9.9020	1.6505	0.657	0.0957	40,858
37	0.59690	4.167	300.0	0.3968	13.5021	1.8370	1.161	0.1560	40,858
38	0.74613	4.167	340.0	0.4497	15.3022	1.8544	1.228	0.1849	40,858
39	0.89535	4.167	360.0	0.4761	16.2005	1.8945	1.408	0.1998	40,858
40	0.19380	4.167	450.0	0.5952	20.2532	1.9853	1.984	0.2533	40,858
41	0.29845	5.000	290.0	0.3835	13.0495	1.6416	0.641	0.1253	49,030
42	0.59690	5.000	380.0	0.5026	17.1022	1.8387	1.167	0.1977	49,030
43	0.74613	5,000	400.0	0.5291	18.0039	1.8461	1.194	0.2098	49,030
44	0.89535	5.000	435.0	0.5753	19.5760	1.7904	1.001	0.2158	49,030
45	1.19380	5,000	520.0	0.6878	23.4041	1.9026	1.445	0.2911	49,030
46	0.29845	5.833	350.0	0.4629	15.7513	1.6409	0.639	0.1502	57,201
47	0.59690	5.833	440.0	0.5820	19.8040	1.7373	0.850	0.2069	57,201
48	0.74613	5.833	470.0	0.6216	25.1515	1.7195	0.804	0.2157	57,201
49	0.89535	5.833	510.0	0.6746	22.9549	1.7590	0.907	0.2448	57,201
50	1.19380	5.833	580.0	0.7671	26.1025	1.8126	1.074	0.2940	57,201

TABLE II

h4
н
ш
ш
_
В
4
1

Stirred Tank for Different Gas Superficial Velocities and Different Agitator Speeds

Impeller Reynolds No. Re _i	19,633 19,633 19,633 19,633 26,168 26,168 26,168 26,168 26,168 26,168 32,722 32,722 32,722 332,722 332,722 339,267 340,275 340	
Inter- facial Area a cm ⁻ l	0.03425 0.05338 0.06105 0.06874 0.08805 0.08805 0.05723 0.05723 0.05723 0.0550 0.06492 0.06492 0.06492 0.08805 0.09970 0.09970 0.09970 0.09970 0.09970 0.09970 0.09970 0.09970 0.09970 0.09970 0.09970	
Av. Conc. of Caustic in Tank C _B av Gm. mol/1	487 487 487 487 487 475 475 475 475 475 475 475 475 475 47	
kla sec - x 10 ³	22.1403 34.4424 39.3643 44.2809 56.5829 56.5829 49.2809 49.2809 49.2826 66.4213 34.4424 49.2027 54.1246 66.4213 34.4424 49.2027 54.1246 66.4213 34.4424 49.2027 54.1246 66.4213 34.4424 49.2027 54.1246 66.4213 34.4424 49.2027 54.1246 66.5829 63.9630 71.3432 81.1870	
Gm Mol CO ₂ Abs. Per Sec. Per Ml X 10 ⁶	0.4152 0.6459 0.6459 0.8304 1.0611 0.8304 0.8304 0.8304 0.8304 0.8304 0.8304 0.8227 1.1534 0.9227 1.1995 0.7843 0.7843 1.1995 1.3379 0.7843 1.1995 1.1995 1.1995 1.1995 1.2918 1.5225	
Titre* of Caustic at Time 30 Sec. Ml	53.55 53.55 53.30 53.30 53.30 53.10 53.30 53.30 53.30 52.55 53.30 52.35 53.30 52.35 53.30 52.35 53.30 52.35 53.30 52.35 53.30 52.35 53.30 52.35 53.30 52.35 53.30 52.35 53.30 52.35 53.30 52.35 53.30 52.35 53.30 52.35 53.30 52.35 53.30 52.35 53.30 52.35 53.30 52.35 53.30 52.35 53.300	
Titre* of Caustic at Time O Sec. Ml	54.0 54.0 54.0 54.0 54.0 54.0 54.0 54.0	
Agitator Speed N revol/sec	2.500 2.500 2.500 2.500 2.500 3.333 5.0000 5.00000 5.00000 5.00000 5.00000000	
Gas Super- ficial Vel. V _s cm/se <u>c</u>	0.29845 0.59690 0.74613 0.89535 0.89535 1.19380 0.29845 0.2984	
Experi- ment Number	51 53 55 55 55 55 55 56 57 77 77 75 75 77 75 75 75 75 75 75 75	

* Titre is M1 of 0.03471 M HC1 necessary to titrate 50 M1 of reactor solution diluted 40 times.

-43-

F	-
ц	ļ
a	j
μ	-

Stirred Tank for Different Gas Superficial Velocities and Different Agitator Speeds

oeller /nolds . Re _i	066 066 066 066 066 066 066 066 066 066
N N N	44644555555555555555555555555555555555
Inter- facial Area a cm-1	0.02568 0.04026 0.04868 0.05735 0.05735 0.05735 0.05156 0.06315 0.06315 0.06893 0.05735 0.06893 0.05735 0.06893 0.05735 0.06893 0.05735 0.05735 0.05735 0.05735 0.07766 0.08367 0.08228
in of I	666666666666666666666666666666666666666
Av. Conc Caustic Tank C _B Gm. mol/	$0.9875 \\ 0.9875 \\ 0.9875 \\ 0.986 \\ 0.986 \\ 0.986 \\ 0.986 \\ 0.986 \\ 0.986 \\ 0.986 \\ 0.986 \\ 0.986 \\ 0.979 \\ 0.978 \\ 0.976 \\ 0.976 \\ 0.970 \\ 0.976 \\ 0.970 \\ 0.970 \\ 0.970 \\ 0.971 \\ 0.970 \\ 0.970 \\ 0.970 \\ 0.970 \\ 0.970 \\ 0.970 \\ 0.970 \\ 0.970 \\ 0.970 \\ 0.970 \\ 0.971 \\ 0.970 \\ 0$
k ^L a-1 sec-1 x 10 ³	12.2175 19.0051 23.0776 27.1501 35.2951 14.9322 21.7201 24.4351 29.8651 38.0102 16.2900 24.4351 27.1501 32.5801 32.5801 32.5801 32.5801 33.5801 35.580
Gm Mol CO ₂ Abs. Per Sec. Per Ml x 10 ⁶	0.2682 0.4172 0.5966 0.5966 0.5966 0.3277 0.37748 0.5364 0.3576 0.5566 0.3576 0.5566 0.5566 0.4768 0.5566 0.4768 0.5566 0.4768 0.5752 0.8642 0.8642 0.8642 0.8642 0.8642 0.9536 1.0132 0.8642 0.8642 0.8642 0.9536
itre* of austic at ime 30 ec. M1	55.45 55.20 55.20 55.20 55.05 55.05 55.00 55.35 54.40 54.40 54.45 54.45 54.45 54.45 54.45 54.45 54.45 54.45 54.45 54.45 54.45 54.45 54.45 54.45 54.45
4 0	
Titre* o Caustic at Time Sec. M1	
Agitator Speed N revol/sec	2.500 2.500 2.500 2.500 3.333 3.333 3.333 3.333 3.333 3.333 3.333 3.333 3.333 3.333 3.333 3.333 3.333 3.333 4.167 5.000 5.000 5.000 5.833 5.000 5.833 5.835 5.833 5.835 5.833 5.8355 5.8355 5.8555 5.85555 5.85555555555
Gas Super- ficial Vel. V _s cm/sec	0.29845 0.59690 0.74613 0.89535 1.19380 0.29845 0.298535 0.29845 0.298535 0.299555 0.29955555555555555555555555555555555555
Experi- ment Number	76 77 77 78 88 88 88 88 88 89 90 92 92 93 93 93 94 94 95 95 94 95 95 94 95 95 95 95 96 97 97 97 97 97 97 97 97 97 97 97 97 97

* Titre is M1 of 0.02235 M HC1 necessary to titrate 50 M1 of reactor solution diluted 40 times.

TABLE V

Predicted Bubble Diameters for Different

Agitator Speeds and Gas Superficial Velocities

Agitator Speed N Revol/Sec	Gas Super- ficial Velocity V _s cm/sec	Predicted Time of Contact from Equation (52) t x 10 ² sec	Predicted Bubble Diameter d cm
2.500 2.500 2.500 2.500 2.500 2.500	0.29845 0.29690 0.74613 0.98535 1.19380	2.095 2.430 2.543 2.640 2.795	0.282 0.327 0.342 0.356 0.376
3.333 3.333 3.333 3.333 3.333 3.333	0.29845 0.59690 0.74613 0.89535 1.19380	1.295 1.490 1.555 1.610 1.710	0.230 0.264 0.276 0.286 0.303
4.167 4.167 4.167 4.167 4.167	0.29845 0.59690 0.74613 0.89535 1.19380	1.000 1.152 1.203 1.250 1.325	0.222 0.256 0.267 0.278 0.294
5.000 5.000 5.000 5.000 5.000 5.000	0.29845 0.59690 0.74613 0.89535 1.19380	0.648 0.745 0.777 0.807 0.857	0.173 0.199 0.208 0.216 0.229
5.833 5.833 5.833 5.833 5.833 5.833	0.29845 0.59690 0.74613 0.89535 1.19380	0.497 0.572 0.597 0.620 0.657	0.154 0.178 0.186 0.193 0.204

agitator is presented in Figures 6, 7 and 8 for absorption of carbon dioxide in 0.085 M, 1.0 M, and 1.5 M caustic respectively. The number of revolutions per minute range from 150 to 350 and the gas superficial velocities used from 0.29845 centimeters per second to 1.1938 centimeters per second. The data for these figures are obtained from Tables II, III and IV.

Effect of Agitator Speed and Gas Superficial Velocities on Contact Time

The effect of the agitator speed and the gas superficial velocities on the time of contact between gas particles and the liquid elements is presented in Figure 9. The range of values used for these two variables is the same as in the case of interfacial areas listed above. These data are obtained from Table I or Table II.

Correlation for Interfacial Areas

The interfacial areas obtained can be correlated on the basis of the equations given by Calderbank [8]. The interfacial areas can be correlated on the basis of the following equation

$$a = A(\frac{N^{3}D^{5}}{g_{c}T^{2}H})^{0.4} (\frac{\rho_{L}}{\sigma})^{0.6} (\frac{V_{s}}{V_{t}})^{0.5}$$
(52)

where D is the agitator diameter, N is the agitator speed in

revolutions per second, T is the tank diameter, H is the height of the liquid in tank, ρ_L is the liquid density, σ is the interfacial tension, V_s and V_t are the gas superficial and terminal velocities, respectively, g_c is the gravitational constant and is equal to one in the cgs system, and A is a dimensionless constant.

The value of the dimensionless constant A varies in the case of absorption with the different solutions and are found to be 1.57, 0.554, and 0.658 for 0.085 M, 1.0 M and 1.5 M caustic solutions, respectively.

Figures 10, 11, and 12 represent the plots of interfacial areas against the term representing all the variables on the righthand side of equation (52). The mean percentage deviation in the scatter of the data is less then eleven percent in all the three cases.

Correlation for Time of Contact

The gas-liquid time of contact can be correlated by the equation

$$t = c \frac{g_{c}^{0.24}}{D^{3.2}} \left(\frac{\sigma}{\rho_{L}}\right)^{0.36} \left(\frac{T^{2}H}{N^{3}}\right)^{0.573} \left(\frac{V_{s}}{V_{t}}\right)^{0.2} \left(\frac{\mu_{d}}{\mu_{c}}\right)^{0.5}$$
(53)

The equation is based on turbulence theory (see Appendix A). The value of the constant C is found to be 8.89 centimeter $^{0.4}$ by fitting the data using the method of least squares.

Figure 13 represents the plots of the time of contact against the term representing the variables on the right-hand side of equation (53).

Predicted Bubble Diameters

Table V and Figure 14 show the predicted bubble diameters as a function of agitator speeds and gas superficial velocities. The bubble diameters are obtained by using the correlation represented by equation (53) or Figure 13 for the time of contact and equation (A-7) or Figure 15 (see Appendix A) given by Schwartzberg and Treybal.

For the range of values of agitator speeds and gas superficial velocities, the predicted bubble diameters range from 0.376 centimeter to 0.154 centimeter, which are of the same order of magnitude as bubble diameters found by other techniques by other workers.



-49-



FIGURE 7. EFFECT OF IMPELLER TIP SPEED AND SUPERFICIAL GAS VELOCITY ON INTERFACIAL AREAS IN 1.0 M CAUSTIC SOLUTION



GURE 8. EFFECT OF IMPELLER TIP SPEED AND SUPERFICIAL GAS VELOCITY ON INTERFACIAL AREAS IN 1.5 M CAUSTIC SOLUTION

-51-



EFFECT OF IMPELLER TIP SPEED AND GAS SUPERFICIAL VELOCITY ON THE TIME OF CONTACT BETWEEN GAS-LIQUID PARTICLES



-53-



FIGURE 11. CORRELATION OF INTERFACIAL AREAS IN 1.0 M CAUSTIC SOLUTION



FIGURE 12. CORRELATION OF INTERFACIAL AREAS IN 1.5 M CAUSTIC SOLUTIONS



FIGURE 13. CORRELATION OF GAS-LIQUID CONTACT TIME



FIGURE 14. LOG-LOG PLOT OF PREDICTED BUBBLE DIAMETER VERSUS IMPELLER TIP SPEED FOR DIFFERENT GAS SUPERFICIAL VELOCITIES

IV. DISCUSSION

In this section of the dissertation, a critical discussion of the procedure used in this investigation, a discussion of the results obtained, and the relevancy of the correlations obtained will be presented.

Discussion of Procedure

Some Comments on the CO₂-NaOH System

The reaction in the liquid phase is second-order and the absorption rate is capable of falling in the different reaction regimes, depending on the actual conditions. When the conditions described by the following two equations exist, viz.

$$\gamma = (k_2 c_B D_A)^{1/2} / k_L \ge 5$$
 (54)

and

$$1 < (\pi/4 k_2 c_B t)^{1/2} < \sqrt{\frac{D_A}{D_B}} + \frac{c_B}{z c_A^*} \sqrt{\frac{D_B}{D_A}}$$
 (55)

the absorption rate is time independent. This exists when the hydroxide concentration is sufficiently high, and/or the temperature of reaction sufficiently high to give a high reaction rate, and/or for long contact times. The rate of absorption is then given by equation (50).

The reaction can become infinitely fast under certain conditions. This is approached when the following constraint is met with

$$(\pi/4 \ k_2 c_B t)^{1/2} >> \sqrt{\frac{D_A}{D_B}} + \frac{c_B}{z c_A^*} \sqrt{\frac{D_B}{D_A}}$$
(56)

and the reaction rate is given by [72]

$$N_{A} = c_{A}^{*} k_{L} \left(\sqrt{\frac{D_{A}}{D_{B}}} + \frac{c_{B}}{zc_{A}^{*}} \sqrt{\frac{D_{B}}{D_{A}}} \right)$$
(57)

Here the rate is solely dependent on the hydrodynamic conditions around the gas bubbles and this occurs when the reaction is very fast, the contact time very long, or the concentration of reactant small. Higher reaction temperatures tend to give this situation in the particular system that is used in this investigation.

We shall see in the next part of the discussion how the above situations are avoided or made use of in this investigation.

A great disadvantage is the high solubility of carbon dioxide, which gives us high reaction rates. Since the reaction is exothermic, the temperature rise of the system becomes a factor to be taken into account. This difficulty is avoided in this investigation by conducting the absorption for short periods of time, so that the temperature change is negligible.

Resistance to mass transfer in the gas phase can become a factor in this investigation if the gas absorbed is mixed with inerts. Besides this problem, is the problem related to gas hold up and the amount of back-mixing of the gas phase produced in the

-59-

stirred tank. Various investigators have analyzed this problem, but definite conclusions still cannot be drawn as to the degree of this back-mixing. In the absence of definite knowledge of this problem of back-mixing in the reactor, the estimation of the value of the carbon dioxide partial pressure in a mixture with an inert component would be quite a dubious proposition. The problem has been avoided in this investigation by the use of undiluted carbon dioxide as the gas phase.

Another phenomenon associated with this system is the change in viscosity with the liquid phase as the concentration of hydroxide or electrolyte changes. For strong solutions of sodium hydroxide, the presumption of hydrodynamic similarity with much weaker electrolyte solutions associated with this reaction becomes a highly dubious proposition. Also, it has been observed that gas bubble diameters are very much dependent on viscosity of the medium they are suspended in.

Experimental Plan

One of the objectives in this investigation is the evaluation of the gas-liquid contact times as a function of the variables that could be encountered in contacting equipment of the type used here. It has already been seen that, when the hydroxide concentration is high and the rate of reaction is fast, the absorption rate can become time independent.

Since the evaluation of contact times is one of the objectives,

-60-

a set of the experiments were conducted with solutions having low hydroxide concentrations. Also, as it is not possible to evaluate contact time independently by itself for each experiment, it was found necessary to conduct another experiment using the same conditions, except that the concentration of the hydroxide in this case is 0, and we consequently have the case of physical absorption. The ratio R of the case with chemical reaction to that without reaction would then be a function of contact time, and if this ratio is known the time of contact can be evaluated.

There is, however, an exception to the above proposition, viz. if the reaction proceeds at a very fast speed or if the contact time is very large, then we have the case of instantaneous reaction, where the rate of absorption is solely determined by the hydrodynamics around the gas bubble as can be seen from equation (57). Then the ratio R becomes independent of contact time, which means that at high reaction rates the value of this ratio approaches an asymptotic value. This would make it impossible to evaluate contact time as

$$R = \sqrt{\frac{D_A}{D_B}} + \frac{c_B}{zc_A^*} \sqrt{\frac{D_B}{D_A}}$$
(58)

To avoid this case of instantaneous reaction, the temperature at which absorption is conducted is kept sufficiently low.

The problem of dynamic similarity in the case of the absorption into 0.085 M hydroxide and water should not occur since the

-61-

viscosity change involved in the two cases is of the order of 4 percent. The Marangoni effect should be a very negligible effect because of two considerations. The change in surface tension is of the order of 1 percent and also the system as a whole is very vigorougly agitated to eliminate what little effect it may have.

In the case of the absorption experiments with the more concentrated hydroxide solutions, there is a great change in the hydrodynamic conditions. The viscosity changes are quite significant. The concept of dynamic similarity with absorption in water cannot be assumed. However, if the values of the contact time of the order of the values of those found in the case of the experiments with 0.085 M hydroxide are substituted into equations (54) and (55), we find that the absorption rate falls into the regime where it is independent of the time of contact. Thus, the interfacial areas can be evaluated directly.

Discussion of Special Technique for Measuring Rates of Absorption

When a gas diffuses into a liquid with which it reacts, the temperature in the neighborhood of the surface will tend to rise because of the phenomenon analogous to condensation which takes place with respect to the gas. This rise in temperature is enhanced if the subsequent reaction that takes place in the liquid phase is exothermic in nature. If this rise in temperature is large enough, it will effect the rate of absorption since solubility, diffusivity and reaction rate of the gas change with temperature.

-62-
To keep constant temperature conditions in the system under investigation, the absorption reaction is conducted for a short enough period so that the temperature change in the reactor is negligible. Yet, the time must be sufficient enough for the gas to establish a uniform pattern of bubbles in the agitated solution and also to allow a sufficient amount of absorption to measure the rate of absorption after the uniform pattern is established.

In general, the temperature changes associated with the absorption in this investigation were of the order of less than 1/2 a degree Centigrade. By trial and error methods, this change had always been divided evenly around the temperature of 25°C, so that the absorption could be assumed to take place at an average temperature of 25°C.

Use of Subsidiary Data

The subsidiary data used in this investigation include the values of the reaction rate constants, diffusivities of carbon dioxide and hydroxide ion, the saturation concentration of carbon dioxide in water and electrolyte solutions, the surface tension and viscosity of hydroxide solutions, and the terminal velocities of the gas bubbles.

The values of the specific rate constant for the reaction between carbon dioxide and sodium hydroxide have been obtained by many workers with slight variations. In this investigation the values obtained by Pinsent, Pearson and Roughton [48] have been

-63-

used for reaction in infinitely dilute solutions. For the effect of ionic strength on reaction rate constants, equation (30) with the appropriate value of the constant has been used.

The value of the diffusivity for carbon dioxide in water given by Davidson and Cullen [13] has been adopted as being the most reliable. For diffusivity of carbon dioxide in alkali solutions, the values have been estimated by using the Nernst-Einstein equation for the estimation of diffusivity through viscosity measurements. The viscosity of the solutions involved was measured by the use of an Oswald Viscometer.

The effective diffusivity of hydroxyl ions used in this investigation is the value reported by Danckwerts, et al [18]. The value of 2.3 x 10^{-5} centimeter square per second has been adopted. Rehm, et al [51] used values between 2.0 x 10^{-5} to 3.0 x 10^{-5} centimeter square per second and found that the calculated rates of absorption were relatively insensitive in this range.

The International Critical Tables gives values of the surface tension of sodium hydroxide solutions at a temperature of 18°C. The values at 25°C used in this investigation are computed by taking the available value at 25° and drawing a parallel line to the line giving the value of surface tension at 18° as a function of concentration.

The terminal gas bubble velocity has been used in the correlations obtained. The value of the terminal velocity used in

-64-

all these cases is 26.5 centimeters per second, which value has been sutstantiated by various investigators for the bubble sizes encountered in this investigation [24].

Discussion of Results

In this section, a discussion of the pertinent results and correlations, the development of the correlations and some general comments on the methods and results of some previous investigators will be dealt with.

Method of Approach Used by Previous Investigators

Most previous workers in this area have evaluated interfacial areas in agitated systems using direct methods of measurement. The direct measurement methods include optical transmittance methods, [8,9,65] optical reflecting and x-ray transmittance, [9] which all give point values. Other direct methods include hold-up and bubble diameter measurements from which interfacial areas can be computed.

The basic weakness in these methods is that the direct determinations give local point-values, which, as has been pointed out by many investigators, vary from point to point in any agitated systems. The evaluation of "average" or representative interfacial values become subject to the number of observations and the actual location of point values. Calderbank [8] has shown that local values of interfacial areas, diameter, and hold-up vary according to radial distance and axial position.

-65-

Another serious limitation of the direct methods is that these methods do not give the actual measure of the "effective" interfacial area, but give an interfacial area based on perfectly round bubbles.

It can easily be seen that the effective interfacial area in an agitated system is dependent on the degree of coalescence of the gas bubbles. Also, in a force field the effective interfacial area is significantly dependent on the axial distortion that the bubbles undergo; that is, the elongation of diameter in one axis as compared to the elongation in the other axis. Areas computed on the basis of diameter of the bubbles generally have the implicit assumption of perfect roundness of the bubbles. Further, the damping effect because of surface tension, density, viscosity differences would contribute some significant changes in effective interfacial areas.

Finally, in most gas-liquid systems the question of the presence of surfactant films in the interface bears some relation to the overall rate of transfer because of either the enhancing or hindering effect. If the presence of these surfactants is viewed as something that reduces the available interfacial area through which transfer does not take place, then the direct method of computing interfacial areas would not give the "effective" interfacial area in any particular gas-liquid system.

From the foregoing observations, it can be seen that the evaluation of effective interfacial areas in gas-liquid agitated

-66-

systems may be more effectively done by the use of chemical methods. Chemical method of evaluation of gas-liquid effective interfacial areas has apparently been resorted to by only two investigators [66,68].

Evaluation of Interfacial Areas and Contact Times by Chemical Methods

..

The application of an absorption model to a known rate of absorption in a particular gas-liquid system gives us the values of the parameters in the model for the system that is being investigated. Thus, the application of the penetration theory to the absorption rates gives the values of the interfacial areas and the contact times.

One common feature in the work of the previous investigators, who used chemical methods of evaluation of interfacial areas, is that they did not evaluate the contact times in the systems they used, and, consequently give no idea of the type of contact times encountered in agitated gas-liquid systems with respect to the variables in these systems. They essentially made the assumption that the regime of absorption which they encounter with their conditions is in the region of absorption which is time independent. This is generally a valid procedure if the concentrations of the hydroxide used in the carbon dioxide-sodium hydroxide system is sufficiently high to prevent depletion of the reactant around the interface and pseudo-first order reaction rate can be assumed. The real difficulty arises when the concentrations involved are not sufficiently high and contact times are relatively long so that depletion of reactant at the interface may be sufficient to put the rate in a time dependent regime.

Besides avoiding a possible error in the method of evaluation of interfacial areas, the evaluation of contact times in any gasliquid work would most likely serve the useful purpose of providing estimates of contact times in terms of variables encountered for comparable hydrodynamic situations. This would make it possible to predict absorption rates in other chemical systems, particularly those where the kinetic rate of reaction is slower so as to make the absorption process time dependent.

Yoshida and Miura [68] who give values of interfacial areas for their work used diluted carbon dioxide in air (1 to 14 percent) as their reacting gas, but did not indicate what type of carbon dioxide partial pressures were used in the calculation of their results. As pointed out earlier, the question of back-mixing of gas in a stirred tank can assume significant dimensions. Danckwerts [16] has shown that, in contrast to the use of log mean values on the basis of inlet and outlet concentrations or the use of outlet concentration values, the use of inlet partial pressure values can be more correct in certain situations.

Westerterp et al [66] performed their work under unspecified conditions of concentration. They did not evaluate contact times, but stated that they made sure that the values of β were greater

-68-

than 2. But if the values are not very much higher than 2, the assumption of time independent reaction rates would be invalid since the concentrations of hydroxide involved would not be high enough to prevent depletion of reactant. With their experiments using the sodium sulfite-oxygen absorption system, Reith [52] considers that the results of Westerterp et al are probably invalidated by misconceptions about the kinetics of sulfite-oxidation reaction used by these workers.

Correlations for Interfacial Areas

On the basis of Hinze's equations (see Appendix A), Calderbank [8] developed correlations to correlate his results on interfacial areas in gas-liquid systems in stirred tanks and sieve plate columns. The interfacial areas obtained through optical methods and x-ray transmittances correlated well with the equation he used:

a = (const)
$$\frac{(P/V)^{0.4} \rho_L^{0.2}}{\sigma^{0.6}} (\frac{V_s}{V_t})^{0.5}$$
 (59)

where the terms have been defined in Appendix A.

This equation is not in a very strict sense correct, since it would give zero specific area at zero impeller speed. A term such as $f(V_s/V_t)^{1/2}$ should be added for the sake of completeness, though this would be unimportant in almost all other cases. The term $(V_s/V_t)^{1/2}$ was added to Hinze's equation in order to account for the influence of the gas flow. Equation (59) is found to be valid for

$$\operatorname{Re}_{i}^{0.7} \times \left(\frac{\mathrm{ND}}{\mathrm{V}_{\mathrm{S}}}\right)^{0.3} < 20,000$$
 (60)

where Re_i is the impeller Reynolds number.

If we substitute the equation for the power input for a turbine impeller (see Appendix A), which is given as

$$P/V = c_1 \frac{\rho_f N^3 D^5}{g_c T^2 H}$$
 (61)

into equation (59), we obtain the following equation in terms of impeller and tank dimensions, fluid properties, and gas superficial velocities for the interfacial area.

$$a = A(\frac{N^{3}D^{5}}{g_{c}T^{2}H})^{0.4} (\frac{\rho_{L}}{\sigma})^{0.6} (\frac{V_{s}}{V_{t}})^{0.5}$$
(62)

As shown by Figures 6, 7, and 8 the interfacial areas are dependent on the degree of agitation and the gas input rate. The interfacial areas obtained in this investigation correlate well with the correlation as represented by equation (62) as can be seen from Figures 10, 11, and 12. The mean deviation of the interfacial areas obtained about the best line through the points by the method of least squares in the three different concentration solutions is less than 12 percent in each case.

The values of the constant A were obtained from equation (62)

for the three different sodium hydroxide concentration solutions, viz. the solutions of caustic strength 0.085 N, 1.0 N, and 1.5 N are 1.57, 0.554, and 0.66, respectively. The values for these constants suggest that for the same impeller speed and gassuperficial velocities, the value of interfacial area is greater in the 0.085 N solution by approximately 1.5 times the value in the more concentrated solutions. The value of the interfacial area in 1.5 N alkali solutions is about 1.2 times the value in the 1.0 N concentrated solution.

It is clear from this that more factors than one are responsible for this wide variation of interfacial areas in the three solutions.

One possible factor that may have a significant effect on the results is the change of surface tension encountered in higher concentration solutions as reactions proceed around the interface. The rate of reaction in the concentrated solutions is anywhere from 5 to 9 times that in 0.085 N sodium hydroxide solutions. It follows from this that there would be relatively greater differences in the species concentration around the interface in the two cases. The surface tension values of sodium hydroxide solutions and sodium carbonate solutions are different from one another, though not very greatly. But the resulting instabilities because of surface tension differences may be enough in the case of the more concentrated solutions to have a higher coalescence rate. A high degree of coalescence and break-up of gas-bubbles tend to give smaller effective

-71-

interfacial areas.

Another possible factor, which may have a significant effect on the results presented here is the effect of surfactants that may be present in the distilled water used. It is easy to visualize the presence of traces of surfactants picked up either as original high-molecular liquids present in the undistilled water or as contaminants present in the reaction vessel and other reagents used.

The presence of surfactant material in the system may be viewed to affect the rate of mass transfer in many ways; it may decrease the rate of change of surface tension with the concentration of diffusing species or it may form a rigid film on the surface and act as a diffusive barrier, interposing as a resistance to transfer. If this diffusive barrier is present only in a limited amount on the interface, that portion of the interface may have a smaller rate of transfer taking place across it. This may be looked on as a reduction in effective interfacial area in the Thompson [62] studied the effect of surfactants on differsystem. ent reagent systems. In the case of the absorption of carbon dioxide in water, he found no reduction in rates of absorption when he introduced surfactants in his system, but in the case of absorption of this gas into 2 N alkali solutions there was a considerable decrease in rates of transfer when surfactant was introduced.

It has been noticed by previous investigators [66] that the bubble sizes in viscous solutions get smaller as the viscosity

-72-

increases. The viscosity differences in the solutions involved in this investigation are quite significant. The change of viscosity is of the order of 30 percent in going from the lowest concentration solution to the highest.

It follows from this that in the case of 1.0 N and 1.5 N alkali solutions, the approximately 25 percent change encountered in the interfacial areas could be explained partially on this basis. If the hold-up of the gas in the reactor does not change, a change in bubble diameter by 10 percent would produce a change of about 10 percent in interfacial areas.

There may well be other factors such as the greater damping effect with more viscous solutions which may tend to give smaller interfacial areas; the greater amount of distortion that takes place in relatively larger bubbles. Li et al [37] showed that if the bubbles rising in liquids are considered to be oblate spheroids, the surface area of these spheroids could be calculated to be greater by as much as 12 percent depending on the degree of deformation.

Reith [52] claims that the interfacial areas he obtained in pure water (which he measured by a photographic technique) are 1 1/2 to 3 times smaller than those obtained in 0.8 M sodium sulphite solutions. He discusses the possibility that every solution will behave differently; if so, experiments designed to give data for scaling-up should be performed with the actual solutions of interest.

-73-

Correlation for Time of Contact

The times of contact obtained for the range of variables used in this investigation is shown in Figure 9. The contact times generally lie between 0.6×10^{-2} seconds to 2.7×10^{-2} seconds, for impeller tip speeds ranging from 24 centimeters per second to impeller tip speeds of 56 centimeters per second and superficial gas velocities in the range of 0.3 to 1.2 centimeters per second.

The contact times correlate well with the following equation as derived in Appendix A.

$$t = C(\frac{\sigma}{\rho_c})^{0.36} (\frac{T^2 H}{N^3})^{0.573} \frac{g_c^{0.24}}{D^{3.2}} (\frac{V_s}{V_t})^{0.2} (\frac{\mu_d}{\mu_c})^{0.25}$$
(63)

where the terms in equation (63) have been defined in Appendix A.

The mean deviation for the contact times about the best fit for the line drawn in Figure 13 is of the order of 20 percent. This is a fairly good fit, considering the fact that two experiments had to be performed for each set of variables to get the ratio R and also considering the fact that t is very sensitive for any variation in the ratio R, which is obtained by trial and error procedure mentioned earlier.

Predicted Bubble Diameters

The predicted bubble diameters for the various superficial gas velocities and impeller tip speeds used range from 0.15

centimeters to about 0.38 centimeters. These values are typical values encountered in gas-liquid agitated systems.

These predicted values make use of the contact times obtained here and the results of Schwartzberg and Treybal who calculated average liquid velocity as represented by equation (A-7) in Appendix A.

The use of contact time in predicting bubble diameters may have advantages over the method making use of interfacial areas and gas hold-up. If part of the interfacial surface is not available for transfer (as is the case when it is partially covered by a diffusive barrier) the interfacial area obtained may be lower than the total bubble surface. This would tend to give greater bubble diameters.

The method using contact times does not have to take the interfacial area into direct consideration. The only assumption that is made here is that the equation

$$t = \frac{d}{U}$$
(64)

given in Appendix A is valid for the computation of contact times.

Equation (64) has been shown to be valid by Hammerton and Garner [25] who studied transfer from rising bubbles in pure water. A similar approach has been successfully used for predicting mass transfer rates during drop formation at a capillary tip by Groothius and Kramers [23].

-75-

The values of the average velocities obtained by Schwartzberg and Treybal were for similar equipment as used in this investigation. The only difference is in the position of the impeller from the bottom of the tank; the position used by the above mentioned workers being about 0.17 of the tank diameter from the bottom. But then if the average velocity in the tank and the power number for the impeller is only dependent on power input and impeller Reynolds number in the system, then the velocities should not be different in the two cases.

Comparison of Results Obtained on Interfacial Areas

As shown by equation (62), the interfacial areas obtained in this investigation show a dependency with respect to impeller tip speeds and gas superficial velocities in the following manner.

$$a \propto N^{1.2} V_s^{0.5}$$
 (65)

The exponents obtained for N and V_s , respectively by Calderbank [8] using direct methods are the same as in equation (65). Yoshida and Miura, using vaned-disc impellers have exponents in the range 0.33 to 0.66 and 0.9 to 0.7 for V_s and N, respectively, while for turbine impellers they obtained exponents of 0.74 and 1.1, respectively. Preen [50] using paddle impellers obtained an exponent of 0.6 for V_s , while Quigley [60] using an unspecified impeller, obtained an exponent 0.715 for V_s . Van Krevelen [60] also using an unspecified impeller obtained an exponent of 0.4 for $\rm V_{S}$. Westerterp does not think that interfacial areas are dependent on $\rm V_{S}$.

It can be seen that the exponents obtained here agree with those of Calderbank's correlation and vary a little with those found by other investigators.

Recommendations

This section contains the recommendations for further studies related to this investigation.

<u>Agitation and Gas Input Range.</u> The investigation conducted shows validity of correlations given in the range of the variables used. To test the correlations further, it is recommended that the agitation rates be substantially increased and the gas superficial velocities be increased further.

Effect of Solute. At this point the effect of solute on the interfacial areas is not very clear. It is possible that different solutes and different solute properties have different effects on the interface. Though Calderbank's correlation for interfacial area has been found to be valid within each solute concentration, it has not been possible to correlate all interfacial areas within the different concentrations in one correlation. It can clearly be inferred from this that some other unknown factors have some effects on the interface.

<u>Effect of the Type of Impellers.</u> Though the validity of the correlations submitted for interfacial areas and times of contact

-77-

has been experimentally verified only for a six-bladed turbine impeller in a fully baffled tank, it appears from the nature of the correlations derived or submitted that these correlations should well be applicable over turbulent range for all agitated systems in which power number is a constant, that is, independent of the impeller Reynolds number. However, it is recommended that more work be conducted using different agitated systems.

Limitations

This investigation was conducted under the following limitations.

1. The rate of transfer was studied in four sets of reacting solutions, viz. 0, 0.085 M, 1.0 M and 1.5 M caustic solutions.

2. Five gas superficial velocities ranging from 0.298 centimeter per second to 1.19 centimeters per second were used.

3. Five agitator speeds ranging from 150 revolutions per minute to 350 revolutions per minute were used.

V. CONCLUSIONS

The determination of interfacial areas and effective contact times for a stirred tank at gas superficial velocities in the range of 0.29 to 1.19 centimeters per second and agitation speeds in the range of 150 to 350 revolutions per minute and 4 concentrations of caustic solutions in the range of 0 to 1.5 molar strengths yielded the following conclusions.

 The interfacial areas depend on agitation intensities and gas superficial velocities.

 The effective time of contact depends on agitation intensities and gas superficial velocities.

3. It is possible to correlate the effective time of contact in a stirred reactor using fluid energy dissipation equation in turbulent regions and using the Kolmogoroff energy distribution law.

4. It is possible to correlate interfacial areas in terms of energy dissipation in the system and gas superficial velocities.

5. There are effects of a solute which are still not known on the interfacial areas.

VI. SUMMARY

The purpose of this investigation was the application of the penetration theory model to gas absorption with chemical reaction in a stirred tank reactor and the evaluation of the parameters of the penetration model, viz. the gas-liquid interfacial area and the contact time between the gas bubbles and liquid elements, for the different agitation intensities and gas rates in the reactor.

The values of these parameters for the model were determined by measuring the rates of absorption of carbon dioxide into aqueous solutions and forcing the model to give values of the parameters consistent with observed rates of absorption.

The contact times and interfacial areas were determined for five agitation rates ranging from 150 revolutions of the agitator to 350 and for five gas input rates ranging from superficial gas velocities of 0.29 centimeter per second to about 1.2 centimeters per second. Model parameters were evaluated for three different caustic strength solutions.

The values of the interfacial areas show that for the same conditions of agitation and gas flow in the reactor the value of the interfacial areas are highest for the lowest caustic concentration and fall as the concentration of caustic increases until it reaches a minimum value and then rises again with increasing concentration. These results, together with the work of another investigator, suggest that, for design and scale-up purposes for

-80-

gas absorption in solutions, experiments should be set up with the solutions of actual interest.

The interfacial areas obtained correlate well with the correlation given by Calderbank, which is based on the work of Hinze on bubble sizes in turbulent regimes.

The gas-liquid particle contact times are found to be dependent on the intensity of agitation and the gas rates. A correlation based on the theory of isotropic turbulence has been proposed and found to correlate the data well.

VII. BIBLIOGRAPHY

- Astarita G., Mass Transfer with Chemical Reaction, Elsev. Pub. (1967).
- Bakowski S.G., Zhur. Priklad, Zhim., <u>39</u>, 29 (1956); Coulson J.M., Richardson J.F., Chemical Engineering, MacMillan Co., N.Y.(1964).
- Bartholomew W.H., Karow E.O., Sfat M.R., Oxygen Transfer and Agitation in Submerged Fermentations, Ind. Eng. Chem., <u>42</u>, 1801-09 (1950).
- Batchelor, G.K., The Theory of Homogeneous Turbulence, p. 103, Cambridge University Press (1963).
- 5. Bieber A.L., Private Communications, May 1970.
- Bird R.B., Stewart W.E., Lightfoot E.N., Transport Phenomena,
 J. Wiley Inc., N.Y. (1960).
- 7. Brian P.L.T., Hurley J.F., Hasseltine E.H., Penetration Theory for Gas Absorption Accompanied by a Second Order Chemical Reaction, A.I.Ch.E.J., <u>7</u>, 226-231 (1961).
- Calderbank P.H., Physical Rate Processes in Industrial Fermentation, Part I, Trans. Inst. Chem. Engr., <u>36</u>, 443-459 (1958).
- Calderbank P.H., Physical Rate Processes in Industrial Fermentation, Part II, Trans. Inst. Chem. Engr., <u>37</u>, 173-185 (1959).
- 10. Calderbank P.H., Moo-Young M.B., The Continuous Phase Heat and Mass Transfer Properties of Dispersions, Chem. Eng. Sc., <u>16</u>, 39-54 (1961).
- 11. Calderbank P.H., Evans F., Rennie J., Proceedings of the International Symposium on Distillation, Brighton, Inst. of Chem. Engrs., London, May 1960.

- Cooper F.M., Fernstrom G.A., Miller S.A., Performance of Gas-Liquid Contactors, Ind. Eng. Chem., <u>36</u>, 504-509 (1944).
- Cullen E.J., Davidson J.F., Absorption of Gases in Liquid Jets, Trans. Faraday Soc., <u>53</u>, 113-120 (1957).
- Danckwerts P.V., Absorption by Simultaneous Diffusion and Reaction, Trans. Faraday Soc., 46, 300-304 (1950).
- Danckwerts P.V., Gas Absorption Accompanied by Chemical Reaction, A.I.Ch.E.J., <u>1</u>, 456-463 (1955).
- Danckwerts P.V., Absorption from Bubbles of Dilute Gas, Chem. Eng. Sc., 20, 785-787 (1965).
- Danckwerts P.V., Kennedy A.M., The Kinetics of Absorption of Carbon Dioxide into Neutral and Alkaline Solutions, Chem. Eng. Sc., <u>8</u>, 201-125 (1958).
- Danckwerts P.V., Kennedy A.M., Roberts D., Kinetics of CO₂ Absorption in Alkaline Solutions, Chem. Eng. Sc., <u>18</u>, 63-72 (1963).
- Davies J.T., Kilner A.A., Ratcliff G.A., The Effect of Diffusivities and Surface Films on Rates of Absorption, Chem. Eng. Sc., 19, 583-590 (1964).
- 20. Eben C.D., Pigford R.L., Gas Absorption with Chemical Reaction on a Sieve Tray, Chem Eng. Sc., <u>20</u>, 803-811 (1965).
- Friedman A.M., Lightfoot E.N., Oxygen Absorption in Agitated Tanks, Ind. Eng. Chem., <u>49</u>, 1227-30 (1957).

- 22. Fortescue G.E., Pearson J.R.A., On Gas Absorption into Turbulent Liquid, Chem. Eng. Sc., 22, 1163-76 (1967).
- Groothius H., Kramers H., Gas Absorption by Single Drops During Formation, Chem. Eng. Sc., 4, 17-25 (1955).
- 24. Haberman W.L., Morton R.K., Report 802, The David Taylor Model Basin, Washington, D.C., U.S. Navy Department.
- Hammerton D., Garner F.H., Trans. Inst. Chem. Engrs. (London), 32, S18-S24 (1954).
- Higbie R., Mass Transfer from Rising Bubbles, Trans. Am. Inst. Chem. Eng., 31, 365 (1935).
- Hinze J.O., Fundamentals of Hydrodynamic Mechanism of Splitting in Dispersion Processes, A.I.Ch.E.J., <u>1</u>, 289-295 (1955).
- Hixson A.W., Gaden E.L., Oxygen Transfer in Submerged Fermentation, Ind. Eng. Chem., <u>42</u>, 1792-1801 (1950).
- 29. Hyman D., Mixing and Agitation, Advances in Chem. Eng., <u>3</u>, 119-202 (1962).
- Hyman D., Bogaerde J.M. van den, Small Bench-Scale Stirred Reactors, Ind. Eng. Chem., <u>52</u>, 751-53 (1960).
- 31. Johnson D.L., Saito H., Polejes J.D., Hougen O.A., Effects of Bubbling and Stirring on Mass Transfer Coefficients in Liquids, A.I.Ch.E.J., <u>3</u>, 411-417 (1957).
- 32. Karwat H., Chem. Ing. Tech., <u>31</u>, 588 (1959).
- 33. Kishinevskii M.K., J. Appl. Chem., U.S.S.R., <u>28</u>, 881 (1955); Coulson J.M., Richardson J.F., Chemical Engineering, MacMillan Co., N.Y. (1964).

- 34. Kishinevskii M.K., Serebryanskii V.T., J. Appl. Chem., U.S.S.R., 29, 29 (1956); Coulson J.M., Richardson J.F., Chemical Engr., MacMillan Co., N.Y. (1964).
- 35. Laity D.S., Treybal R.E., Dynamics of Liquid Agitation in the Absence of Air-Liquid Interface, A.I.Ch.E.J., 3, 176-180 (1957).
- 36. Leibson I., Holcomb E.G., Caeoso A.G., Jamie J.J., Rate of Flow and Mechanics of Bubble Formation from Single Submerged Orifices, A.I.Ch.E.J., 2, 296-306 (1956).
- 37. Li P.S., West F.B., Vance W.H., Moulton R.W., Unsteady State Mass Transfer from Gas Bubbles Liquid Phase Reaction, A.I.Ch.E.J., <u>11</u>, 581-587 (1965).
- 38. Maxon D.W., Johnson M.J., Aeration Studies on Propagation of Bakers's Yeast, Ind. Eng. Chem., 45, 2554-60 (1953).
- 39. Michel B.J., Miller S.A., Power Requirements of Gas-Liquid Agitated Systems, A.I.Ch.E.J., 8, 262-266 (1962).
- 40. Moelwyn-Hughes E.A., The Kinetics of Reaction in Solution, Oxford (1947).
- 41. Nijsing R.A.T.O., Hendriksz R.H., Kramers H., Absorption of CO₂ in Jets and Falling Films with and without Chemical Reaction, Chem. Eng. Sc., <u>10</u>, 89-104 (1959).
- 42. Oldshue J.Y., Role of Turbine Impellers in Aeration of Activated Sludge, Ind. Eng. Chem., <u>48</u>, 2194-98 (1956).
- 43. Payne J.W., Dodge B.F., Rate of Absorption of Carbon Dioxide in Water and Alkaline Media, Ind. Eng. Chem., <u>24</u>, 630-637 (1932).

- 44. Pearson J.R.A., Diffusion of One Substance into a Semi-Infinite Medium Containing Another with a Second Order Reaction, Appl. Sc. Res., Sec. A, <u>11</u>, 321-340 (1962-63).
- 45. Perry R.H., Pigford R.L., Kinetics of Gas-Liquid Reactions, Ind. Eng. Chem., 45, 1247-53 (1953).
- Phillips D.H., Johnson M.J., Oxygen Transfer in Agitated Vessels, Ind. Eng. Chem., <u>51</u>, 83-92 (1959).
- Pigford R.L., Diffusion and Chemical Kinetics, Univ. of Delaware, 1950.
- 48. Pinsent B.R.W., Pearson L., Roughton F.J.W., The Kinetics of Combination of Carbon Dioxide with Hydroxide Ions, Trans. Faraday Soc., 52, 1512-1520 (1956).
- 49. Polejes J.D., Ph.D. Thesis, Univ. of Wisconsin (1959).
- 50. Preen B.V., Ph.D. Thesis, Univ. of Durham, South Africa (1961); Sideman S., Hortacsu O., Fulton J.W., Ind.Eng.Chem.,<u>58</u>,32-47(1966).
- 51. Rehm T.R., Moll A.J., Babb A.L., Unsteady State Absorption of Carbon Dioxide by Dilute Sodium Hydroxide Solutions, A.E.Ch.E.J., 9, 760-765 (1963).
- 52. Reith, T., Physical Aspects of Bubble Dispersions in Liquids, Doctor's Thesis, Delft (1968).
- 53. Rushton J.H., Mixing, Ind. Eng. Chem., <u>48</u>, 552-555 (1956).
- 54. Rushton J.H., Costich E.W., Everett H.J., Power Characteristics of Mixing Impellers, Chem. Eng. Progr., <u>46</u>, 395-404 (1950).

- 55. Schultz J.S., Gaden E.L., Jr., Sulfite Oxidation as a Measure of Aeration Effectiveness, Ind. Eng. Chem., <u>48</u>, 2209-2212 (1956).
- 56. Schwartzberg H.G., Treybal R.E., Fluid and Particle Motion in Turbulent Stirred Tanks, Ind. Eng. Chem. Fundam., 7, 1-6 (1968).
- Seidell A., Linke W.F., Solubilities of Inorganic and Organic Compounds, D. van Norstad and Co., N.Y. (1952).
- Sherwood T.K., Pigford R.L., Absorption and Extraction, McGraw-Hill, N.Y. (1952).
- 59. Shinnar A., Church J.M., Predicting Particle Sizes in Agitated Dispersions, Ind. Eng. Chem., <u>52</u>,253-256 (1960).
- Sideman S., Hortacsu O., Fulton J.W., Mass Transfer in Gas-Liquid Contacting Systems, Ind. Eng. Chem., <u>58</u>, 32-47 (1966).
- 61. Smith R.K., Wills G.B., Application of Penetration Theory to Gas Absorption on a Sieve Tray, Ind. Eng. Chem. Proc. Des. and Dev., <u>5</u>, 39-44 (1966).
- Thompson D.W., Effect of Interfacial Mobility on Mass Transfer in Gas-Liquid Systems, Ind. Eng. Chem. Fundam., 9, 243-248 (1970).
- 63. Toor H.L., Marchello J.M., A Mixing Model for Transfer near a Boundary, Ind. Eng. Chem. Fundam., <u>2</u>, 8-12 (1963).
- 64. van Krevelen D.W., Hoftizer P.J., Chim. Ind. XXI^{me} Congress Int. Chim. Ind., p. 168 (1948).

- 65. Vermuelen T., Williams G.M., Langlois G.E., Interfacial Area in Liquid-Liquid and Gas-Liquid Agitation, Chem. Eng. Progr., <u>51</u>, 85F-94F (1955).
- 66. Westerterp K.R., van Dierendonck L.L., de Kraa J.A., Interfacial Areas in Agitated Gas-Liquid Contactors, Chem. Eng. Sc., 18, 157-176 (1963).
- 67. Yoshida F., Ikeda A., Imakawa S., Miura Y., Oxygen Absorption Rates in Stirred Gas-Liquid Contactors, Ind., Eng. Chem., 52, 435-440 (1960).
- Yoshida F., Miura Y., Gas Absorption in Agitated Gas-Liquid Contactors, Ind. Eng. Chem. Proc. Des. Dev., <u>2</u>, 263-268 (1963).
- Yoshida F. Yoshiharu M., Effective Interfacial Area in Packed Columns for Absorption with Chemical Reaction, A.I.Ch.E.J.,
 <u>9</u>, 331-337 (1963).

Addenda

- 70. Whitman W.G., Prediction of Mass Transfer Coefficients for Two Films, Chem. and Met. Eng., 29, 146 (1923).
- 71. Foust H.C., Mack D.E., Rushton J.H., Gas-Liquid Contacting by Mixers, <u>36</u>, 517-522 (1944).
- 72. Danckwerts P.V., Gas-Liquid Reactions, McGraw-Hill, Inc. (1967).
- 73. International Critical Tables, Vol. 4 (1933).

APPENDIX A

DEVELOPMENT OF CORRELATION FOR THE PREDICTION OF TIME OF CONTACT

DEVELOPMENT OF CORRELATION FOR THE PREDICTION OF TIME OF CONTACT

The time rate of decrease of kinetic energy or the dissipation of fluid energy per unit volume for geometrically similar configurations is governed by a relationship of the following type [6]:

$$P/V = \frac{\rho_f U^3 \phi(Re_s)}{g_c L}$$
(A-1)

where U is a characteristic stream velocity, L a characteristic stream dimension, ρ_{f} the fluid density, $\phi(\text{Re}_{s})$ is some function of the stream Reynolds number, and P/V is power dissipated per unit volume.

The nature of the function $\phi(\text{Re}_s)$ is dependent on the type of flow geometry and the particular characteristic velocity used. This characteristic may be the average velocity \overline{U} , or the root mean square fluctuating velocity, U.

Batchelor [4] has shown that experimentally the rate of decrease of kinetic energy of an isotropic, grid-generated turbulence is of the order of U^3/L_e and gives the following relationship:

$$\frac{d}{dt} (U^2) = \frac{-AU^3}{L_e}$$
 (A-2)

This equation can be transformed in terms of P/V by writing it in

-90-

the following way:

$$P/V = \frac{A\rho_f U^3}{g_c L_e}$$
 (A-3)

where the constant A equal to $\phi(\text{Re}_{S})$ is known approximately to be of the order of unity, L_{e} is the Eulerian integral scale, a measure of the size of the main energy containing eddies.

It has been shown by dimensional analysis that the power number N_p in geometrically similar stirred tanks stirred by turbine impellers can be expressed as a function of Reynolds and Froude numbers [54].

$$N_{p} = \frac{Pg_{c}}{D^{5}N^{3}\rho_{f}} = f(Re, Fr, other geom. factors)$$
(A-4)

The Froude number in the relationship above represents the gravity forces acting in the stirred tank, which accounts for the appearance of the vortex. Because of the existence of the vortex, it is difficult to conceive of two dynamically similar situations in a stirred tank. This vortex is eliminated by the introduction of radial baffles in the stirred tank so that equation (A-4) for the power number becomes independent of the Froude number [35,54]. Thus for geometrically similar tanks stirred by a turbine type of impeller the following equation can be written [56]:

$$P/V = \frac{c_1 \rho_f N^3 D^5}{g_c T^2 H}$$
 Re₁ > 10,000 (A-5)

The right hand side of equation (A-1) can be equated to the right hand side of equation (A-5). Equation (A-5) is independent of Re_i above Reynolds numbers of 10,000.

$$\frac{\rho_{f} U^{3} \phi(\text{Re}_{s})}{g_{c}^{L}} = \frac{C_{1} \rho_{f} N^{3} D^{5}}{g_{c} T^{2} H}$$
(A-6)

where C_1 is a constant, T is tank diameter, and H is the liquid height in the tank.

Any reasonable consistent stream dimension may be used for L, provided (Re_{s}) is adjusted for the exact dimension. The width of the impeller discharge stream is of the order of and proportional to the impeller blade width, 0.20 D. Cutter [56] has shown that for turbine impellers L_e is approximately 0.4D/5. When a value with any linear proportionality is used, the velocity U can be written as

$$U = \frac{C_2 ND^2}{(T^2H)^{1/3}} \qquad \text{Re}_i > 10,000 \qquad (A-7)$$

Schwartzberg and Treybal [56] studied the variation of total velocity and the other variables represented in equation (A-7) for turbine impellers and found the value of C_2 to be 1.586. Their



ND²/(T²H)^{1/3} [ENLARGED FROM SCHWARTZBERG AND TREYBAL [57]]

calculated data is shown in Figure 15 and has a mean deviation of 5.7 percent.

Gas Bubble Diameter

Hinze [27] showed that three kinds of forces act on a globule in a flow field: a viscous stress or dynamic pressure τ from the surrounding continuous phase, a surface tension force, and a viscous stress in the globule. If d is the diameter of the globule and σ the interfacial tension, the surface tension force will be of the order of σ/d . The viscous stresses set up in the globule is given by

$$\frac{\mu_d}{d} \left(\frac{\tau}{\rho_d}\right)^{1/2}$$
(A-8)

where μ is the viscosity and the subscript d refers to the dispersed phase. In general, it can be said that the greater the external force τ compared with the counteracting interfacial tension force σ/d the greater the globule deformation. At a critical Weber number (We)_{cr} break up occurs.

If bubble coalescence is neglected, then the size of the largest bubble would be dependent on the dynamic pressure. This yields

$$(We)_{cr} = \frac{\rho_c U^2 d_{max}}{\sigma}$$
 (A-9)

where U^2 is the average value of the square of the velocity over a

distance equal to d_{max} ; these velocity differences being due to turbulent fluctuations. If turbulence is assumed to be isotropic (which is true at least on a local level), the Kolmogoroff energy distribution law will be valid in this region and the turbulence pattern will be determined solely by energy input per unit mass and time, ε . Kolmogoroff has shown that local isotropy can be assumed at high Reynolds numbers (which usually exist in stirred tanks). It can be proved then that

$$U^2 = const (\epsilon d)^{2/3}$$
 (A-10)

If we substitute this into equation (A-9)

$$\frac{\rho_{c} d_{max}}{\sigma} (\epsilon d)^{2/3} = (const)_{l}$$
 (A-11)

or

$$d_{\max}(\rho_c/\sigma)^{3/5} (\epsilon)^{2/5} = \text{const}$$
 (A-12)

It is often convenient to express energy input in terms of unit volume rather than unit mass to give

$$d_{max} = const \frac{\sigma^{0.6}}{(P/V)^{0.4} \rho_c^{0.2}}$$
 (A-13)

The neglect of coalescence in obtaining the above equation is probably less serious than one might predict, since in many actual instances coalescence is hindered by the presence of impurities and surfactants. Shinnar and Church [59] developed another relationship for the case where two bubbles or globules may collide. If d_{min} is the diameter of the smallest bubble for which coalescence will be prevented by turbulence, then Shinnar and Church showed that

$$d_{min} = const \frac{A(h_o)^{3/8}}{(P/V)^{2/8} p_c^{1/8}}$$
 (A-14)

where $A(h_0)$ is the energy of adhesion between two spherical bubbles of unit diameter separated by a distance h and is uniquely defined by the properties of the fluid. If it can be made to be related with surface tension, then by dimensional considerations, it should be possible to make it proportional to σd , so that equation (A-14) becomes

$$d_{\min} = \text{const} \frac{\sigma^{0.6}}{(P/V)^{0.4} \rho_c^{0.2}}$$
 (A-15)

which is similar to the equation for the non-coalescing situation. The constants would probably be different in the two cases.

Calderbank [8] obtained correlations on the basis of Hinze's equations for gas-liquid systems in stirred tanks and modified these equations to support his experimental data. For dispersions in electrolyte solutions he proposed the following equation for the mean bubble diameter of the gas dispersion.

$$d_{bm} = (const) \frac{\sigma^{0.6}}{(P/V)^{0.4} \rho_c^{0.2}} \phi^{0.4} (\frac{\mu_d}{\mu_c})^{0.25}$$
(A-16)

where $\boldsymbol{\varphi}$ is the reaction of gas hold-up in the dispersion.

The gas hold-up was also similarly correlated by the equation

$$\phi = \left(\frac{V_{s}\phi}{V_{t}}\right)^{1/2} + c_{1} \frac{(P/V)^{0.4}\rho_{c}^{0.2}}{\sigma^{0.6}} \left(\frac{V_{s}}{V_{t}}\right)^{0.5}$$
(A-17)

where C_1 is a dimensional constant having the dimensions of $(length)^1$.

At high power dissipation, however, the first term in equation (A-17) is negligible, so that

$$\phi = C_1 \frac{(P/V)^{0.4} \rho_c^{0.2}}{\sigma^{0.6}} (\frac{V_s}{V_t})^{0.5}$$
(A-18)

This equation is similar to the equations obtained by Foust et al [71].

If equation (16) and (18) are combined together, an equation for the mean bubble diameter independent of the term ϕ can be obtained.

$$d_{bm} = C_2 \frac{\sigma^{0.36}}{(P/V)^{0.24} \rho_c^{0.12}} (\frac{V_s}{V_t})^{0.2} (\frac{\mu_d}{\mu_c})^{0.25}$$
(A-19)

where C_2 is a dimensional constant.

-97-

Gas-Liquid Contact Time

The contact time of a diffusing gas from a bubble to a turbulent fluid element is an important parameter for the Higbie penetration model, both physical as well as chemical absorption of a gas into a liquid. If d is the average diameter of the gas bubble in a dispersion and U is the velocity of the liquid element, then the contact time is given by

$$t = d/U \qquad (A-20)$$

If equations (A-5), (A-7), (A-19), and (A-20) are combined, the time of contact in the stirred tank can be expressed in terms of the tank dimensions, stirrer dimensions and the physical properties of the system to give

$$t = C(\frac{\sigma}{\rho_c})^{0.36} (\frac{T^2 H}{N^3})^{0.573} \frac{g_c^{0.24}}{D^{3.2}} (\frac{V_s}{V_t})^{0.2} (\frac{\mu_d}{\mu_c})^{0.25}$$
(A-21)

where C in this case is a constant comprising the constants from the equations used.

There are some assumptions implicit in this derivation:

(1) The velocity of the bubble in the dispersion is much smaller compared to the velocity of the liquid particles.

(2) The impeller Reynolds number is sufficiently high for a constant power number.
APPENDIX B

.

CALIBRATION DATA AND PROCEDURES

CALIBRATION DATA AND PROCEDURES

Calibration of Oricemeter

The saturation column is kept circulating with water at 25°C from the temperature bath. The wet-test meter is hooked up to the gas line. The carbon dioxide from the cylinder is bubbled through the saturation column at constant upstream line pressure of 15 psig from the orifice-meter. The time taken for a certain number of revolutions of the wet-test meter needle is noted and the mercury differential in the manometer across the orifice-meter and the wettest meter are noted. The procedure is repeated for each successive calibration point. Table VI and Figure 16 show the data and results of the orifice-meter calibrations.

Calibration of Agitator Motor Gear

The gear is set at a particular position and the stroboscopic light is synchronized on a spot marked on the agitator stem. The syncronous frequency at which the stroboscopic light matches the agitator revolutions per minute is noted for the different gear readings. Table VII and Figure 18 give the results of these calibrations.

Calibration of Caustic Rotameter

The overhead supply bottle is filled with the requisite strength caustic. The needle-valve controlling the flow through the rotameter is set at a certain position and the caustic is allowed to flow into

TABLE VI

Calibration Data and Results for Orificemeter

Orifice Manometer Reading	Wet-test Meter Reading in. Hg	Time, sec.	Number of Revolutions of Wet-test meter	Calculated Gas Flow Rate ml/sec
1.5	0.7	74	8	786
0.5	0.2	57	4	500
0.3	0.1	74	4	382
1.0	0.4	43	4	667
2.5	1.0	46	6	954
2.0	0.9	50	6	875
3.5	1.3	59	8	1003
5.0	1.9	57	8	1055

.

with Carbon Dioxide Gas





ML OF CAUSTIC PER MIN

-103-

a graduated cylinder for one minute. The reading of the float on the rotameter stem is noted for each flow rate. In the case of the higher flow rates the flow rate is kept constant by manipulating the needle-valve. Figure 17 shows the results of the rotameter calibration. -105-

TABLE VII

Calibration of Agitator Gear

Gear Reading	Agitator rpm
4.05	150
5.0	182
6.0	220
7.0	265
8.0	305
9.0	342
12.0	441
13.0	481
14.0	520
11.0	409





.

.....

APPENDIX C

EQUIPMENT AND APPARATUS AND MATERIALS

EQUIPMENT AND APPARATUS

The equipment and apparatus used in this investigation are listed and described in the following section.

<u>Agitator Motor</u> Manufactured by Chemineer Inc., Dayton, Ohio. Maximum power 1/4 horsepower, serial no. G-1741, maximum rpm 3450, model ELB-AFC-ES1. Used as a driver for agitator shaft.

<u>Beckman pH Meter</u> Model Beckman, glass electrode pH meter, serial no. 36147, manufactured by Beckman Instruments, Inc., South Pasadena, California. Used for obtaining end points in titration of reactor solutions and standard solutions.

<u>Burets</u> Kimax, teflon stopper titration burets, 50 milliliters, 0.10 milliliter graduations. Used to hold and measure titrating solutions.

<u>Double Arm Balance</u> 0-1000 gramas, 1.0 gram increments. Manufactured by Fisher Scientific Co., Pittsburg, Pa. Used to weigh hydroxide for reactor solutions.

<u>Metler Balance</u> Analytical, dampened, 0 to 150 grams, 0.00001 gram increments, serial no. 3636000. Manufactured by Scientific Products, Evanston, Ill. Used for weighing reagents for preparation of standard solutions.

<u>Magnetic Stirrer</u> Manufactured by Fisher Scientific Co. Used for stirring of solutions during titration using pH meter.

Orifice-meter 1/8 inch sharp-edged orifice made of copper plate. Pressure taps 1 1/2 and 4 1/2 inches up and downstream,

respectively. Manufactured in the machine shop, Department of Chemical Engineering, Virginia Polytechnic Institute and State University. Used to measure gas flow rate into absorption tank.

<u>Pressure Gauge</u> Range 0-30 psig. Manufactured by Norgram Co., Denver, Colorado. Used to keep upstream orificemeter gas pressure constant.

<u>Pump</u> Centrifugal, model D-11, serial no. C-8F-1111, type 100, manufactured by Eastern Industries, Hamden, Conn. Used to circulate temperature bath water into saturation column.

<u>Rotameter</u> Tube no. 2-F-1/4-20-5/70, manufactured by Fisher and Porter Co. Used to measure hydroxide rate into reactor vessel.

<u>Stroboscope</u> Type 1531-A, manufactured by General Radio Co., Concord, Mass. Range 0-6000 rpm. Used to calibrate agitator motor gear for agitator revolutions.

<u>Water Bath</u> Continuous-intermittent unitized bath with heating element. Manufactured by Fisher Scientific Co., Pittsburg, Pa. Used to keep saturation tower water temperature constant.

MATERIALS

The materials used in this investigation are listed below. <u>Buffer Solution Powders</u> Manufactured by Fisher Scientific Company, Fairlawn, N.J. Used to make buffer solutions for the calibration of pH meter.

<u>Carbon Dioxide</u> Regular grade. Specifications: 99.5 percent by volume of carbon dioxide, the remainder being mostly nitrogen with some oxygen and a trace of argon. Manufactured by Pure Carbonic Co., New York and supplied by Industrial Gas and Supply Co., Bluefield, West Virginia. Used as absorbing gas.

<u>Distilled Water</u> Distilled from water supplied by the Virginia Polytechnic Institute and State University Water Supply Authority in a single still in a tin-coated condenser.

<u>Hydrochloric Acid</u> Reagent Grade A.C.S., lot no. 784096. Manufactured by Fisher Scientific Co., N.J. Used for the analysis of HCl solutions.

Potassium Hydrogen Phthalate Reagent grade. Manufactured by Fisher Scientific Co. Used for the standardization of HCl solutions.

<u>Sodium Hydroxide</u> Certified A.C.S., lot no. 785654. Manufactured by Fisher Scientific Co. Minimum NaOH 98.3 percent. Maximum impurities: chlorine 0.001 percent, sodium carbonate 0.4 percent, sulphate 0.002 percent, phosphate 0.005 percent, ammonium hydroxide 0.02 percent, heavy metals 0.0004 percent, potassium 0.004 percent, Ni 0.0005 percent and iron 0.0005 percent.

APPENDIX D

SAMPLE CALCULATIONS

-113-

SAMPLE CALCULATIONS

<u>Sample Calculations for Absorption in Water and 0.085 M</u> <u>Caustic</u> Consider experiment number 12 for the case of absorption without reaction and experiment 37 for absorption with reaction. Both these experiments are for the same impeller speed and gas superficial velocity.

For experiment 12,

Amount of 1 M caustic added to tank/min = 110 ml. Absorption of CO_2 in gm. mole per sec. per ml

$$= \frac{110}{1000} \times \frac{1}{60} \frac{1}{(tank vol)}$$

$$= \frac{110}{1000 \times 60 \times 18,900}$$

 $= 0.2160 \times 10^{-6}$

 $k_{La} = \frac{0.2160 \times 10^{-6}}{(\text{sat conc. of } CO_2 \text{ in water}) \times \text{partial pr. of } CO_2}$

$$= \frac{0.2160 \times 10^{-6}}{3.37 \times 10^{-5} \times (\frac{P_{atm} - P_{w-vap.}}{760})}$$
$$= \frac{0.2160 \times 10^{-6} \times 760}{(705 - 24.0)}$$
$$= 7.1535 \times 10^{-3} \text{ sec}^{-1}$$

For experiment 37 similarly,

Amount of 3 M caustic added to tank/min = 300 ml. Absorption of CO₂ in gm mole per sec per ml

 $= \frac{300}{1000} \times 3 \times \frac{1}{2} \times \frac{1}{60} \times \frac{1}{18,900}$

$$= 0.2968 \times 10^{-6}$$

=
$$13.5021 \times 10^{-3} \text{ sec}^{-1}$$

R = rate of absorption with reaction rate of absorption without reaction

$$= \frac{0.3968 \times 10^{-6}}{0.2160 \times 10^{-6}}$$

= 1.8370

From Figure 5,

t = time of contact = 1.161×10^{-2} sec. For the case of physical absorption

$$N_{A}a = 2a \sqrt{\frac{D_{A}}{\pi t}} = 0.2160 \times 10^{-6} \frac{\text{gm mol}}{(\text{sec})(\text{ml})}$$



Sample Calculations for Absorption in 1.5 M Caustic For experiment 69,

Difference in titre reading after 30 sec

$$= (54.0 - 527) \text{ m} = 1.3 \text{ m}$$
.

Rate of Absorption in gm mol of CO₂ per ml per sec

$$=\frac{1.3}{30} \times \frac{\gamma}{s} \times M \times 10^{-3}$$

where in this case γ is the number of times the reactor solution is diluted, s is the amount in ml of diluted reactor solution titrated and M is the molarity of HCl solution used for the titration.

Rate of Absorption in gm mol of CO₂ per ml per sec

$$= \frac{1.3}{30} \times \frac{40}{50} \times 0.03471 \times 10^{-3}$$

$$k'_{L}a = \frac{0.9227 \times 10^{-3}}{2.093 \times 10^{-5} \times \frac{681}{760}} = 49.2027 \times 10^{-3} \text{ sec}^{-1}$$

$$N_{A}a = (k_{2}c_{B}D_{A})^{1/2} a c_{A}^{*} = 0.9227 \times 10^{-3} \frac{\text{gm mol}}{(\text{sec})(\text{ml})}$$

$$a = \frac{0.9927 \times 10^{-3}}{(20,670 \times 10^{3} \times 1.472 \times 10^{-3} \times 1.36 \times 10^{-5})^{1/2} 1.8573 \times 10^{-5}}$$

$$= 0.08465 \text{ cm}^{-1}$$

.

APPENDIX E

PHYSICO-CHEMICAL PROPERTIES OF SOLUTIONS USED

TABLE VIII

Physico-Chemical Properties of Caustic Solutions Used

Caustic Strength in moles/liter	0.085	1.0	1.5
Estimated Experimental Viscosity at 25°C in c.p.	0.941	1.152	1.260
Estimated Surface Tension at 25°C in dymes/cm	72.15	73.85	74.8
Estimated Experimental Density at 25°C in gm/cm ³	1.001	1.042	1.063
Estimated Specific Rate Constants for Reaction with CO ₂ at 25°C in 1/gmol.	8,865	15,330	20,620
Estimated Solubility of Carbon Dioxide in gmol/ml	3.28x10 ⁻⁵	2.45×10 ⁻¹	⁵ 2.093x10 ⁻⁵
Estimated Diffusivity of CO_2 in cm ² /sec	1.805x10 ⁻⁵	1.488×10 ⁻⁴	5 1.36×10 ⁻⁵

-118-

=]]9-

VITA

The author was born in Medan, Indonesia on December 6, 1941. He attended a series of schools in Southeast Asia up to the high school level.

In December 1959, he was awarded the General Certification of Education of the University of Cambridge, England. He joined St. Xavier's College, one of the colleges affiliated with the University of Bombay, in June 1960 and received the Intermediate Science Certificate in May 1962. In June 1962, he joined the Department of Chemical Technology, University of Bombay and received the degree of the Bachelor of Chemical Engineering in April 1966. The author joined Tennessee Technological University in September 1966 and received the degree of Master of Science in Chemical Engineering in August 1967.

The author joined the Department of Chemical Engineering, Virginia Polytechnic Institute and State University in September 1967. The author expects to receive the degree of Doctor of Philosophy in Chemical Engineering from Virginia Polytechnic Institute and State University in June 1971.

Brahm to. Frashe

GAS ABSORPTION WITH CHEMICAL REACTION IN AN AGITATED REACTOR

Ьy

Brahm D. Prasher

ABSTRACT

The purpose of this investigation is the application of the penetration model for gas absorption with chemical reaction in a stirred reactor and the evaluation of the parameters of the penetration model, viz. the gas-liquid interfacial area and gas-liquid particle contact time, for the different agitation intensities and gas rates.

The values of these parameters for the model were determined by measuring the rates of absorption of carbon dioxide into caustic solutions and then forcing the model to give values of the parameter consistent with observed rates of absorption.

The contact times and interfacial areas were determined for five agitation rates ranging from 150 revolutions of the agitator to 350 and for five gas input rates ranging from superficial gas velocities of 0.29 centimeter per second to about 1.2 centimeters per second. These parameters were evaluated for three different caustic strengths.

The interfacial areas show discrepancies in values for the three different caustic strengths. These results, together with the work of an earlier investigator, seem to suggest that, for design and scale-up purposes for gas absorption in solutions, experiments be set up with the solutions of actual interest.

The interfacial areas obtained correlate well with the correlations given by Calderbank, which is based on the work of Hinze on bubble sizes in turbulent regimes.

The gas-liquid particle contact times are again found to be dependent on the intensity of agitation and the gas rates. A correlation based on the theory of isotropic turbulence has been proposed and found to correlate the data well.