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AND
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CHEMICAL REACTION ENGINEERING LABORATORY

REPORT FOR THE PERIOD

JUNE 1, 1980 - MAY 31, 1981

Report

June, 1980 - May, 1981

CHEMICAL REACTION ENGINEERING LABORATORY

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INTRODUCTION

This report covers the major development in the Chemical Reaction Engineering Laboratory (CREL) for the period June 1, 1980 through May 31, 1981. During this period we maintained the continuity of projects in the areas of multiphase reactors (trickle-beds in particular) and gas-solid noncatalytic reactions. Active projects, major accomplishments and sponsorship are summarized in Table I.

The primary mission of the Laboratory remained to provide an excellent environment for graduate research and to train graduate students. Fundamental approach to problem solution was emphasized but selection of industrially relevant problems for thesis topics encouraged. Feedback from participating companies was actively sought and always appreciated. We are especially indebted to Mr. Alan Pearson of Alcoa, Dr. John Schwarz of Amoco Oil, Dr. Arnold Hershman and Dr. Dave Gross of Monsanto Corporate Research, Dr. Darwin Novak and Dr. Louis Bosanquet of Monsanto Corporate Engineering, and Dr. Chandler Barkeley of Shell Development for providing us with valuable advice and help during the past year. We are thankful to Dr. David Golland and Dr. John DeLuca of Monsanto Commercial Products for providing the funding in exciting new research areas of gas-melt contacting.

The industrial contacts and industrial support of our research have also been very valuable in attracting American graduate students. At one point during the past year, when there were only six American graduate students in the department (out of about 36 graduate students), four were working in CREL (H. Erk, J. Evans, P. Mills, J. Weston). With increased industrial participation and funding we are confident that we can attract quality American graduate students. These students seem particularly interested in industrial relevance of their work and in establishing industrial contacts. The contribution of foreign students was significant and we will continue to encourage the very

best among them to work in CREL as we have done in the past.

During the past year the operation of the Laboratory was supported almost entirely by industrial contributions (Alcoa, Amoco Oil, Monsanto Company, Shell Development Company) and departmental funds. A minor portion of the support came from NSF through a grant for improving the Laboratory experimental and educational facilities. Proposals to DOE and NSF have been submitted and the decision on funding is expected in Fall 1981.

During the past year Patrick L. Mills received his D.Sc. degree upon completing his thesis in CREL on trickle-bed reactors. He worked for several months at the General Electric Company and has recently joined Monsanto Corporate Research. Henry Erk completed his M.S. thesis on gas-solid noncatalytic reactions in Fall 1980 and joined the Semiconductors Division of the Monsanto Company. Joe Evans is graduating in August 1981 having completed his M.S. thesis on effective diffusivity of liquids in porous catalysts. Dr. Ashok Gokarn from the National Chemical Laboratory in Poona, India has joined CREL for a year at the end of April 1981 to work on problems of gas-melt contacting.

In activities outside Washington University, M. P. Duduković presented seminars at Rice University, University of Maine, University of Wyoming, Oregon State University and a paper with P. L. Mills at the Annual AIChE Chicago Meeting. Mike Duduković also visited Shell Development, Mobil Research and Development, Gulf Research and Development, Amoco Oil Research and Development and the Alcoa Technical Center in order to exchange ideas and explore topics of common interest. Several papers were published and a number submitted for publication.

A brief summary of research projects follows. More detailed description of results and findings for any particular project is available upon request.

TABLE I

Active Projects in the Chemical Reaction Engineering Laboratory June, 1980-present

AREA I: MULTIPHASE REACTORS

Project	Funding	Investigators	Major Results, Publications and Presentations
<p>1. Liquid-Solid Contacting and Liquid Holdup in Trickle-Bed Reactors</p> <p>Relevance: Trickle-bed design and scale-up. Desulfurization of petroleum and coal derived liquids. Hydrogenation of chemicals. Oxidation of waste products. Development of key design parameters.</p>	<p>Industrial Amoco Monsanto Shell</p>	<p>M. P. Duduković P. L. Mills A. El-Hisnawi J. Kang</p>	<p>a) Development of a tracer method for evaluation of liquid-solid contacting.</p> <p>b) Development of a correlation for dynamic saturation and external liquid-solid contacting in trickle-flow regime.</p> <p>c) Development of a correlation for dynamic saturation in gas-liquid interacting (pulsing) regime.</p> <p>d) Quantification of the effect of physical properties (density, viscosity, surface tension) and particle size and shape on dynamic saturation and liquid-solid contacting.</p>

TABLE I. (Cont.)

Active Projects in the Chemical Reaction Engineering Laboratory June, 1980-present

AREA I: MULTIPHASE REACTORS

Project	Funding	Investigators	Major Results, Publications and Presentations
<p>1. Liquid-Solid Contacting and Liquid Holdup in Trickle-Bed Reactors (Continued)</p>			<p>1. P. L. Mills and M. P. Duduković, "Analysis of Catalyst Effectiveness in Trickle-Bed Reactors Processing Volatile and Nonvolatile Liquid Reactants", Chem. Eng. Science 35(11), 2267-2280 (1980).</p> <p>2. P. L. Mills, H. F. Erk, J. Evans and M. P. Duduković, "Some Comments on Models for Evaluation of Effectiveness Factors in Trickle-Bed Reactors", Chem. Eng. Science 36(5), 947-950 (1981).</p> <p>3. P. L. Mills and M. P. Duduković, "Evaluation of Liquid-Solid Contacting in Trickle-Bed Reactors by Tracer Methods", AIChE J. (accepted for publication 1981).</p> <p>4. P. L. Mills and M. P. Duduković, "Reactor Modelling and Parameter Estimation by Time Domain Analysis of Impulse Response Data", AIChE J. (submitted 1981).</p>

TABLE I. (Cont.)

Active Projects in the Chemical Reaction Engineering Laboratory June, 1980-present

AREA I: MULTIPHASE REACTORS

Project	Funding	Investigators	Major Results, Publications and Presentations
<p>2. Prediction of Trickle-Bed Performance</p> <p>Relevance: Prediction of performance of an integral trickle-bed reactor when kinetics, operating conditions and physical properties are known. Reactor model development.</p>	<p>Industrial Amoco Monsanto Shell</p>	<p>M. P. Duduković A. El-Hisnawi D. O'Connor</p>	<p>a) Kinetic studies of hydrogenation of α-methylstyrene in a slurry reactor on Pd/Aℓ_2O$_3$ in four different solvents completed. Kinetic forms and activation energies evaluated. Effect of solvent and impurities determined.</p> <p>b) Apparent rate data gathered in a basket type reactor and effectiveness factor of completely wetted catalyst pellets determined.</p> <p>c) Tracer and reaction studies in trickle-beds are completed. Holdup and contacting effectiveness determined. Conversion data obtained.</p> <p>d) A model for performance of an isothermal trickle-bed reactor in case of a gas limiting reactant developed and checked against experimental data.</p> <p>Papers for publication are in preparation.</p>

TABLE I. (Cont.)

Active Projects in the Chemical Reaction Engineering Laboratory June, 1980-present

AREA I: MULTIPHASE REACTORS

Project	Funding	Investigators	Major Results, Publications and Presentations
<p>3. Evaluation of Diffusivity of Liquids in Solid Catalysts by Dynamic Methods</p> <p><u>Relevance:</u> Evaluation of diffusional resistance for desulfurization and coal hydrogenation catalysts. Assessment of transient methods in evaluation of effective diffusivities in extrudates.</p>	<p>Industrial Alcoa</p>	<p>M. P. Duduković J. Evans</p>	<p>a) Development of a packed bed with large recycle with a dynamic response of a stirred tank for evaluation of effective diffusivities in HDS catalysts.</p> <p>b) Development of on-line data acquisition, processing and parameter estimation procedures.</p> <p>c) Experimental data for the four different catalysts obtained and effective diffusivities evaluated. Inadequacy of a one parameter model for describing effective diffusivity demonstrated. Publication in preparation.</p>

TABLE I. (Cont.)

Active Projects in the Chemical Reaction Engineering Laboratory June, 1980-present

AREA I: MULTIPHASE REACTORS

Project	Funding	Investigators	Major Results, Publications and Presentations
<p>4. Static Mixers in Gas-Liquid Contacting</p> <p><u>Relevance:</u> Improved energy efficiency of gas-liquid contactors. Comparison of interfacial area and power input per unit volume required in static mixers and gas-liquid contactors.</p>	Industrial Monsanto	M. P. Duduković J. Weston	<p>a) Development of experimental set-up to measure volumetric mass transfer coefficients and interfacial area for transfer (via chemical method) by CO₂ absorption in buffered arsenite solution completed.</p> <p>b) Preliminary data indicate higher energy efficiency of static mixers for interfacial area generation than in other gas-liquid contactors.</p>
<p>5. Gas-molten metal contacting.</p> <p><u>Relevance:</u> Metallurgical processes. Manufacture of semiconductors.</p>	Industrial Monsanto	M. P. Duduković A. Gokarn I. P. Wang	<p>Review of bubble formation and growth in media of high surface tension and low viscosity. Formulation of key dimensionless groups and appropriate models.</p> <p>Project initiated in April 1981.</p>

TABLE I (Cont.)

Active Projects in the Chemical Reaction Engineering Laboratory June, 1980-present

AREA II: GAS-SOLID NONCATALYTIC REACTIONS

Project	Funding	Investigators	Major Results, Publications and Presentations
<p>1. Parameter Estimation in Gas-Solid Non-catalytic Reactions</p> <p><u>Relevance:</u> Model selection and parameter estimation for various gas-solid adsorptions and reactions.</p>	<p>Industrial</p>	<p>M. P. Duduković H. Erk</p>	<p>a) Formulation of an algorithm for parameter estimation based on modified Marquardt's, Newton-Raphson and steepest descent method.</p> <p>b) Formulation of a library of models for gas-solid reactions and algorithms based on orthogonal collocation for computation of time-conversion relationships.</p> <p>c) Testing and verification of the algorithm using experimental data for a $CCl_4 + BaF_2$ reaction. Kinetic constants and diffusivities determined. Guidelines for model discrimination provided.</p>
<p>2. Modeling of the "Rotten Apple" Phenomenon</p>		<p>M. P. Duduković H. Erk</p>	<p>a) Explanation of the phenomenon of the solid reacting from inside-out based on diffusion with simultaneous reaction model with a self-inhibited rate form. Publication in preparation.</p>

TABLE I (Cont.)

Active Projects in the Chemical Reaction Engineering Laboratory June, 1980-present

AREA II: GAS-SOLID NONCATALYTIC REACTIONS

Project	Funding	Investigators	Major Results, Publications and Presentations
<p>3. Thermodynamics of the Si/H/C% System Relevance: Production of semiconductor silicon. Examination of the effect of errors in thermodynamic data on equilibrium yields. Exploration of potential for new routes to silicon.</p>	<p>Industrial Monsanto</p>	<p>M. P. Duduković I. P. Wang</p>	<p>a) A fast, simple program for evaluation of equilibrium compositions in the Si/H/C% system developed. b) Effect of errors in thermodynamic data assessed. c) Potential for some new routes to silicon assessed.</p>

AREA I. MULTIPHASE REACTORS

Project 1. Liquid-Solid Contacting and Liquid Holdup in Trickle-Bed Reactors

A. Problem Definition

All processes taking place in trickle-bed reactors in chemical and petroleum industry can be divided into two main groups. In one case a nonvolatile liquid reactant is rate limiting, in the other a gas reactant (or volatile liquid reactant) is rate limiting. In either event overall reaction rate and reactor performance depend on the fraction of the catalyst that is actively wetted by liquid. Hence, liquid-solid contacting efficiency and liquid holdup are important design parameters.

B. Research Objectives

1. Development of a reliable method for evaluation of contacting efficiency.
2. Evaluation of all the available data (from this study and in the literature) for the trickle-flow regime and development of a correlation for contacting effectiveness.
3. Evaluation of all the available data and development of a liquid holdup correlation in trickle-flow regime.
4. Evaluation of data and development of a liquid-holdup correlation for the gas-liquid interacting (pulsing) regime.

C. Research Accomplishments

The experimental setup, presented in Figure 1.1, which was developed by P. Mills and reported on in the last annual report, was used to perform dynamic tracer tests.

Experiments were performed with hexane, cyclohexane, toluene and 2-propanol as carrier liquids with helium, nitrogen or argon as the gas phase. Pentane was used as tracer. Catalyst particles used were 1/16" to 1/32" extrudates, had different composition, 0.5% Pd to 2.5% Pd on alumina, and different pore

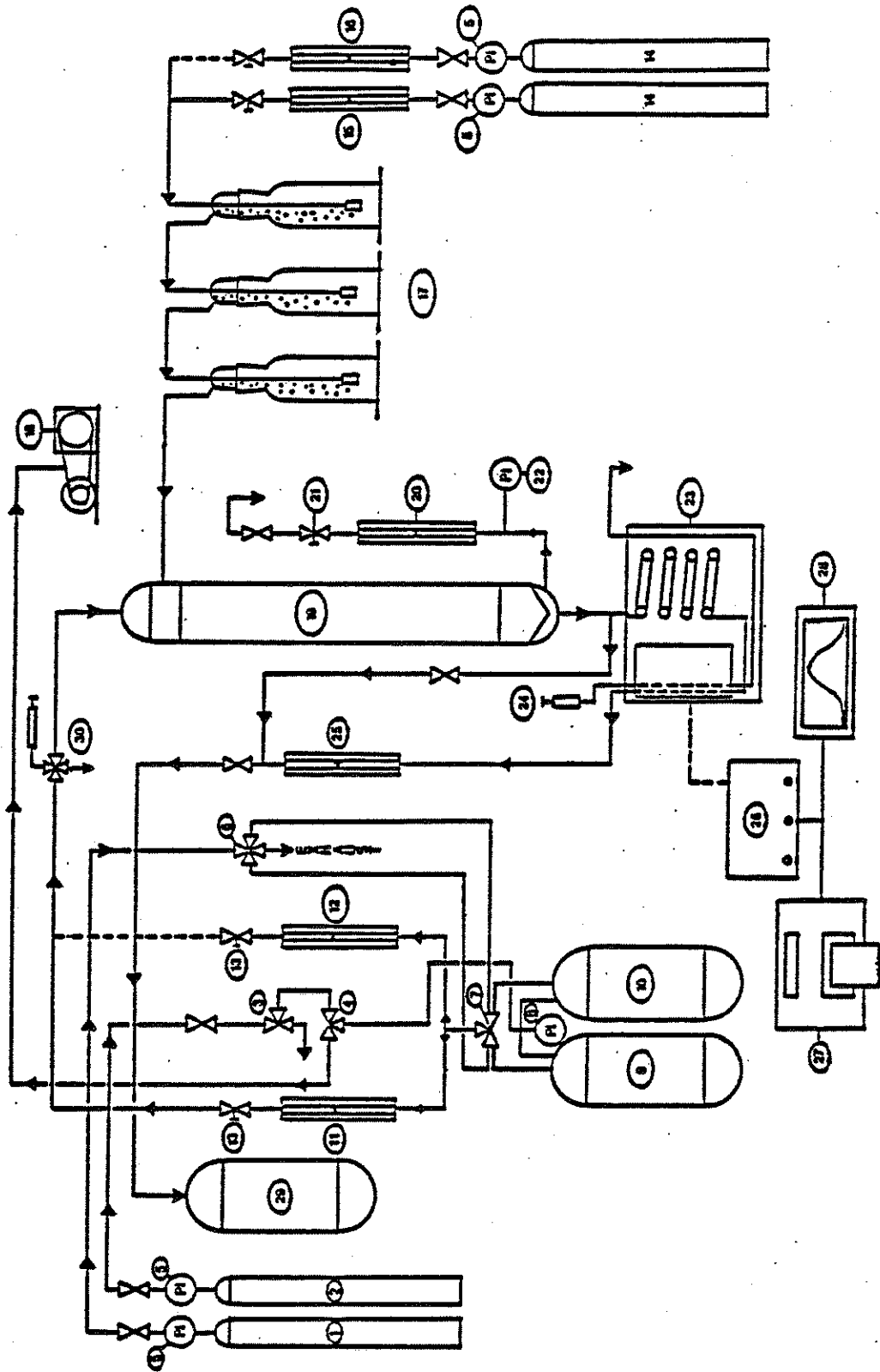


Figure 1.1 Experimental Apparatus for Tracer Studies in Trickle-Bed Reactors.

List of Equipment Items for Figure 1.1

<u>No.</u>	<u>Item</u>	<u>No.</u>	<u>Item</u>
1	Step Valve Supply Pressure Cylinder	15	Low Range Gas Flowmeter
2	Feed Tank Supply Pressure Cylinder	16	High Range Gas Flowmeter
3	3-Way Ball Valve (Pressure/Bleed)	17	Inlet Gas Bubblers
4	3-Way Ball Valve (Pressure/Vacuum)	18	Vacuum Pump
5	Cylinder Pressure Indicator and Regulator	19	Trickle-Bed Column
6	4-Way Ball Valve	20	Outlet Gas Flowmeter
7	3-Way Pneumatic Switching Ball Valve	21	Outlet Gas Metering Valve
8	Feed Tank Pressure/Vacuum Gauge	22	Column Pressure Indicating Gauge
9	Solvent Supply Tank	23	Refractometer Water Bath
10	Solvent/Tracer Supply Tank	24	Refractometer Reference Side Liquid
11	Low Range Liquid Flowmeter	25	Refractometer Outlet Liquid Flowmeter
12	High Range Liquid Flowmeter	26	Control Module
13	Liquid Inlet Metering Valve	27	Voltmeter/Printer/Microprocessor
14	Inlet Gas Supply Cylinders	28	Recorder
		29	Waste Tank
		30	Tracer Injection Valve

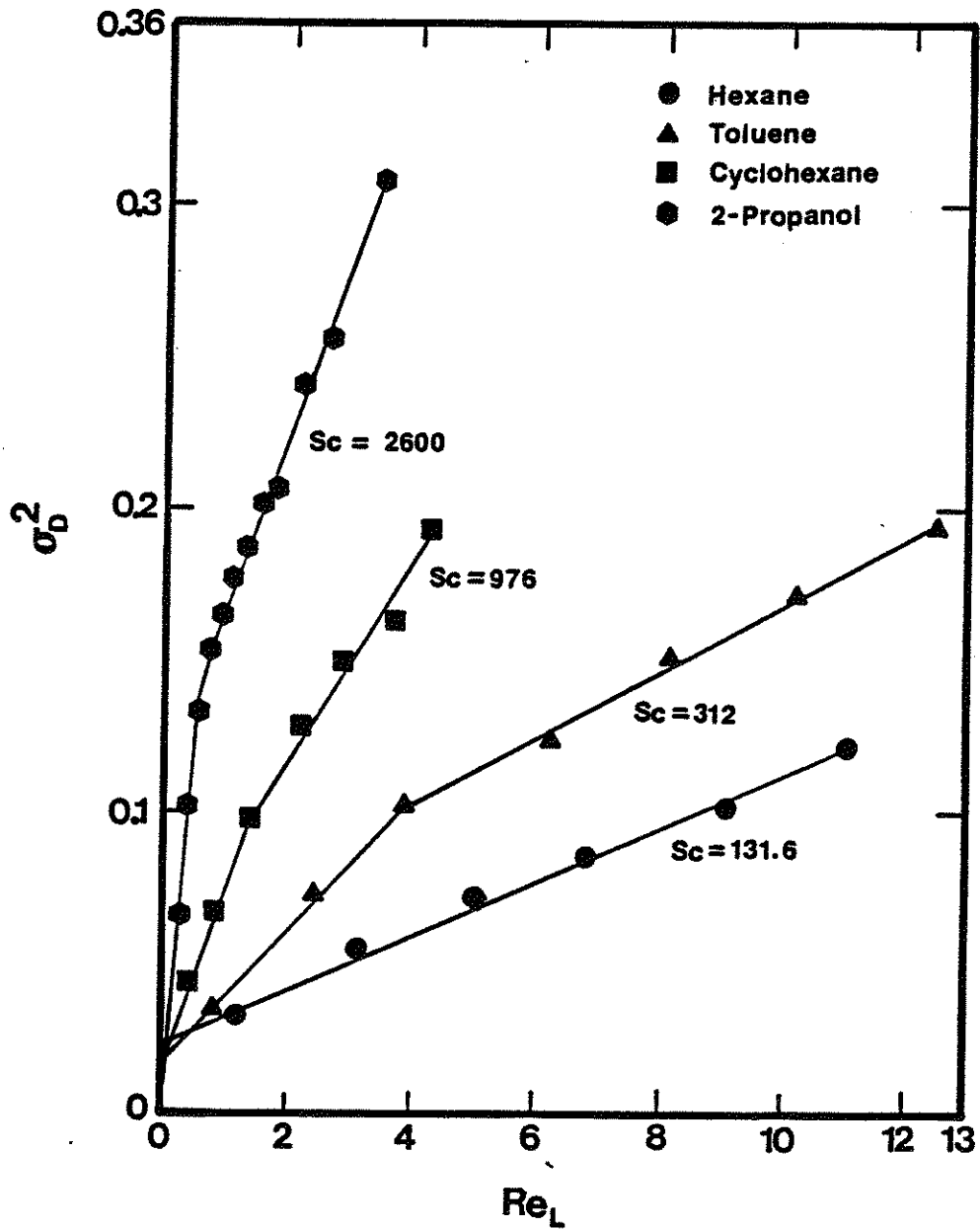


Figure 1.2 Dimensionless Variance for Tracer Impulse Response as a Function of Reynolds Number and Schmidt Number.

ω_D , and external liquid solid contacting, η_{CE} , based on slightly over 100 data points in the trickle-flow regime.

$$\omega_D = 2.02 \text{Re}_L^{0.344} \text{Ga}_L^{-0.197} \quad (1.2)$$

$$\eta_{CE} = 1.60 \text{Re}_L^{0.160} \text{Ga}_L^{-0.0729} \quad (1.3)$$

or

$$\eta_{CE} = 0.957 \text{Re}_L^{0.0598} \omega_D^{0.171} \quad (1.3a)$$

where

$$\text{Re}_L = \frac{u_{SL} \rho_L d_{pe}}{\mu_L} \quad ; \quad d_{pe} = \frac{6 V_p}{S_{ex}}$$

$$\text{Ga}_L = \frac{d_{pe}^3 g \rho_L^2}{\mu_L} \quad ; \quad \omega_D = \frac{H_D}{\epsilon_B}$$

These correlations are valid in the trickle-flow regime (low gas-liquid interaction regime on the flow map of Charpentier presented as Figure 1.4).

No clear effect of the groups containing surface tension such as the Weber number or Capillary number was obtained. Introduction of such additional groups into the correlation improved the matching of data at best marginally. This may be due to the fact that all the data used are based on hydrocarbons and water and the surface tension was varied only from about 18 dyn/cm to 75 dyn/cm. No effect of the packing characterization factor $a_t d_{pe} / \epsilon_B$ was observed either. The value of this group ranges between 7 and 11 for the data considered.

5. The following correlation was obtained for liquid saturation in the pulsing regime (high gas-liquid interaction regime presented in Figure 1.4).

$$\omega_D = 1.52 \text{Ca}^{0.0516} \text{Re}_g^{-0.138} \text{Ga}_L^{-0.0625} \quad (1.4)$$

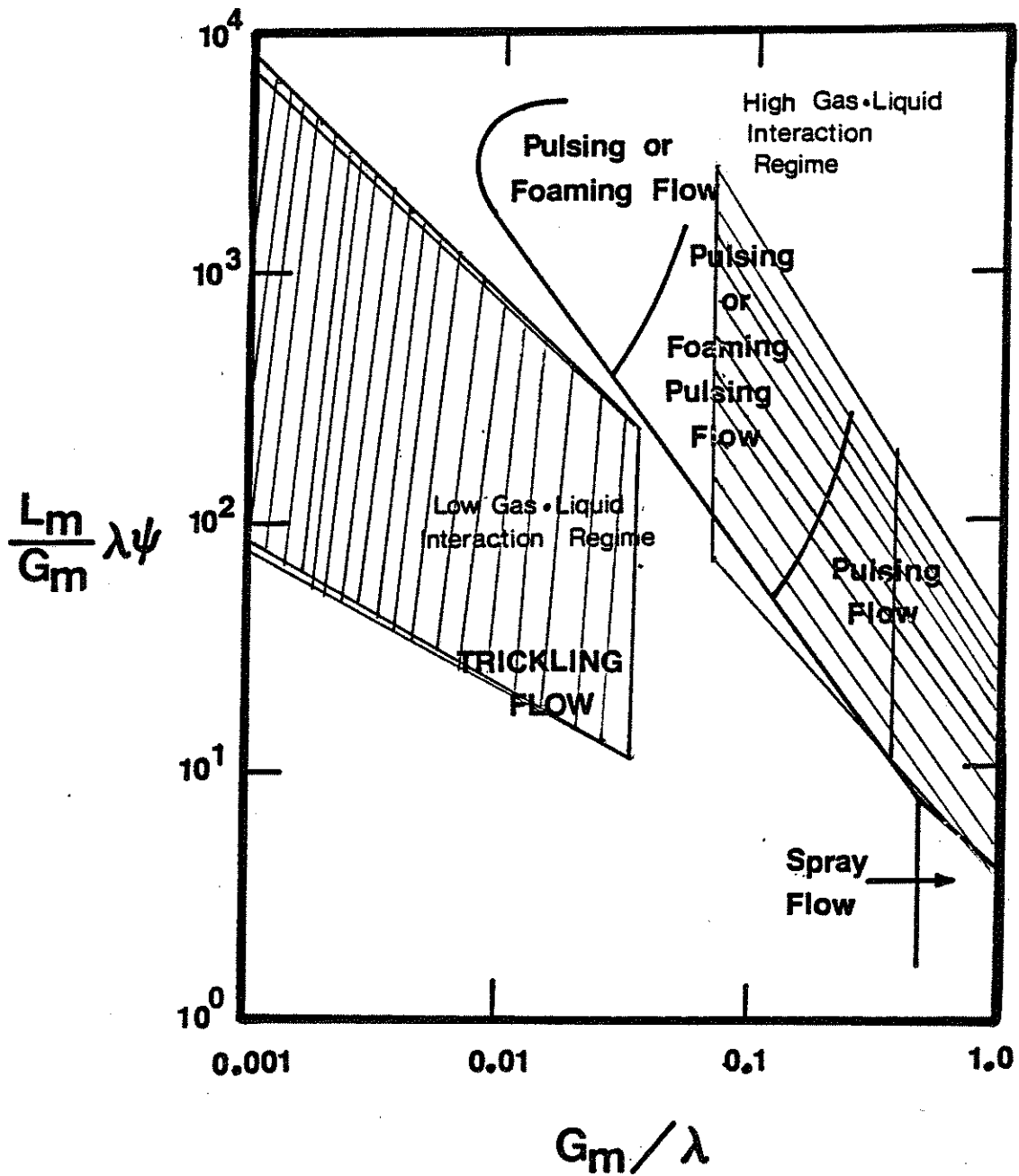


Figure 1.4 Flow Regimes in Trickle-Bed Reactors

- ////// Region of the data used for low gas-liquid interaction regime correlations.
- ////// Region of the data used for high gas-liquid interaction regime correlations.

where:

$$Ca = \frac{\mu_L u_{SL}}{\sigma} ; \quad Re_g = \frac{u_{sg} \rho_g d_{pe}}{\mu_g}$$

All the details of the analysis, range of variables, average errors and standard deviations are in preparation for publication and are available upon request. They are also part of the thesis of A. El-Hisnawi.

D. Further Research Plan

1. Extension of experiments and correlations from isothermal to adiabatic situations.
2. Formulation of a hydrodynamic model to explain and bridge the differences between low and high gas-liquid interaction regime.

Project 2. Prediction of Trickle-Bed Performance

A. Problem Definition

In order to be able to design and scale-up trickle-bed reactors it is desirable to first be able to predict their performance for well understood test reactions. In this project the goal is to examine how well can one predict the performance of a trickle-bed operating at substantial conversion of the liquid reactant, based on the known kinetics (as determined in a slurry reactor), known effectiveness factor of completely wetted catalyst (as determined in a stirred tank reactor) and independently measured contacting efficiency (determined by the tracer technique). The basic premise is that dispersion effects are unimportant except at very high conversion (as documented repeatedly in our Laboratory) and that correct prediction of reactor performance for reactions of known kinetics is achievable if particle scale contacting efficiency and the resulting catalyst effectiveness factor are correctly assessed. This last information depends on the accuracy of gas-liquid and liquid-solid mass transfer coefficients in trickle-bed reactors. Hydrogenation of α -methylstyrene on Pd/Al₂O₃ in various organic solvents as carriers was selected for a test reaction.

B. Research Objectives

1. Development of a model for an isothermal trickle-bed reactor with gas-limiting reactant.
2. Comparison of model predicted and experimental reactor performance.

C. Research Accomplishments

1. The kinetics of α -methylstyrene hydrogenation in various solvents (hexane, cyclohexane, toluene, 2-propanol) was determined in a slurry reactor. The reaction was found to be approximately first order with respect to hydrogen and zero order with respect to α -methylstyrene.

The rate forms obtained are presented in Table 2.1. The effect of impurities is discussed in the thesis by El-Hisnawi.

2. Determination of reaction rates in completely wetted catalyst pellets was done in a stationary basket type reactor described in the last annual report. The effectiveness factors of 1/8" to 1/16" extrudates with different catalyst loading (0.5% Pd to 2.5% Pd) were found to vary from 0.012 to 0.21 at temperatures between 15°C and 30°C.
3. Liquid holdup and catalyst contacting were determined by tracer tests on 0.5% Pd and 2.5% Pd 1/16" catalyst particles in the region of interest and found to be in good agreement with the proposed correlations.
4. The proposed model for the trickle-bed is based on the following assumptions: *i*) plug flow, *ii*) isothermal, *iii*) excess gas reactant in gas phase, *iv*) complete internal catalyst wetting, *v*) no reactor scale incomplete contacting, *vi*) zeroth order reaction with respect to liquid reactant, first order in gas reactant.

Assumptions *iv*) and *v*) were verified by tracer studies and assumption *vi*) by our kinetic studies. Pure hydrogen feed or hydrogen/nitrogen mixtures used satisfied assumption *iii*). Due to the presence of the solvent and small feed concentrations of α -methylstyrene assumption *ii*) is satisfied. Assumption *i*) holds, as proven by tracer studies, except at very low liquid velocities.

The equation for conversion of α -methylstyrene, X_α , takes the following form:

$$\frac{C_{\alpha 0} U_L X_\alpha}{L \eta k (1-\epsilon) C_{ge}} = (1-\eta_{CE}) \left\{ \frac{1}{1 + \frac{\eta k V_P}{k_{gs} S_{ex}}} \right\} + \eta_{CE} \left\{ \frac{1}{\left(1 + \frac{\eta k V_P}{k_{LS} S_{ex}}\right)^\lambda} \left[\frac{(C_{gi}/C_{gl})^{\lambda-1}}{\frac{k_{gl} a_{gl} L}{U_L}} - \frac{k_{gl} a_{gl} L}{U_L} \right] + 1 \right\} \quad (2.1)$$

Table 2.1

Summary of Intrinsic Reaction Rate

Forms in Various Solvents



Solvent	Rate Form	
	0.5% Pd	2.5% Pd
Cyclohexane	$10.25 \times 10^5 e^{-\frac{10,200}{RT}} P_{\text{H}_2}$	Same as with 0.5% Pd.
Hexane (u.v) grade	$2.307 \times 10^4 e^{-\frac{8000}{RT}} P_{\text{H}_2}$	Same as with 0.5 %
Hexane (ACS) grade	$7.1 \times 10^4 e^{-\frac{9280}{RT}} P_{\text{H}_2}$	$2.724 \times 10^4 e^{-\frac{8180}{RT}} P_{\text{H}_2}$
Toluene	$5.04 \times 10^3 e^{-\frac{8353}{RT}} P_{\text{H}_2}$	$4.99 \times 10^2 e^{-\frac{6100}{RT}} P_{\text{H}_2}$
2-propanol	$3.477 \times 10^5 e^{-\frac{10,800}{RT}} P_{\text{H}_2}$	$1.091 \times 10^4 e^{-\frac{8000}{RT}} P_{\text{H}_2}$

$$\lambda = 1 + \frac{k_{LS} a_{LS}}{k_{gl} a_{gl}} \frac{\frac{\eta k V_p}{k_{LS} S_{ex}}}{1 + \frac{\eta k V_p}{k_{LS} S_{ex}}}$$

The length of the bed, L , and its porosity, ϵ , is known. The feed α -methylstyrene concentration, $C_{\alpha O}$, and hydrogen concentration in the liquid feed, C_{gi} , are known for each run as well as catalyst particle dimensions, V_p and S_{ex} . Reaction rate constant, k , and hydrogen solubility, C_{ge} , are also known at desired temperatures. The effectiveness factor of completely wetted catalyst, η , was determined by our kinetic studies and catalyst contacting, η_{CE} , is available from tracer studies or correlations. The success of formula (2.1) in predicting experimental results depends on the accuracy of the available correlations for gas-liquid, $k_{gl} a_{gl}$, and liquid-solid volumetric mass transfer coefficients, $k_{LS} a_{LS}$.

It was shown by El-Hisnawi that using any of the available correlations for $k_{ge} a_{ge}$ and $k_{LS} a_{LS}$ greatly underpredicts the observed conversion data. However, when these parameters are adjusted upward by roughly a factor of five, data in all solvents can be predicted well with no additional adjustable parameters. Comparison of model predictions and experimental conversions is illustrated in Figures 2.1 and 2.2.

D. Further Research Plan

1. Extension to adiabatic conditions with small and large percent of solvent volatization.
2. Evaluation of a liquid-limiting reactant case such as H_2O_2 decomposition.

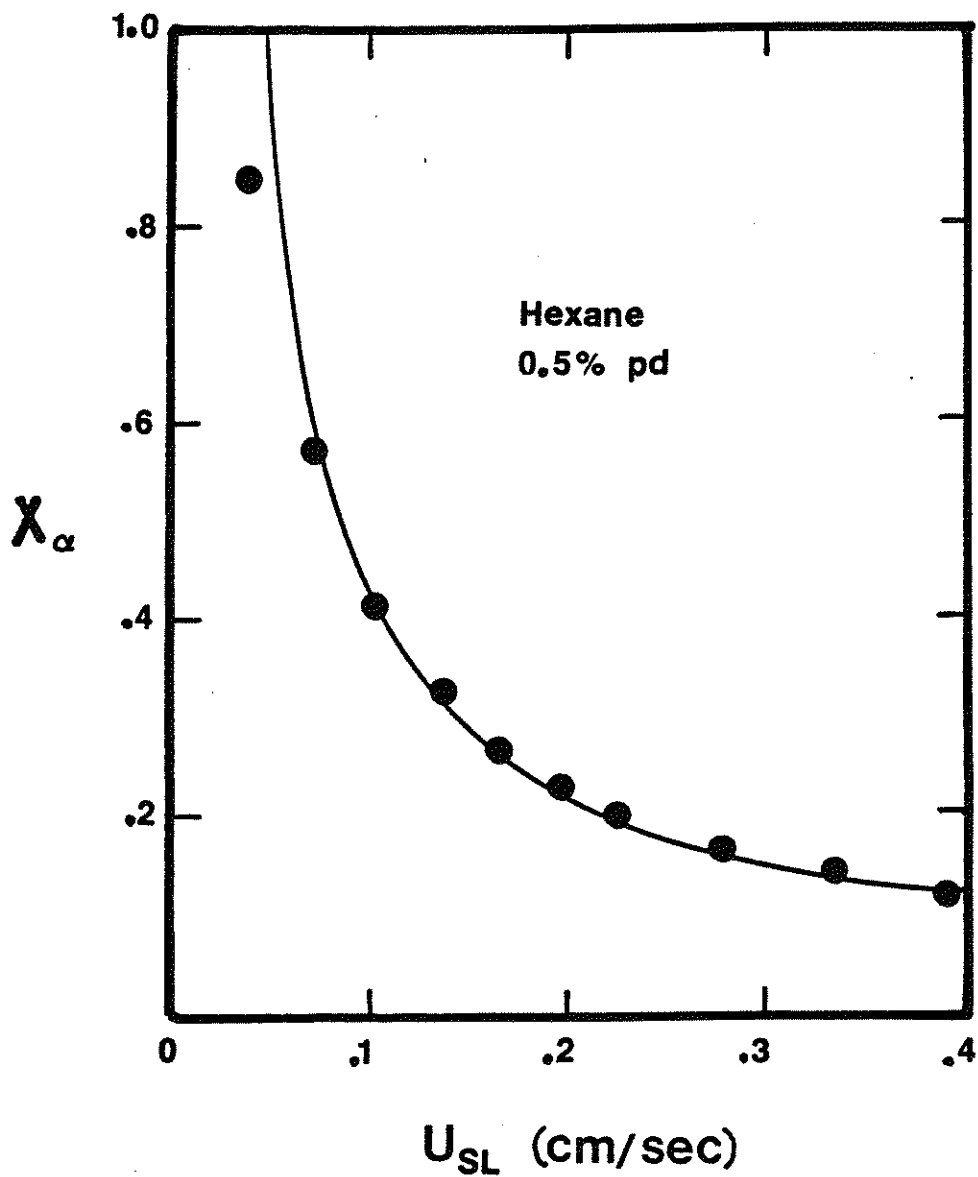


Figure 2.1 Comparison of Model Predicted and Experimental Conversion in a Trickle-Bed Reactor (Hexane Solvent, 0.5% Pd on Al_2O_3 catalyst).

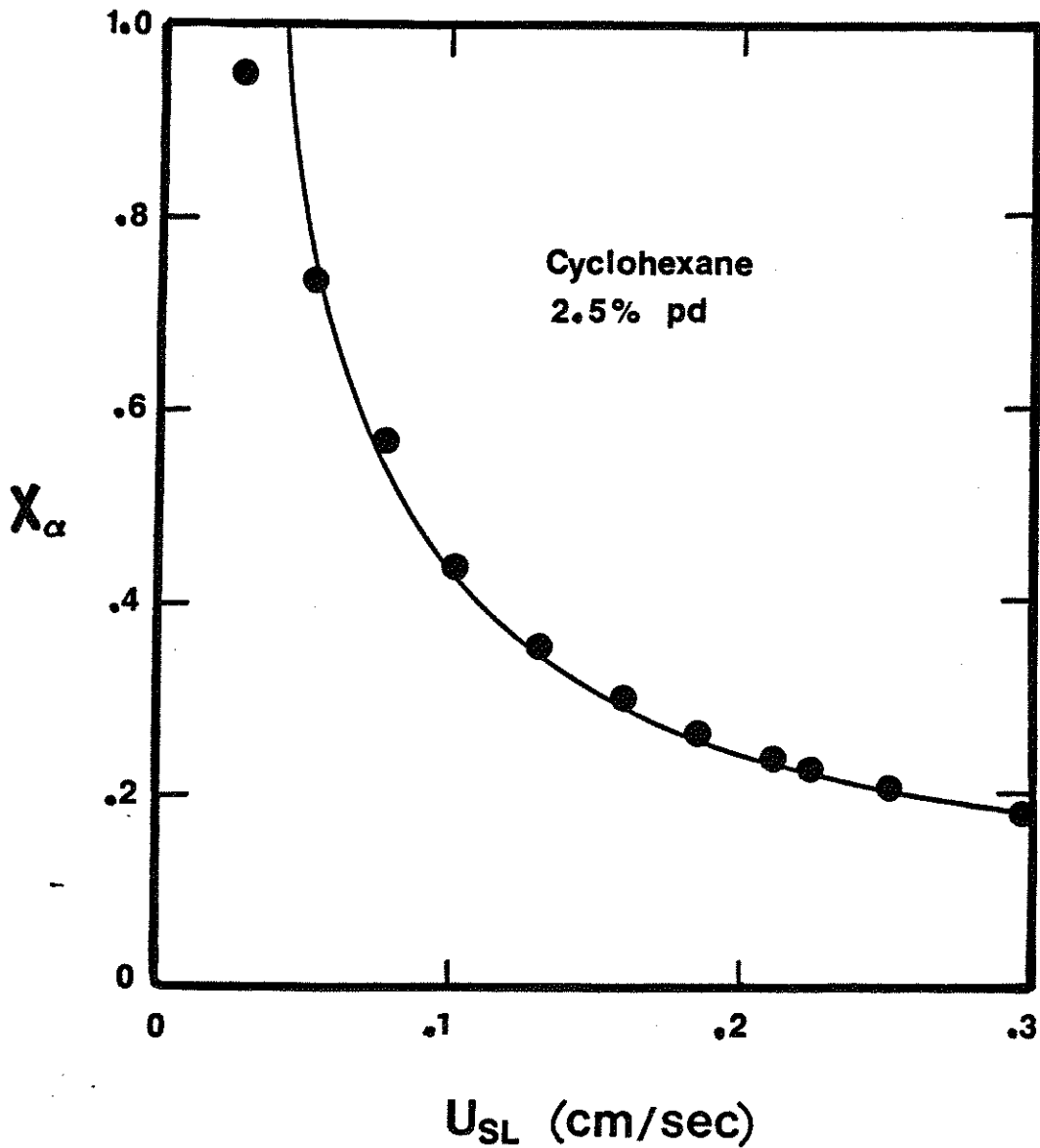


Figure 2.2 Comparison of Model Predicted and Experimental Conversion in a Trickle-Bed Reactor (Cyclohexane Solvent, 2.5% Pd on Al_2O_3 catalyst).

Project 3. Effective Diffusivity of Liquids in Solid Catalysts

A. Problem Definition

Knowledge of effective diffusivities of liquids in porous catalysts is necessary for proper estimation of catalyst effectiveness factors. This information is also necessary in assessing the contribution of internal pellet diffusion to tracer response curves. Finally, for HDS or H-coal catalysts it is of interest to know whether effective diffusivities in fresh and spent catalysts are the same. Evaluation of effective diffusivity can be obtained from dynamic tracer testing and the experiments can be best performed in vessels that, when packed with nonporous packing, give exponential residence time distributions.

B. Research Objectives

1. Development of on-line data acquisition and computerized data processing capabilities for determination of effective diffusivities from transient responses.
2. Development of a method for evaluation of effective diffusivities from transient data based on direct time-domain matching of experimental and model responses.
3. Development of a method for evaluation of effective diffusivities from transient data based on the method of moments.
4. Critical evaluation of the methods, apparatus and models used in the evaluation of effective diffusivity of liquids by transient methods.

C. Research Accomplishments

The equipment for evaluation of effective diffusivity is shown in Figure 3.1. It was demonstrated that when the vessel is filled with glass beads the response of a stirred tank reactor is obtained. This is illustrated by Figure 3.2 where step-up, step-down and impulse responses for the open system are

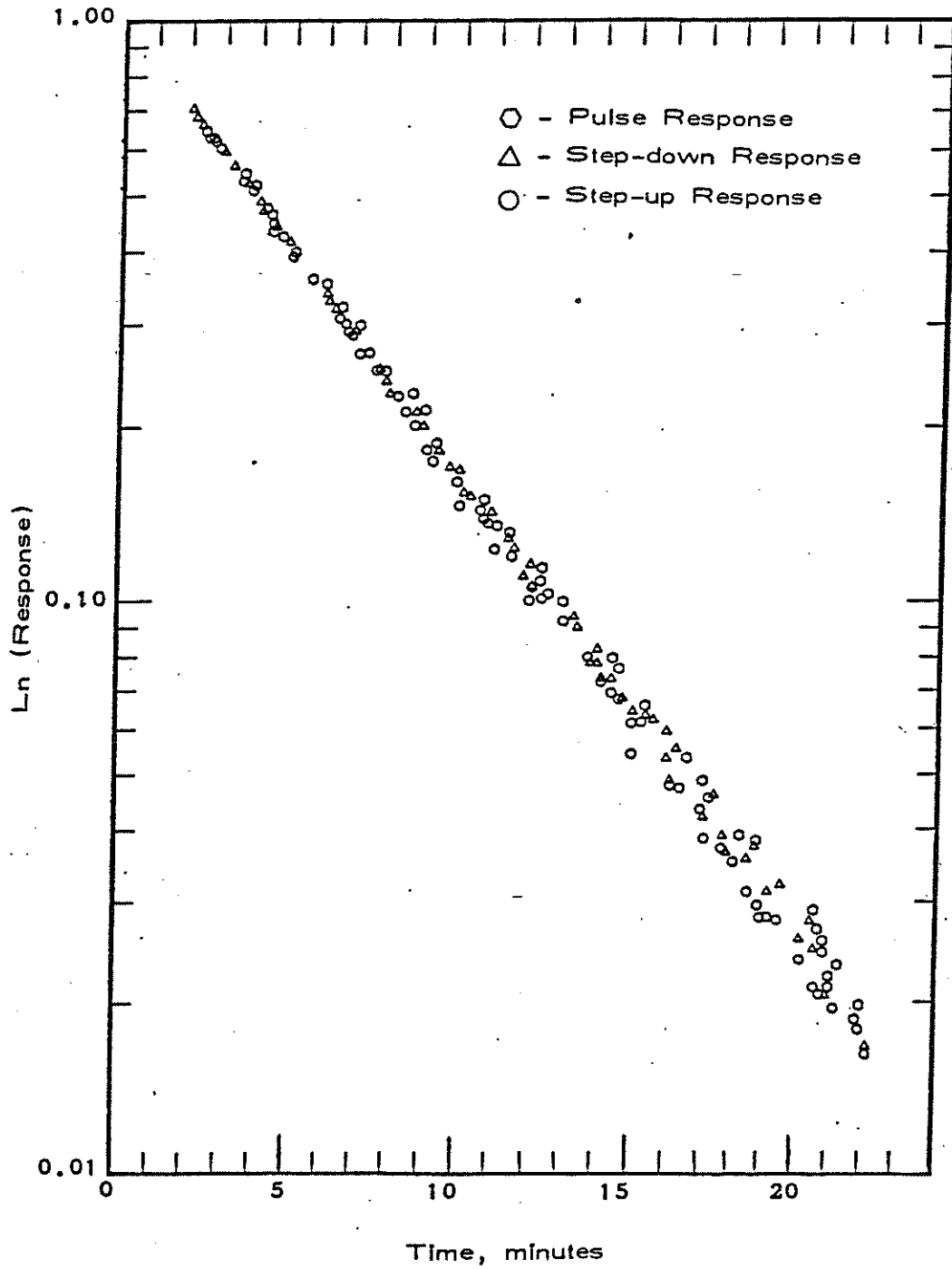


Figure 3:2 Impulse, Step-down and Step-up Response of the System.

presented. For evaluation of effective diffusivities a known amount of catalyst particles was interdispersed among the glass beads and the system was operated in a closed mode subject to impulse tracer injections. Cyclohexane was used as solvent and tetrahydronaphthalene as tracer. Several different catalysts were tested. Details are provided in the thesis by J. Evans.

1. On-line data acquisition was accomplished by interfacing an Apple II microcomputer with the spectrophotometer. Data were stored on disks and via a modem were transferred to a DEC 20 computer for processing and parameter estimation.
2. An algorithm was developed for direct parameter estimation (effective diffusivity and adsorption equilibrium constant) by minimizing the sum of the squares of the errors between experimental and model predicted data. The model is based on diffusion of tracer from a well mixed, finite volume of fluid into a porous particle with co-current instantaneous and reversible adsorption. The diffusion process is described by a single effective diffusivity. Model solutions are based on particle shapes of spheres or infinite cylinders.
3. An algorithm based on the method of moments was developed for evaluation of effective diffusivities, D_e , and adsorption equilibrium constants, K_A , from experimental transient data. The method of moments included models based on spherical, infinite cylinder and finite cylinder particles of different aspect ratio $P = R/L$. In order to implement the method of moments the steady state response upon tracer injection, C_∞ , has to be estimated and subtracted from the response. The theoretical curves for various particle shapes are presented in Figure 3.3.

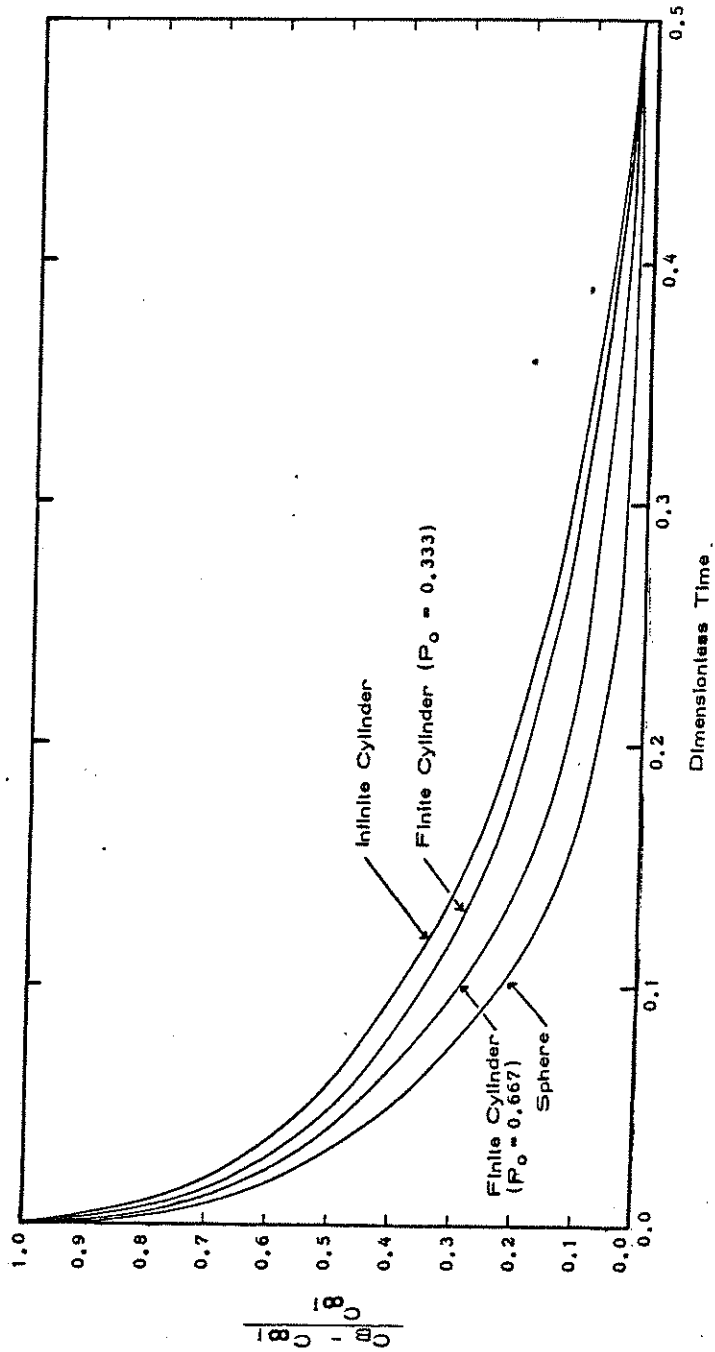


Figure 3.3 Concentration Profiles Computed from the Model Response.

4. Comparison of the time-domain matching and method of moments was performed. A typical result is presented in Table 3.1. The reproducibility of each method is good. Effective diffusivities determined by direct time-domain parameter estimation and method of moments are always within 15% of each other. Thus, either method could be used for evaluation of effective diffusivities. However, the adsorption equilibrium constants varied by up to 60% depending on the method used for their evaluation. The values determined by time-domain matching are closer to the ones obtained from batch adsorption isotherms. An analysis, presented in Figure 3.4, indicates that an underestimate in C_{∞} of 5 - 10% causes at most an overestimate of diffusivity of up to 12%, but the overestimate in equilibrium constant may be anywhere from 30% to 70%. Figure 3.4 indicates that for accurate estimates of effective diffusivity by the method of moments one should underestimate C_{∞} , while an overestimate of C_{∞} is needed for better estimates of the adsorption equilibrium constant.
5. Measurements with two different particle sizes of the same catalyst showed an increase in effective diffusivity with increased particle size. For a particle size ratio of two the ratio of the determined effective diffusivities was 3.65 which is close to the particle size ratio squared. This points out the inadequacy of the model based on single effective diffusivity in interpreting experimental data and throws serious doubts on all the data reported in the literature. A bidisperse pore structure, skin effect etc., leading to systems with two time constants may be helpful in explaining our experimental data. Additional effects of catalyst loading and

Table 3.1

Effective Diffusivity and Adsorption Equilibrium Constant for 0.1588 cm Diameter Catalysts (Amoco)

Run Number	Tracer Injected (grams)	Injection Number	γ	Time-Domain k_A	Matching $D_e \times 10^6$	Method of Moments k_A $P = 0$	Method of Moments k_A $P = 0.19$	
28	.348	1	0.0451	5.69	5.83	7.29	9.07	
31	.348	1	0.0458	5.53	6.20	6.35	7.74	
34	.348	1	0.0454	5.91	6.16	7.82	9.73	
37	.348	1	0.0458	6.16	5.75	8.28	10.70	
Average \pm Standard Deviation				5.82 \pm .27	5.99 \pm .23	7.44 .83	9.31 \pm 1.24	6.22 \pm .37

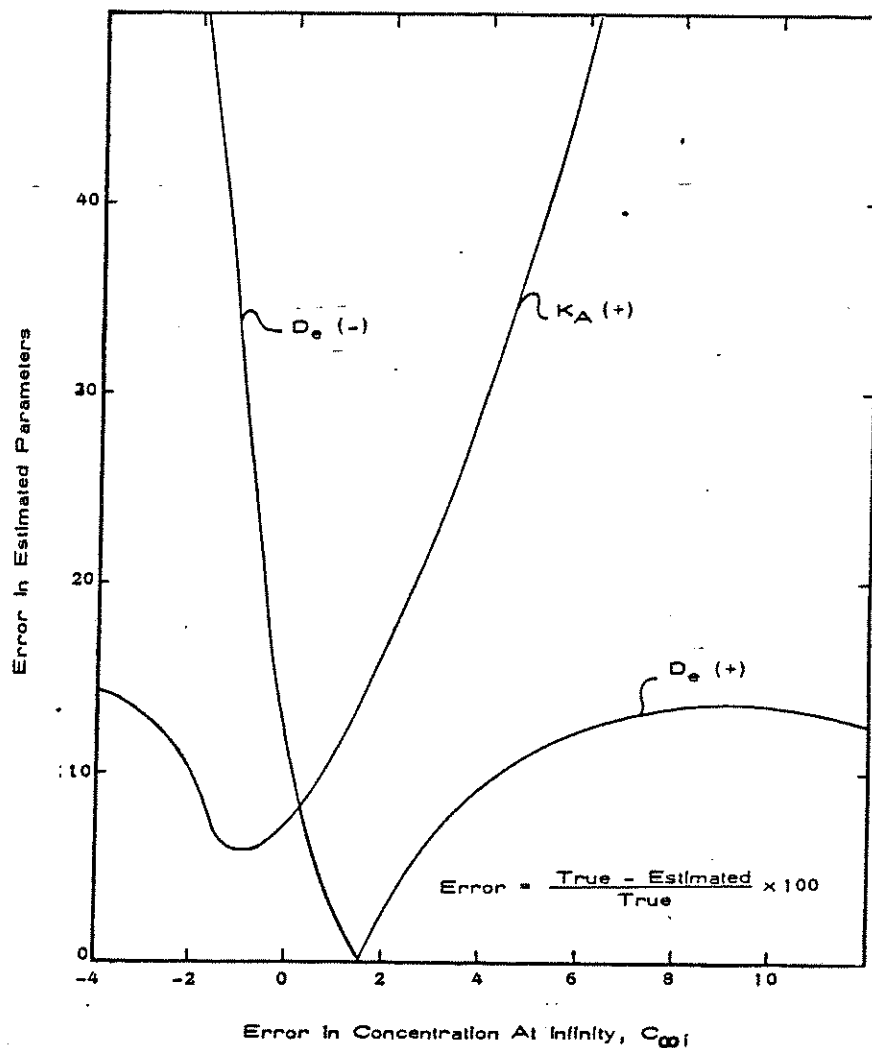


Figure 3.4 Effect of the Error in Steady State Concentration (Final Concentration Value) on Estimated Diffusivity and Adsorption Equilibrium Constant by the Method of Methods (Three digit accuracy of the response signal is used as produced by the spectrophotometer).

repeated tracer injection on effective diffusivity were observed and could not be explained based on a single diffusivity model.

Details are provided in the thesis by Joe Evans.

D. Further Research Plan

1. Examination of alternative models capable of eliminating the effect of particle size, catalyst loading (volume of catalyst/volume of liquid) and repeated tracer injections on diffusivity.

Project 4. Static Mixers in Gas-Liquid Contacting

A. Problem Definition

Static mixers are motionless in-line mixers composed of separate inserts (elements) which vary from helixes to dense, corrugated panels. The advantage of static mixers in blending highly viscose fluids and in creating liquid-liquid dispersions has been documented.

It is of interest to determine whether static mixers are viable contacting devices for gas-liquid reactions. It is particularly important to evaluate whether they can provide large volumetric mass transfer coefficients and interfacial areas for transfer at lower power input per unit volume of liquid than traditional gas-liquid contacting devices such as stirred tanks, packed and bubble columns, ejectors, venturris, etc.

B. Research Objectives

1. Development of an experimental set-up for evaluation of different types of static mixers for gas-liquid contacting.
2. Evaluation of pressure drop and gas holdup correlations for static mixers.
3. Determination of interfacial areas and required power input and comparison to other gas-liquid contacting devices.

C. Research Accomplishments

1. An experimental set-up has been developed as shown in Figure 4.1.
2. Preliminary data on pressure drop and gas holdup is shown in Figures 4.2 and 4.3. This data was obtained with a Kenics mixer (180° helical elements) and shows that the pseudo homogeneous model predicts better the observed phenomena than the Lockhart-Martinelli correlation.
3. It was shown that absorption of carbon dioxide in water catalyzed by buffered arsenite solutions can be used to obtain interfacial areas, a_{GL} . This chemical method was used by other investigators and it was

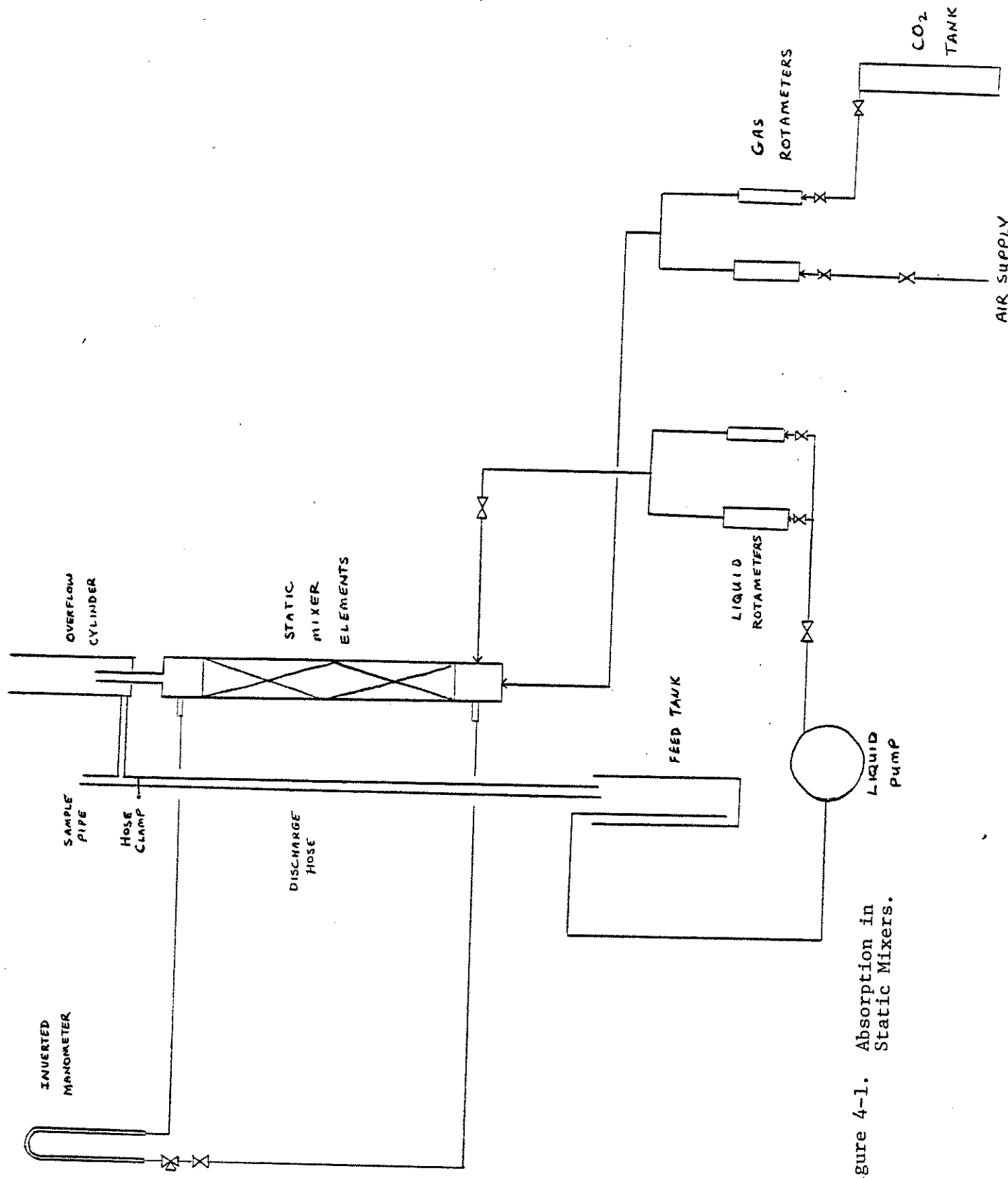
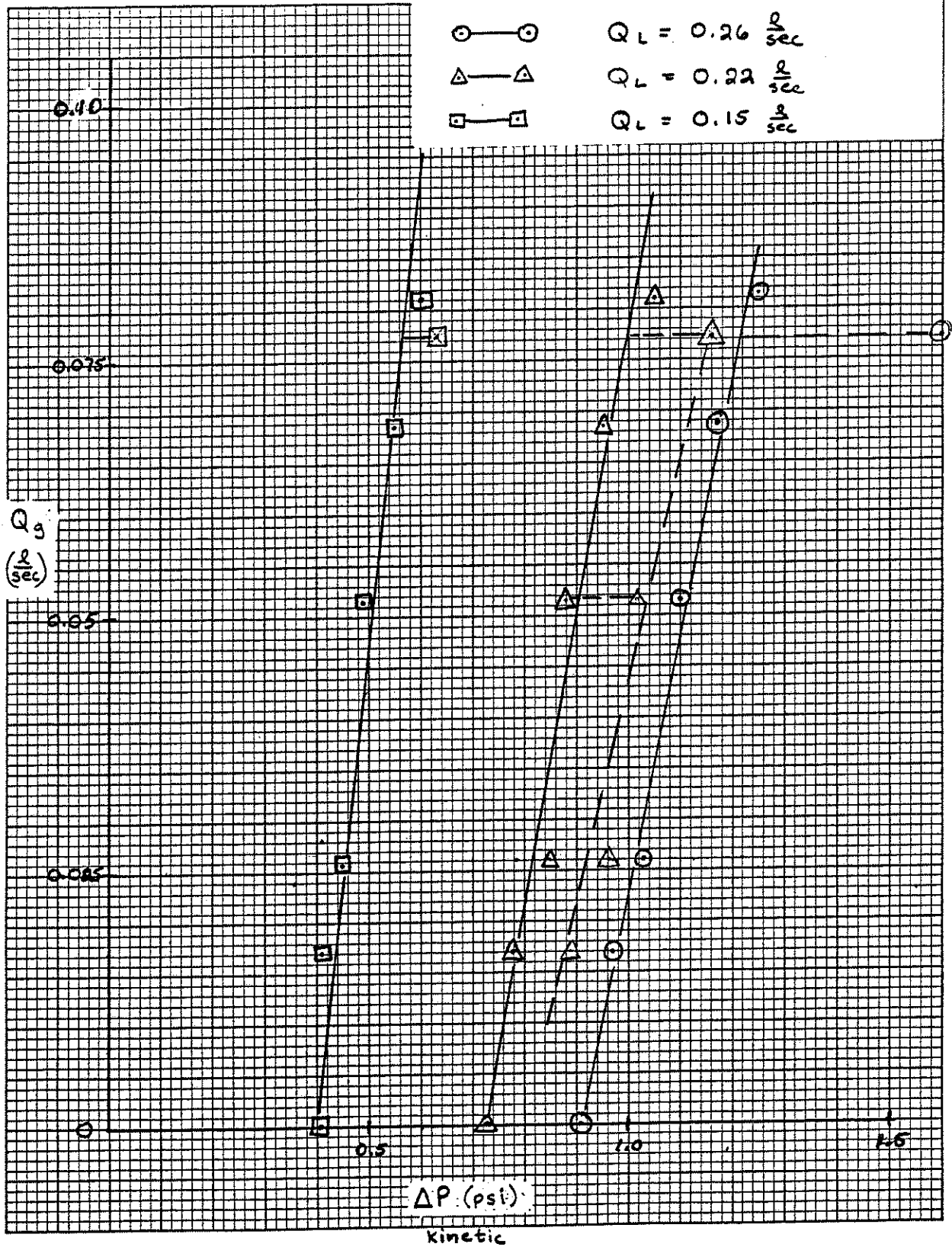


Figure 4-1. Absorption in Static Mixers.

Kinetic ΔP as a Function of Gas and Liquid Flowrates.



K₂E 5 X 8 TO THE CENTIMETER 48 1612
 MADE IN U.S.A.
 KEUFFEL & ESSER CO

Figure 4.2. Pressure Drop as a Function of Operating Conditions.

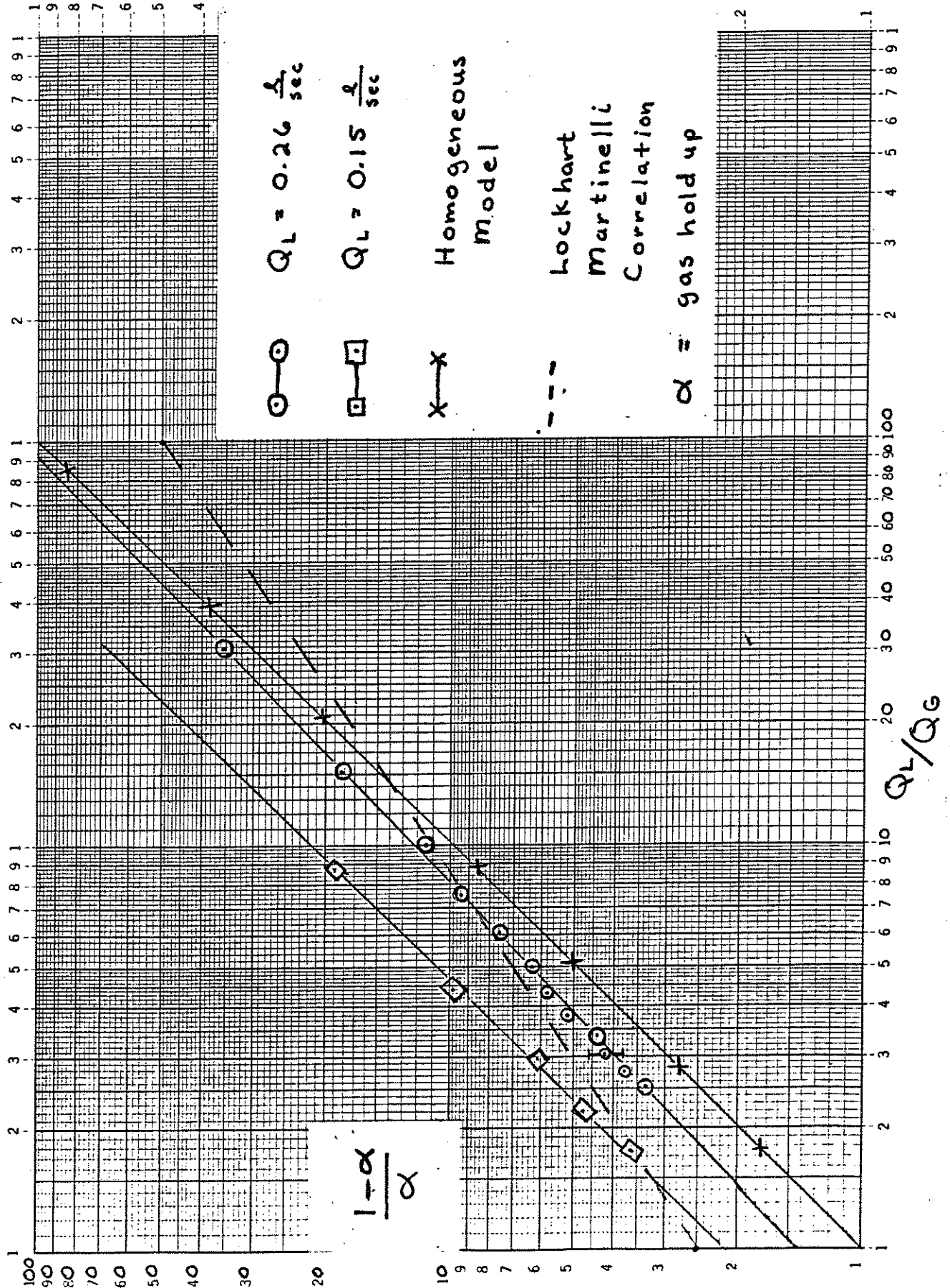


Figure 4.3. Gas Holdup as Function of Operating Conditions.

shown that the following representation of data is possible:

$$\left(\frac{R a_{LG}}{C_A^*} \right)^2 = D_L k_2 C_B a_{LG}^2 + (k_L a_{LG})^2 \quad (4.1)$$

Since $(R a_{LG}/C_A^*)$ and C_B are obtained from the experiments and data for D_L and k_2 are available in the literature both interfacial area a_{LG} and mass transfer coefficient, k_L , can be determined.

Preliminary runs indicate that the Kenics mixer may provide more interfacial area at a given power input than other gas-liquid contacting devices.

D. Further Research Plan

1. To complete research objectives stated above under B. as part of John Weston's M.S. thesis requirements.
2. To examine the utility of surfaces and edges i.e. of inducing secondary shear flows and turbulence on creating gas-liquid interfacial area and suggest an improved static mixer for gas-liquid operation.

Project 5. Gas-Molten Metal Contacting

A. Problem Definition

Relatively cold gases are introduced into molten metals in a number of metallurgical processes. Supersonic and subsonic impinging jets and submerged spargers are used for this introduction of the gas into the melt. Some semi-quantitative, empirical information exists on oxygen lancing in steel making processes. The usual chemical engineering correlations for bubble columns are not readily extrapolated to molten metals since these have very high surface tension. This whole area of gas-melt contacting needs a systematic study in order to allow rational design for these systems.

B. Research Objectives

1. Review the current state of the art in gas-melt contacting.
2. Formulate a model to assess the key factors determining bubble formation, growth, size and rise velocity when a cold gas is introduced into hot, molten metal from a submerged sparger.
3. Formulate a model to determine criteria for jet penetration and breakup for supersonic and subsonic impinging jets.
4. Formulate a model to determine gas-melt interactions and capture by the melt of the particulates carried by the feed gas.
5. Verify models by studies on model systems.

C. Research Accomplishments

The project was initiated in January 1981 and work started at the end of April 1981.

1. The review of the state of the art in gas-melt contacting has been completed and is in preparation.

D. Further Research Plan

As indicated above under B.

AREA II. GAS-SOLID NONCATALYTIC REACTIONS

Project 1. Parameter Estimation in Gas-Solid Noncatalytic Reactions

A. Problem Definition

Reactions of solid particles play an important role in ore roasting and leaching, in coal conversion, pollution abatement and in a number of chemical processes. Reliable reactor design depends on proper understanding of rate limiting steps and quantification of the rate expression for reaction of a single solid particle.

Traditionally a single pellet reactor is used in the laboratory to produce conversion-time data. A fit of various models for reactions of solid particles can then be attempted to such data. This often requires nonlinear parameter estimation procedures.

B. Research Objectives

1. Development of a "library" of models for gas-solid noncatalytic reactions.
2. Development of a numerical algorithm for nonlinear least squares parameter estimation from conversion-time data.

C. Research Accomplishments

Both research objectives have been accomplished. Details are available in Henry Erk's M.S. thesis.

A powerful program, which utilizes orthogonal collocation, is available and on file in the laboratory for evaluation of rate and diffusion constants from time-conversion data for a single, isothermal, gas-solid reaction.

D. Further Research Plan

Extension to multiple gas-solid reactions if funding becomes available.

Project 2. Modeling of the "Rotten Apple" Phenomenon

A. Problem Definition

Some gas-solid reactions systems exhibit a peculiar behavior that the solid reacts from inside-out ("rotten apple" phenomenon) contrary to models for the diffusion with simultaneous reaction. Various consecutive reaction schemes are sometimes hypothesized to explain the phenomenon. It is of interest to determine whether any other explanations are plausible.

B. Research Objectives

1. Evaluation of the self-inhibited rate form as an explanation for "rotten apple" phenomenon.
2. Evaluation of possibility of multiple reaction paths for solid particles under identical conditions in case of self-inhibited rate forms.

C. Research Accomplishments

1. The following model containing a self-inhibited rate expression (such as the one found in catalytic oxidation of CO and Pt) with respect to the gas reactant has been proposed as a possible explanation for the "rotten apple" phenomenon.

$$\nabla^2 y - \frac{\phi^2 z^\rho y}{(1 + \bar{K}y)^2} = 0$$

$$\frac{\partial z}{\partial \theta} = - \frac{z^\rho y}{(1 + \bar{K}y)^2}$$

where ∇^2 is the Laplacian operator, y -dimensionless concentrations of the gas reactant, z -dimensionless concentration of the solid reactant, θ -dimensionless time, ϕ^2 -Thiele modulus, \bar{K} -dimensionless inhibition constant, ρ -parameter with values $0 \leq \rho \leq 1$.

Solid conversion as a function of time is given by:

$$X(\theta) = 1 - (\nu + 1) \int_0^1 \xi^\nu z(\xi, \theta) d\xi$$

where ξ is dimensionless position within the solid pellet and $\nu = 0, 1, 2$ is the shape factor for the solid pellet.

The model was solved by orthogonal collocation and it was shown that for certain values of parameters ρ , \bar{K} and ϕ^2 the solid may indeed react from inside out as illustrated in Figure II-2.1.

2. It has also been shown that multiple gas reactant concentration profiles within the pellet are possible for certain parameter range as shown in Figure II-2.2.
3. Multiple conversion-time histories are also possible but are practically indistinguishable from each other.

Details and further discussion is provided in Henry Erk's thesis.

D. Further Research Plan

Extension to the shrinking core model.

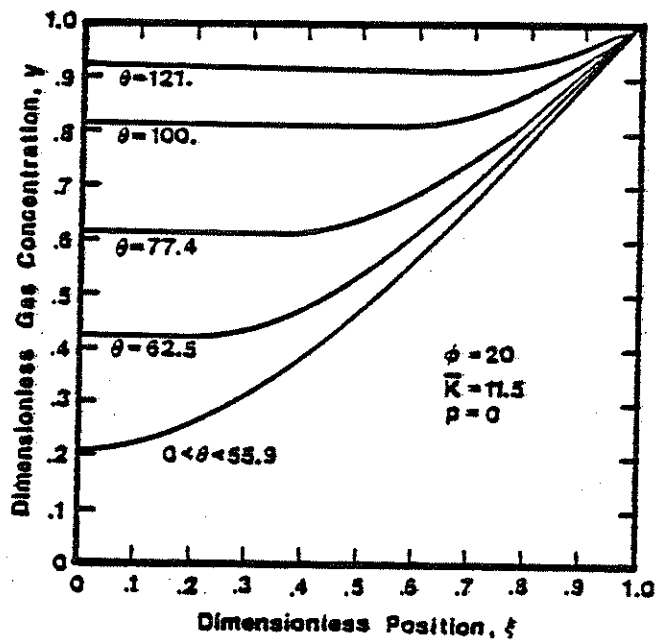
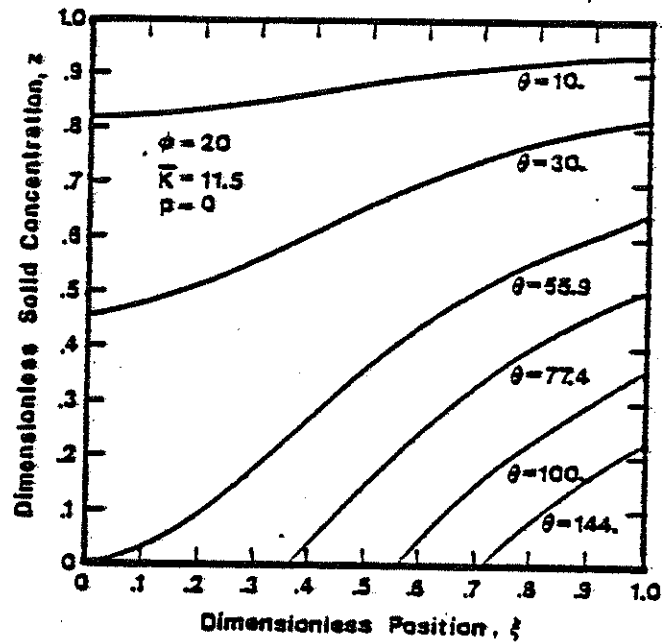


Figure II-2.1 Solid and gas concentration profiles in a case of a self-inhibited rate form.

(θ is dimensionless time, ϕ is Thiele modulus for the particle, \bar{K} is the dimensionless inhibition constant and p is the order with respect to solid reactant).

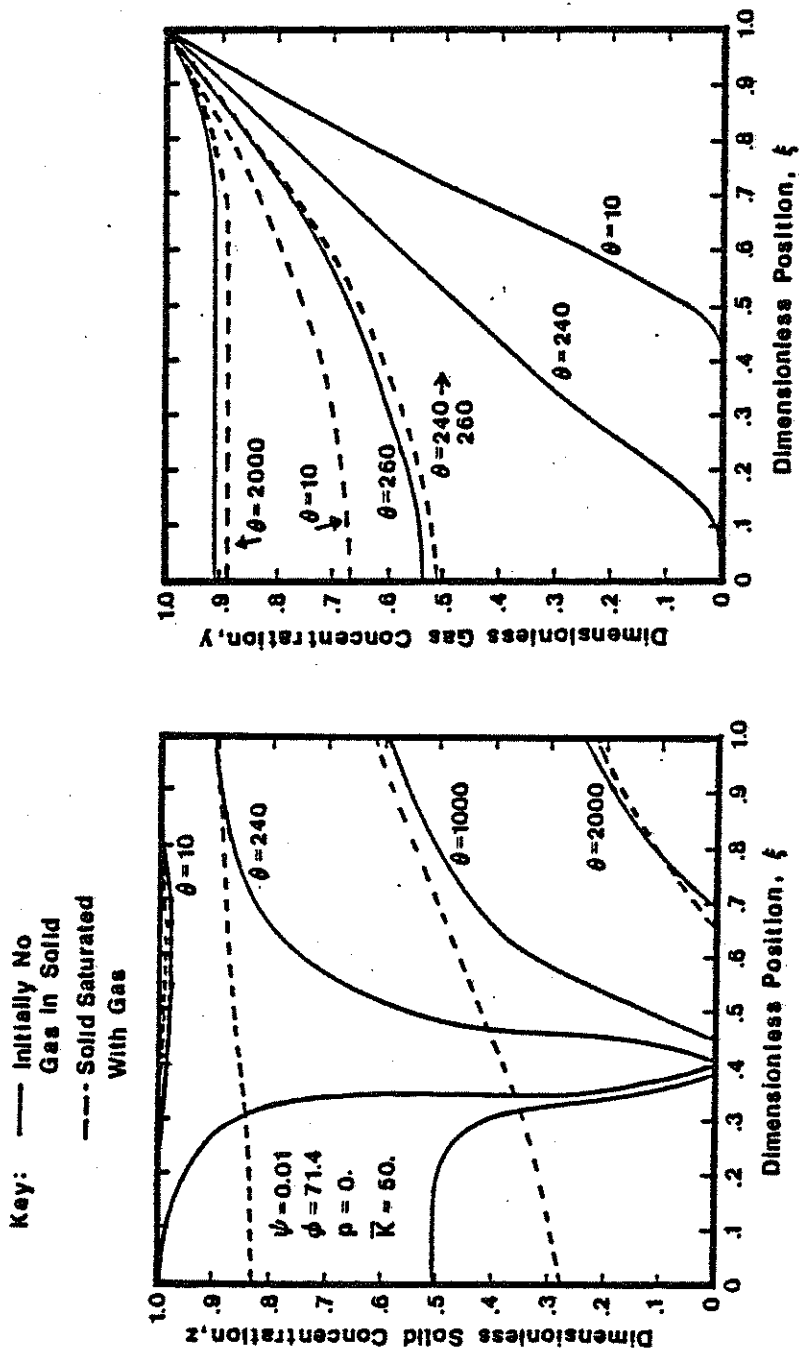


Figure II-2.2 Multiple gas and solid concentration profiles.

Project 3. Thermodynamics of the Si/H/Cl System

A. Problem Definition

Solar and semiconductor grade silicon is produced by reactions of hydrogen and chlorosilanes or of silane. Chlorosilanes, in turn, are obtained by gas-solid reactions between silicon and hydrochloric acid or other chlorosilanes. A variety of processes and process conditions are possible. In order to assess their feasibility and potential it is necessary to understand the thermodynamics of the Si/H/Cl system.

B. Research Objectives

1. Develop a simple and fast algorithm for evaluation of equilibrium composition in the Si/H/Cl system.
2. Plot charts of (Si/Cl) vs. Cl/H ratio as a function of temperature at different pressures. Prepare tables of detailed gas composition.
3. Evaluate the effect of the uncertainty in thermodynamic data on equilibrium composition.

C. Research Accomplishments

All of the above objectives have been achieved. A sample equilibrium chart is given in Figure II-3.1.

A report to the sponsor is in preparation.

D. Further Research Plan

None in this area. Gas-solid reactions of silicon will be studied.

1 0

ATM

500	X	⊙
600	X	⊙
700	X	⊙
800	X	⊙
900	X	⊙
1000	X	⊙
1100	X	⊙
1200	X	⊙
1300	X	⊙

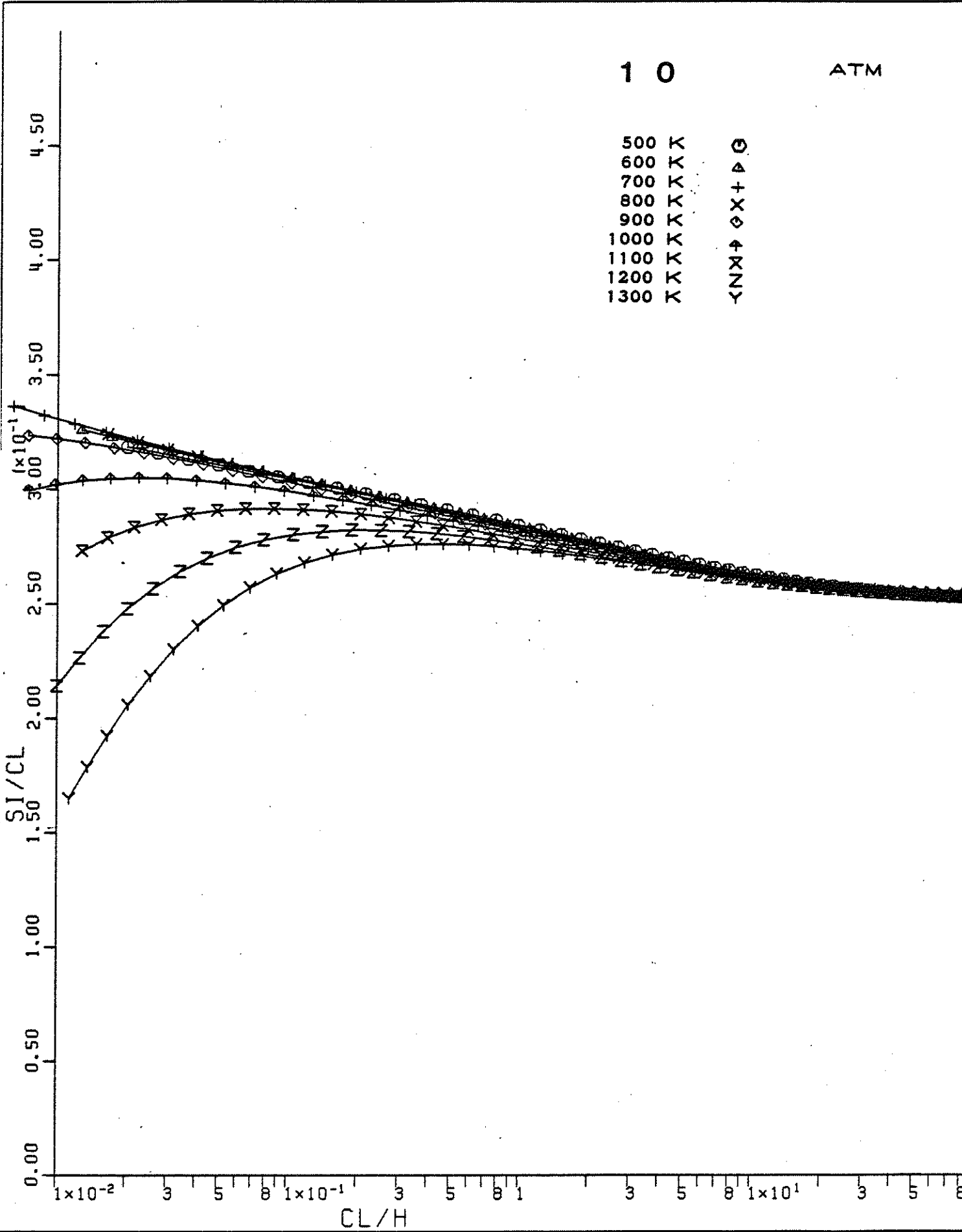


Figure II-3.1. Equilibrium Diagram for the Si/H/Cl Systems at P = 10 atm.

CURRENT STAFF

During the period covered by this report the following individuals have worked in the laboratory.

A. Faculty

Dr. Milorad (Mike) Duduković

Dr. Ahsok Gokarn

B. Graduate Students

A. A. El-Hisnawi

H. F. Erk

J. Evans

P. L. Mills

I. P. Wang

J. Weston

C. Undergraduate Students

J. Kang

D. O'Connor

CURRENT FUNDING

The external support of the laboratory during the past year was derived from industrial contributions (Alcoa, Amoco, Monsanto, Shell) totalling \$40,000.

In addition a grant was obtained from Monsanto Commercial Products Company for \$74,000.

Proposals with DOE and NSF are pending.

PAPERS AND PRESENTATIONS

A. PAPERS

1. Mills, P. L. and M. P. Duduković, "Application of the Method of Weighted Residuals to Mixed Boundary Value Problems I. Dual Series Relations", Chem. Eng. Science 35(7), 1557-1570 (1980).
2. Mills, P. L. and M. P. Duduković, "Analysis of Catalyst Effectiveness in Trickle-Bed Reactors Processing Volatile and Nonvolatile Liquid Reactants", Chem. Eng. Science 35(11), 2267-2280 (1980).
3. Hsu, Y. C. and M. P. Duduković, "Liquid Recirculation in Gas-Lift Reactors", in Proc. 2nd Multiphase Flow and Heat Transfer Symposium (T. N. Veziroglou, editor), Hemisphere Publ. Co., pp. 1757-1775 (1980).
4. Mills, P. L., Erk, H. F., Evans, J. and M. P. Duduković, "Some Comments on Models for Evaluation of Catalyst Effectiveness Factors in Trickle-Bed Reactors", Chem. Eng. Science 36(5), 947-950 (1981).
5. Linek, F. and M. P. Duduković, "Representation of Breakthrough Curves for Fixed-Bed Adsorbers and Reactors using Moments of the Impulse Response", Chem. Eng. J. in print.
6. Garza-Garza, O. and M. P. Duduković, "Some Observations on Gas-Solid Noncatalytic Reactions with Structural Changes", Chem. Eng. Science, in print.
7. Duduković, M. P., "On Heating of an Insulated Slab by Non-uniform Heat Generation", Comp. and Chem. Engineering, in print.

B. PRESENTATIONS

1. Mills, P. L. and M. P. Dudukovic, "Reactor Modelling and Parameter Estimation by Time-Domain Analysis of Impulse Response Data", AIChE 73rd Annual Meeting, Chicago, November 16-20, 1980.

2. Duduković, M. P. Seminars on trickle-bed reactors at

Exxon Research and Development

Mobil Research and Development

Oregon State University

Rice University

Shell Development

University of Maine

University of Wyoming

