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CHEMICAL REACTION ENGINEERING LABORATORY

REPORT FOR THE PERIOD

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Report

June, 1979 - June, 1980

CHEMICAL REACTION ENGINEERING LABORATORY

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INTRODUCTION

This report covers the major developments in the Chemical Reaction Engineering Laboratory (CREL) for the period June 1, 1979 through May 31, 1980. The work in CREL, like in the last years, is still concentrated in two major areas of multiphase reactors and gas-solid noncatalytic reactions.

In the area of multiphase reactors, catalyst effectiveness and contacting efficiency in trickle-bed reactors were studied together with kinetics of some model reactions in slurry and basket reactors. Tracer methods were used to develop a correlation for dynamic holdup and external catalyst contacting in trickle flow regime. The effect of solvent (physical properties variation), catalyst and reactant concentrations on kinetics of hydrogenation of α -methylstyrene was studied in a slurry reactor. Effectiveness factors of catalyst pellets to be used in trickle-bed reactors were evaluated in a basket reactor. The correlations for prediction of holdup, pressure drop and liquid recirculation in gas-lift reactors were finalized. Work on determination of effective diffusivities of liquids in HDS catalysts is in progress and a study of static mixers as gas-liquid contacting devices has been initiated.

In the area of gas-solid noncatalytic reactions the emphasis was on development of a sophisticated parameter estimation routine. The goal is to establish a whole library of plausible models for gas-solid reactions and evaluate the feasibility of a particular model by extracting some of its parameters by the parameter estimation technique from experimental conversion-time curves. At the same time the closeness

of the fit of a particular model to experimental data is to be established. Some effort was also spent on modeling and explaining the so-called "rotten apple" phenomenon whereby the solid reactant appears to react from inside towards the outside.

The summary of all the projects which are active or have been completed is given in Table I.

During the past year the operation of the Laboratory was maintained by industrial support (Alcoa, Amoco Oil, Monsanto and Shell Development Company) and departmental funds. A more active pursuit of federal funding (NSF and DOE) is planned for the coming year.

One doctoral student (P. L. Mills) completed his thesis during the past year in the Laboratory. Currently, three graduate students are working in the Laboratory and a number of undergraduates. Dr. S. P. Waldram, from University College London, who spent a year in the Department of Chemical Engineering, worked with the students in CREL on some projects related to diffusion in porous media.

In activities outside Washington University M. P. Duduković presented seminars at University of Houston, Purdue and University of Illinois at Urbana. P. L. Mills gave a seminar at General Electric and Y. C. Hsu presented a paper at the 6th International Symposium on Chemical Reaction Engineering in Nice, France. Several papers were published and a number has been submitted for publication.

In summary, one could say that excellent progress has been made in the area of trickle-bed and gas-lift reactors. Considerable progress has been made in other areas. The main and only problem appears to be an inadequate funding level and steps are being taken to correct that.

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, 1979-present

AREA I: MULTIPHASE REACTORS

Project	Funding	Investigators	Major Results, Publications and Presentations
<p>1. Liquid-Solid Contacting and Liquid Catalyst <i>Holdup</i> Effectiveness 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.</p> <p>Mixed boundary value problems and parameter estimation procedures.</p> <p><i>Development of very design parameters.</i></p>	<p>Industrial Amoco Monsanto Shell</p>	<p>M. P. Duduković P. L. Mills A. El-Hisnawi J. Kang</p>	<p><i>Part 1</i></p> <p>a) Complete development of an experimental set-up for tracer studies in multiphase flow. Automation of data acquisition and processing.</p> <p>b) Evaluation of the effect of particle scale in complete contacting on catalyst effectiveness. Development of an analytical approximate formula for effectiveness factor of partially wetted catalyst.</p> <p>c) Development of a correlation for holdup and external contacting for the trickle flow regime.</p> <p>d) Development of Fast Fourier Transform algorithms for transfer function inversion and for deconvolution coupled with smoothing algorithms. Development of time domain parameter estimation using tracer data.</p> <p>e) Development of a correlation for holdup and external contacting for the trickle flow regime.</p>

TABLE I. (Cont.)

Active Projects in the Chemical Reaction Engineering Laboratory June, 1979-present

AREA I: MULTIPHASE REACTORS

Project	Funding	Investigators	Major Results, Publications and Presentations
<p>1. Liquid-Solid Contacting and <i>Liquid</i> Catalyst <i>Method</i> Effectiveness in Trickle-Bed Reactors (Continued)</p>			<p>1. P. L. Mills and M. P. Duduković, "A Dual-Series Solution for Effectiveness Factor of Partially Wetted Catalysts in Trickle-Bed Reactors". <u>I&EC Fundamentals</u>, 18(2), 139-149 (1979).</p> <p>2. P. L. Mills and M. P. Duduković, "A Modified Differential Refractometer for Continuous Liquid-Phase Residence Time Distribution Studies", <u>I&EC Fundamentals</u> 18(3), 292-296 (1979).</p> <p>3. P. L. Mills, W. P. Wu and M. P. Duduković, Tracer Analysis in Systems with Two-Phase Flow", <u>AIChE Journal</u> 25(5), 885-890 (1979).</p> <p>4. J. G. Schwartz and M. P. Duduković, "Comments on Transport Rates by Moment Analysis of Dynamic Data", <u>I&EC Fundamentals</u> 18(2), 198 (1979).</p> <p>5. P. L. Mills and M. P. Duduković, "Analysis of Catalyst Effectiveness in Trickle-Bed Reactors Processing Volatile and Nonvolatile Liquid Reactants", <u>Chem. Eng. Sci.</u>, (accepted for publication, 1979).</p>

TABLE I. (Cont.)

Active Projects in the Chemical Reaction Engineering Laboratory, June, 1979-present

AREA I: MULTIPHASE REACTORS

Project	Funding	Investigators	Major Results, Publications and Presentations
<p>1. Liquid-Solid Contacting and Catalyst Effectiveness in Trickle-Bed Reactors (Continued)</p>			<p>6. P. L. Mills and M. P. Duduković, "Application of the Method of Weighted Residuals to Mixed Boundary Value Problems: Dual Series Relations", Chem. Eng. Sci., (accepted for publication, 1979).</p> <p>7. P. L. Mills and M. P. Duduković, "Triple Series Relations: Solution by the Method of Weighted Residuals", Proc. 2nd Int. Conf. on Math. Modeling, St. Louis, July 11-13 (1979), pp. 231-243.</p> <p>Three additional papers in preparation.</p>

Can trace →

TABLE I (Cont.)

Active Projects in the Chemical Reaction Engineering Laboratory June, 1979-present

AREA II: GAS-SOLID NONCATALYTIC REACTIONS

Project	Funding	Investigators	Major Results, Publications and Presentations
<p>1. Gas-Solid Non-catalytic Reactions - Parameter Estimation from Conversion-Time Data</p> <p>Relevance: 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><i>c) Testing and verification of the algorithm using experimental data for a $CO_2 + BaO_2$ reaction. Kinetic constants and differential equations determined. Guidelines for model development provided.</i></p>
<p>2. Modeling of the "Rotten Apple" Phenomenon</p>		<p>M. P. Duduković H. Erk</p>	<p>a) Explanation of the phenomenon based on diffusion with simultaneous reaction model with a self-inhibited rate form.</p> <p><i>Publication in preparation</i></p>

TABLE I (Cont.)

Active Projects in the Chemical Reaction Engineering Laboratory June, 1979-present

AREA II: GAS-SOLID NONCATALYTIC REACTIONS

Project	Funding	Investigators	Major Results, Publications and Presentations
<p>3. Effective Diffusivity of Gases in Porous Solid Pellets</p> <p>Relevance: Verification of existing theories, development of a reliable experimental technique for diffusivity evaluation</p>		<p>M. P. Duduković S. P. Waldram</p>	<p>Development of a novel test cell for measurement of diffusivities in a single solid pellet of commercially made catalysts or other solid materials in the presence or in absence of superimposed pressure difference and by steady or unsteady state method. Apparatus development and construction 100% completed.</p> <p>1. S. P. Waldram and M. P. Duduković, "The Dynamic Response of a Single Catalyst Pellet", <u>Chem. Eng. Sci.</u>, 34(7), 1361-1362 (1979).</p>

Fixed 3

AREA I. MULTIPHASE REACTORS

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

A. Problem Definition

Trickle-bed reactors represent an important class of three-phase reactors used for liquid-gas contacting in the presence of a catalyst. The use of this reactor type is widely spread in petroleum industry and shows promise for coal liquefaction and chemical processing also, provided its scale-up and design can be facilitated.

The most important parameters for design of trickle-bed reactors are the catalyst area that is effectively wetted by liquid (contacting efficiency) and the effectiveness factor of such partly wetted catalyst in case of nonvolatile or volatile liquid reactants.

B. Research Objectives

1. Development of a reliable method for evaluation of contacting efficiency and interpretation of tracer (dynamic) data.
2. Development of a correlation for contacting efficiency as a function of operating conditions and physical properties of the system.
3. Analysis of the effect of catalyst contacting on catalyst effectiveness factor in case of nonvolatile and volatile liquid reactants and development of a formula for effectiveness factor calculation.

C. Research Accomplishments

1. An experimental set-up for tracer studies in multiphase flow (trickle and pulsed flow in particular) was developed. (Figure 1

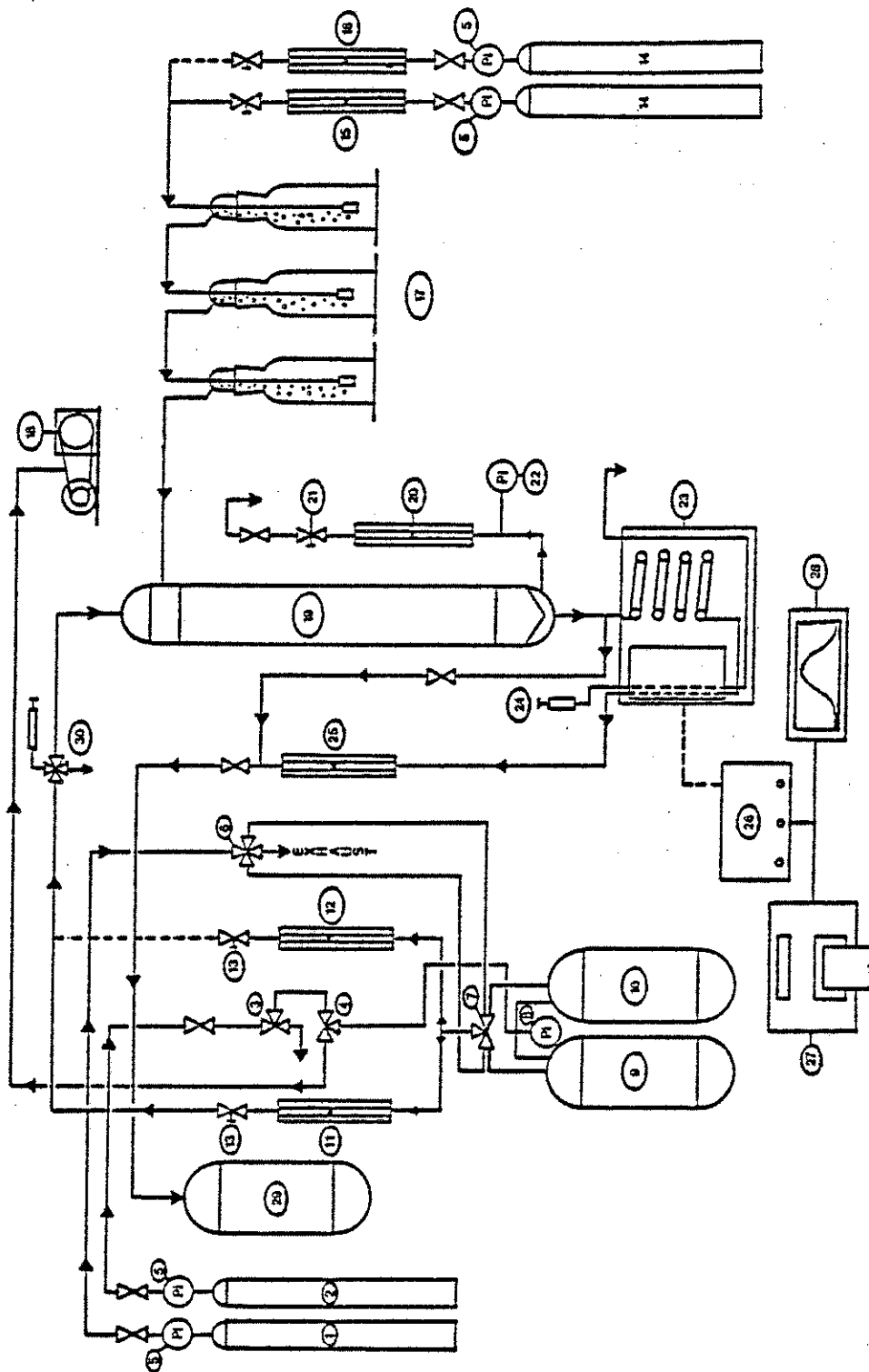


Figure 1. Experimental Equipment For Tracer Studies.

Table 1
List of Key Equipment Items

<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

and Table 1). Another view of the apparatus and the range of liquid and gas superficial velocities that can be covered is given in Appendix I.

2. On line data collection, data smoothing, tail extrapolation and evaluation of the moments of the tracer impulse responses was established. The basic outline of the main computer program and associated subroutines together with a sample output are enclosed in Appendix I. The fully documented program is available upon request.
3. A program for time-domain analysis and parameter estimation was developed including the use of Fast Fourier Transform and smoothing algorithms that allow efficient deconvolution procedures as schematically presented in Figure 2. A fully documented program can be obtained upon request.
4. It was established that tracer methods can distinguish between external incomplete catalyst contacting by liquid and partial internal liquid fill-up. From the first moment of an adsorbable tracer impulse response curve in two-phase flow and in liquid filled column operated at same liquid mass velocity one can extract the information on internal pore fill-up or total (B.E.T.) catalyst area contacted by liquid. It was shown that internal pore fill-up is always complete (see $(K_A)_{app.} / (K_A)_{LF}$ line in enclosed Figure 3) under the conditions of this study given in Table 2. The fraction of external catalyst area contacted by liquid can be determined by comparing second moments of the tracer response curve in two phase flow and liquid filled column. It was shown that external contacting increases with liquid mass velocity (see η_{CE} line in Figure 3).

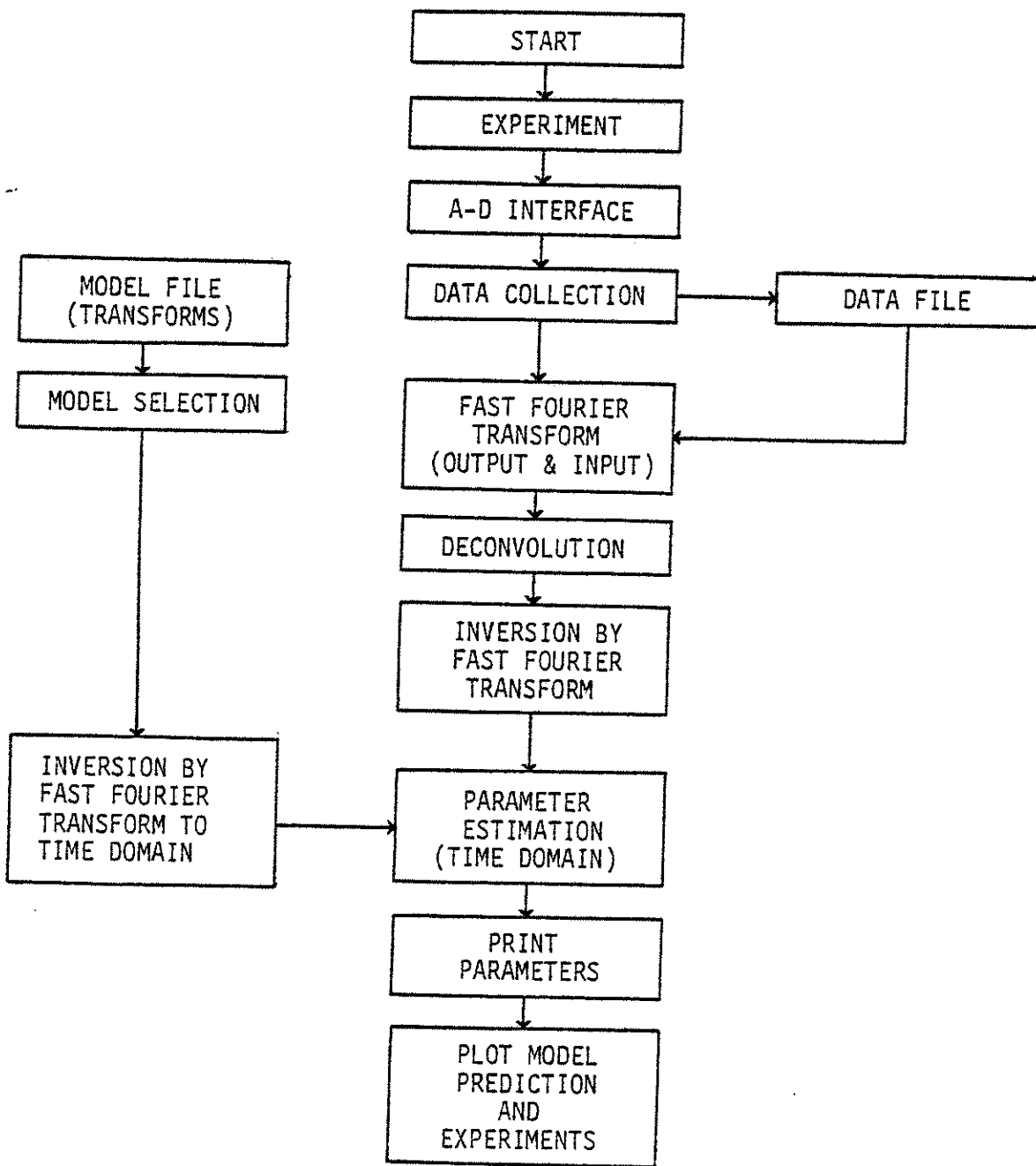


Figure 2. Logic Diagram For Time-Domain Analysis of Impulse Response Data and Models.

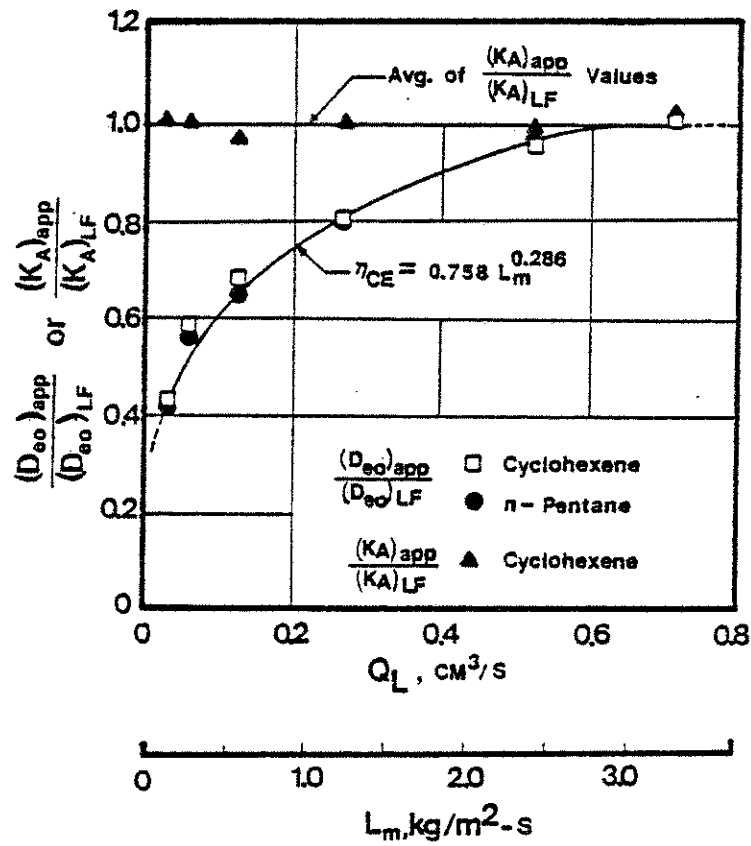


Figure 3. Comparison of $(D_{eo})_{app} / (D_{eo})_{LF}$ and $(K_A)_{app} / (K_A)_{LF}$ Values For Cyclohexene and n-Pentane Tracers.

Table 2

Range of Variables and Physical Properties

Variable	Units	Minimum	Maximum
Re_L	---	0.33	7.91
L_m	$\frac{kg}{m^2 \cdot s}$	0.146	3.478
G_m	$\frac{kg}{m^2 \cdot s}$	1.191×10^{-3}	1.983×10^{-3}
Q_L	cm^3/s	0.032	0.758
Q_G	cm^3/s	1.03	1.72
u_L	cm/s	0.022	0.529
u_G	cm/s	0.72	1.20

$\sigma_L = 18.2 \text{ dynes/cm}$

$\mu_L = 0.316 \text{ cp}$

$\rho_L = 0.657 \text{ g/cm}^3$

$d_p = \begin{cases} 0.0718 \text{ cm (alumina)} \\ 0.30 \text{ cm (glass beads)} \end{cases}$

5. The following correlation for external catalyst contacting was developed in terms of dimensionless variables based on the data taken in our studies and all the data available in the literature:

$$\eta_{CE} = 1.0 - \exp \left[-2.602 \text{Re}_L^{0.395} \text{Fr}_L^{0.316} \text{We}_L^{-0.137} \left(\frac{a_t d_p}{\epsilon_B} \right)^{-0.11} \right] \quad (1)$$

The agreement of the correlation with the data is given in Figure 4. The correlation is based on data that cover the following parameter range.

$$0.33 \leq \text{Re}_L \leq 31.9$$

$$2.6 \times 10^{-5} \leq \text{Fr}_L \leq 2.2 \times 10^{-3}$$

$$3.4 \times 10^{-7} \leq \text{We}_L \leq 9.0 \times 10^{-4}$$

$$1.9 \leq a_t d_p / \epsilon_B \leq 8.1$$

$$18.7 \leq \sigma_L \leq 72.4 \text{ dynes/cm}$$

$$0.667 \leq \rho_L \leq 0.998 \text{ g/cm}^3$$

$$0.316 \leq \mu_L \leq 0.958 \text{ cp}$$

$$0.0714 \leq d_p \leq 0.41 \text{ cm}$$

In the above equation Re_L is the Reynolds number based on particle diameter and liquid superficial velocity; Fr_L is the Froude number for the liquid defined by $a_t L_m^2 / \rho_L^2 g$ where a_t is packing external area per unit volume of reactor, L_m is liquid mass superficial velocity, ρ_L is liquid density and g is gravitational acceleration; We_L is the liquid Weber number; ϵ_B is bed porosity and d_p is mean particle diameter.

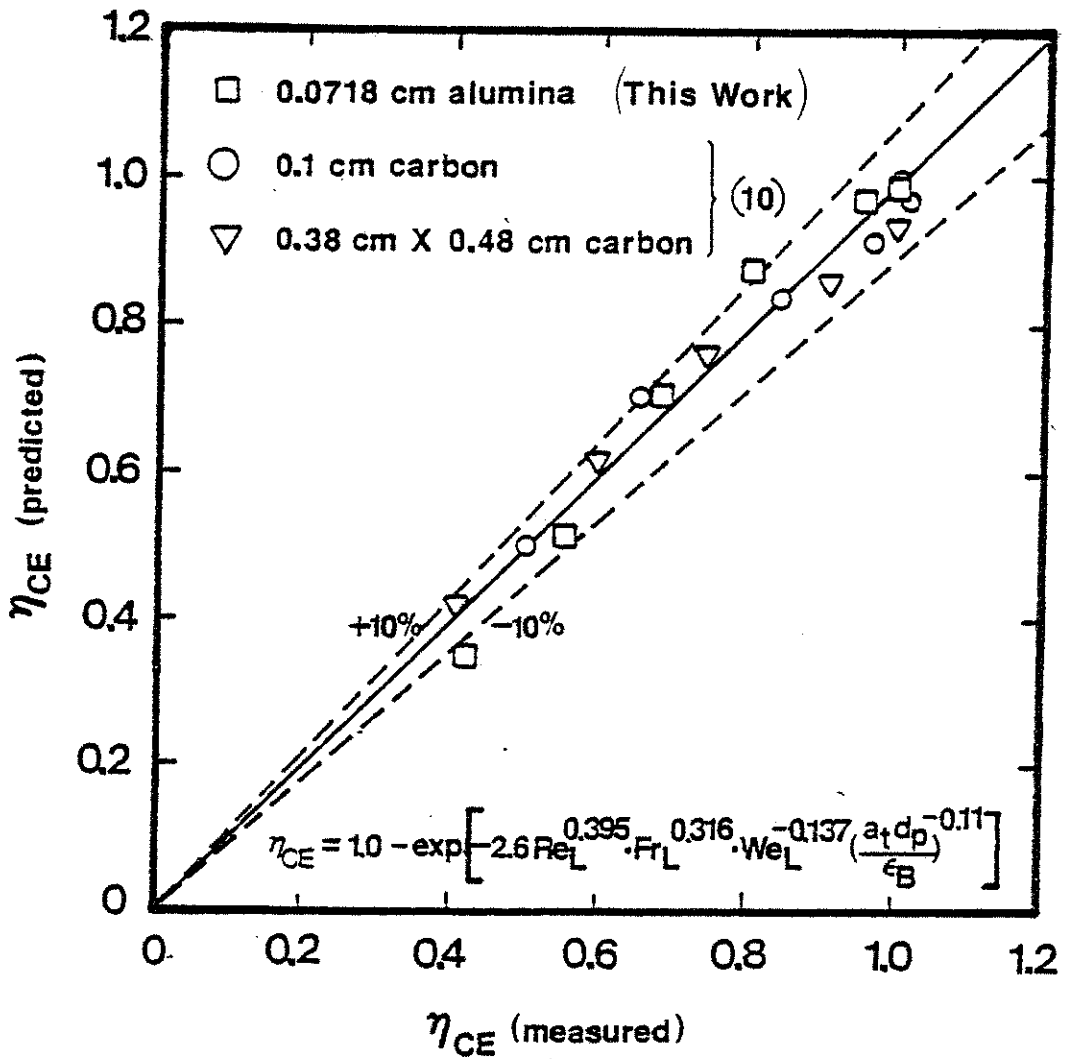


Figure 4. Comparison of Predicted to Measured Values For Solid-Liquid Contacting Correlation.

6. The problem of the catalyst effectiveness factor of partially externally wetted catalyst pellets was solved for both non-volatile and volatile liquid reactants. The governing equations are described in Table 3 and the resulting dual series in Table 4. Various possible limiting cases are discussed in Table 5. It was shown that for small modulus $\Lambda < 5$ (especially $\Lambda < 1$) a complete solution is necessary in order to assess catalyst effectiveness within 25% accuracy or better. A general algorithm for solution of dual series was developed and is sketched out briefly in Appendix II. For high values of the modulus $\Lambda > 5$ (especially $\Lambda > 10$) it was shown that an approximate formula shown below allows accurate estimation of the effective factor η_{TB}

$$\eta_{TB} = \frac{\eta_{CE}}{\frac{\Lambda^2}{\tilde{Bi}_w} + \frac{\Lambda}{\tanh \Lambda}} + \frac{(1-\eta_{CE})\epsilon}{\frac{\Lambda^2}{\tilde{Bi}_d} + \frac{\Lambda}{\tanh \Lambda}}$$

In the above equation η_{CE} is the fraction of external catalyst area wetted (obtainable from equation (1)), Λ is the Thiele modulus generated for any particle shape by taking the characteristic distance to be volume of particle/external particle surface; \tilde{Bi}_w and \tilde{Bi}_d are modified Biot numbers for the wetted and dry particle surface, respectively, while ϵ is the ratio of the bulk concentrations of the limiting reactant in gas and liquid phase.

Summary of Governing Equations and Boundary Conditions for Partially Wetted Catalyst Pellets

Table 3

Geometry	Governing Equation	Boundary Conditions for Gaseous (I=A) or Liquid (I=B) Reactant Limiting Cases	Range of Validity
Slab	$\frac{\partial^2 u_1}{\partial \xi_1^2} + \frac{\partial^2 u_1}{\partial \xi_2^2} - \phi_1^2 u_1 = 0$ <p>1 = A Gaseous Reactant 1 = B Liquid Reactant</p>	$\xi_1 = 0 \left\{ \begin{array}{l} - \frac{1}{\left[\frac{B_1}{d} \right]} \frac{\partial u_1}{\partial \xi_1} + u_1 = 1 \text{ or } c \\ - \frac{1}{\left[\frac{B_1}{v} \right]} \frac{\partial u_1}{\partial \xi_1} + u_1 = 1 \end{array} \right.$	$\xi_0 < \xi_2 \leq 1$ $0 \leq \xi_2 < \xi_0$
		$\xi_1 = 1 \quad \frac{\partial u_1}{\partial \xi_1} = 0$	$0 \leq \xi_2 \leq 1$
		$\xi_2 = 0, 1 \quad \frac{\partial u_1}{\partial \xi_2} = 0$	$0 \leq \xi_1 \leq 1$
Cylinder	$\frac{1}{\rho} \frac{\partial}{\partial \rho} \left(\rho \frac{\partial u_1}{\partial \rho} \right) + \frac{1}{\rho^2} \frac{\partial^2 u_1}{\partial \phi^2} - \phi_1^2 u_1 = 0$	$\rho = 1 \left\{ \begin{array}{l} - \frac{1}{\left[\frac{B_1}{d} \right]} \frac{\partial u_1}{\partial \rho} + u_1 = 1 \text{ or } c \\ - \frac{1}{\left[\frac{B_1}{v} \right]} \frac{\partial u_1}{\partial \rho} + u_1 = 1 \end{array} \right.$	$\alpha < 0 \leq \pi$ $0 \leq \theta < \pi$
Sphere	$\frac{1}{\rho} \frac{\partial}{\partial \rho} \left(\rho^2 \frac{\partial u_1}{\partial \rho} \right) + \frac{1}{\rho^2} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial u_1}{\partial \theta} \right) - \phi_1^2 u_1 = 0$	$\rho = 0 \quad \lim_{\rho \rightarrow 0} \rho^2 \frac{\partial u_1}{\partial \rho} = 0 \quad \begin{array}{l} \nu=1 \text{ cylinder} \\ \nu=2 \text{ spheres} \end{array}$ $\theta = 0, \pi \quad \frac{\partial u_1}{\partial \theta} = 0$	$0 \leq \theta \leq \pi$ $0 \leq \rho \leq 1$

Table 4

Dual Series Equations

Geometry	Dual Series Equations	Range of Validity
Slab	$d_1 \left\{ \frac{1}{(B1)_{w1}} + \frac{\coth \phi_1}{\phi_1} \right\} + \sum_{n=2}^{\infty} d_n \left\{ \frac{1}{(B1)_{w1}} + \frac{\coth r_n}{r_n} \right\} \cos[(n-1)\pi\xi_2] = 1$ $d_1 \left\{ \frac{1}{(B1)_{d1}} + \frac{\coth \phi_1}{\phi_1} \right\} + \sum_{n=2}^{\infty} d_n \left\{ \frac{1}{(B1)_{d1}} + \frac{\coth r_n}{r_n} \right\} \cos[(n-1)\pi\xi_2] = 1 \text{ or } \epsilon$ <p style="text-align: center;">where $r_n = \sqrt{[(n-1)\pi]^2 + \phi^2}$</p>	$0 \leq \xi_2 < \xi_0$ $\xi_0 < \xi_2 \leq 1$
Cylinder	$e_1 \left\{ \frac{1}{(B1)_{w1}} + \frac{1}{\phi_1} \frac{I_0(\phi_1)}{I_1(\phi_1)} \right\} + \sum_{n=2}^{\infty} e_n \left\{ \frac{1}{(B1)_{w1}} + \frac{1}{\phi_1} \frac{I_{n+1/2}(\phi_1)}{I_n(\phi_1)} + n-1 \right\} \cos[(n-1)\theta] = 1$ $e_1 \left\{ \frac{1}{(B1)_{d1}} + \frac{1}{\phi_1} \frac{I_0(\phi_1)}{I_1(\phi_1)} \right\} + \sum_{n=2}^{\infty} e_n \left\{ \frac{1}{(B1)_{d1}} + \frac{1}{\phi_1} \frac{I_{n+1/2}(\phi_1)}{I_n(\phi_1)} + n-1 \right\} \cos[(n-1)\theta] = 1 \text{ or } \epsilon$	$0 \leq \theta < \alpha$ $0 < \theta \leq \pi$
Sphere	$\sum_{n=0}^{\infty} g_n \left\{ \frac{1}{(B1)_{w1}} + \frac{1}{\phi_1} \frac{I_{n+1/2}(\phi_1)}{I_{n+1/2}(\phi_1)} + n \right\} P_n(\cos \theta) = 1$ $\sum_{n=0}^{\infty} g_n \left\{ \frac{1}{(B1)_{d1}} + \frac{1}{\phi_1} \frac{I_{n+3/2}(\phi_1)}{I_{n+1/2}(\phi_1)} + n \right\} P_n(\cos \theta) = 1 \text{ or } \epsilon$	$0 \leq \theta < \alpha$ $\alpha < \theta \leq \pi$

Table 5
Summary of Limiting Cases

<u>Case Designation</u>	<u>Liquid Reactant Limited</u>	<u>Gaseous Reactant Limited</u>
A $Bi_d \rightarrow 0$ $Bi_w \rightarrow \infty$	Nonvolatile liquid reactant; negligible vapor-liquid-solid or liquid-solid mass transfer resistance.	Not applicable.
B $Bi_d \rightarrow \infty$ $Bi_w \rightarrow 0$	Not applicable.	Negligible gas-solid mass transfer resistance; no gas- liquid-solid mass transfer.
C Bi_d is finite $Bi_w \rightarrow \infty$	Liquid reactant is appreciably volatile; negligible vapor-liquid- solid or liquid-solid mass trans- fer resistance.	Significant gas-solid mass transfer resistance; negli- gible gas-liquid-solid mass transfer resistance.
D $Bi_d \rightarrow \infty$ Bi_w is finite	Highly volatile liquid reactant; some vapor-liquid-solid or liquid-solid mass transfer resistance.	Negligible gas-solid mass transfer resistance; some gas-liquid-solid mass transfer resistance.
E $Bi_d \rightarrow 0$ Bi_w is finite	Nonvolatile liquid reactant; some vapor-liquid-solid or liquid-solid mass transfer resistance.	Not applicable.
F Bi_d is finite $Bi_w \rightarrow 0$	Not applicable.	Significant gas-solid mass transfer resistance; no gas- liquid-solid mass transfer.
G Bi_d is finite Bi_w is finite	Both vapor-liquid-solid or liquid-solid and vapor-solid mass transfer are important.	Both gas-liquid-solid and gas-solid mass transfer are important.

The behavior of catalyst effectiveness with contacting efficiency for nonvolatile liquid limiting reactant and gas limiting reactant is shown in Figures 5 and 6, respectively. Dramatically different behavior is noticed. In case of non-volatile liquid limiting reactant effectiveness factor, η_{TB} , increases with increased external contacting, η_{CE} , while for gas limiting (or volatile liquid limiting reactant) the effectiveness factor decreases with increased external contacting.

Additional information on holdup correlation, etc., is available.

D. Further Research Plan

1. Extension of holdup and contacting correlation to other flow regimes downflow-pulsing, upflow, etc.
2. Development of theory to explain the correlations and reinforce their validity.
3. Evaluation of heat transfer, hot spot formation and their effect on contacting.

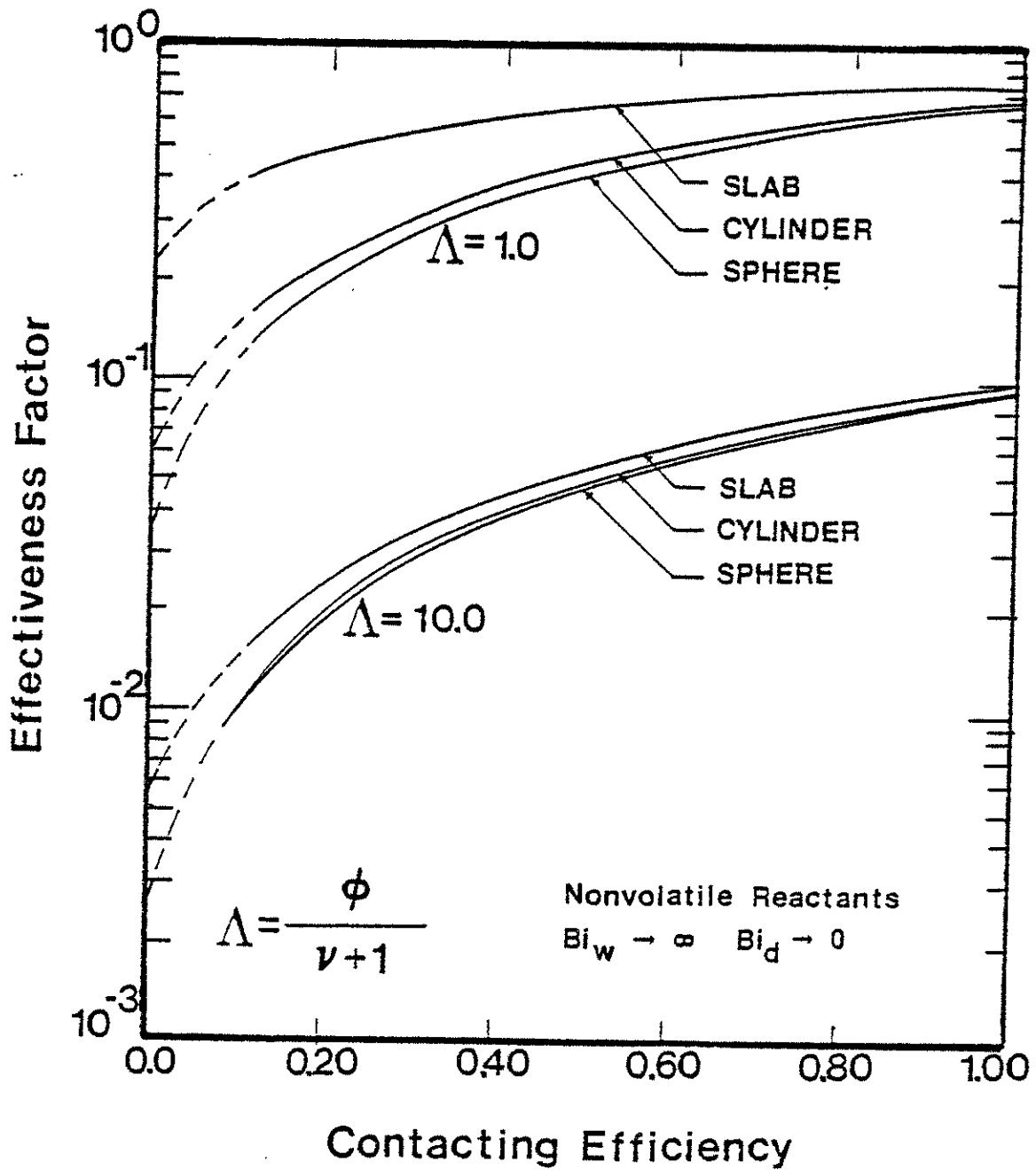


Figure 5. Effectiveness Factor as a Function of External Contacting Efficiency for Nonvolatile Liquid Reactant Limited Case.

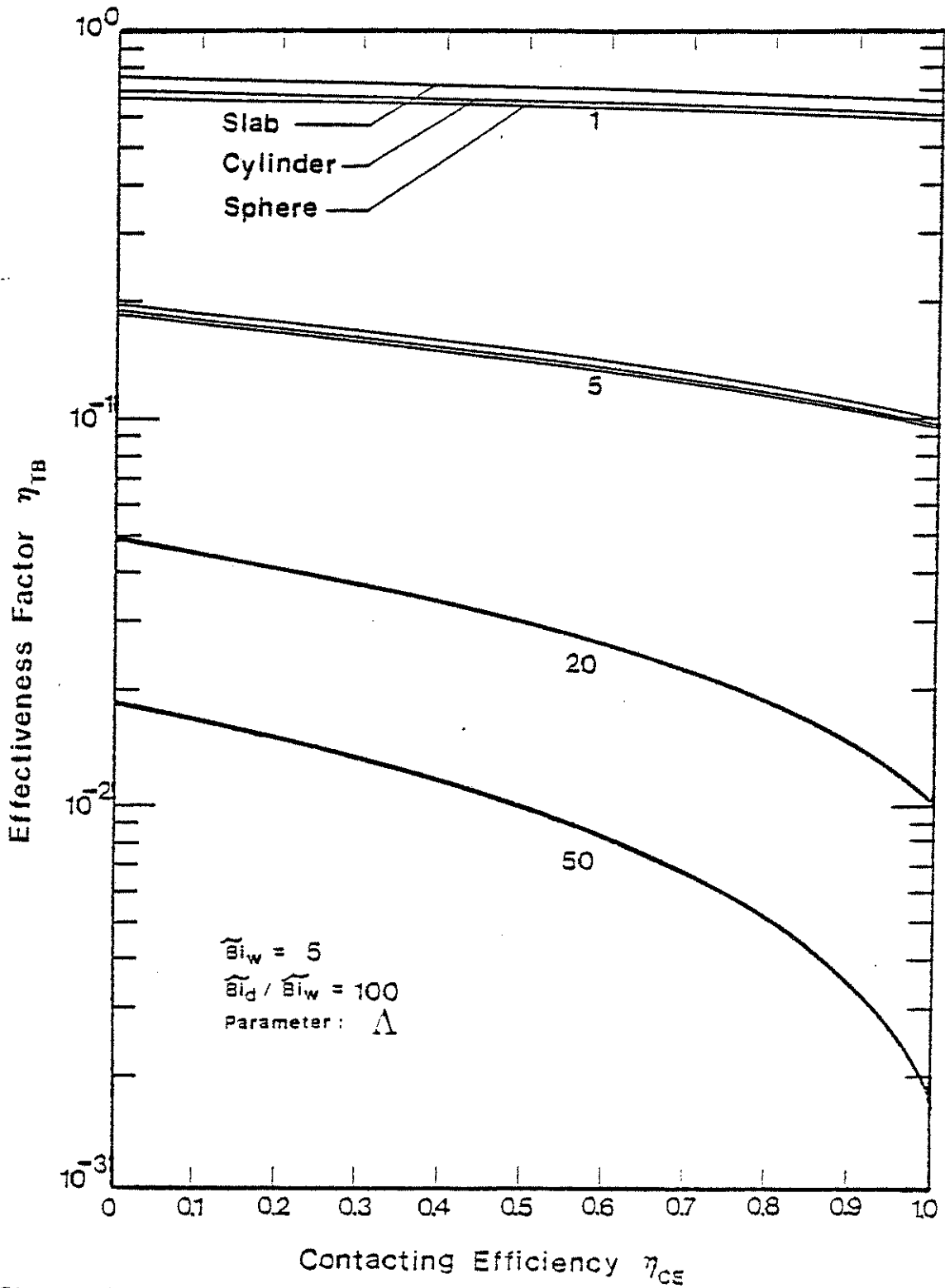


Figure 6. Effectiveness Factor as a Function of External Contacting Efficiency For a Typical Gas Reactant Limited Case.

Project 2. Model Reactions for Trickle-Bed Reactors

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 ^{moderate} ~~large~~ 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} ~~one~~ 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. Comparison of predicted and actual performance of an integral trickle-bed reactor for reaction of known kinetics.
2. Experimental confirmation of the utility of the contacting efficiency and catalyst effectiveness correlation developed in Project 1 for systems of varying physical properties (varying solvents).

C. Research Accomplishments

1. The kinetics of hydrogenation of α -methylstyrene at low concentrations (less than 10^{-2} gmol/cm³) in various organic solvents (cumene, cyclohexane, benzene, heptane, glycol, etc.) was determined on small catalyst particles (less than 30 μ) of Pd on Al₂O₃. First order behavior with respect to hydrogen and zeroth order with respect to α -methylstyrene was found in all solvents and at catalyst concentrations of 0.5% and 2.5% Pd. It was shown that the reaction is structure insensitive. The experiments were performed in the semi-batch slurry reactor shown in Figure 2-1 (with the basket (9) removed). Care was taken to show that external mass transfer was not limiting the reaction rate (see Figure 2-2). It was found that the activation energy and frequency factor vary somewhat from solvent to solvent and are most likely related to the temperature dependence of hydrogen solubility and adsorption isotherm in various solvents. An illustration of the variation in rates and activation energies obtained in various solvents is given in Figure 2-3.
2. Apparent rate studies were done in the reactor of Figure 2-1 with cylindrical particles 1/16" and 1/32" in diameter, which will be utilized in trickle-bed experiments, and it was found that the effectiveness factors are low (less than 10^{-2}) so that the approximate formula for the effectiveness factor of partly wetted particles, developed in Project 1 and reported as equation (2), can be used with confidence for interpretation of trickle-bed data.

#	ITEM
PI	PREASURE INDICATOR AND REGULATOR
T1	TEMPERATURE INDICATOR
PR	BACK PREASURE REGULATOR
1	STIRRER MOTOR
2	WATER TEMPERATURE BATH
3	STEEL BEARING
4	SAMPLE OUTLET
5	REACTOR SUPPORT RING
6	BAFFLES
7	CONSTANT TEMPERATURE COIL
8	FOUR-BL ADDED FLAT TURBINE
9	STATIONARY BASKET
10	WATER MANOMETER
11	SHUT-OFF VALVE
12	FLOW METER
13	MOISTURE FILTER
14	REFLUX CONDENSOR
15	METERING VALVE

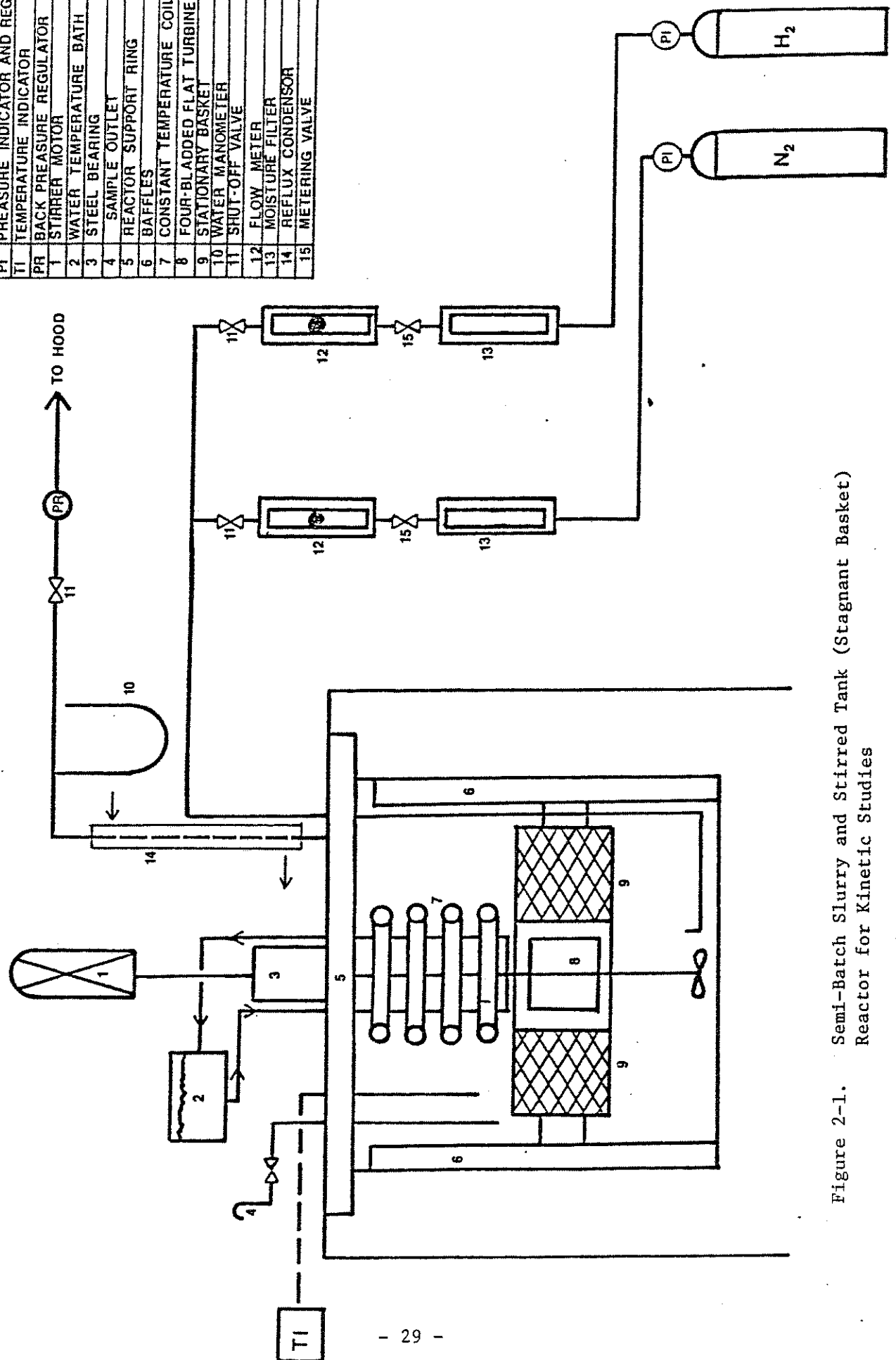
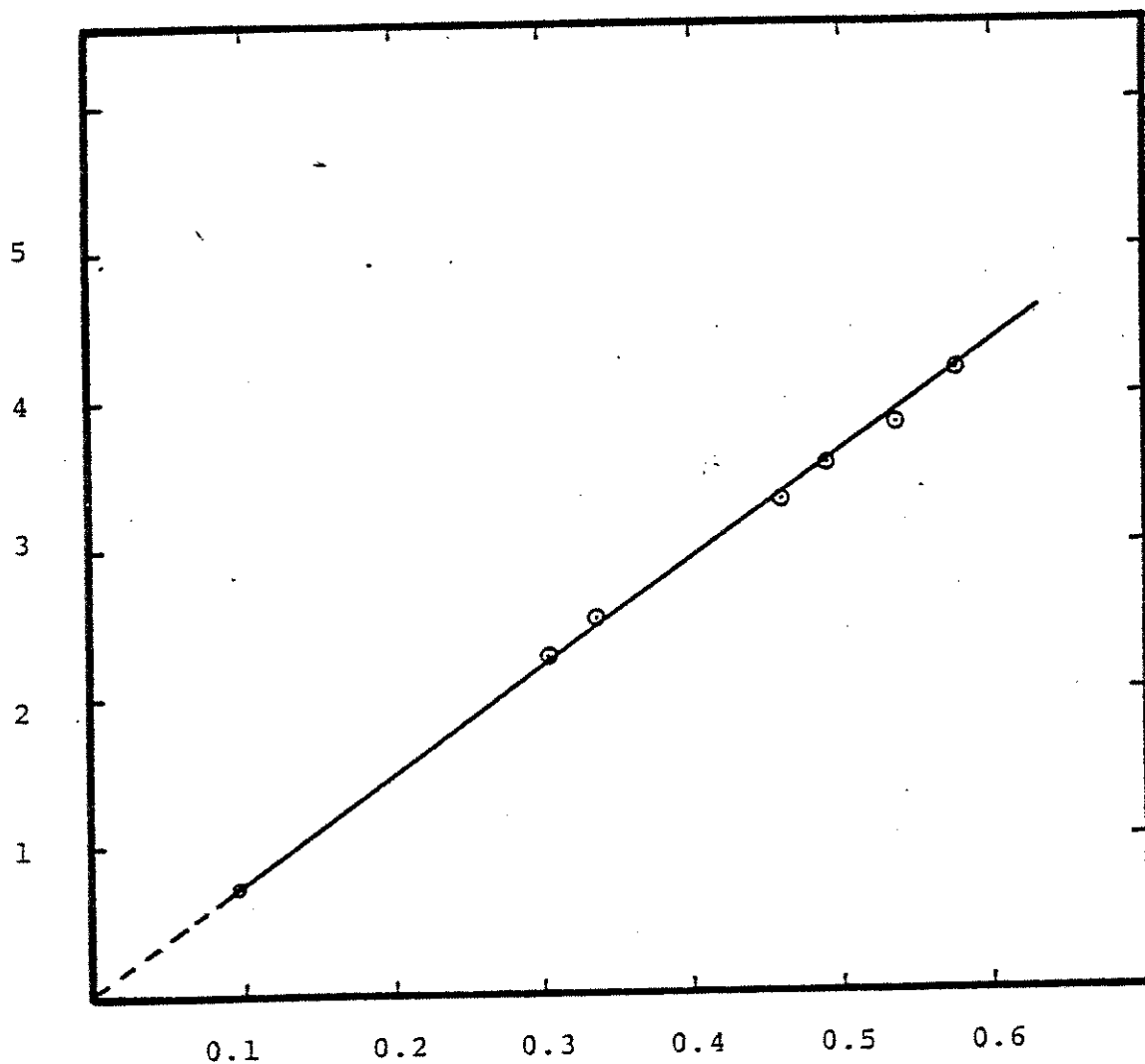


Figure 2-1. Semi-Batch Slurry and Stirred Tank (Stagnant Basket) Reactor for Kinetic Studies

Reciprocal of reaction rate $\left(\frac{1}{-r_m}\right) \times 10^{-5} \left(\frac{\text{sec}}{\text{g-mole}}\right)$



Reciprocal of Catalyst loading $\left(\frac{1}{m}\right)$ $\left(\frac{\text{l}}{\text{grams}}\right)$

Figure 2-2. Reciprocal of reaction rate as function of reciprocal catalyst loading (Set B).

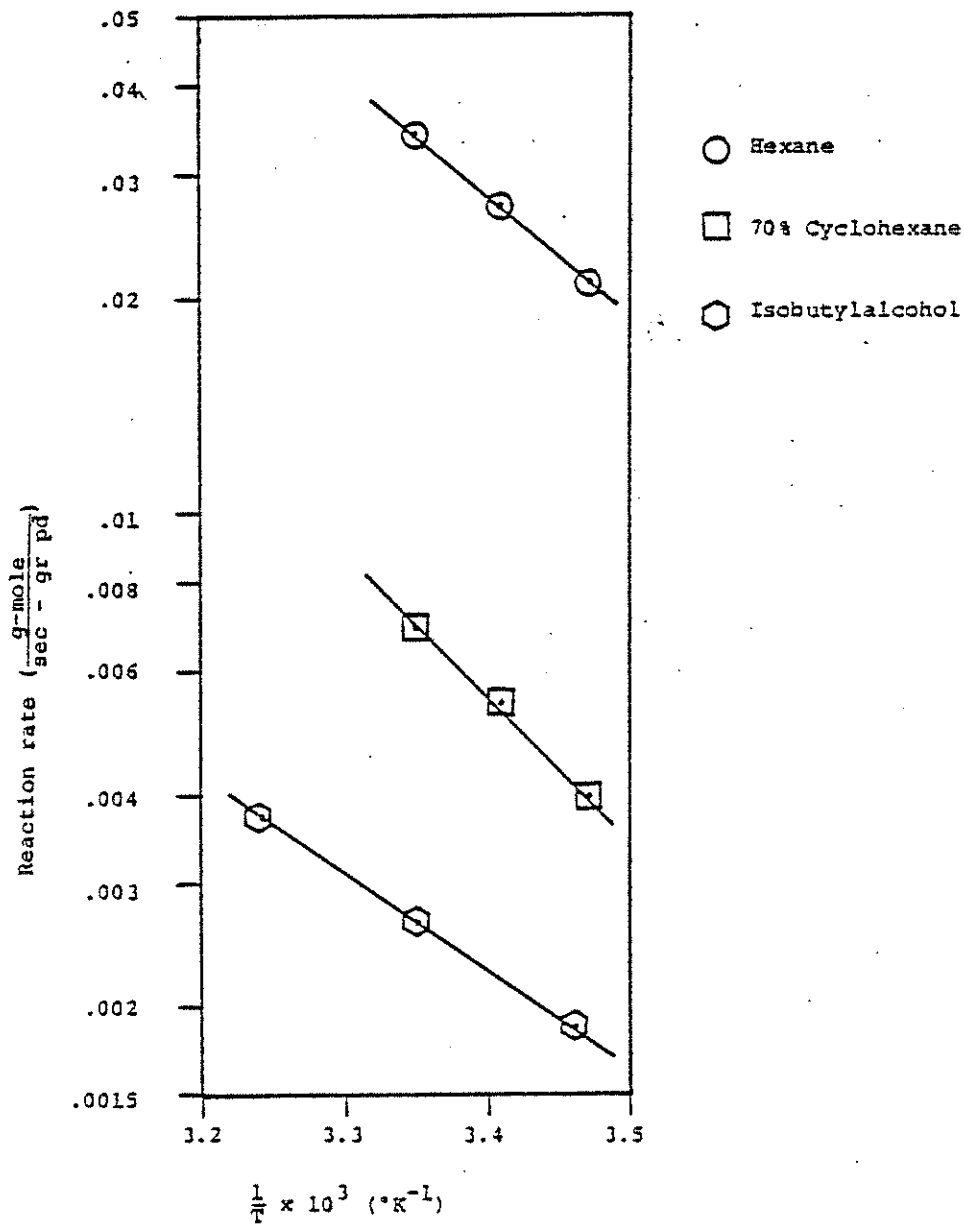


Figure 2-3. Reaction rate in different solvents as function of temperature.

D. Further Research Plan

1. Determination of contacting in trickle-bed reactor via tracer studies.
2. Reaction studies in trickle bed reactors and comparison to predicted performance.

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.

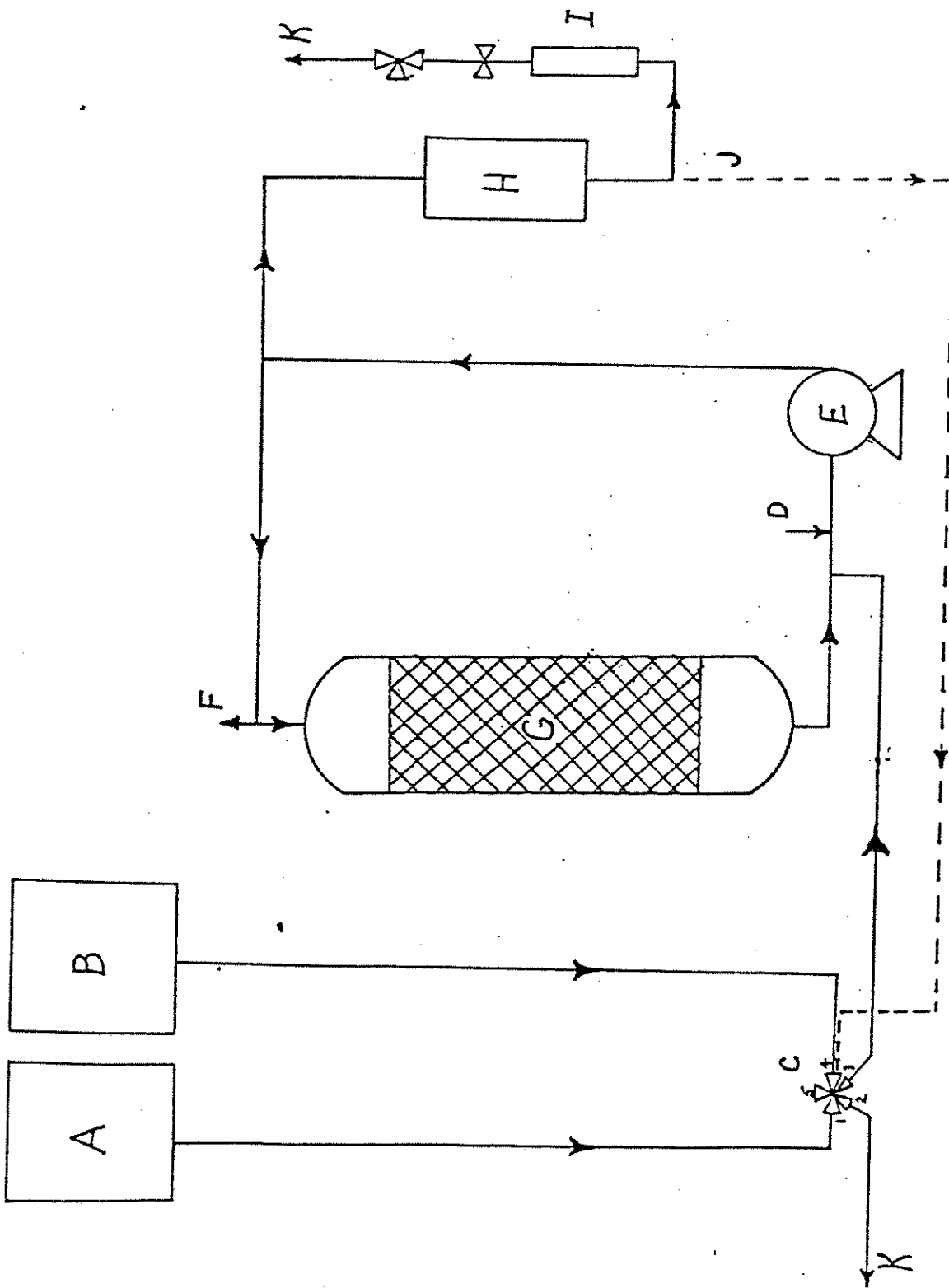
B. Research Objectives

1. Development of an experimental set-up for evaluation of liquid effective diffusivities and adsorption isotherms on porous solid catalysts.
2. Development of a computerized data reduction procedure and parameter estimation algorithm.

C. Research Accomplishments

The equipment for evaluation of effective diffusivities, schematically represented in Figure 3-1, was constructed and tested. Exponential residence time distribution of the equipment when operated as an open system with the bed consisting of nonporous glass beads was demonstrated.

The equipment can be operated as an open system with a new flow in coming from tank A or B and net outflow exiting through port K upon passing through the spectrophotometer H. The recycle flow created by



- A. SOLVENT TANK
- B. SOLVENT + TRACER TANK
- C. SWITCHING VALVE
- D. INJECTION PORT
- E. PUMP
- F. VENT
- G. PACKED COLUMN
- H. SPECTROPHOTOMETER WITH FLOW-THROUGH CELL
- I. FLOWMETER
- J. RECYCLE STREAM FOR A CLOSED SYSTEM
- K. DRAIN

Figure 3-1. Apparatus for Measurement of Effective Diffusivity of Liquids in Porous Catalysts

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 larger volumetric mass transfer coefficients and interfacial areas for transfer ~~per unit of~~ ^{at lower} liquid processed ~~and for power input~~ ^{per unit volume of liquid than} ~~required as compared to more~~ 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. Selection of a gas-liquid absorption system with reaction in the liquid for evaluation of volumetric mass transfer coefficients and interfacial areas for transfer.
3. Evaluation of pressure drops and mass transfer coefficients.

C. Research Accomplishments

1. Kenics (180° helical elements), Ross (semieliptical elements) and Koch (corrugated panels) mixers have been obtained.
2. Preliminary experimental set-up (as shown in Figure 4-1) has been assembled and some test runs performed. Larger capacity pump is needed to achieve the recommended flow regime.

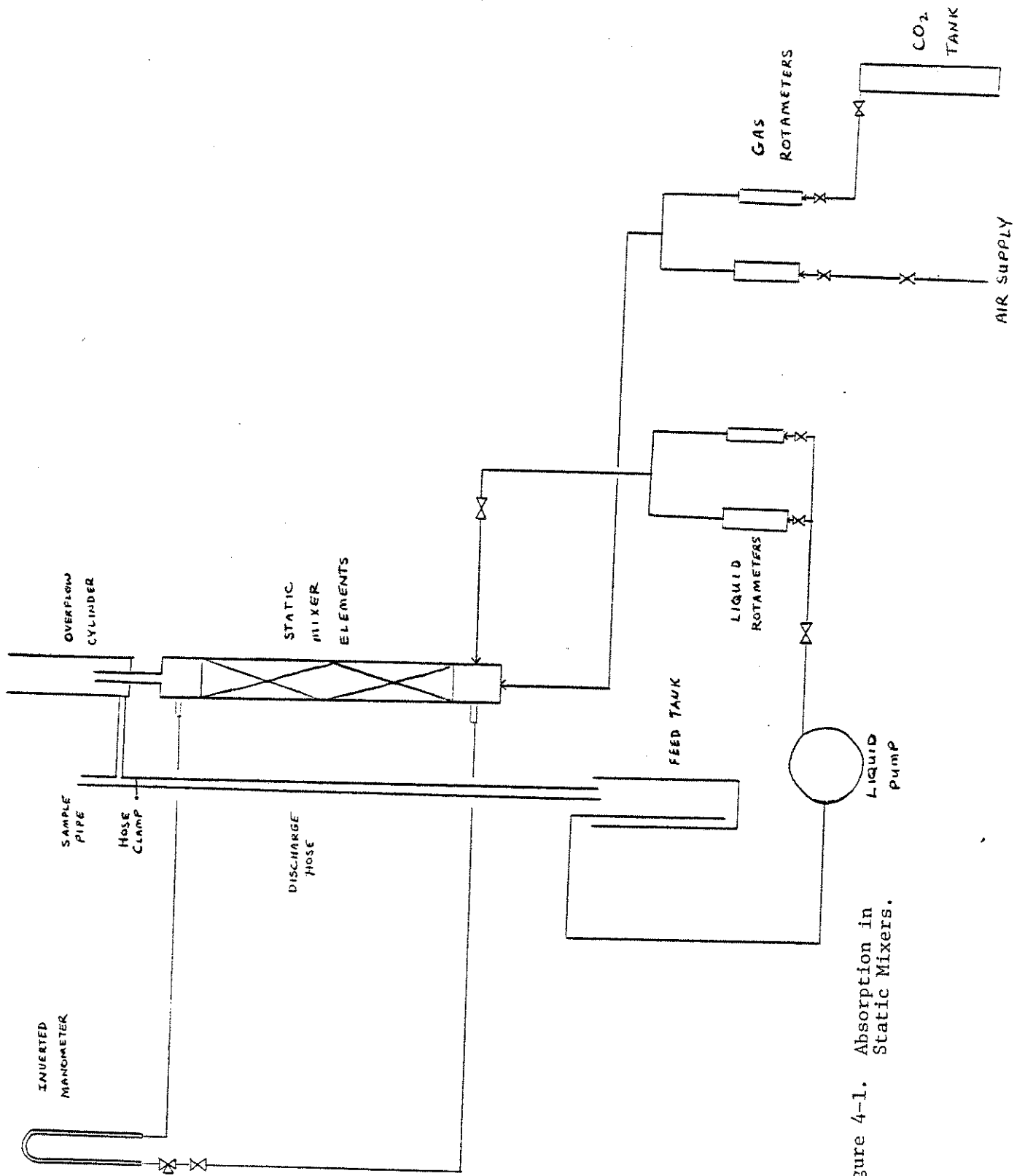
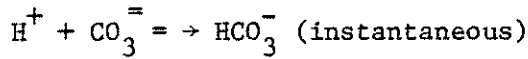
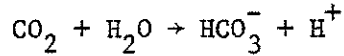


Figure 4-1. Absorption in Static Mixers.

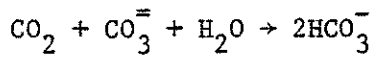
3. Absorption of carbon dioxide into a buffer solution of sodium carbonate/sodium bicarbonate catalyzed by arsenite ion

$A_s(OH)_2O^-$ has been selected as the test system.

The reaction proceeds according to the following scheme:



which leads to the following overall scheme:



Reaction rate is given as:

$$r = K_1 + K_c C_{\text{diss. ars.}}$$

$$\text{where } C_{\text{diss. ars.}} = C_{\text{tot. ars.}} \frac{K_{\text{ars}} (\text{BR})}{1 + K_{\text{ars.}} (\text{BR})}$$

(BR) = $(CO_3^{=}/HCO_3^-)$ - buffer ratio, K_{ars} is the ratio of the first and second dissociation constants of arsenious acid and can be taken as 10.6 and the values for K_1 and K_c are given in the literature.

The rate of absorption per unit interfacial area as given by Danckwerts surface renewal model is:

$$R = A^* \sqrt{D_L K_2 B + K_L^2}$$

where A^* is the equilibrium concentration of dissolved CO_2 , D_L is the diffusivity of CO_2 in the liquid, K_L is the liquid side mass transfer coefficient and $K_2 B = K_{OH}^-(OH^-) + K_c (A_s(OH)_2O^-)$.

Measuring the total rate of absorption, R_a , at various catalyst (arsenite) concentrations leads to the set of data that can be plotted as a straight line according to the following equation:

$$\left(\frac{R_a}{A^*}\right)^2 = D_L K_2 B a^2 + (K_L a)^2$$

A plot of $\left(\frac{R_a}{A^*}\right)^2$ vs $K_2 B$ should give a straight line with the slope $D_L a^2$ and the intercept $(K_L a)^2$. Values of A^* , D_L , K_2 are available in the literature. In this manner the volumetric mass transfer coefficient, $K_L a$, and interfacial area for transfer, a , can be determined.

4. A set of experimental runs were performed to test the equipment.
5. An analytical method for determining the difference in carbonate in concentration and from it the amount of CO_2 absorbed has been developed.

D. Further Research Work

1. Modification of equipment, installation of a large capacity pump and a better manometer.
2. Further refinement and calibration of the procedure for evaluation of carbonate ion concentration in presence of bicarbonate and arsenite ion.
3. Experimental testing of Kenics, Ross and Koch mixers; evaluation of pressure drop, volumetric mass transfer coefficients and interfacial area for transfer.

Project 5. Gas-Lift Recirculation Reactor

A. Problem Definition

Gas-lift-slurry reactors represent another alternative to trickle-beds for gas-liquid contacting in the presence of solid catalysts. This reactor configuration is very useful for operation at terminal conditions as it can be operated at large recycle ratios as a stirred tank without moving parts.

Although bubble columns with suspended slurries have been extensively investigated, almost no experimental information is available on gas-lift reactors where liquid velocity in the up-leg can be order of magnitude greater than in bubble columns. Therefore, it is of interest to determine how liquid holdup and liquid-gas mass transfer depend on liquid recirculation.

B. Research Objectives

1. Determination of reliable correlations for pressure drop, gas holdup and liquid recirculation in the bubble flow regime.
2. Determination of mass transfer coefficients and effect of liquid velocity, solids size and concentration.

C. Research Accomplishments

1. Experimental investigations of pressure drop, gas holdup and liquid recirculation in gas-lift up-legs from 0.75" to 2" in diameter with L/D ratios from 38 to 90 were completed. Liquid densities were varied from 0.8 to 1.3 g/cm³, surface tension from 29 to 73 dynes/cm and viscosity from 0.8 to 56 cps. The schematic of the apparatus used is shown in Figure 5-1.

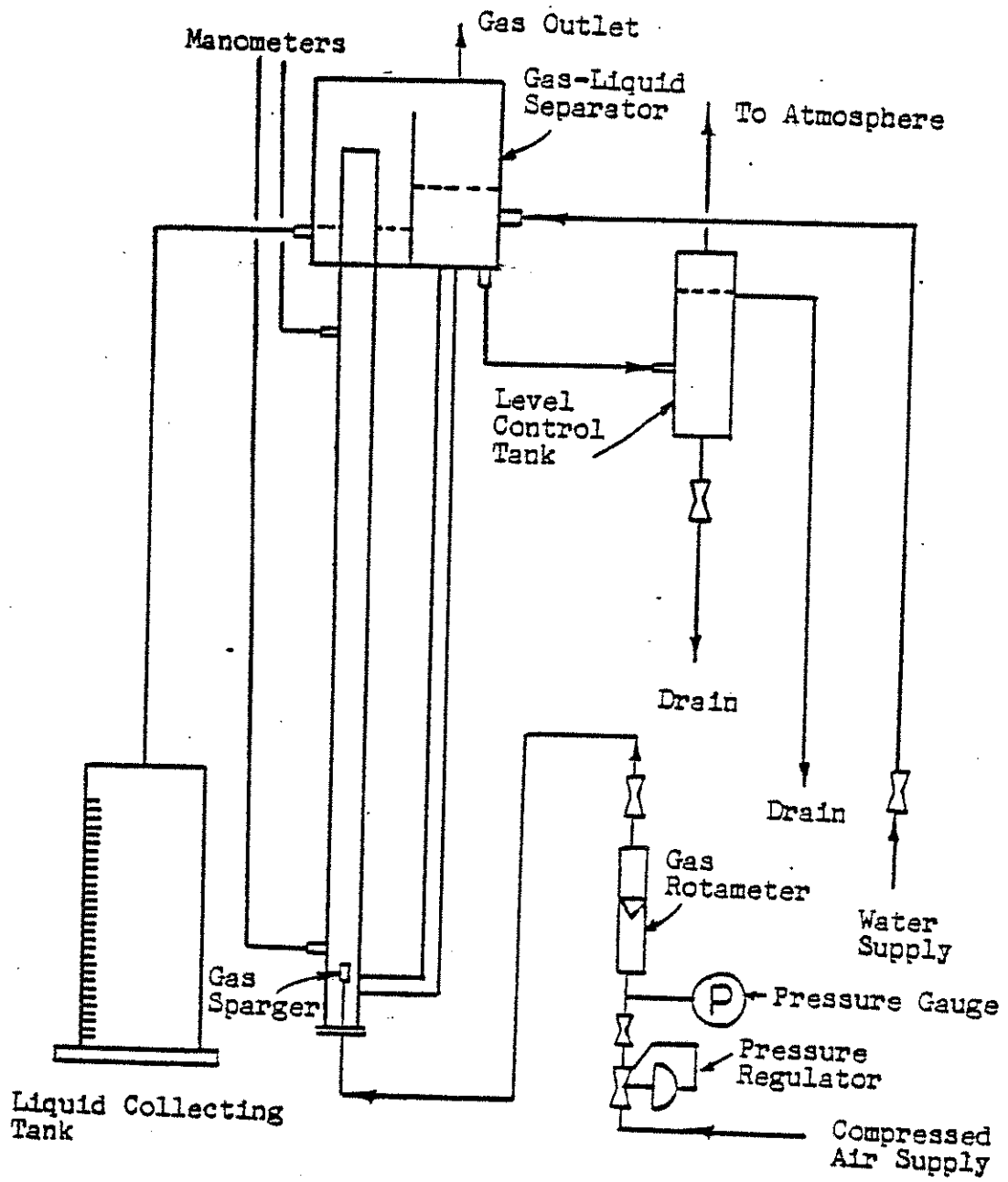


Figure 5-1. Apparatus for Pressure Drop, Holdup and Liquid Recirculation Studies in Gas-Lift Reactors.

2. Two phase flow pressure drop correlation for bubble flow regime was developed and is given below:

$$\frac{f_{TP}}{f_L} = 6.42 (Fr_{TP})^{-0.213} (Re_{TP})^{-0.056} (We_{TP})^{-0.157};$$

$$(Re_M \geq 1,000)$$

The correlation predicts pressure drop of all data available within 30%.

3. Gas holdup correlation was developed for the bubble flow regime and is given below:

$$\frac{1-\epsilon_G}{\epsilon_G} = 4.6 Z^{0.9} e^{0.47D}; \quad 2 \leq D \leq 5 \text{ cm}$$

$$\frac{1-\epsilon_G}{\epsilon_G} = 30 Z^{0.9} e^{0.063D}; \quad 5 \leq D \leq 30 \text{ cm}$$

where Z is a dimensionless group given by:

$$Z = \left(\frac{V_L}{V_G}\right) \left(Fr_{TP}\right)^{0.36} \left(Re_{TP}\right)^{0.006} \left(We_{TP}\right)^{-0.57}$$

The agreement with data is shown in Figure 5-2.

4. An algorithm based on a one dimensional momentum balance and developed correlations for holdup and pressure drop was constructed for prediction of liquid recirculation velocities. It was shown that the algorithm should predict liquid velocities in large scale reactors within 20% while much larger errors are

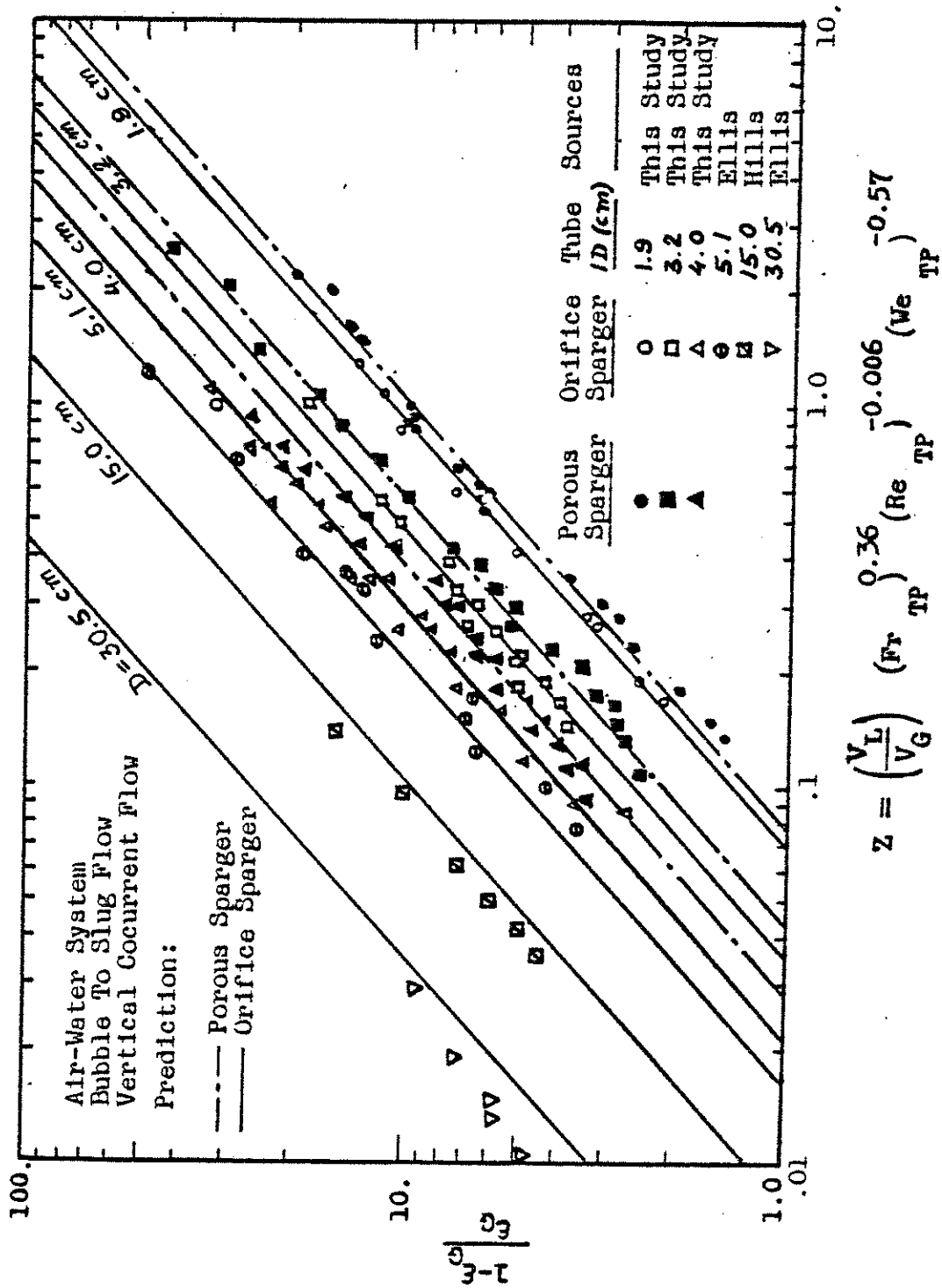


Figure 5-2. Comparison of Holdup Correlation with Data.

possible in small scale bench equipment as used in this study.
The comparison of predicted and actual liquid recirculation
velocity is shown in Figure 5-3.

D. Further Research Plan

Pursuit of the second objective i.e. determination of mass transfer
coefficients and assessment of the effect of liquid velocity, solids
size and concentration on them has been abandoned for lack of funding.

No research is planned in this area in the immediate future.

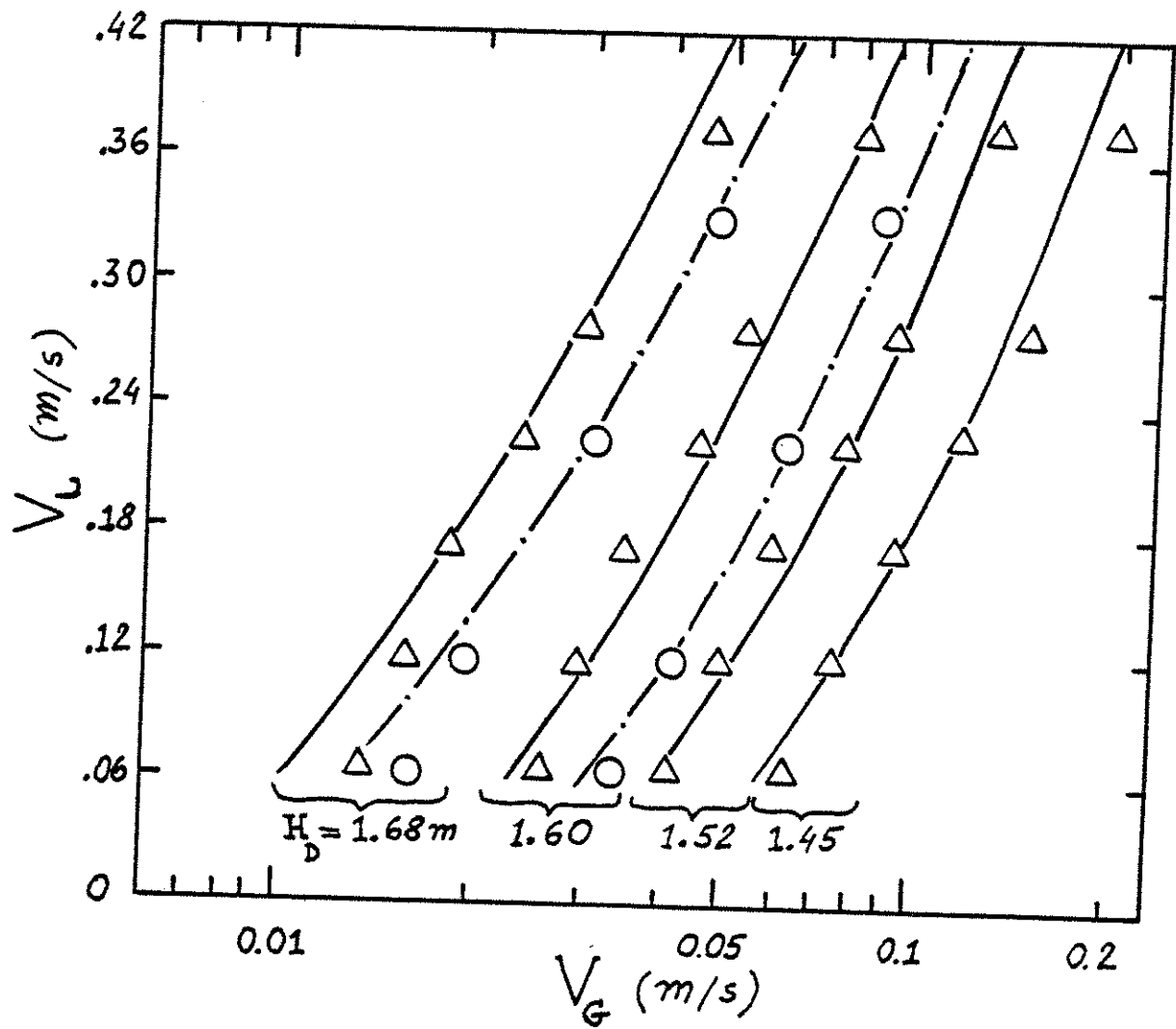


Figure 5-3. Comparison of Predicted and Measured Liquid Recirculation Velocity.

AREA II. GAS-SOLID NONCATALYTIC REACTIONS

Project 1. Parameter Estimation From Conversion Time Data

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

The project has been initiated this spring. Various popular models for gas-solid reactions have been completed. Further work is in progress.

D. Further Research Plan

Accomplishment of research objectives stated above.

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.

D. Further Research Plan

Accomplishment of research objectives stated above.

3. Multiple conversion-time histories are also
possible and are practically indistinguishable
from each other.

Details of the further research is provided in
Appendix B.

E. Further Research Plan

Extension to the shrinking core model

$\bar{K} = 10; \quad \phi = 20; \quad \rho = 0$

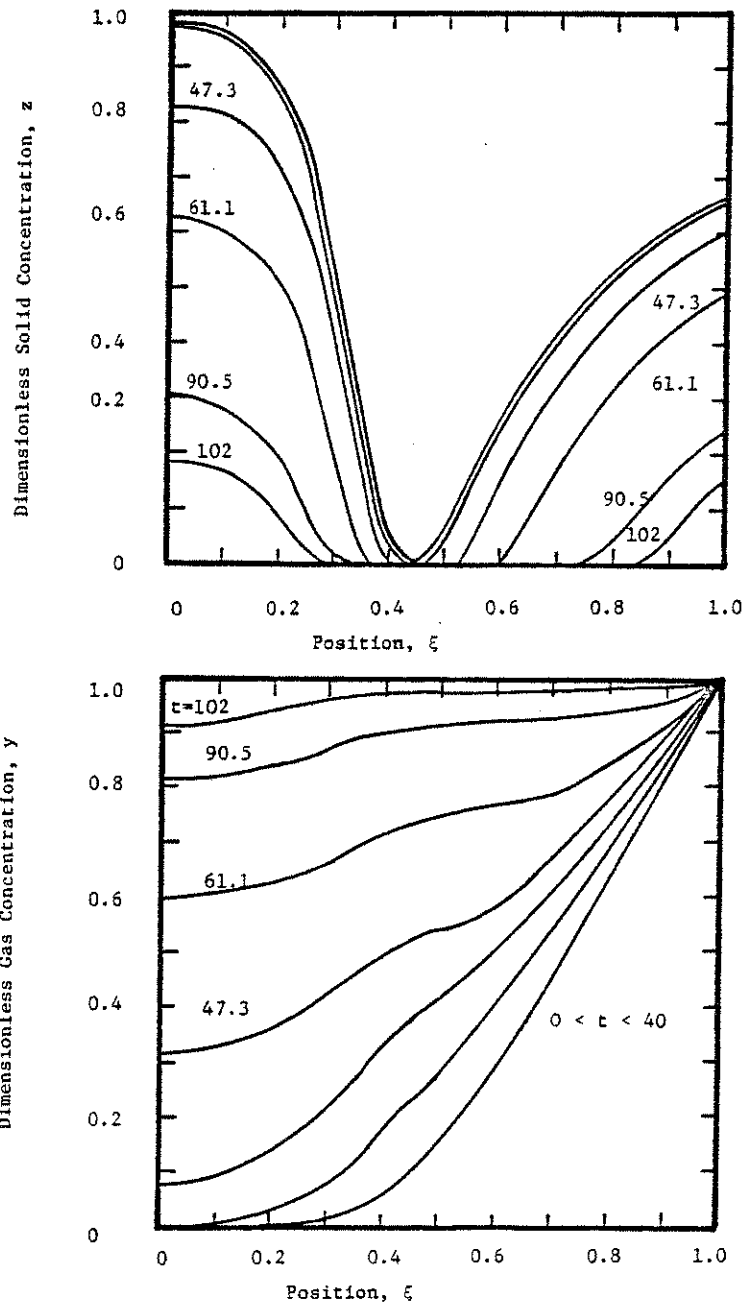


Figure II-2-1. Solid and Gas Reactant Concentration Profiles in a Solid Pellet in Case of Self-inhibited Rate Form.

Project 3. Effective Diffusivity of Gases in Porous Solid Pellets

A. Problem Definition

In many applications it is important to know effective diffusivities in porous solid pellets precisely. This is the case when one deals with the manufacture of novel or routine catalyst and/or adsorbent pellets or when one studies gas-solid noncatalytic reactions or catalytic reactions in a single pellet reactor. The existing theories (dusty gas model) and models (random pore model etc.) cannot yield predictions of sufficient accuracy. Thus, it is necessary to measure effective diffusivities experimentally.

In determination of effective diffusivities it is important to be able to evaluate the diffusivity of the actual pellets of interest, rather than of specially prepared samples, and under conditions similar to those under which the pellet will be ultimately used. Almost none of the current techniques can satisfy both requirements. This, and the necessity of knowing effective diffusivities accurately in our work with gas-solid noncatalytic reactions provided the incentive for development of a novel apparatus for determination of effective diffusivities.

B. Research Objectives

1. Development of a novel apparatus for evaluation of effective diffusivity of gases in binary gas mixtures in single commercial catalyst pellets.
2. Comparison of diffusivities determined by steady state and transient method.

C. Research Accomplishments

The experimental setup for evaluation of effective diffusivities in presence and absence of superimposed pressure difference across the

pellet was constructed and is presented schematically in Figures II-3-1 to II-3-3. The current test cell composed of two half-cells (14) can handle a 1/4" cylindrical or granular pellet and can be adapted to house other pellets of commercially used sizes. The pellet is currently held in tygon tubing which is sleeved onto the half-cells. Other housing will be developed also. The dead volume in each half-cell is minimal and a micro TC detector (12) is placed adjacently to each half-cell. A micro pressure transducer (8) is imbedded into each half-cell. Flow controls allow regulated flow of gas on each side of the pellet.

Both steady state and transient tests in presence and in absence of pressure differences across the pellet are possible.

For example, in a steady state test a mixture of two gases can be passed continuously on one side of the pellet through a half-cell and a pure gas can be fed into the half-cell on the other side of the pellet. The TC-cells on the exits of both half-cells determine the change in concentration of both gas streams. From this information and based on the known gas flow rates and the expression for a steady state diffusion flux effective diffusivity can be calculated. Experimental runs can be repeated in presence and in absence of pressure differences across the pellet thus providing a test for the dusty gas model.

Transient experiments can be performed by utilizing the fast actuating solenoid valve (6) which can provide a step change in gas concentration. The step change tests are designed to minimize flow and pressure disturbances by using large coils of gases in front of the solenoid valve. This test can provide a verification whether effective

diffusivities determined by steady state and transient methods agree well with each other which has been a topic of controversy for quite some time. The interpretation of transient tests has been developed and involves more sophisticated mathematics. Transient tests can also be conducted in presence and absence of pressure differences across the pellet.

The equipment is ready for testing. Only some experiments with brass pellets to test for presence of leaks have been performed so far.

D. Further Research Plan

None due to temporary lack of funds.

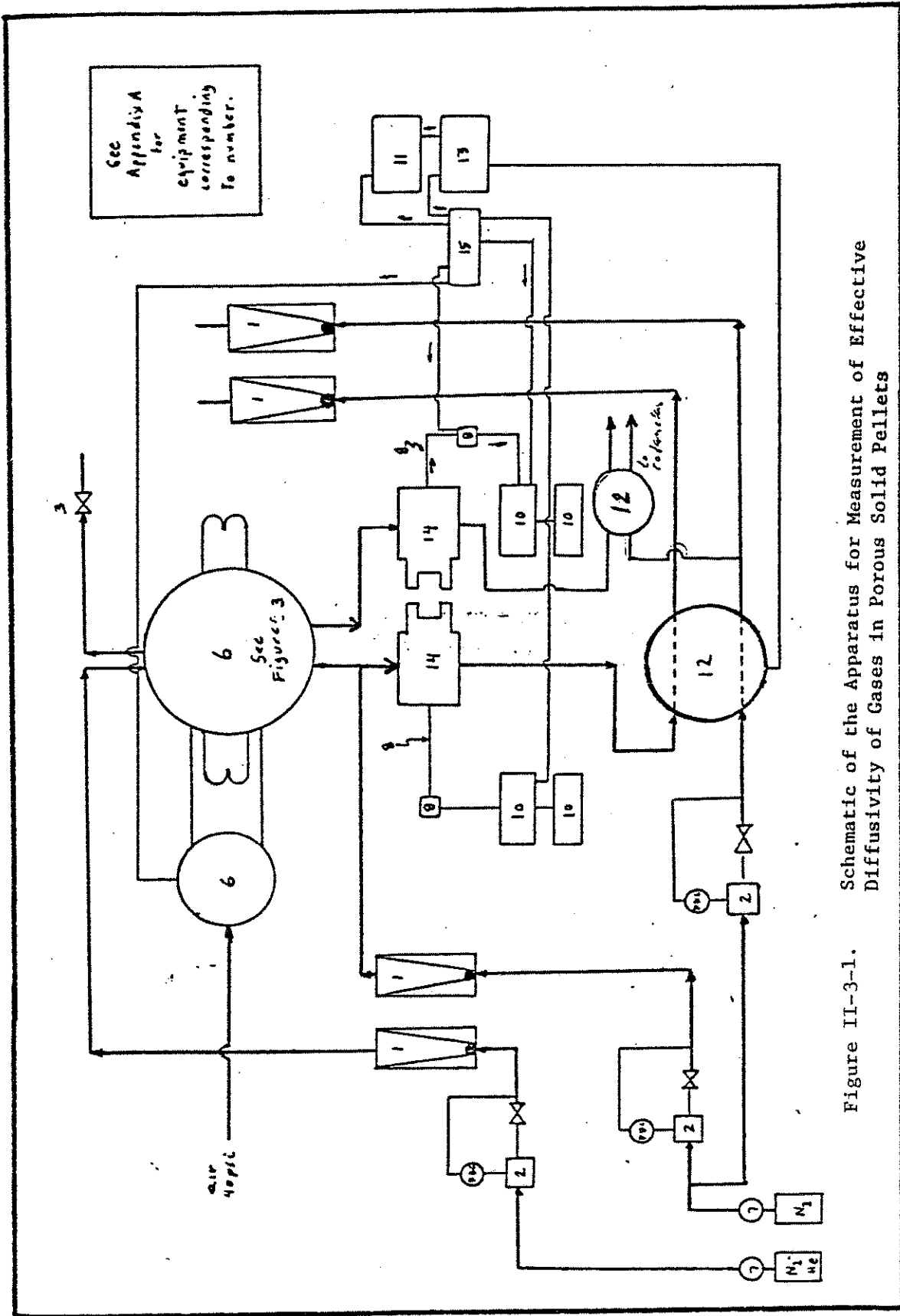


Figure II-3-1. Schematic of the Apparatus for Measurement of Effective Diffusivity of Gases in Porous Solid Pellets

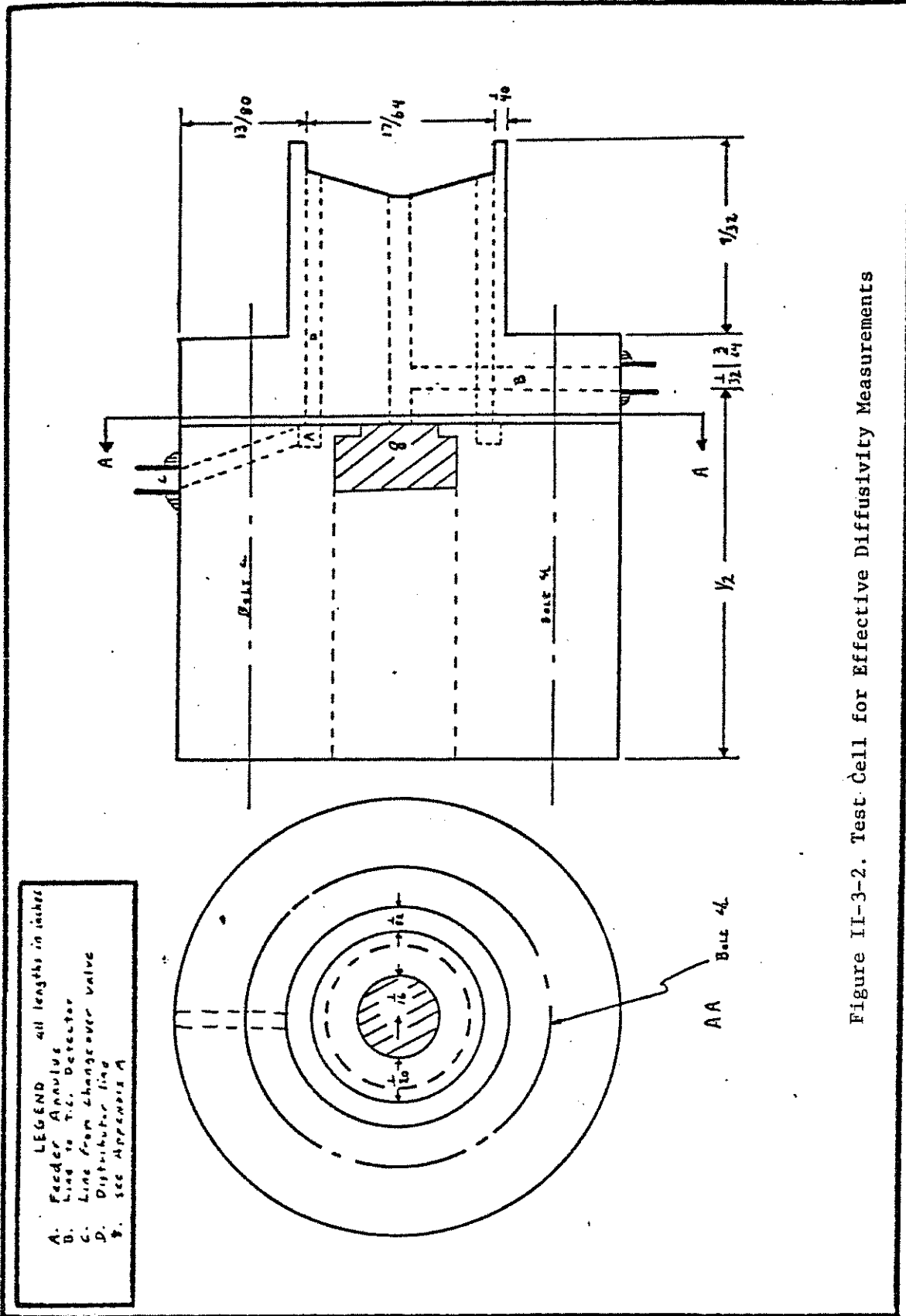


Figure II-3-2. Test Cell for Effective Diffusivity Measurements

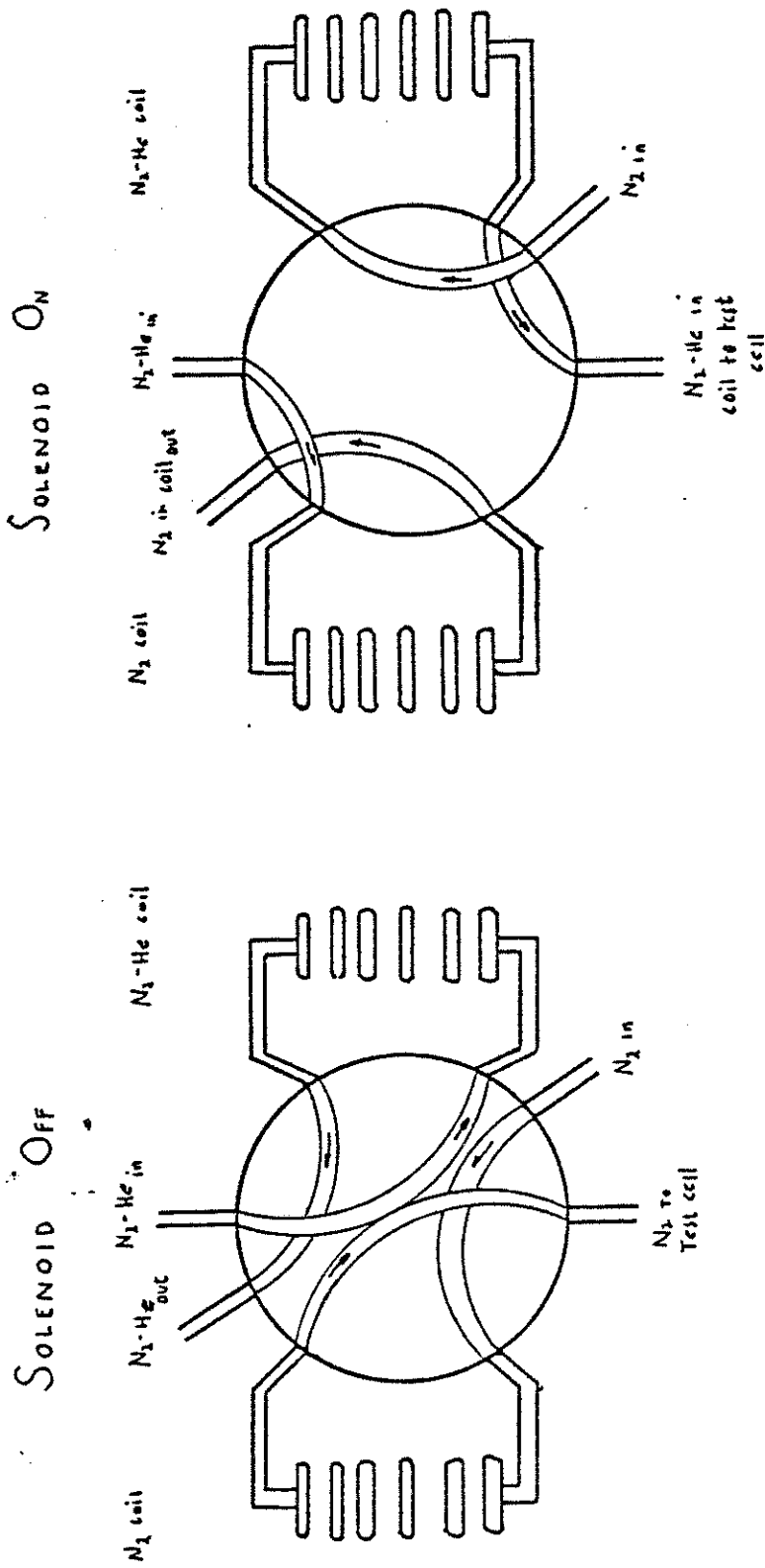


Figure II-3-3. Solenoid Valve Schematic for Effective Diffusivity Measurements

LISTING OF ITEMS FOR Figure II-3-1 to II-3-3.

- (1) Rotameter
- (2) Flow Controller
- (3) Needle Valve
- (4) Copper Coil
- (6) 8-Port Injection Valve
- (7) Pressure Regulator
- (8) Pressure Transducer
- (9) Power Supply
- (10) Digital Voltmeter
- (11) Chart Recorder
- (12) Thermal Conductivity Cell
- (13) Power Supply
- (14) Test Cell

CURRENT STAFF

The staff of the Laboratory during the period covered by this report consisted of the following members of the Chemical Engineering Department.

A. Faculty

Dr. Milorad (Mike) P. Duduković, Associate Professor of Chemical Engineering.

Dr. Simon P. Waldram, Visiting Associate, Professor of Chemical Engineering (June 1979 - August 1979).

B. Graduate Students

A. A. El-Hisnawi.

H. Erk.

J. Evans.

H. C. Kao (June 1979 - December 1979).

G. Maxwell (June 1979 - August 1979).

P. L. Mills (graduated in April 1980 with a D.Sc. degree).

C. Undergraduate Students

J. Kang.

K. Mowery.

L. Windes.

CURRENT FUNDING

The support for the Laboratory during the past year was derived from industrial contributions (Alcoa, Amoco, Monsanto, Shell) totalling \$28,000.

No federal grants were sought or obtained during the past year.

Federal grants in the area of multiphase reactors (DOE, NSF) and gas-solid reactions (DOE) are being sought this year.

Appendix I

Liquid - Solid Contacting and
Catalyst Effectiveness in Trickle-Bed Reactors

Schematic of the Apparatus (2 Figures)

Range of Achievable Operation Conditions (2 Tables)

Data Reduction - Program Outline (1 Figure)

Sample Program Output (1 Figure)

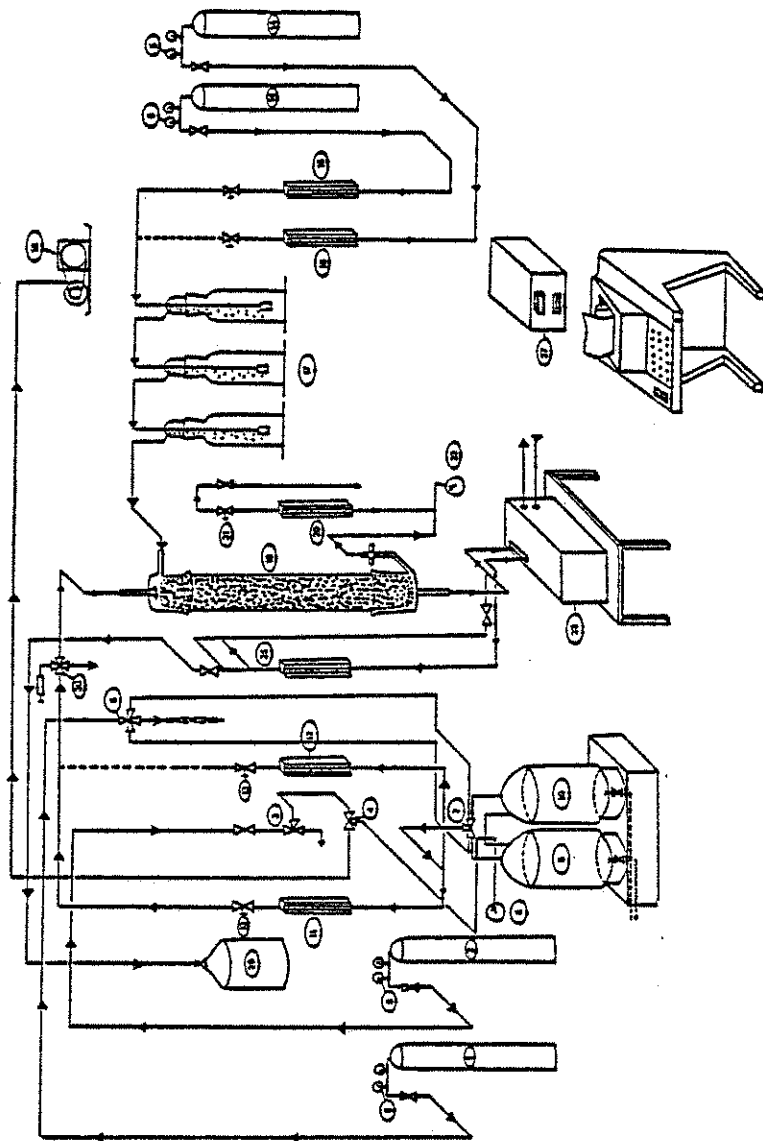


Figure AI-1. Three-Dimensional View of the Experimental Equipment For Tracer Studies.

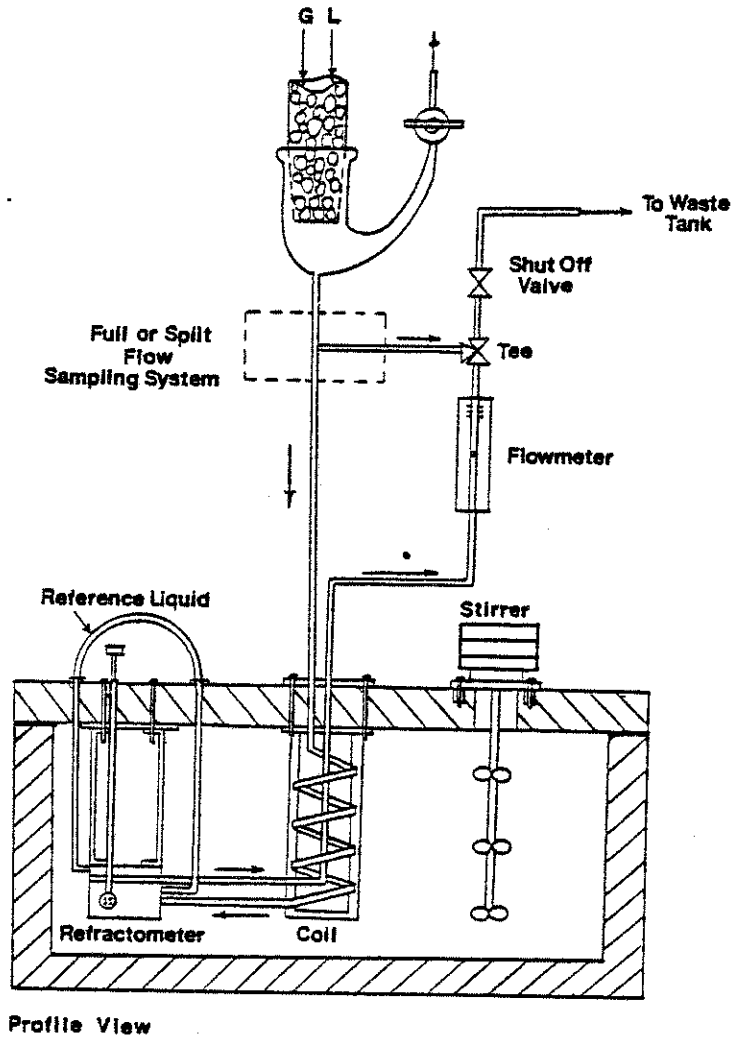


Figure AI-2. Details of the Lower End of the Trickle-Bed Column.

Figure AI-1.

Range of Possible Liquid Superficial Velocities

Reactor Inner Diameter		Liquid Superficial Velocity, $\frac{\text{kg}}{\text{sq.m.}\cdot\text{sec.}}$			
		(Based on water with $\rho = 1.0 \text{ gm/cu.cm.}$)			
<u>cm</u>	<u>in.</u>	<u>R-2-15A*</u>	<u>R-2-15C</u>	<u>R-6-15A</u>	<u>R-6-15B</u>
1.27	0.5	6.08	28.68	101.6	271.0
2.54	1.0	1.52	7.17	25.39	67.76
5.08	2.0	0.38	1.79	6.35	16.94
7.62	3.0	0.17	0.80	2.82	7.53
10.16	4.0	0.09	0.45	1.59	4.23

* Denotes Brooks rotameter tube size designation.

Table AI-2.

Range of Possible Gas Superficial Velocities

Reactor Inner Diameter		Gas Superficial Velocity, $\frac{\text{kg}}{\text{m}^2\text{-s}}$ (Based on Air at T = 25°C)			
		R-2-15AAA*	R-2-15AA	R-2-15A	R-6-15A
1.27	0.5	0.023	0.041	0.262	2.555
2.54	1.0	5.68×10^{-3}	0.010	0.422	0.639
5.08	2.0	1.42×10^{-3}	2.58×10^{-3}	0.016	0.160
7.62	3.0	6.32×10^{-4}	1.15×10^{-3}	7.27×10^{-3}	0.071
10.16	4.0	3.55×10^{-4}	6.45×10^{-4}	4.09×10^{-3}	0.040

* Denotes Brooks rotameter tube size designation.

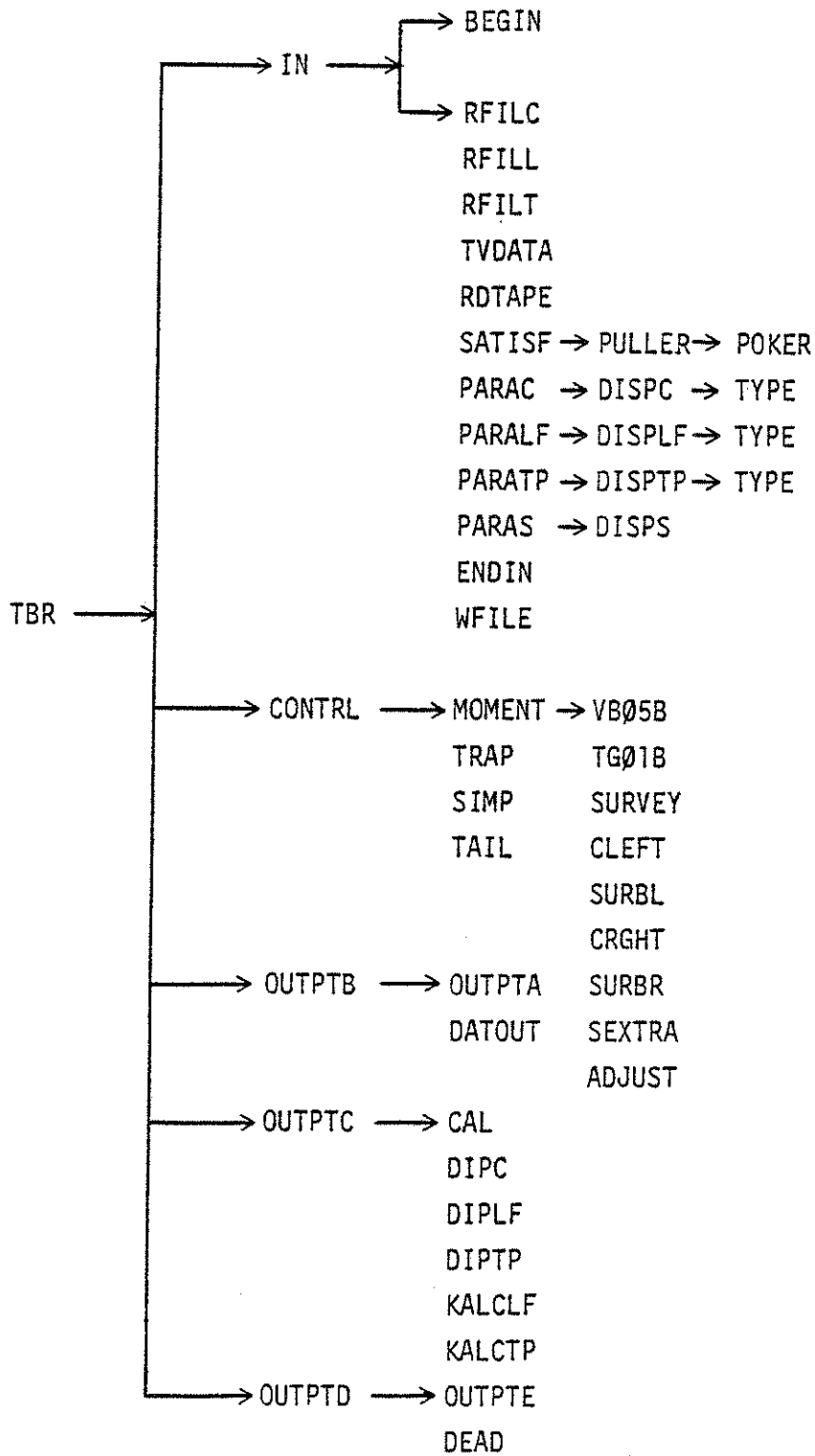


Figure AI-3. Main Program and Associated Subroutines Used in Data Reduction.

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*ERROR*CHECK**ERROR*CHECK**ERROR*CHECK**ERROR*CHECK**ERROR*CHECK*

INDEX	SIGNIFICANCE
1	FIRST POINT IN SET
1	MINIMUM POINT
1	STARTING AVERAGE
2	BEGINNING OF RESPONSE
7	MAXIMUM POINT
10	START OF EXTRAPOLATION
25	TERMINATION OF RESPONSE
25	END AVERAGE
25	LAST POINT IN SET

INTERMEDIATE CALCULATIONS

START RESPONSE TIME =	0.0	START AVERAGE =	0.000
INIT. RESPONSE TIME =	3.0	INITIAL RESPONSE =	0.000
TIME OF MAXIMUM =	18.0	ABSOLUTE MAXIMUM =	58.900
TIME OF MINIMUM =	0.0	ABSOLUTE MINIMUM =	0.000
TAIL STARTING TIME =	27.0	START OF TAIL =	42.000
FINAL RESPONSE TIME =	72.0	FINAL RESPONSE =	0.000
RESPONSE END TIME =	72.0	END AVERAGE =	0.000

BASE-LINE CORRECTION

DO YOU WISH A (STRAIGHT LINE) BASE DRIFT CORRECTION
WITH SLOPE= 0.0000000 Y-INTERCEPT = 0.00000
ENTER (YES OR NO)=

Figure AI-4. Sample Output From TBR.

 TAIL EXTRAPOLATION CALCULATIONS

 TRIAL NUMBER 1

POINT INDEX OF LOWEST SUGGESTED EXTRAPOLATION POINT = 7
 POINT INDEX OF HIGHEST SUGGESTED EXTRAPOLATION POINT = 25
 INITIAL POINT INDEX OF EXTRAPOLATION ARRAY = 11
 FINAL POINT INDEX OF EXTRAPOLATION ARRAY = 19

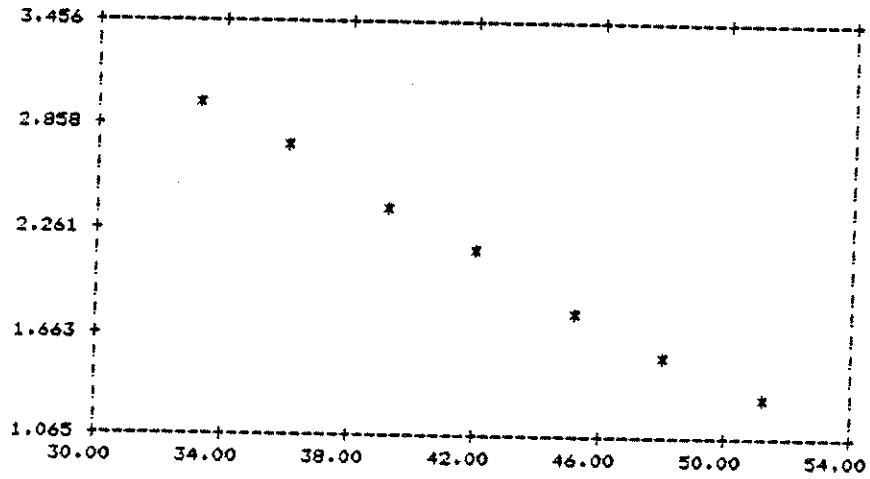
 SELECTED TAIL POINTS

INDEX	TIME	VOLTAGE
11	30.00	31.70
12	33.00	20.00
13	36.00	14.90
14	39.00	10.60
15	42.00	8.50
16	45.00	6.20
17	48.00	4.90
18	51.00	3.70
19	54.00	2.90

 SELECTED PLOT POINTS

INDEX	TIME	VOLTAGE	LN(VOLTAGE)
1	30.00	31.70	3.4563
2	33.00	20.00	2.9957
3	36.00	14.90	2.7014
4	39.00	10.60	2.3609
5	42.00	8.50	2.1401
6	45.00	6.20	1.8245
7	48.00	4.90	1.5892
8	51.00	3.70	1.3083
9	54.00	2.90	1.0647

Figure AI-4. (continued)



TAIL FIT PARAMETERS

MULTIPLIER = 0.94515E+03 EXPONENTIAL CONSTANT = -0.112025E+00
 RESIDUAL = 5.98230

	ZERO	FIRST	SECOND
TAIL MOMENTS	2.650	214.454	17566.216
CURVE MOMENTS	1479.600	32360.400	878846.410
TOTAL MOMENTS	1482.250	32574.854	896412.630

--SUMMARY OF EXTRAPOLATION RESULTS--

INDEX	RESIDUAL
19	5.98230

 *CALCULATIONS*COMPLETED**CALCULATIONS*COMPLETED**CALCULATIONS*COMPLETED*

Figure AI-4. (continued)

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=====
DATA SET NAME : NA21          MODE OF OPERATION: PULSE INPUT OF TRACER
SAMPLING METHOD: FIXED TIMING  SMOOTHING METHOD : NONE USED
EXPERIMENT TYPE: TWO-PHASE FLOW
=====

```

EXPERIMENTAL DATA

INDEX	TIME (SEC)	ORIGINAL VOLTAGE (MV)	ADJUSTED VOLTAGE (MV)	TRACER CONCENTRATION (GHS/CC)	EXIT-AGE DISTRIBUTION (1./SEC.)
1	0.00	0.00	0.00	0.0000E+00	0.0000E+00
2	3.00	0.00	0.00	0.0000E+00	0.0000E+00
3	6.00	15.50	15.50	0.1550E-02	0.1046E-01
4	9.00	45.20	45.20	0.4520E-02	0.3049E-01
5	12.00	54.80	54.80	0.5480E-02	0.3697E-01
6	15.00	57.50	57.50	0.5750E-02	0.3879E-01
7	18.00	58.90	58.90	0.5890E-02	0.3974E-01
8	21.00	57.40	57.40	0.5740E-02	0.3872E-01
9	24.00	53.20	53.20	0.5320E-02	0.3589E-01
10	27.00	42.00	42.00	0.4200E-02	0.2834E-01
11	30.00	31.70	31.70	0.3170E-02	0.2139E-01
12	33.00	20.00	20.00	0.2000E-02	0.1349E-01
13	36.00	14.90	14.90	0.1490E-02	0.1005E-01
14	39.00	10.60	10.60	0.1060E-02	0.7151E-02
15	42.00	8.50	8.50	0.8500E-03	0.5735E-02
16	45.00	6.20	6.20	0.6200E-03	0.4183E-02
17	48.00	4.90	4.90	0.4900E-03	0.3306E-02
18	51.00	3.70	3.70	0.3700E-03	0.2496E-02
19	54.00	2.90	2.90	0.2900E-03	0.1956E-02
20	57.00	2.30	2.30	0.2300E-03	0.1552E-02
21	60.00	1.70	1.70	0.1700E-03	0.1147E-02
22	63.00	1.10	1.10	0.1100E-03	0.7421E-03
23	66.00	0.40	0.40	0.4000E-04	0.2699E-03
24	69.00	0.20	0.20	0.2000E-04	0.1349E-03
25	72.00	0.00	0.00	0.0000E+00	0.0000E+00

Figure AI-4. (continued)

 ** OPERATION PARAMETERS **

1.) CALIBRATION FACTOR (GM/CC/HV) = 0.1000E-03

---SUMMARY OF ROTAMETER SETTINGS AND VOLUMETRIC FLOW RATES---

			FLOW RATES		
			SETTING	CC/SEC	CC/MIN
2.)	LIQUID INLET	=	12.000 ST	0.537	32.246
3.)	REFRACTOMETER	=	14.200 GL	1.070	64.210
4.)	GAS INLET	=	9.000 GL	1.035	62.092

---LIQUID PHYSICAL PROPERTIES---

5.) LIQUID DENSITY (GM/CC) = 0.6570
 6.) LIQUID VISCOSITY (CP) = 0.3157

---GAS PHYSICAL PROPERTIES---

7.) GAS DENSITY (GM/CC) = 0.0002
 8.) GAS VISCOSITY (CP) = 0.0180

---REACTOR DIMENSIONS---

9.) REACTOR DIAMETER (CM) = 1.350
 10.) REACTOR VOLUME (CC) = 51.60
 11.) PACKED BED HEIGHT (CM) = 40.00

---PACKING PROPERTIES---

12.) PARTICLE DIAMETER (CM) = 0.0718
 13.) PARTICLE DENSITY (GM/CC) = 1.5780
 14.) PARTICLE POROSITY (CC/CC) = 0.4950
 15.) PACKING WEIGHT (GMS) = 51.00

---MISCELLANEOUS QUANTITIES---

16.) NOISE FACTOR = 0.0010
 17.) TRACER INLET CONC (GM/CC) = 0.2500
 18.) INJECTION LOOP VOL (CC) = 0.6060

Figure AI-4. (continued)

 ** CALCULATED PARAMETERS **

.....

A)	LIQUID HOURLY SPACE VELOCITY (1/HR)	=	74.663
B)	MASS SUPERFICIAL VELOCITY (KG/SQ.M/SEC) --LIQUID	=	4.912
C)	--GAS	=	0.1446E-02
D)	MASS SUPERFICIAL VELOCITY (KG/SQ.M/MIN) --LIQUID	=	294.723
E)	--GAS	=	0.8676E-01
F)	SUPERFICIAL VELOCITY (CM/SEC) --LIQUID	=	0.748
G)	--GAS	=	0.723
H)	SUPERFICIAL VELOCITY (CM/MIN) --LIQUID	=	0.087
I)	--GAS	=	43.379
J)	REYNOLDS NUMBERS --LIQUID	=	11.172
K)	--GAS	=	0.5768E-01
L)	BED PROPERTIES --BED POROSITY	=	0.374
M)	TRACER MASS BALANCE (GMS) --MASS INJECTED	=	0.1515E+00
N)	--MASS EXITING	=	0.1586E+00
O)	-- ERROR (%)	=	-0.4704E+01

.....

Figure AI-4. (continued)

```

=====
NAME=NA21
TYPE=1
EVENLY SPACED TIME?YE   DELTA-T=   3.000   IEXP= 3
=====
DESIGNATION=N-HEPTANE-TP-8X-1   PACKING=POROUS F-1 ALUMINA
SOLVENT   =N-HEXANE             TRACER  =N-HEPTANE
=====

```

```

DEAD VOLUME - MEAN RESIDENCE TIME =      SEC      MIN
                                      7.6371      0.1273
- VARIANCE                          =      SQ SEC   SQ MIN
                                      1.0389      0.0003

```

.....

RESULTS

```

ZEROTH MOMENT           =      1482.25
FIRST MOMENT            =      32574.85
SECOND MOMENT           =      896412.63

MEAN RESIDENCE TIME     =      SEC      MIN
CORRECTED MEAN RESIDENCE TIME =  21.98   0.3663
                                      14.34   0.2390

VARIANCE                =      SQ SEC   SQ MIN
CORRECTED VARIANCE     =  121.79   0.0338
                                      120.75   0.0335

DIMENSIONLESS VARIANCE =      0.5873

```

Figure AI-4. (continued)

Appendix II

Liquid - Solid Contacting and
Catalyst Effectiveness in Trickle Bed Reactors

Dual Series Program (Sample Output)

Table AII-1.

Dual Trigonometric Series Solved by DTRIGS*

<u>Type</u>	<u>Dual Series Equations</u>
1 a b	$\sum_{n=1}^{\infty} a_n u_{n1} \frac{\cos}{\sin} [(n-1)\pi x] = f_1(x) \quad , \quad 0 \leq x < c$ $\sum_{n=1}^{\infty} a_n u_{n2} \frac{\cos}{\sin} [(n-1)\pi x] = f_2(x) \quad , \quad c < x \leq 1$
2 a b	$\sum_{n=1}^{\infty} a_n u_{n1} \frac{\cos}{\sin} [(n-1/2)x] = f_1(x) \quad , \quad 0 \leq x < c$ $\sum_{n=1}^{\infty} a_n u_{n2} \frac{\cos}{\sin} [(n-1/2)x] = f_2(x) \quad , \quad c < x \leq \pi$

* Code Name for Dual Trigonometric Series

** SOLUTION OF DUAL-SERIES EQUATIONS BY THE METHOD OF WEIGHTED RESIDUALS **

PLEASE ANSWER THE FOLLOWING QUESTIONS!

WHAT SOLUTION METHOD DO YOU WISH TO USE?

- 1.) GALERKIN METHOD
- 2.) COLLOCATION METHOD
- 3.) LEAST-SQUARE METHOD

PLEASE ENTER THE TYPE NUMBER (1, 2, OR 3) = 3

WHAT IS THE FORM OF THE SERIES KERNEL?

- 1.) $\cos((N-1)*\pi*x)$
- 2.) $\sin((N-1)*\pi*x)$
- 3.) $\cos((N-1/2)*x)$
- 4.) $\sin((N-1/2)*x)$
- 5.) $\cos((N-1)*\theta)$
- 6.) $\sin((N-1)*\theta)$

PLEASE ENTER THE TYPE NUMBER (1-6) = 1

DO YOU WANT TO PERFORM A CALCULATION WITH THE SERIES COEFFICIENTS?

PLEASE ANSWER YES OR NO = YES

DO YOU WANT THE SERIES COEFFICIENTS PRINTED OUT?

PLEASE ANSWER YES OR NO = YES

DO YOU WANT TO EVALUATE THE SERIES AT SELECTED BASE POINTS?

PLEASE ANSWER YES OR NO = YES

Figure AII-1. Computer Output from DTRIGS.

PLEASE ENTER THE FOLLOWING SERIES COMPUTATIONAL PARAMETERS

1.) NUMBER OF MATRICE SIZES = 1

<u>NUMBER</u>	<u>SIZE</u>
1	50

2.) NUMBER OF PARAMETERS TO BE VARIED IN THE SERIES MODIFIER = 1

<u>PARAMETER NUMBER</u>	<u>PARAMETER VALUE</u>
1	5.0

3.) SERIES INTERVAL BREAK POINT = 0.5

4.) NUMBER OF BASE POINTS IN SERIES EVALUATION = 100

5.) ENTER THE VALUES OF C1 AND C2: 1.0 , 0.0

PLEASE ENTER THE NAME OF THE OUTPUT FILE: SLAB

STOP

END OF EXECUTION
CPU TIME: 6.45 ELAPSED TIME: 18.22
EXIT

Figure AII-1. (continued)

DEGREE OF MATRIX = 50

SERIES FUNCTIONAL VALUES AT SELECTED BASE POINTS

1	0.0000000E+00	0.9921222E+00
2	0.1010101E-01	0.9995691E+00
3	0.2020202E-01	0.1007993E+01
4	0.3030303E-01	0.1001626E+01
5	0.4040404E-01	0.9923340E+00
6	0.5050505E-01	0.9975275E+00
7	0.6060606E-01	0.1007589E+01
8	0.7070707E-01	0.1003682E+01
9	0.8080808E-01	0.9929870E+00
10	0.9090909E-01	0.9953288E+00
11	0.1010101E+00	0.1006756E+01
12	0.1111111E+00	0.1005708E+01
13	0.1212121E+00	0.9941059E+00
14	0.1313131E+00	0.9935711E+00
15	0.1414141E+00	0.1005417E+01
16	0.1515152E+00	0.1007697E+01
17	0.1616162E+00	0.9958574E+00
18	0.1717172E+00	0.9917803E+00
19	0.1818182E+00	0.1003451E+01
20	0.1919192E+00	0.1009500E+01
21	0.2020202E+00	0.9983287E+00
22	0.2121212E+00	0.9902789E+00
23	0.2222222E+00	0.1000726E+01
24	0.2323232E+00	0.1010999E+01
25	0.2424242E+00	0.1001814E+01
26	0.2525253E+00	0.9893928E+00
27	0.2626263E+00	0.9969771E+00
28	0.2727273E+00	0.1011751E+01
29	0.2828283E+00	0.1006604E+01
30	0.2929293E+00	0.9897962E+00
31	0.3030303E+00	0.9920243E+00
32	0.3131313E+00	0.1011015E+01
33	0.3232323E+00	0.1013123E+01
34	0.3333333E+00	0.9929123E+00
35	0.3434343E+00	0.9857789E+00
36	0.3535354E+00	0.1006961E+01
37	0.3636364E+00	0.1021554E+01
38	0.3737374E+00	0.1002267E+01
39	0.3838384E+00	0.9796924E+00
40	0.3939394E+00	0.9953607E+00
41	0.4040404E+00	0.1029876E+01
42	0.4141414E+00	0.1027318E+01
43	0.4242424E+00	0.9845161E+00
44	0.4343434E+00	0.9672588E+00
45	0.4444444E+00	0.1019296E+01
46	0.4545455E+00	0.1094613E+01
47	0.4646465E+00	0.1105417E+01
48	0.4747475E+00	0.1018298E+01
49	0.4848485E+00	0.8776883E+00
50	0.4949495E+00	0.7464552E+00

Figure AII-1. (continued)

SERIES FUNCTIONAL VALUES FOR SELECTED BASE POINTS

51	0.5050505E+00	-0.6329751E-01
52	0.5151515E+00	0.1441271E-01
53	0.5252525E+00	0.3479296E-01
54	0.5353535E+00	-0.3550789E-01
55	0.5454545E+00	0.1484114E-02
56	0.5555555E+00	0.2720250E-01
57	0.5656566E+00	-0.1092434E-01
58	0.5757576E+00	-0.1550163E-01
59	0.5858586E+00	0.1533223E-01
60	0.5959596E+00	0.9604974E-02
61	0.6060606E+00	-0.1410805E-01
62	0.6161616E+00	-0.3704797E-02
63	0.6262626E+00	0.1391902E-01
64	0.6363636E+00	0.1350905E-02
65	0.6464646E+00	-0.1162857E-01
66	0.6565657E+00	0.1566898E-02
67	0.6666667E+00	0.1083059E-01
68	0.6767677E+00	-0.2380853E-02
69	0.6868687E+00	-0.8853289E-02
70	0.6969697E+00	0.3905745E-02
71	0.7070707E+00	0.8128776E-02
72	0.7171717E+00	-0.4073562E-02
73	0.7272727E+00	-0.6595919E-02
74	0.7373737E+00	0.4910864E-02
75	0.7474747E+00	0.6033076E-02
76	0.7575758E+00	-0.4818463E-02
77	0.7676768E+00	-0.4863961E-02
78	0.7777778E+00	0.5304243E-02
79	0.7878788E+00	0.4442063E-02
80	0.7979798E+00	-0.5110485E-02
81	0.8080808E+00	-0.3538846E-02
82	0.8181818E+00	0.5411218E-02
83	0.8282828E+00	0.3222049E-02
84	0.8383838E+00	-0.5197356E-02
85	0.8484849E+00	-0.2508422E-02
86	0.8585859E+00	0.5400024E-02
87	0.8686869E+00	0.2265936E-02
88	0.8787879E+00	-0.5192821E-02
89	0.8888889E+00	-0.1685706E-02
90	0.8989899E+00	0.5344931E-02
91	0.9090909E+00	0.1486769E-02
92	0.9191919E+00	-0.5161188E-02
93	0.9292929E+00	-0.9912791E-03
94	0.9393939E+00	0.5294291E-02
95	0.9494950E+00	0.8240714E-03
96	0.9595960E+00	-0.5127830E-02
97	0.9696970E+00	-0.3743500E-03
98	0.9797980E+00	0.5262384E-02
99	0.9898990E+00	0.2214505E-03
100	0.1000000E+01	-0.5117128E-02

Figure AII-1. (continued)

SOLUTION VECTOR

```

-----
A( 1) = 0.2932391E+01
A( 2) = 0.3367606E+01
A( 3) = -0.7223145E+00
A( 4) = -0.1444209E+01
A( 5) = 0.5442275E+00
A( 6) = 0.1105960E+01
A( 7) = -0.4031803E+00
A( 8) = -0.9737340E+00
A( 9) = 0.2829635E+00
A(10) = 0.9046599E+00
A(11) = -0.1726718E+00
A(12) = -0.8594419E+00
A(13) = 0.6675524E-01
A(14) = 0.8219234E+00
A(15) = 0.3738476E-01
A(16) = -0.7832484E+00
A(17) = -0.1402608E+00
A(18) = 0.7382145E+00
A(19) = 0.2416085E+00
A(20) = -0.6830093E+00
A(21) = -0.3400451E+00
A(22) = 0.6146218E+00
A(23) = 0.4332172E+00
A(24) = -0.5309250E+00
A(25) = -0.5181021E+00
A(26) = 0.4303247E+00
A(27) = 0.5908970E+00
A(28) = -0.3114239E+00
A(29) = -0.6458175E+00
A(30) = 0.1750022E+00
A(31) = 0.6770983E+00
A(32) = -0.2229586E-01
A(33) = -0.6771942E+00
A(34) = -0.1437242E+00
A(35) = 0.6357917E+00
A(36) = 0.3151316E+00
A(37) = -0.5422759E+00
A(38) = -0.4793423E+00
A(39) = 0.3838550E+00
A(40) = 0.6129121E+00
A(41) = -0.1494699E+00
A(42) = -0.6749432E+00
A(43) = -0.1629738E+00
A(44) = 0.5919173E+00
A(45) = 0.5186104E+00
A(46) = -0.2305694E+00
A(47) = -0.7274837E+00
A(48) = -0.5909532E+00
A(49) = -0.2184202E+00
A(50) = -0.2074624E-01

```

Figure AII-1. (continued)

