WASHINGTON UNIVERSITY
SEVER INSTITUTE OF TECHNOLOGY

EFFICIENCY OF STATIC MIXERS AS GAS / LIQUID CONTACTORS

by

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Prepared under the direction of Professor M. Duduković

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ABSTRACT

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Gas-liquid interfacial areas and liquid side mass transfer coefficients were measured in three types of static mixers. Carbon dioxide absorption catalyzed by arsenite was used as a test reaction. The liquid and gas velocities were varied from 0.19 m/s to 0.63 m/s and from 0.07 m/s to 0.32 m/s, respectively. Holdup and pressure drops were also determined and correlated.

The mass transfer coefficient was constant at 1.84×10^{-4} m/s. The Koch CY mixer was superior to the Kenics and Ross LLPD mixers and competitive with traditional two phase contactors in producing interfacial area per unit dissipated power.

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EFFICIENCY OF STATIC MIXERS AS GAS / LIQUID CONTACTORS

1. INTRODUCTION

1.1 GENERAL

Static mixers are stationary baffle-like units which effect the mixing of flowing materials with the aid of the fluid's own kinetic energy. These mixers are not an innovation but are simply a practical engineering design that has worked in many mixing situations and are now becoming a technology. Today, there are many companies which are producing different types of static mixers and providing technical literature.

The advantages which these static mixers boast over dynamic mixers are the following:

1) Narrow residence time distribution;

2) Use of a wide range of viscosities (gases to highly viscous polymer melts) as well as use for varied continuous to dispersed phase viscosity ratios from 10^{-2} to 10^{6});

3) Ready adaptation to existing pipe systems;

4) Smaller space requirements;

5) Negligible maintainance and wear, due to the absence of moving parts;

6) Low capital investments, operating costs and energy requirements;

7) Availability in many types of materials from aluminum to teflon.

They also have shown the ability to be used in industry for a multitude of applications. The main mixing applications include blending, dispersion and homogenization. The following section describes these applications and cites specific examples.

1.1.1 Industrial Applications of Static Mixers.

Blending is the process of mixing two soluble fluids together. This includes gas/gas blending, liquid/liquid blending, and solid/solid blending. Companies are using static mixers to:

1) Dilute 50% caustic solution by blending with water;

2) Blend various gasoline stocks as well as different lubricating oils in the petroleum industry;

3) Blend fertilizers, cement, and feed grains.

The unique advantages of static mixers in blending were demonstrated by a plant in France which had to blend three hot and explosive gases (1)*. The solution was a 16 inch

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* The numbers in parentheses in the text indicate references in the Bibliography.

diameter, 15 foot long static mixer. They achieved a uniform temperature and composition with the following advantages:

1) Elimination of leak hazard with explosive gases;

2) No explosion risk due to hot spots generated by by moving parts;

3) No moving parts, hence no part replacement;

4) No external power other than gas pressure; and

5) Reduced space requirements.

Dispersions occur when two immiscible fluids are combined and droplets, bubbles or particles of one phase are formed within the other continuous phase, where the two phases could be gas/liquid, liquid/liquid, solid/liquid. Some examples of this application include:

1) Soapstock acidulation for the production of high quality fatty acids by dispersing H_2SO_4 in soapstock;

2) Dispersion of CO_2 into soft drinks; and

3) Elimination of Na_2SO_3 by dispersing oxygen into the mainstream to produce Na_2SO_4.

A subcase of dispersions is the application of static mixers for high viscosity polymer melts intended for fiber, film or bulk plastic production. Some examples include:

1) Dispersion of immiscible droplets of anti-static or anti-soiling agents of much lower viscosity;

2) Break up and dispersion of unwanted immiscible gel structures of high viscosity polymers resulting from cross-linking or polymer degradation;

3) Blending of immiscible polymer systems to form controlled two phase structures of unique physical, optical or electrical properties.

The last major application is homogenization. Homogenization of polymers to eliminate radial temperature profiles is important for processing, spinning and extruding. This application is also important for the proper thermal control for many reactions. Fluids which have a tendency to separate in transfer lines before they are processed or before sampling by an on-line instrument can be homogenized by static mixers. Since the homogenization occurs in the radial direction the fluid flow approaches ideal plug flow which is also valuable for many reactions in which the desired product is an intermediate.

These are the basic uses for static mixers. There are many other more imaginative applications in the literature such as catalyst support or as a pressure reducing device to throttle superheated steam to a precise temperature and pressure (as opposed to a simple throttling valve that wears out after use). It is apparent from this brief list that the applications of static mixers are numerous and that the differences in fluid properties cover an extremely wide range.

This laboratory was particularly interested in the use of static mixers as a gas/liquid reactor. The benefits of plug flow charateristics, easier thermal control for the reactor and a design that permits easier scale up made the idea of static mixers as chemical reactors appealing. However, there are over 20 types of static mixers currently available each with their own distinct designs. Moreover, it is not known which is the optimal design. The next section briefly describes the three static mixer designs that were studied by this laboratory.

1.1.2 Static Mixer Designs

This study was only involved with three different static mixer designs from the following three companies:

1) Charles Ross and Son Co. (Ross LLPD mixer)
2) Chemineer/Kenics (Kenics mixer)
3) Koch Engineer Co. (Koch CY mixer)

The Ross LLPD Mixer is constructed of semi-elliptical panels. Two panels are connected together in the middle at a 120° angle and this is called one element (Figure 1). Each element is fitted in a pipe with each neighboring element reversed and rotated 90° along the linear axis.

The Kenics Mixer is constructed of a series of 180° twisted helical elements (Figure 2), alternating right hand twist and left hand twist, enclosed in a tube with each element rotated 90° relative to its neighbor. The interesting feature of this mixer is the radial mixing caused by the twist of each element. The flow in each channel circulates around its own hydraulic center causing radial mixing. Since for each element the rotation is in the opposite direction than in the previous element the shear forces at the interface of the two becomes great.

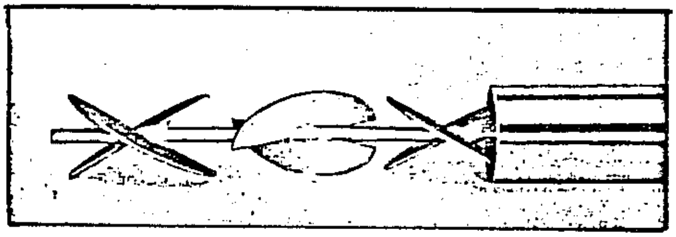


Figure 1. The LLPD Ross Mixer

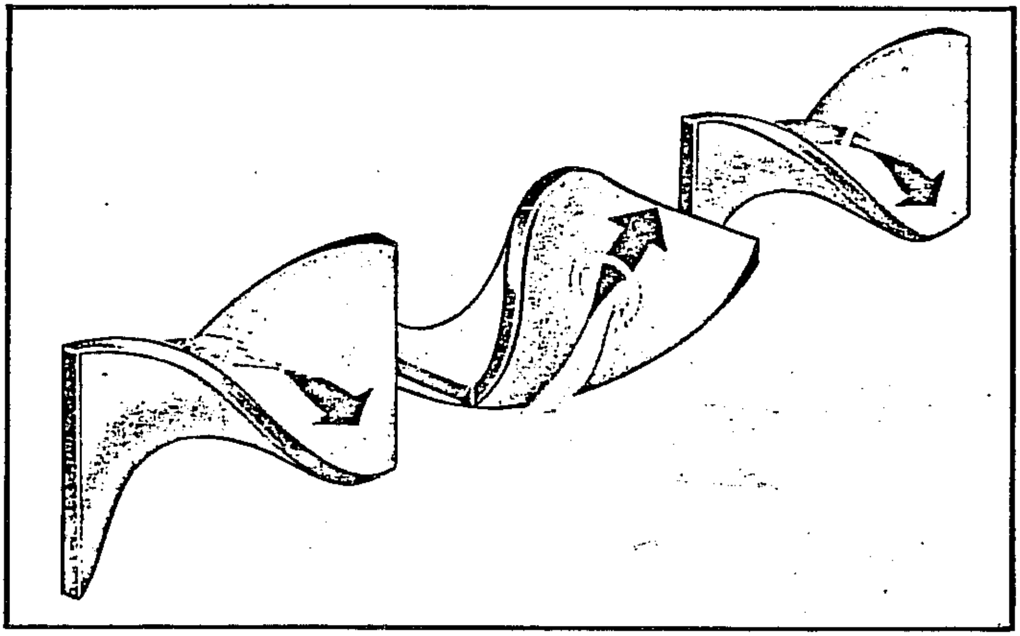


Figure 2. The Kenics Mixer

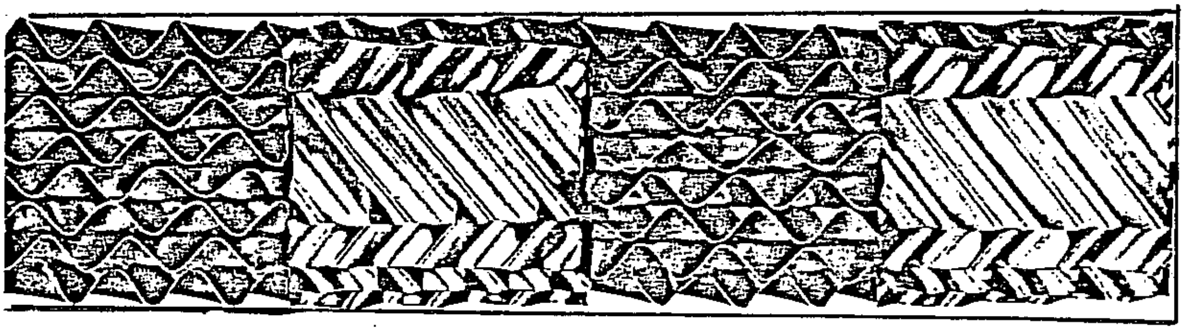


Figure 3. The Koch Mixer

The Koch Mixer is constructed of corrugated panels with the corrugations at a 45° angle to the linear axis. Separate panels, all one diameter long, are welded together lengthwise, with each panel having the corrugations running in a perpendicular direction to its neighbor (Figure 3). This set of panels, defined as one element, cause a two dimensional mixing pattern. Successive elements are rotated 90° forming one long unit as well as a third mixing dimension. The CY mixer is the second most compact type made by Koch. Each corrugation layer is 1/8 inch thick. The mixer has a hydraulic diameter of 0.15 inches and a void fraction of 0.72.

The Koch mixer comes in several sizes besides the CY mixer. The Koch AY mixer, which is most often studied in the literature, has corrugation layers that are 1/2 inch thick. This mixer has a hydraulic diameter of 0.66 inches and a void fraction of 0.92.

1.2 RESEARCH OBJECTIVES AND SCOPE

The primary goal of this study was to evaluate the efficiency of static mixers as gas/liquid contactors. Their efficiency will be defined by the amount of surface area per unit reaction volume per power input necessary to create this surface area. By using this definition comparisons between three different brands of static mixers at various flow conditions as well as other conventional gas/liquid contactors can be made. Another goal was to evaluate the static mixers' efficiency in eliminating the resistance to mass transfer in the liquid phase through the simultaneous evaluation of the liquid mass transfer coefficient.

The general objectives of this study were

1) To experimentally determine liquid holdup and total pressure drop at various liquid and gas flowrates for three different vertical static mixers.

2) To experimentally determine simultaneous values for interfacial area per unit liquid volume, a (m^2/m^3), and the liquid side mass transfer coefficient, k_L (m/s), at various gas and liquid flowrates for the same three static mixers.

3) To compare the experimental efficiencies of the three static mixers to each other and to the efficiencies of other conventional gas/liquid contactors extracted from the literature.

1.3 LITERATURE SURVEY

The literature is fairly scarce on gas/liquid contacting in static mixers and especially on the measurement of interfacial area in static mixers. Up to now most of the research has been concerned mainly with measuring pressure drops, residence times, and holdup for gas/liquid systems (2, 3, 4, 5). The Kenics Company (6) has done some studies on gas dispersion and bubble sizes with the use of photographic techniques and found that the data can be correlated with the following equation for the Kenics Mixer:

$$\frac{d_B}{d} = 0.39\ We^{-0.43} \tag{1}$$

where d_B = Sauter mean drop size, (m);
d = Inside diameter of the mixer, (m);
We = Weber number.

F. Strieff (7) published a study in the Sulzer Technical Review in which he reported a similar drop size correlation for Sulzer (Koch) mixers in a horizontal pipe:

$$\frac{d_B}{d_h} = 0.21\ We^{-0.50}\ Re^{0.15} \tag{2}$$

where d_h = Mixing element hydraulic diameter, (m);
We = Weber No. = $\rho_L V_L^2 d_h / \sigma$
Re = Reynolds No. = $\rho_L V_L d_h / \mu_L$
ρ_L = Density of the liquid phase, (kg/m^3);
V_L = Liquid phase superficial velocity, (m/s);
σ = Surface tension, (N/m);
μ_L = Liquid viscosity, (Pa·s).

This result was based on the measurement of drop size by photographic methods for different liquid/liquid systems and one gas/liquid system.

Although no work has been done to evaluate surface area in static mixers, there have been some studies of the overall mass transfer coefficients in static mixers. In 1977, K. B. Wang and L. T. Fan published a paper in Chemical Engineering Science in which they measured the volumetric liquid mass transfer coefficient, (k_La), for the absorption of pure oxygen into water in a bubble column packed with Koch AY mixers (8). They presented how k_La and gas holdup, ϵ, were affected by superficial gas and liquid velocity and also the affect of adding spacers in between the Koch mixers in the column. The spacers had a negligible affect and representative correlations for k_La and ϵ are as follows:

$$k_La = 4.35 \times 10^{-3} V_L^{0.631} V_g^{0.589} \qquad (3)$$

$$\epsilon = 5.16 \times 10^{-2} V_L^{-0.102} V_g^{0.588} \qquad (4)$$

where V_L and V_G have units cm/s.

Their results also showed a significant increase in k_La with the mixers as opposed to without the mixers.

J. C. Middleton is currently conducting studies of liquid mass transfer coefficients in an oxygen/water system for several static mixers, including Kenics and Sulzer mixers (3). His preliminary results suggest that all static mixers as well as some other conventional gas/liquid contactors can be correlated by one single correlation given below:

$$k_La = 1.74 \times 10^{-4} \left(\frac{E}{V_R}\right)^{0.8} \qquad (5)$$

where E/V_R (W/m^3) is the rate of energy dissapation per unit mixer volume. The final results are yet unpublished.

A recent report by Holmes and Chen of the Koch Engineering Company based on data obtained from oxygen absorption in water experiments in a horizontal pipe filled with AY Koch mixers presented a method to predict mass transfer coefficients, k_La, in such systems (9).

These equations, their sources and the conditions from which they were derived are given in Table 1. This concludes the literature survey related to the determination of a or k_La in static mixers.

Table 1

Equations for Prediction of Volumetric Mass Transfer Coefficients, k_La, for Koch Static Mixers

(2)	$d_B = 5330\ d_h (We)^{-0.5} (Re)^{0.17}$	Strieff (1977)	Horizontal bubble flow, liquid/liquid and gas/liquid
(4)	$\epsilon = 0.0516\ V_L^{-0.102}\ V_G^{0.588}$	Wang and Fan (1978)	Bubble flow in vertical pipe filled with Koch A Y mixers
(6)	$k_L = \frac{2}{\sqrt{\pi}} \frac{D_A\ \Delta V}{d_B}$	Cichy and Russell (1969)	Bubble flow in empty pipe using penetration theory
(7)	$a = \frac{6\ \epsilon}{d_B}$	Sauter	Spherically shaped bubbles
(8)	$\Delta V = 692.8\ d_B^{1.5284}$ $100\ \mu m < d_B < 500\ \mu m$ $\Delta V = 89.3\ d_B^{0.8457}$ $500\ \mu m < d_B < 2000\ \mu m$	Motarjemi and Jameson (1978)	Bubble flow in vertical empty pipe with stagnant liquid phase

2. METHODOLOGY

2.1 LIQUID HOLDUP AND POWER INPUT

Liquid holdup is defined as the volume of liquid per unit volume of total reactor. In this study, the liquid holdup is determined experimentally by quickly closing shut off valves to the reactor at various gas and liquid rates and then measuring the remaining volume of liquid in the column.

The dissipated power density is defined by the following expression:

$$P_\omega = \frac{\Delta P_k \cdot Q_L}{V_R \cdot (1-\epsilon)} \tag{9}$$

where ΔP_k = The pressure drop across the reactor due to kinetic energy loss, (N/m^2);

Q_L = Liquid volumetric flow rate, (m^3/s);

V_R = Volume of the total reactor, (m^3);

$(1-\epsilon)$ = Liquid holdup.

The kinetic pressure drop is calculated from the difference of the experimentally measured total pressure drop across the length of the reactor and the static pressure drop

$$\Delta P_s = [\rho_g \epsilon + \rho_L (1-\epsilon)] \cdot g \cdot H \tag{10}$$

where ρ_g = Density of the gas, (kg/m^3);

ρ_L = Density of the liquid, (kg/m^3);

ϵ = Gas holdup;

g = Acceleration of gravity, (m/s^2);

H = Height difference of the inlet and outlet of the reactor, (m).

It is important to realize not only that the static pressure drop has been subtracted off but that the power needed to push the gas through the reactor has been neglected.

2.2 DETERMINATION OF THE MASS TRANSFER COEFFICIENT AND INTERFACIAL AREA

The following text is a brief description of the options open to the experimenter wanting to determine the liquid side mass transfer coefficient, k_L and interfacial area, a.

2.2.1 Measurement of Interfacial Area

There are a few methods and procedures to choose from in order to determine droplet or bubble size, or interfacial surface area, such as photography, light scattering and various chemical means. Photography and light scattering are physical methods which can be used readily and that introduce no foreign matter such as electrolytes. A good article by Landau, et al. (10) compares these methods.

Photography not only gives data for bubble size but also yeilds information about bubble size distribution and bubble shape. However, the information obtained pertains to the hydrodynamics at the wall at a particular part of the reactor and is not necessarily representative of the entire reactor or of a particular whole cross section. Also the analysis of the photographs is very time consuming and can produce misleading results if the photographs are not properly done.

The light scattering technique avoids the long analysis of results and provides good data with adequate instrumentation. However, this technique involves placing a probe in the reactor which can cause mixing effects of its own. It also is a technique that gives point values for holdup and bubble size, not averages for the whole reactor. In addition the techniques has problems evaluating high magnitudes of surface areas above 800 m^{-1}. (10)

Chemical methods have the advantage of giving results that are a representative of averages for the total reactor, although the results can be interpreted only for a particular system and cannot be accurately extrapolated to gas/liquid systems having different physical characteristics such as viscosity and surface tension. The experiments are often more complex and time consuming than when dealing with physical methods.

2.2.2 Determination of Volumetric Liquid Side Mass Transfer Coefficient

The liquid side mass transfer coefficient, k_L, is determined usually by measuring the interfacial area, a, by the methods presented above and then can dividing an experimentally determined k_La by a. The volumetric coefficient, k_La, can basically be determined in two ways: physical absorption and chemically enhanced absorption. Just as in the case of the determination of the interfacial area, both have disadvantages and advantages. The physical method is easier and quicker experimentally, while the chemical method can often be much more complicated due to the increase of electrolytes in solution. However, there is a fundamental advantage that the chemical method has over the physical methods (11).

The rate of absorption for a gas A being physically absorbed into a liquid B with no mass transfer resistance in the gas phase can be represented by:

$$N_A a = k_L a \; (C_{A_i} - C_{A_b}) \tag{11}$$

where $N_A a$ = Volumetric rate of absorption of A, (mole/m^3s);

C_{A_i} = Concentration of A at the A/B interface, (mole/m^3);

C_{A_b} = Bulk concentration of A in B, (mole/m^3);

This equation relates $k_L a$ to several experimentally measurable quantities. In efficient contacting devices the two phases approach equilibrium conditions so C_{A_b} approaches C_{A_i}. Since the value of $k_L a$ depends on the difference of C_{A_b} and C_{A_i}, extremely accurate measurements of C_{A_b} and C_{A_i} are required in order to avoid a large error for efficient contacting devices. With chemical methods, the reaction regime is controlled so that C_{A_b} approaches zero and this fundamental problem is avoided. At this point, it would be beneficial to introduce some background for these chemical methods.

2.2.3 Chemical Methods

Briefly, for gas/liquid systems of any kind there are three different models used today to describe the physical action at a gas-liquid interface:

1) Two Film Model.
2) Higbie's Surface Renewal Model.
3) Danckwerts' Surface Renewal Model.

The descriptions of the models can be found in any good reaction engineering text book involving gas/liquid reactions (12, 13).

The main differences that these models, have besides their conceptual differences, are the definition of the liquid-side mass transfer coefficient, k_L. Two film theory leads to

$$k_L = \frac{D_A}{\delta_L} \tag{12}$$

where δ_L is the width of the liquid film, while Danckwerts' theory gives

$$k_L = (D_A \cdot s)^{1/2} \tag{13}$$

where s is the surface renewal frequency or the frequency at which the interface is renewed with an element of unreacted liquid. Higbie's theory, the least used of the three, gives

$$k_L = 2\ (D_A/\theta)^{1/2} \tag{14}$$

where θ is the exposure time of a fluid element at the interface. The important point from the above is that in film theory k_L varies with D_A but in the surface renewal theories k_L varies with $D_A^{½}$. The surface renewal theories predict the experimentally determined dependence of k_L on D_A.

Although the three models are different conceptually and give different absorption rate equations, the numerical values for absorption rates of a particular single reaction gas/liquid chemical system are quite similar regardless of model used. In fact, in some cases the models can be interchanged depending on which model is more convienient.

For studies involving the evaluation of the mass transfer parameters the most common type of chemical system used is one in which a pure gas A undergoes an irreversible second-order reaction with a liquid or component in the liquid phase, B, that has the following stoichiometry:

$$A + zB \longrightarrow \text{Products}$$

and rate equation:

$$-R_A = r' C_A C_B \tag{15}$$

An exact analytical solution for the rate of absorption, N_A, for this system is not possible. However, there are approximate solutions which are summarized by the following simple equation:

$$N_A = E_L k_L C_{A_i} \tag{16}$$

The enhancement factor, E_L, is a not so simple function of various physical dimensionless parameters, the Hatta number

$$Ha = (D_A r' C_{B_b})^{½} / k_L \tag{17}$$

the instantaneous enhancement factor

$$E_i = 1 + D_B C_{B_b}/z\ D_A C_{A_i} \qquad (18)$$

and the ratio between the volume of liquid associated with unit interface area and the film thickness parameter

$$Z = (\epsilon k_L)/(a D_A) \qquad (19)$$

Figure 4 presents the plot of the enhancement factor versus the Hatta number with E_i and Z as parameters (14). Basically, the magnitude of the Hatta number is an indication of the speed of the reaction relative to the speed of physical absorption. The higher the Hatta number is the faster the reaction progresses, and, therefore, the shorter the distance away from the interface the reactant A can travel before it is used up by the reaction.

Figure 4 is broken up into four basic reaction regions. In each region, the reaction occurs at a different speed, relative to diffusion, and consequently at different places in the liquid. Figure 5, based on the two film model, displays the concentration profiles in each region (14). In region A, the reaction rate is slow and nearly all the reaction occurs in the bulk. In region D, the reaction rate is fast and all the reaction occurs in the film. The other two regions have rates in between these two extremes.

In each reaction region, the enhancement factor is a different function of the physical parameters. Because of this fact, the information that can be extracted by

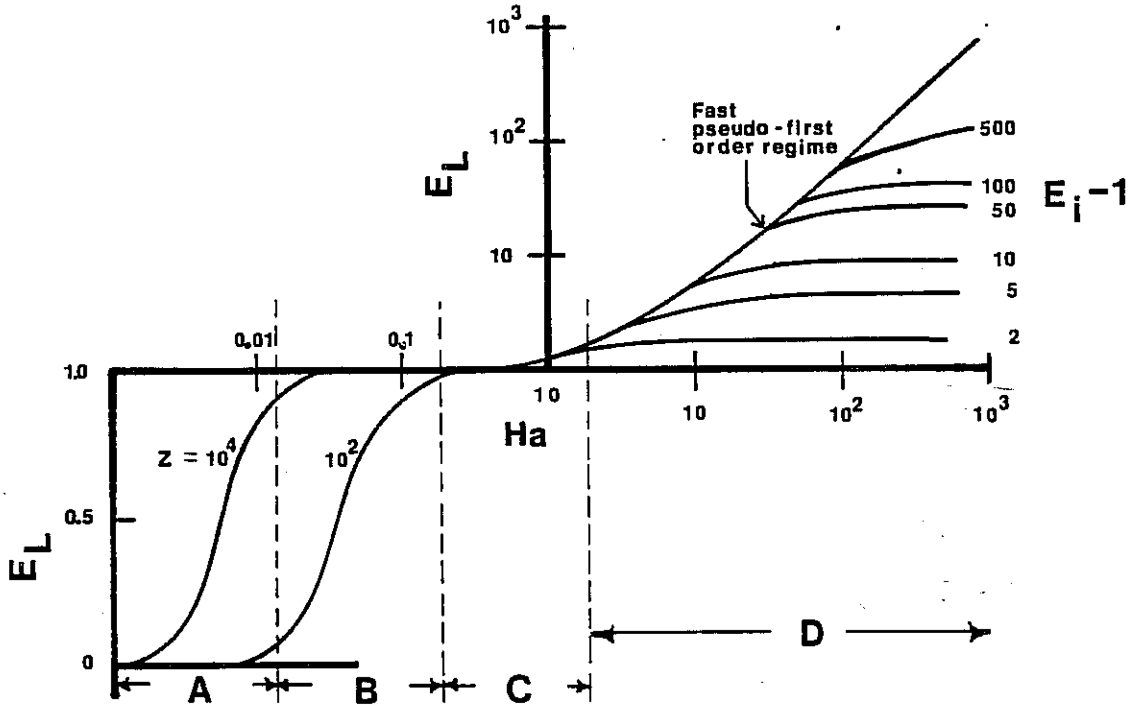
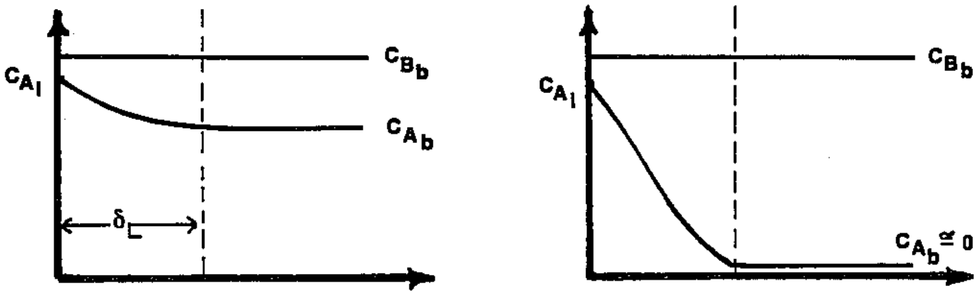
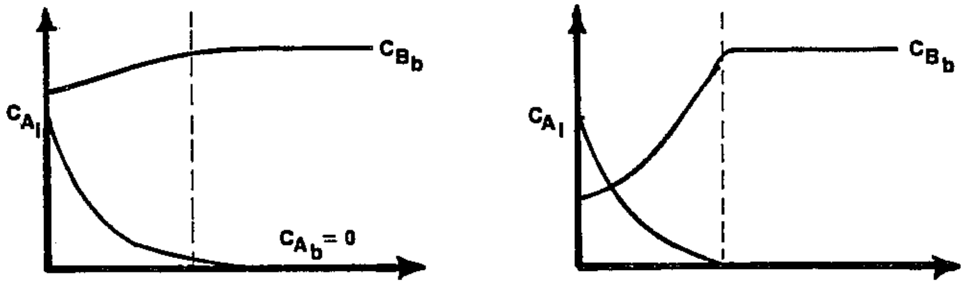


Figure 4. Enhancement Factor for Second Order Reaction



Region A: Ha < 0.02   Region B: 0.02 < Ha < 0.3



Region C: 0.3 < Ha < 3   Region D: Ha > 3

Figure 5. Liquid Phase Concentration Profiles at Various Hatta Numbers

absorption experiments is different for each region. For example, if an experimenter does absorption experiments in region B and $Z > 10,000$ then $E_L = 1$ and the measured overall reaction rate is given by the following equation:

$$N_A a = k_L a \, C_{A_i} \tag{20}$$

Therefore, $k_L a$ can be evaluated directly if C_{A_i} is known. If however, the experimenter has a reaction system that can be operated in region D and if $E_i/2 \gg Ha$ (in the pseudo-first order reaction regime) then

$$E_L = \sqrt{1 + Ha^2} \tag{21}$$

and

$$N_A a = k_L a \, C_{A_i} \sqrt{1 + Ha^2} \tag{22}$$

By substituting for Ha and rearranging terms the following equation is obtained:

$$N_A a = a \, C_{A_i} \sqrt{k_L^2 + D_A \, r} \tag{23}$$

or

$$(N_A a)^2 = a^2 \, C_{A_i}^2 \, (k_L^2 + D_A r) \tag{24}$$

It is apparent from this equation that for known values of D_A and C_{A_i}, $(N_A a)^2$ can be plotted versus r on linear paper to obtain $(k_L a)^2$ from the intercept and a^2 from the slope. Such a plot is referred to as a Danckwerts' plot. This chemical method is very powerful since the interfacial area and mass transfer coefficient can be obtained jointly.

The above examples are just two examples of the various chemical methods used to evaluate mass transfer parameters. In fact, every parameter (a, k_La, k_Ga, k_L, k_G) can be evaluated by selecting the proper chemical system. Charpentier gives a complete synopsis of all the methods, the information that can be obtained for each method as well as the parameters needed, and the requirements that need to be met for the various dimensionless parameters (12).

This study uses the above mentioned Danckwerts' type plot to determine k_La and a simultaneously. The advantage of this method is that a and k_La are measured under the same physical and chemical constraints, so that the final value of k_L will be accurate or meaningful for that chemical system. The reason that it is beneficial to measure a and k_La under the same conditions, as explained by Charpentier (14), is that those experimental quantities can be affected by the means of evaluation. For instance, if k_La is measured by physical absorption and a is measured by chemically enhanced absorption the resulting k_L will not necessarily be correct.

Appendix 7.1 gives a complete derivation of the mathematics of the method, the assumptions made and the necessary requirements for Ha and E_i.

2.3 THE CHEMICAL SYSTEM

A suitable chemical system for the method of simultaneous measurement of k_L and a must satisfy the required restraints on E_i and Ha as given in Appendix 7.1. Generally, the chemical system involves a chemical absorption in which the gas undergoes an irreversible pseudo-first order reaction preferably promoted by a catalyst in the liquid phase. The catalyst should be sufficiently powerful so that the reaction rate can be varied over a wide range without substantially altering the physical characteristics of the solution. Also, the system should have a negligible gas phase mass transfer resistance.

Charpentier lists a few candidates in Table XI from his review article. (14) Of the four systems listed, the two most popular are the following:

a) Oxygen absorption into a sodium sulphite solution with a cobalt sulphate catalyst.

b) Carbon dioxide absorption in a sodium carbonate bicarbonate buffer solution with a sodium arsenite catalyst.

Both systems have been studied extensively in the literature as well as been used successfully to evaluate the mass transfer parameters in packed columns and other conventional contacting devices.

System a) has been reviewed very completely by Linek and Vacek (15). The benefits of this system include:

1) Economy of the solutions;

2) Lack of toxicity;

3) Fire safety; and

4) Small concentrations of catalyst needed ($<10^{-4}$M).

However, as pointed out in Linek's review, this system lacks clear and accurate kinetic data. The kinetics of the reaction

$$SO_3^{=} + 1/2\ O_2 \xrightarrow{Co^{2+}} SO_4^{=} \qquad (25)$$

change significantly with reactant concentrations and catalyst concentrations. Also many of the studies done with this system are in error according to Linek because they did not properly account for these changes in kinetics.

System b) has the following benefits:

1) Substantiated kinetics and kinetic data as well as experimental results on a wetted-wall column (16) and jet apparatus (17);

2) Process is being used industrially;

3) Carbon dioxide can be used safely; and

4) Possibility of determining the rate through analysis of changes in carbon dioxide concentration in the gas phase (or simply to close the mass balance).

The detrements of the system include:

1) Large concentrations of catalyst needed (up to 0.5 M);

2) Analysis of absorbed carbon dioxide in the liquid phase with arsenite catalyst is complicated; and

3) Sodium arsenite is highly poisonous and expensive.

This system was chosen for this study, because of the relatively uncomplicated kinetics and the confidence in the kinetic parameters and physical constants presented in the literature. Also, the problem of economics was partially overcome by reusing the solutions.

The fundamental overall reaction of the system is (12):

$$CO_2(g) + CO_3^{=} + H_2O \xrightarrow{H_2A_sO_3^-} 2\ HCO_3^- \qquad (26)$$

The rate of absorption of carbon dioxide could be determined from measuring inlet and outlet flowrates of the pure gas stream or by determining the change of concentration of bicarbonate in the solution. Experimentally, it seemed more feasible to measure the liquid side absorption because the experimental setup and flowrates chosen complicated the measurement of the outlet gas flowrate. Also due to the expense of the arsenite catalyst, the solutions were reused so the work necessary to determine the final concentrations had to be done whether the rate was measured from the gas side or the liquid side.

The only practical method for determining the concentration of bicarbonate was by titration, similar to a method suggested by Vogel (18). Generally, a known excess amount, v1, of NaOH is added to a sample of reaction solution which converts all of the HCO_3^- to $CO_3^=$. Then an excess amount of $BaCl_2$ is added to precipitate out all the $CO_3^=$ as $BaCO_3$ leaving only the excess NaOH in solution. Finally the NaOH is titrated to an endpoint with HCl, v2, using a mixed indicator of cresol red and thymol blue. The concentration of the HCO_3^- equals (v1 x [NaOH]) - (v2 x [HCl]), where [ ] indicates concentrations. Modifications of this method had to be developed due to the fact that the presence of the arsenite broadened the titration end point. A complete description of the titration method is given in Appendix 7.2.

Once the type of chemical system had been selected, it was still necessary to determine the particular concentrations of all the species of the system. Only a few sets of concentrations had been studied in the literature and had all the physical constants evaluated. This study used the concentration set that had the most available literature values for the constants as well as the one that allowed the highest concentration range for the catalyst (17). The concentrations for the chosen system are given as follows:

$[CO_3^=] = 0.6$ M Buffer system maintains
$[HCO_3^-] = 0.2$ M pH = 10.0
$0.0 \text{ M} < [\text{Arsenite}] < 0.5 \text{ M}$
$0.0 \text{ M} < [Na^+Cl^-] < 0.5 \text{ M}$
$[\text{Arsenite}] + [Na^+Cl^-] = 0.5 \text{ M}$

The sodium chloride concentration is changed as the catalyst concentration is changed in order to maintain a constant ionic strength of 2.5. It is important to keep the ionic strength of the system constant, because the physical constants for this system are affected more by the ionic strength (19)

$$I = 1/2 \ \Sigma C_j z_j^2 \tag{27}$$

where C_j = Concentration of the jth species, (mole/m^3);
z_j = The ionic charge of the jth species;

than by the buffer ratio, $[CO_3^=]/[HCO_3^-]$ (20).

The constants for this system came from two sources. From Danckwerts and Sharma (17), the constants $C_{A_i}\sqrt{D_A}$ and r are obtained as:

$$C_{A_i}\sqrt{D_A} = 7.7 \times 10^{-8} \ (\text{gmole/cm}^2 s^{1/2})$$

at T = 25°C and

$$r = 2.2 + 224.5 \ [\text{Arsenite}] \quad (s^{-1})$$

From Danckwerts and Kennedy (20), the diffusivity of carbon dioxide in solution was obtained as:

$$D_A = 1.38 \times 10^{-5} \quad (cm^2/s).$$

After some preliminary experiments with the selected system, it was determined that the reaction had to be run in a semi-batch mode in order to get a significant bicarbonate concentration change. Therefore, the overall rate of absorption was calculated by the following equation:

$$N_A a = \frac{\Delta[HCO_3^-] \cdot V_b}{2 \cdot V_R \cdot (1-\epsilon) \cdot t} \tag{28}$$

where V_b = Total volume of the batch solution, (m^3);

$V_R(1-\epsilon)$ = Volume of the liquid in the reactor, (m^3);

t = Total time of operation, (s);

$\Delta[HCO_3^-]$ = Change in bicarbonate ion concentration during time t, ($gmole/m^3$).

The final topic for the methodology of the experimental study is that of how much absorption of carbon dioxide can be tolerated. A significant change in the bicarbonate concentration is neccessary to ensure low analytical errors in titration. However as carbon dioxide is absorbed into solution, everything changes, i.e. the buffer ratio and the ionic strength. As the buffer ratio changes the pH changes and because the actual catalyst is the dissociated arsenite ion, the concentration of the active catalyst changes. As the ionic strength changes, the physical constants are changed. The magnitudes of these changes are presented in Table 2 along with the possible errors in titration. This table shows that in order for the total error to be less than 15% each run should not exceed a bicarbonate concentration of 0.4 M. This total error is not the actual error for each data point but is an approximate deviation from the optimal conditions or the conditions at the start of each run. When this is done, Figure 6 displays that although things seem to be changing the overall reaction rate stays constant, as it should.

For economy reasons, the solutions are reused and the amount of absorption will depend on the next desired catalyst concentration. For example, the experiment may be started with the following conditions:

$[CO_3^{=}]$ = 0.6 M $[HCO_3^{-}]$ = 0.2 M
[catalyst] = 0.5 M   [NaCl] = 0.0 M

and the desired conditions to run the second experiment are as follows:

$[CO_3^{=}]$ = 0.6 M $[HCO_3^{-}]$ = 0.2 M
[catalyst] = 0.4 M   [NaCl] = 0.1 M

All that can be done to reuse the solution after the end of the first run is dilution of the total mixture and addition of any of the solutes with the exception of the expensive catalyst. This implies that the maximum final concentration of bicarbonate for the first experiment is 0.25 M. This is

Table 2

Changes in Parameters with Time due to the Absorption of Carbon Dioxide into a Buffer Solution

Time (min)	$[CO_2]$ Absorbed (moles/ℓ)	%	$[HCO_3^-]$ moles/ℓ	$\left(\frac{[CO_3^=]}{[HCO_3^-]}\right)$	$[A_{rs}^-]$ moles/ℓ	%	I	%	Total % Deviation
0	0	—	0.18	2.89	0.193	0	2.24	0	—
3	0.03	10	0.24	2.80	0.193	0	2.24	0	10
11	0.045	7	0.27	1.76	0.190	2	2.20	2	11
15	0.040	8	0.26	1.76	0.190	2	2.20	2	12
20	0.095	3	0.37	1.15	0.185	5	2.14	5	13
30	0.105	3	0.39	1.06	0.184	5	2.14	5	13
60	0.240	1	0.65	0.45	0.165	15	2.05	9	25
90	0.381	1	0.78	0.18	0.127	34	2.00	11	46