EXPERIMENTAL AND THEORETICAL STUDY OF A TUBULAR FLOW REACTOR: HOMOGENEOUS LIQUID-PHASE REACTION

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To my parents,
my husband
and my children.

ABSTRACT

An experimental and theoretical study has been carried out for the evaluation of concentration and temperature profiles for non-isothermal liquid-phase reactions taking place in a vertical tubular reactor. Theoretically homogeneous, irreversible first- and second-orders reactions were investigated. Three different flow models were assumed: (1) plug flow, (2) laminar flow and (3) laminar flow accompanied by radial diffusion. In addition, two modes of reactor operations were considered: adiabatic and constant-wall-temperature (CWT) reactors with the hydrolysis of acetic anhydride being chosen as the reference reaction. The effects of flow model, reaction kinetics, reaction conditions and reactant concentrations on conversion and temperature rises were then investigated.

Point concentration and temperature profiles were computed together with the corresponding flow average values. The results showed that under adiabatic reaction conditions, radial concentration and temperature profiles were greatly affected by both reaction conditions and flow model with the heat of reaction group, G_4, having the most significant effect. It was also observed that large radial diffusion effects could significantly influence overall conversions. In the CWT reactor, curves were found to show a characteristic maximum which were again highly dependent on G_4. It was found that in a CWT reactor, radial temperature variation could be expected even in plug flow and under laminar flow conditions, large G_4 values increased conversions over those calculated for plug flow conditions. Inlet concentration effects were noted for both the adiabatic and the CWT reactors with reaction kinetics significantly affecting reactor performance.

Experimental runs were carried out on a vertical reactor 250 cm. long and 1.865 cm. I.D. The inlet acetic anhydride concentration ranged from 0.291 to 1.470 mole/ℓ and the Reynolds number from 88 to 346. Temperatures varied from 25.57 to 38.91°C and the average velocity from 0.402 to 1.316 cm./sec. The reactor was operated under adiabatic and constant-wall-temperature conditions. Temperature rises were limited to 7°C in accordance with the assumptions formulated in theoretical models.

Experimental results indicated that radial temperature profiles tended to be flat but showed some difference between the wall temperature and the centreline temperature compared to the value predicted by the plug flow model. The laminar flow model gave the closest agreement with experimental results. Six causes are possible for the observed difference between experimental and predicted results. However, the presence of acetic acid is considered to be the most influential.

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NOMENCLATURE

a	dimensionless radial distance
A_o	frequency factor in equation (III-26), (sec^{-1})
A_I	frequency factor for a first-order reaction, equation (III-3), (sec^{-1})
A_{II}	frequency factor for a second-order reaction, equation (III-4), (cm^3/g.mole sec)
C_A	concentration of component A, (g.mole/10 ml.)
C_{A_o}	concentration of component A at the entrance of the mixing chamber, (g.mole/10 ml.)
C_P	specific heat, (cal./g.mole °K)
D_{AM}	effective diffusivity of A in reaction mixture, (cm^2/sec)
E	activation energy, (cal./g.mole)
G_1	Lewis Number as defined by equation (III-22)
G_2	activation energy group as defined by equation (III-23)
G_3	frequency factor group as defined by equation (III-24) or (III-25)
G_4	heat of reaction group as defined by equation (III-27) or (III-28)
Gr	Grashof number as defined in appendix 2
h	dimensionless radial increment
ΔH	heat of reaction per mole of reactant A, (cal./g.mole)
j_A	radial movement of material as defined in equation (III-8) or (III-9)
k	dimensionless axial increment
k_I	reaction rate constant for a first-order reaction, (sec^{-1})
k_{II}	reaction rate constant for a second-order reaction, (cm^3/g.mole sec)
k_c	thermal conductivity, (cal./sec.cm. °K)

NOMENCLATURE

(continued)

M_A	molecular weight of component A, (g./g.mole)
mf_A	mole fraction of component A
r	radial distance, (cm)
r_A	reaction rate for component A in equation (III-1), (g.mole/sec.cm^3)
r_o	inside tube radius, (cm)
R	gas constant, (cal./g.mole °K)
Re	Reynolds number, $= 2r_o \langle u \rangle \bar{\rho}/\mu$
S_c	rate of heat generation by chemical reaction, (cal./sec.cm^3)
t	time, (sec)
T	absolute temperature, (°K)
T_o	initial temperature, (°K)
u	axial velocity, (cm/sec)
$\langle u \rangle$	average velocity, (cm/sec)
V_A	molar volume at normal boiling point for component A, (cm^3/g.mole)
w	dimensionless axial distance as defined in equation (III-30)
x, y	dimensionless concentration as defined in equations (III-31) and (III-32)
x_o	inlet mole fraction of component A
$\langle x \rangle$	ratio of outlet to inlet concentration of component A
z	reactor length, (cm)

NOMENCLATURE

(continued)

Greek Letters

ρ	molal density of the solution, (g.mole/cm^3)
$\bar{\rho}$	density of the solution (g./cm^3)
ρ_A	concentration of component A, (g.mole/cm^3)
ρ_{Ao}	inlet concentration of component A, (g.mole/cm^3)
ρ_B	concentration of component B, (g.mole/cm^3)
ρ_{Bo}	inlet concentration of component B, (g.mole/cm^3)
Θ	dimensionless temperature defined by equation (III-34)
μ	viscosity of reacting mixture, (g./cm.sec)

Subscripts

A	component A
m	radial position
n	axial position
w	wall position

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I. INTRODUCTION

The problem of predicting conversions in tubular flow reactors and the effect of mixing and heat transfer has attracted considerable attention in the past(1-8). These studies have tended to simplify the mathematical analysis as far as possible and the investigations have shown that conversions were dependent not only on the residence time distribution but also on the temperature rises.

Cleland and Wilhelm(4) represented analytically a first-order reaction taking place in an isothermal laminar flow reactor. The equation was solved numerically assuming constant physical properties and fully developed flow. They showed the effect of diffusion on conversion and supported their theoretical solution with experimental data. A similar study was carried out by Vignes and Trambouze(5) who considered an isothermal second-order reaction system. The equation was solved analytically.

Rothenberg and Smith(6-7) investigated a first-order gas-phase reaction taking place under non-isothermal conditions. In particular the effect of heat transfer characteristics of the reactor was studied. Radial and axial profiles of concentration and temperature were predicted but no experimental data were presented.

Shinohara(8) carried out an experimental and theoretical study of a laminar flow constant-wall-temperature (CWT) reactor. The calculations included both first- and second-order reactions. Experimental data were obtained for the saponification of ethyl acetate.

The present study was undertaken to extend this previous work to non-isothermal liquid-phase reactions taking place in adiabatic and CWT reactors. Liquid-phase reactions were selected as they have an advantage over gas-phase reactions, i.e., reaction kinetics can be easily varied while experimentally, reactions can be carried out at low temperatures making measurement of temperatures and concentrations less complicated.

The reference reaction considered in this study was the hydration of acetic anhydride. The parameters used were evaluated for the system acetic anhydride-water-acetic acid and calculations were carried out for both first- and second-order reaction kinetics. Concentrated solutions were employed in order to investigate the effect of the heat of reaction.

Previous investigations(1-8) have shown that flow conditions influence conversions. Three flow models were therefore chosen for study: (i) plug flow, (ii) laminar flow, (iii) laminar flow accompanied by radial diffusion. Plug flow (case 1) can be expected to be present under turbulent conditions or in a packed reactor and is the simplest model available. At low flow rates, however, as were anticipated in the present study, the plug flow model does not take into account any variation of the axial velocity in the radial direction. This can be considered in two ways: parabolic velocity profile or laminar flow (case 2) and laminar flow accompanied by radial movement of material (case 3). The latter model can be considered to be the most realistic but mathematically is the most complicated.

This investigation was divided into three parts. First a theoretical study performed by computer and applicable to any homogeneous liquid-phase reaction was undertaken to investigate the influence of:

i) reaction conditions
ii) reaction kinetics
iii) flow conditions and
iv) reactant concentrations

on conversion and temperature rises. This theoretical study was then applied to the particular case of acetic anhydride hydrolysis by substituting kinetic data and heat of reaction values published by different authors (eqn. V-4). Predicted results were compared with experimentally obtained data.

II. LITERATURE SURVEY

Considerable attention has recently been paid to laminar flow tubular reactors(1-17). Studies were extended from isothermal to non-isothermal reactors assuming different flow models in order to predict overall conversions and temperature rises.

Bosworth(1) investigated the effect of radial diffusion in a tubular flow reactor and showed under what conditions radial diffusion can be neglected. He defined a dimensionless number DL/u_oR^2 and stated that when this number is less than 3.1×10^{-3} diffusion is negligible.

D : reactant diffusivity
L : reactor length
u_o: fluid velocity at centre of tube
R : tube radius

An alternate method of comparing laminar and plug flow reactors was given by Denbigh(2-3) for a second-order reaction in which diffusions of reactant and product were neglected. His method of solving the kinetics of homogeneous second-order reactions in tubular reactors rested upon a statistical distribution of residence times in the reactor from a knowledge of the parabolic laminar flow profile.

Cleland and Wilhelm(4) solved numerically the isothermal problem for a first-order reaction under laminar flow in a tubular reactor. They supported their theoretical model with experimental data. The reaction studied was the hydrolysis of acetic anhydride. They concluded in an alternate approach to Bosworth's that radial diffusion can be neglected when DL/u_oR^2 is smaller than 1.95×10^{-3}. They also found that predicted theoretical results were in good agreement with the experimental results obtained from the smaller reactor. Reactors studied were 1/4 - and 1/2 - in. - diameter horizontal reactors. Later, Lauwerier(9) solved the conservation equation for the reactant analytically in terms of an infinite series of eigenfunctions. However, application of his result is difficult.

Using the finite-difference method, Vignes and Trambouze(5) solved the equation of species continuity for a second-order homogeneous isothermal reaction for the special case of equimolar concentration of reactants. Experimental results obtained from the saponification of ethyl acetate were presented. They suggested a simple method of predicting conversion using the ideal plug-flow and laminar-flow models. Based on the works of Bosworth(1) and Cleland and Wilhelm(4), they concluded that in systems where radial diffusion cannot be neglected, their correlation agrees within an average of 1.1 percent deviation with the experimental results when the value of the effective diffusivity is taken as ten times the average of the molecular diffusivities of the reactants.

Sandru and Smith(10) have studied the photopolymerization of acrylamide in an annular flow reactor; temperature conditions were assumed to be isothermal. Rates of this polymerization reaction were measured quantitatively. It was shown that the rate data could be used to evaluate various models of polymerization kinetics. Shiraishi(11) examined experimentally the effect of free convection at low Reynolds numbers (Re = 3-38) in seven types of vertical and inclined tubular reactors. The reaction studied was the hydrolysis of acetic anhydride. It was found that free convection accompanied by the reaction occurred in the reactor and that by-pass, circular and eddy flows were present due to the increase of liquid density with the reaction. It was also shown that conversion was determined by the size and stability of the by-pass.

Non-isothermal systems were first studied by Chambré$^{(12)}$ who used a perturbation technique and obtained an approximated solution valid at very low Damkohler numbers $(k_{II}\ r_o^2\ \rho_{A_o}/D_{AM})$. The study was based on the assumption of fully developed velocity profiles and Lewis number $(\rho C_p\ D_{AM}/k_c)$ of unity. Trombetta and Happel$^{(13)}$ studied the analysis and design of gas flow reactors with applications to hydrocarbon pyrolysis. They presented their results as factors which can be used to correct calculations made with the plug flow assumption.

Rothenberg and Smith$^{(6,7)}$ studied a first-order homogeneous gas-phase reaction taking place in a laminar flow reactor. They solved the equations of change numerically using a finite-difference method to give radial profiles of concentration and temperature. Average "cup-mixing" concentrations and temperatures were also evaluated and the effect of system parameters investigated. The results showed that the temperature rise was extremely dependent on the heat of reaction parameter $-\Delta H.\ \rho_{A_o}/\ \rho C_p T_o$.

Andersen and Coull(14) compared the two different solutions of Trombetta and Happel(13) and Rothenberg and Smith(6,7) to the analysis of a tubular gas flow reactor. They showed that finite-difference solution for radial profiles is superior to the power-series approximation of radial temperature and composition profiles. They also concluded that the temperature dependency of diffusivity has a negligible effect on conversion.

Merrill and Hamrin(15) studied the industrially important demethylation of toluene to benzene. They presented their results in the form of concentration and temperature profiles in laminar and plug flow. They found for a specific set of isothermal operating conditions that a 12% loss in conversion is suffered in going from turbulent to laminar flow. Polymerization in a tubular reactor was studied by Lynn and Huff(16). They were concerned with the temperature dependency of the viscosity of the solution. These studies showed that appreciable temperature effects would be expected but no experimental data were presented.

Shinohara(8) carried out an experimental and theoretical study of a laminar flow reactor. In developing the theoretical model, the temperature dependency of the physical properties was taken into consideration in both the equation of motion and the equation of energy. In the experimental study, cup-mixed exit concentrations and temperatures were measured, but as dilute solutions were employed, the influence of the heat of reaction was negligible. He concluded that free convection in an upward-flow reactor increases conversion for heating systems and decreases that for cooling systems.

Santarelli and Foraboschi(17) examined the effects of natural convection on conversion in a homogeneous tubular reactor for a first-order irreversible reaction. Adiabatic conditions and laminar flow were assumed. Numerical results pointed out that for dilute solutions, natural convection can modify conversion in the same extent as parabolic velocity profile does.

III. THEORETICAL

III-A Development of Equations

The differential equations used for prediction of concentration and temperature profiles were developed from continuity and energy equations of Bird, Stewart and Lightfoot(18) namely:

$$\frac{D\rho_A}{Dt} = D_{AM} \nabla^2 \rho_A + r_A \qquad \text{(III-1)}$$

and

$$\rho \hat{c}_p \frac{DT}{Dt} = k_c \nabla^2 T + S_c \qquad \text{(III-2)}$$

In writing these equations, the following assumptions were made:

i) In the energy equation, it was assumed heating effects due to expansion, viscous dissipation, free convection and thermodynamic coupling effects were negligible.

ii) The physical properties of the system were constant, that is the effects of variation of density, specific heat, thermal conductivity and viscosity on concentration and temperature profiles were negligible compared to the effect of the chemical reaction.

iii) The variation of reaction rate constant with temperature could be described using the Arrhenius relationship, thus for a first-order reaction $A \rightarrow C$:

$$r_A = -k_I \rho_A = -A_I e^{-E/RT} \cdot \rho_A \qquad \text{(III-3)}$$

while for a second-order reaction, A + B → C:

$$r_A = -k_{II}\,\rho_A\,\rho_B = -A_{II}\,e^{-E/RT}\,\rho_A\,\rho_B \qquad \text{(III-4)}$$

iv) The heat of reaction was constant over the temperature rises encountered and for an exothermic reaction, the rate of evolution of heat due to chemical reaction for the first-order reaction would be:

$$S_c = \Delta H\,A_I\,e^{-E/RT}\,\rho_A \qquad \text{(III-5)}$$

and for the second-order reaction:

$$S_c = \Delta H\,A_{II}\,e^{-E/RT}\,\rho_A\,\rho_B \qquad \text{(III-6)}$$

v) The velocity profiles were constant and fully developed throughout the reactor. Then for plug flow, $u = \langle u \rangle$ and for laminar flow $u = 2\,\langle u \rangle\,[1 - (\frac{r}{r_o})^2]$ (III-7)

vi) Axial mass and energy transport due to diffusion and conduction were negligible when compared to convective transport.

vii) The effect of temperature rise on the diffusion coefficient was neglected. In addition, stoichiometric diffusion was assumed such that the radial velocity vector could be taken as zero. Then for the first-order reaction, the radial movement of material becomes by Ficks' law:

$$j_A = -D_{AC}\,\frac{\partial \rho_A}{\partial r} \qquad \text{(III-8)}$$

where D_{AC} is taken as constant, and for the second-order reaction:

$$j_A = -D_{AM} \frac{\partial \rho_A}{\partial r} \qquad \text{(III-9)}$$

where D_{AM} is the stoichiometric mean diffusion coefficient and was calculated from the Hayduk-Laudie correlation(19). D_{AM} would normally be expected to vary but the effect of this variation was assumed to be negligible.

The resulting steady-state continuity and energy equations for both first- and second-order reaction kinetics under the three different flow conditions are shown in Table III-1.

III-B-1 Numerical Solution

No readily integrable analytical solution could be obtained for the derived differential equations. Approximate solutions were obtained by numerical integration of corresponding difference equations. Before proceeding with the finite-difference method, the differential equations were first written in dimensionless form and the groups and variables selected were the same as those used by previous workers(6,7) so that results could be readily compared, namely:

$$\text{Lewis Number, } G_1 = \frac{\rho C_p D_{AM}}{k_c} \qquad \text{(III-22)}$$

$$\text{Activation Energy Group, } G_2 = E/RT_o \qquad \text{(III-23)}$$

$$\text{Frequency Factor Group, } G_3 = r_o^2 \rho C_p A_I/k_c \quad \text{1st-order reacti} \qquad \text{(III-24)}$$

TABLE III-1

PARTIAL CONSERVATION EQUATIONS FOR DIFFERENT FLOW MODELS

Flow Model	First-Order Reaction	Second-Order Reaction
Plug Flow	$<u> \frac{d\rho_A}{dz} + A_I \ \rho_A e^{-E/RT} = 0$ (III-10) $<u> \frac{\partial T}{\partial z} = \frac{k_c}{\rho C_p} \left(\frac{1}{r} \frac{\partial}{\partial r} \cdot \frac{r\partial T}{\partial r}\right) + \frac{\Delta H \rho_A A_1 e^{-E/RT}}{\rho C_p}$ (III-11)	$<u> \frac{d\rho_A}{dz} + A_{II} \ \rho_A \rho_B e^{-E/RT} = 0$ (III-16) $<u> \frac{\partial T}{\partial z} = \frac{k_c}{\rho C_p} \left(\frac{1\partial}{r\partial_r} \cdot \frac{r\partial T}{\partial r}\right) + \frac{\Delta H \rho_A \rho_B A_{II} e^{-E/RT}}{\rho C_p}$ (III-17)
Laminar Flow	$2<u> \ [1 - (r/r_o)^2] \frac{d\rho_A}{dz} + A_I \rho_A e^{-E/RT} = 0$ (III-12) $2<u> \ [1 - (r/r_o)^2] \frac{\partial T}{\partial z} = \frac{k_c}{\rho C_p}\left(\frac{1}{r} \frac{\partial}{\partial r} \cdot \frac{r\partial T}{\partial r}\right) + \frac{\Delta H \rho_A \ A_I e^{-E/RT}}{\rho C_p}$ (III-13)	$2<u>[1 - (r/r_o)^2]\frac{d\rho_A}{dz} + A_{II}\rho_A \cdot \rho_B e^{-E/RT} = 0$ (III-18) $2<u>[1 - (r/r_o)^2]\frac{\partial T}{\partial z} = \frac{k_c}{\rho C_p}\left(\frac{1}{r} \frac{\partial}{\partial r} \cdot \frac{r\partial T}{\partial r}\right) + \frac{\Delta H \rho_A \cdot \rho_B \ A_{II} e^{-E/RT}}{\rho C_p}$ (III-19)
Laminar Flow accompanied by radial diffusion	$2<u> \ [1 - r/r_o)^2] \ \frac{\partial \rho_A}{\partial z} = D_{AM}\left(\frac{1}{r} \frac{\partial}{\partial r} \cdot r\frac{\partial \rho_A}{\partial r}\right) - A_I \rho_A e^{-E/RT}$ (III-14) $2<u> \ [1 - (r/r_o)^2] \ \frac{\partial T}{\partial z} = \frac{k_c}{\rho C_p}\left(\frac{1}{r} \frac{\partial}{\partial r} \cdot \frac{r\partial T}{\partial r}\right) + \frac{\Delta H \rho_A \ A_I e^{-E/RT}}{\rho C_p}$ (III-15)	$2<u>[1 - (r/r_o)^2]\frac{\partial \rho_A}{\partial z} = D_{AM}\left(\frac{1}{r} \frac{\partial}{\partial r} \cdot r\frac{\partial \rho_A}{\partial r} \right) - A_{II}\rho_A \cdot \rho_B e^{-E/RT}$ (III-20) $2<u>[1 - (r/r_o)^2]\frac{\partial T}{\partial z} = \frac{k_c}{\rho C_p}\left(\frac{1}{r} \frac{\partial}{\partial r} \cdot \frac{r\partial T}{\partial r}\right) + \frac{\Delta H \rho_A \cdot \rho_B \ A_{II} e^{-E/RT}}{\rho C_p}$ (III-21)

Frequency Factor Group, $G_3 = r_o^2 \rho C_p A_o/k_c$ 2nd-order reaction (III-25)

where $A_o = A_{II}(\rho_{Ao} + \rho_{Bo})$ (III-26)

Heat of Reaction Group, $G_4 = -\Delta H \rho_{Ao}/\rho C_p T_o$ 1st-order reaction (III-27)

$= -\Delta H(\rho_{Ao} + \rho_{Bo})/\rho C_p T_o$ 2nd-order reaction (III-28)

T_o = initial or entrance temperature

Radial Position, $a = r/r_o$ (III-29)

Axial Position, $w = k_c z/2 r_o^2 \langle u \rangle C_p \cdot \rho$ (III-30)

Dimensionless Concentration, $x = \dfrac{\rho_A}{\rho_{Ao}}$ 1st-order reaction (III-31)

$y = \dfrac{\rho_A}{\rho_{Ao} + \rho_{Bo}}$ 2nd-order reaction (III-32)

$\Delta y = (\rho_{Bo} - \rho_{Ao}) / (\rho_{Ao} + \rho_{Bo})$ (III-33)

Dimensionless Temperature, $\theta = (T - T_o)/T_o$ (III-34)

These values were used to develop the required dimensionless continuity and energy equations shown in Table III-2.

TABLE III-2

DIMENSIONLESS CONTINUITY AND ENERGY EQUATIONS

Flow Model	First-Order Reaction	Second-Order Reaction
Plug Flow	$\frac{dx}{dw} + 2\ x\ G_3 e^{-G_2/(\theta+1)} = 0$ (III-35) $\frac{\partial\theta}{\partial w} = 2(\frac{1}{a}\frac{\partial}{\partial a} \cdot \frac{a\partial\theta}{\partial a}) + 2\ x\ G_3.G_4 e^{-G_2/(\theta+1)}$ (III-36)	$\frac{dy}{dw} + 2y(y + \Delta y)G_3.e^{-G_2/(\theta+1)} = 0$ (III-41) $\frac{\partial\theta}{\partial w} = 2(\frac{1}{a}\frac{\partial}{\partial a} \cdot \frac{a\partial\theta}{\partial a}) + 2y(y + \Delta y)G_3.G_4 e^{-G_2/(\theta+1)}$ (III-42)
Laminar Flow	$\frac{dx}{dw} + \frac{xG_3 e^{-G_2/(\theta+1)}}{(1 - a^2)} = 0$ (III-37) $\frac{\partial\theta}{\partial w} = \frac{1}{(1 - a^2)}(\frac{1}{a}\frac{\partial}{\partial a} \cdot \frac{a\partial\theta}{\partial a}) + \frac{xG_3.G_4 e^{-G_2/(\theta+1)}}{(1 - a^2)}$ (III-38)	$\frac{dy}{dw} + \frac{y(y + \Delta y)G_3.e^{-G_2/(\theta+1)}}{(1 - a^2)} = 0$ (III-43) $\frac{\partial\theta}{\partial w} = \frac{1}{(1 - a^2)}(\frac{1}{a}\frac{\partial}{\partial a} \cdot \frac{a\partial\theta}{\partial a}) + \frac{y(y + \Delta y)G_3.G_4 e^{-G_2/(\theta+1)}}{(1 - a^2)}$ (III-44)
Laminar flow accompanied by radial diffusion	$\frac{\partial x}{\partial w} = \frac{G_1}{(1 - a^2)}(\frac{1}{a}\frac{\partial}{\partial a} \cdot \frac{a\partial x}{\partial a}) - \frac{xG_3 e^{-G_2/(\theta+1)}}{(1 - a^2)}$ (III-39) $\frac{\partial\theta}{\partial w} = \frac{1}{(1 - a^2)}(\frac{1}{a}\frac{\partial}{\partial a} \cdot \frac{a\partial\theta}{\partial a}) + \frac{xG_3.G_4 e^{-G_2/(\theta+1)}}{(1 - a^2)}$ (III-40)	$\frac{\partial y}{\partial w} = \frac{G_1}{(1 - a^2)}(\frac{1}{a}\frac{\partial}{\partial a} \cdot \frac{a\partial y}{\partial a}) - \frac{y(y + \Delta y)G_3.e^{-G_2/(\theta+1)}}{(1 - a^2)}$ (III-45) $\frac{\partial\theta}{\partial w} = \frac{1}{(1 - a^2)}(\frac{1}{a}\frac{\partial}{\partial a} \cdot \frac{a\partial\theta}{\partial a}) + \frac{y(y + \Delta y)G_3.G_4.e^{-G_2/(\theta+1)}}{(1 - a^2)}$ (III-46)

III-B-2 Boundary Equations

In order to develop the algebraic equations to solve the differential equations given in Table III-2, it was necessary to modify the equations, (1) at the centreline of the reactor and (2) at the reactor wall, i.e., a = 0 and a = 1, respectively.

At the reactor centreline, the conditions imposed were:

$$\left(\frac{\partial x}{\partial a}\right)_{a=0} , \left(\frac{\partial y}{\partial a}\right)_{a=0} = 0 \qquad \text{(III-47)}$$

and

$$\left(\frac{\partial \theta}{\partial a}\right)_{a=0} = 0 \qquad \text{(III-48)}$$

An indeterminate form $\left(\frac{1}{a}\frac{\partial \theta}{\partial a}\right)_{a=0}$ was obtained and the problem was solved by applying L'Hôpital's rule.

$$\lim_{a \to 0} \frac{1}{a}\frac{\partial \theta}{\partial a} = \frac{\partial^2 \theta}{\partial a^2} \qquad \text{(III-49)}$$

These boundary conditions were then inserted in the equations of Table III-2.

III-B-2-1 Reactor Centreline: At the reactor centreline, the corresponding dimensionless equations were:

First-order Kinetics:

Case 1 $$\frac{\partial \theta}{\partial w} = 4\frac{\partial^2 \theta}{\partial a^2} + 2x\, G_3 G_4 e^{-G_2/(\theta+1)} \qquad \text{(III-50)}$$

Cases 2 & 3 $$\frac{\partial \theta}{\partial w} = 2\frac{\partial^2 \theta}{\partial a^2} + x\, G_3 G_4 e^{-G_2/(\theta+1)} \qquad \text{(III-51)}$$

Case 3 $$\frac{\partial x}{\partial w} = 2G_1 \frac{\partial^2 x}{\partial a^2} - G_3\, x\, e^{-G_2/(\theta+1)} \qquad \text{(III-52)}$$

Second-order Kinetics:

Case 1 $$\frac{\partial\theta}{\partial w} = 4\frac{\partial^2\theta}{\partial a^2} + 2\,G_3G_4\,y(y+\Delta y)e^{-G_2/(\theta+1)} \quad \text{(III-53)}$$

Cases 2 & 3 $$\frac{\partial\theta}{\partial w} = 2\frac{\partial^2\theta}{\partial a^2} + G_3G_4\,y(y+\Delta y)e^{-G_2/(\theta+1)} \quad \text{(III-54)}$$

Case 3 $$\frac{\partial y}{\partial w} = 2\,G_1\frac{\partial^2 y}{\partial a^2} - G_3\,y(y+\Delta y)e^{-G_2/(\theta+1)} \quad \text{(III-55)}$$

III-B-2-2 Reactor Wall: At the reactor wall, the boundary conditions depended on both the assumed flow model and the reaction conditions and are shown in Table III-3. The equations to be solved were parabolic(20) and are summarized as follows:

First-order Kinetics:

1. Adiabatic Reactor

Cases 2 & 3 $$\frac{\partial^2\theta}{\partial a^2} + G_3G_4\,x\,e^{-G_2/(\theta+1)} = 0 \quad \text{(III-56)}$$

Case 3 $$G_1\frac{\partial^2 x}{\partial a^2} - G_3\,x\,e^{-G_2/(\theta+1)} = 0 \quad \text{(III-57)}$$

2. CWT Reactor

Case 3 $$G_1\frac{\partial^2 x}{\partial a^2} - G_3\,x\,e^{-G_2} = 0 \quad \text{(III-58)}$$

Second-order Kinetics:

1. Adiabatic Reactor

Cases 2 & 3 $$\frac{\partial^2\theta}{\partial a^2} + G_3G_4\,y(y+\Delta y)e^{-G_2/(\theta+1)} = 0 \quad \text{(III-59)}$$

Case 3 $$G_1\frac{\partial^2 y}{\partial a^2} - G_3\,y(y+\Delta y)e^{-G_2/(\theta+1)} = 0 \quad \text{(III-60)}$$

2. CWT Reactor

Case 3 $$G_1\frac{\partial^2 y}{\partial a^2} - G_3\,y(y+\Delta y)e^{-G_2} = 0 \quad \text{(III-61)}$$

TABLE III-3

WALL BOUNDARY CONDITIONS

Flow Model	Adiabatic Reaction	Constant-wall-temperature Reactor
Plug Flow	$\frac{\partial\theta}{\partial a} = 0$ $a = 1$	$\theta = 0$ $a = 1$
Laminar Flow	$x = 0,\ y = 0,\ \frac{\partial\theta}{\partial a} = 0$ $a = 1$	$x = 0,\ y = 0$ $\theta = 0$ $a = 1$
Laminar Flow accompanied by radial diffusion	$\frac{\partial x}{\partial a},\ \frac{\partial y}{\partial a} = 0,\ \frac{\partial\theta}{\partial a} = 0$ $a = 1$	$\frac{\partial x}{\partial a},\ \frac{\partial y}{\partial a} = 0,\ \theta = 0$ $a = 1$

III-B-3 Finite-Difference Equations

An implicit method, the Crank-Nicholson method[20,21] was used to develop the required algebraic equations. Full details are given in Appendix 6. Considering a point $x_{m,n}$ in the reactor (see Figure III-1) the following numerical approximations were made:

$$x \simeq \frac{x_{m,n+1} + x_{m,n}}{2} \qquad \text{(III-62)}$$

$$\frac{\partial x}{\partial w} \simeq \frac{x_{m,n+1} - x_{m,n}}{k} \qquad \text{(III-63)}$$

$$\frac{\partial x}{\partial a} \simeq \frac{1}{4h}(x_{m+1,n+1} - x_{m-1,n+1} - x_{m-1,n} + x_{m+1,n}) \qquad \text{(III-64)}$$

$$\frac{\partial^2 x}{\partial a^2} \simeq \frac{1}{2h^2}(x_{m+1,n+1} - 2x_{m,n+1} + x_{m-1,n+1} + x_{m+1,n} - 2x_{m,n} + x_{m-1,n}) \qquad \text{(III-65)}$$

$e^{-G_2/(\theta_{m,n}+1)}$ was taken as constant over an axial increment k.

At the wall, explicit formulations were used in Cases 2 and 3.

$$\frac{\partial^2 x}{\partial a^2} \simeq \frac{-x_{m+2,n+1} + 16x_{m+1,n+1} - 30x_{m,n+1} + 16x_{m-1,n+1} - x_{m-2,n+1}}{12h^2} \qquad \text{(III-66)}$$

Similar equations were written for θ.

Typical algebraic equations are shown in Table III-4 for the plug flow reactor and are given in full in Appendix 6. The two sets of algebraic equations developed were solved alternately, the calculations being carried out on an IBM 360/65

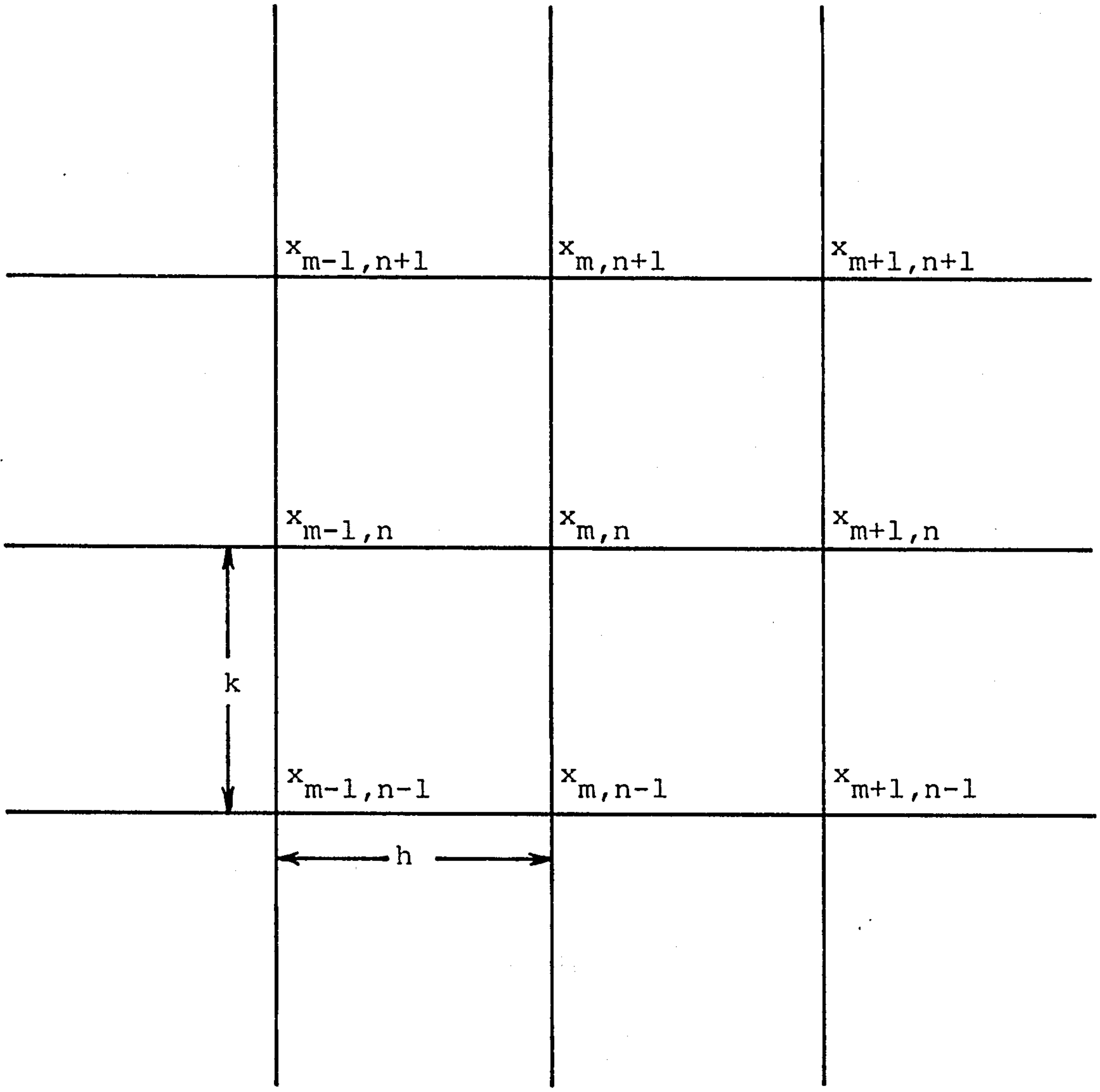

FIGURE III-1 FINITE-DIFFERENCE GRID

TABLE III-4

FINITE-DIFFERENCE EQUATIONS FOR THE PLUG FLOW REACTOR

1. First-Order Kinetics

1. CWT Reactor $0 \leq a \leq 1$ $$A_1 x_{m,n+1} = A_2 x_{m,n} \quad \text{(III-67)}$$

$0 < a < 1$ $$A_3\theta_{m+1,n+1} + A_4\theta_{m,n+1} + A_5\theta_{m-1,n+1} = A_6 \quad \text{(III-68)}$$

$a = 0$ $$A_7\theta_{2,n+1} + A_8\theta_{1,n+1} = A_9 \quad \text{(III-69)}$$

2. Adiabatic Reactor $$\theta_{n+1} = \theta_n + kG_3G_4(x_{n+1} + x_n)e^{-G_2/(\theta_n + 1)} \quad \text{(III-70)}$$

2. Second-Order Kinetics

1. CWT Reactor $0 \leq a \leq 1$ $$x_{m,n+1} = (-D_2 + \sqrt{D_2^2 - 4D_1D_3})/2D_1 \quad \text{(III-71)}$$

$0 < a < 1$ $$D_4\theta_{m+1,n+1} + D_5\theta_{m,n+1} + D_6\theta_{m-1,n+1} = D_7 \quad \text{(III-72)}$$

$a = 0$ $$D_8\theta_{2,n+1} + D_9\theta_{1,n+1} = D_{10} \quad \text{(III-73)}$$

2. Adiabatic Reactor $$\theta_{n+1} = \theta_n + \tfrac{1}{2}kG_3G_4(x_n + x_{n+1})(x_n + x_{n+1} + 2\Delta x)\, e^{-G_2/(\theta_n + 1)} \quad \text{(III-74)}$$

Note: Referring to equation (III-67)

$$A_1 = 1 + kG_3\, e^{-G_2/(\theta_{m,n} + 1)}$$

$$A_2 = 1 - kG_3\, e^{-G_2/(\theta_{m,n} + 1)}$$

The remaining parameters A_3 to A_9 and D_1 to D_{10} are as defined in Appendix 6.

computer. Firstly, the concentration change was calculated for an axial increment and the corresponding temperature rise evaluated. The temperature rise was required before the next concentration change could be calculated. This procedure was repeated along the length of the reactor. In determining the concentration profiles for the first-order reaction, computational procedures were straight-forward, a standard Gauss-Jordan elimination sub-routine being required for the third flow model. This sub-routine was also employed in determining temperature profiles. In the case of the second-order reaction, the numerical equations involved the square of the concentration. This problem was overcome for plug flow and laminar flow by only taking the positive root and putting y = 0 when both roots became negative. For the case of laminar flow accompanied by radial diffusion, the above technique could not be used and an iterative method had to be employed. Two to three iterations were required for each axial increment. Bulk or "cup-mixing" concentrations and temperatures were computed from the radial concentration and temperature profiles respectively using Simpson's rule to evaluate the integral, that is,

Plug flow:
$$\langle x \rangle = 2 \int_0^1 x\, a\, da \qquad \text{(III-75)}$$

$$\langle \theta \rangle = 2 \int_0^1 \theta\, a\, da \qquad \text{(III-76)}$$

Laminar flow:
$$\langle x \rangle = 4 \int_0^1 x(1-a^2) a\, da \qquad \text{(III-77)}$$

$$\langle \theta \rangle = 4 \int_0^1 \theta(1-a^2) a\, da \qquad \text{(III-78)}$$

Other numerical methods using Romberg's integration and the Gauss quadrature were investigated but showed only marginal improvement or were inferior to Simpson's rule(22). Numerical calculations were then carried out to determine the effects of varying parametric groups, reaction conditions, reaction kinetics, flow conditions and inlet reactant concentration on conversions and temperature rises along the reactor.

IV. THEORETICAL RESULTS AND DISCUSSION

IV-A INTRODUCTION

Before carrying out detailed numerical computations, comparisons were made with the work of previous investigators(4-8) (see Appendix 1). Figure IV-1 shows the results reported by Rothenberg(6,7) for a first-order reaction taking place in a constant-wall-temperature (CWT) reactor. Calculations predicting the variation of both cup-mixing temperatures, $<\theta>$ and cup-mixing concentrations, $<x>$ with the axial distance, w, were compared. The results are in good agreement and in addition, the instabilities reported by Rothenberg for G_4 values greater than 0.37 have been eliminated. The results were also compared with data reported by Cleland and Wilhelm(4) for the hydration of dilute solutions of acetic anhydride under isothermal conditions, the agreement was very good. The results obtained by Vignes and Trambouze(5) and Shinohara(8) for a second-order reaction, the saponification of ethyl acetate, were also found to be in good agreement with results computed from the equations developed in this investigation.

IV-A-1 Effect of Reaction Conditions

The behaviour of an adiabatic and a CWT reactors is shown in Figure IV-2. In the CWT reactor, the temperature profile exhibited a characteristic maximum whereas in the adiabatic reactor, the average temperature, $<\theta>$ is found to

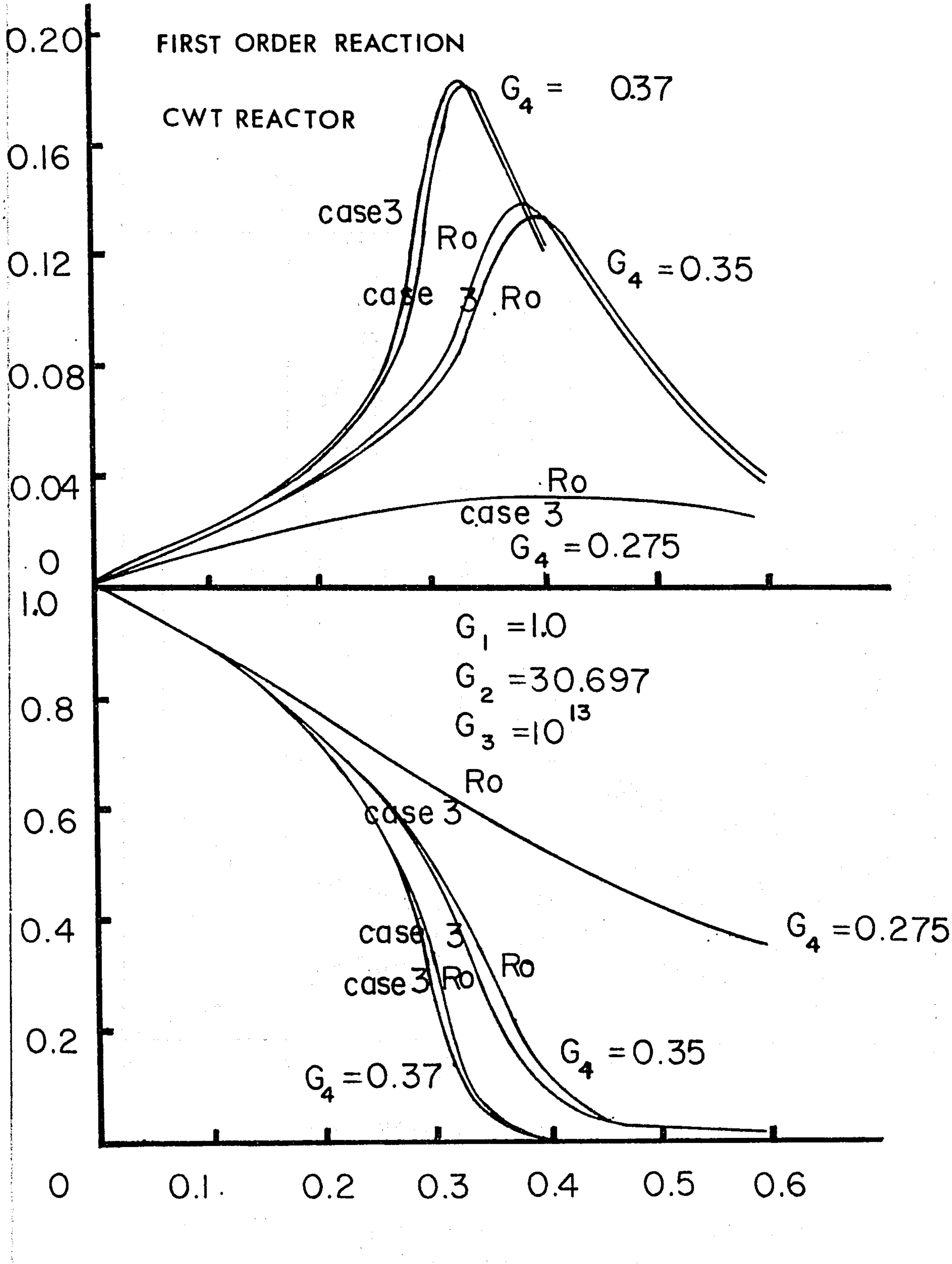

FIGURE IV-1 TEMPERATURE RISES AND CONVERSIONS. CWT REACTOR.

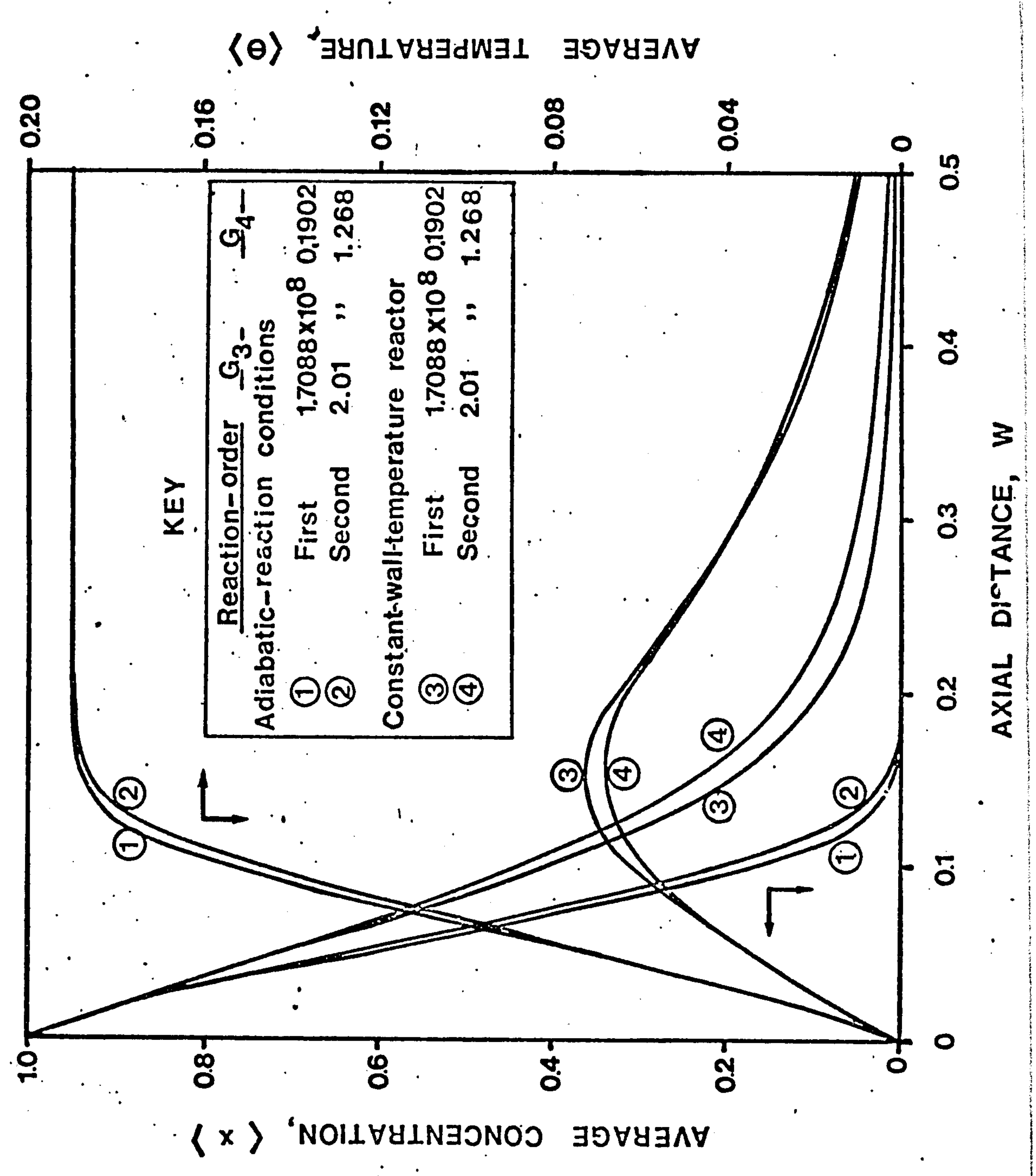

FIGURE IV-2 TEMPERATURE RISES AND CONVERSIONS. ADIABATIC AND CWT REACTORS.

increase with the axial distance and then flatten and remain constant. The calculations showed that under normal conditions, in order to achieve a given degree of conversion, higher residence time is required in a CWT reactor than if the reaction is carried out under adiabatic conditions. In comparing results, it was found to be more convenient in all cases to plot <x> values rather than the <y> values calculated for the second-order reaction.

IV-A-2 Effect of Reaction Kinetics

The effects on concentration and temperature profiles investigated in this study were generally of the same form for both first- and second-order reactions. However, in the adiabatic and CWT reactors for a given axial distance, w, first-order kinetics always gave higher conversions than second-order kinetics, (Figure IV-2). Also, for the adiabatic reactor, the corresponding temperatures were always greater for a first-order reaction than for a second-order reaction until they both converged to the maximum temperature attainable, (Figure IV-2) while for the CWT reactor, a first-order reaction was found to result in a higher maximum temperature (Figure IV-2).

IV-B Adiabatic Reactor

IV-B-1 Effect of Flow Model

As a general rule, the more uniform the velocity profile, the higher the conversion. This is shown in Figure IV-3 where at a given axial distance, w, the plug flow model gave a higher average temperature, $\langle\theta\rangle$ and a higher conversion than Case 3 and Case 2.

IV-B-2 Effect of Lewis Number, G_1

When radial movement of material took place, the velocity profile became more uniform and conversion increased as can be seen in Figure IV-4 where G_1 was varied from 0.00659 to 6.59. However, at very low values of G_1, increasing G_1 ten fold did not change the temperature and concentration profiles appreciably and it was only when G_1 values where increased by a factor of 100 that an effect of radial movement on conversion and temperature became significant. These results indicate that temperature effects on the diffusion coefficient can be ignored in liquid systems in developing the transport equations and confirm the results reported by Shinohara(8).

IV-B-3 Effect of Activation Energy Group, G_2 and Frequency Factor Group, G_3

When studying the effects of G_2 and G_3, the energy of activation group and the frequency factor group, respectively, the products $G_3e^{-G_2}$ were held constant at 3.316. The results were similar to those obtained with the CWT reactor and will be discussed in section IV-C-3. Tabulated results appear in Appendix 1.

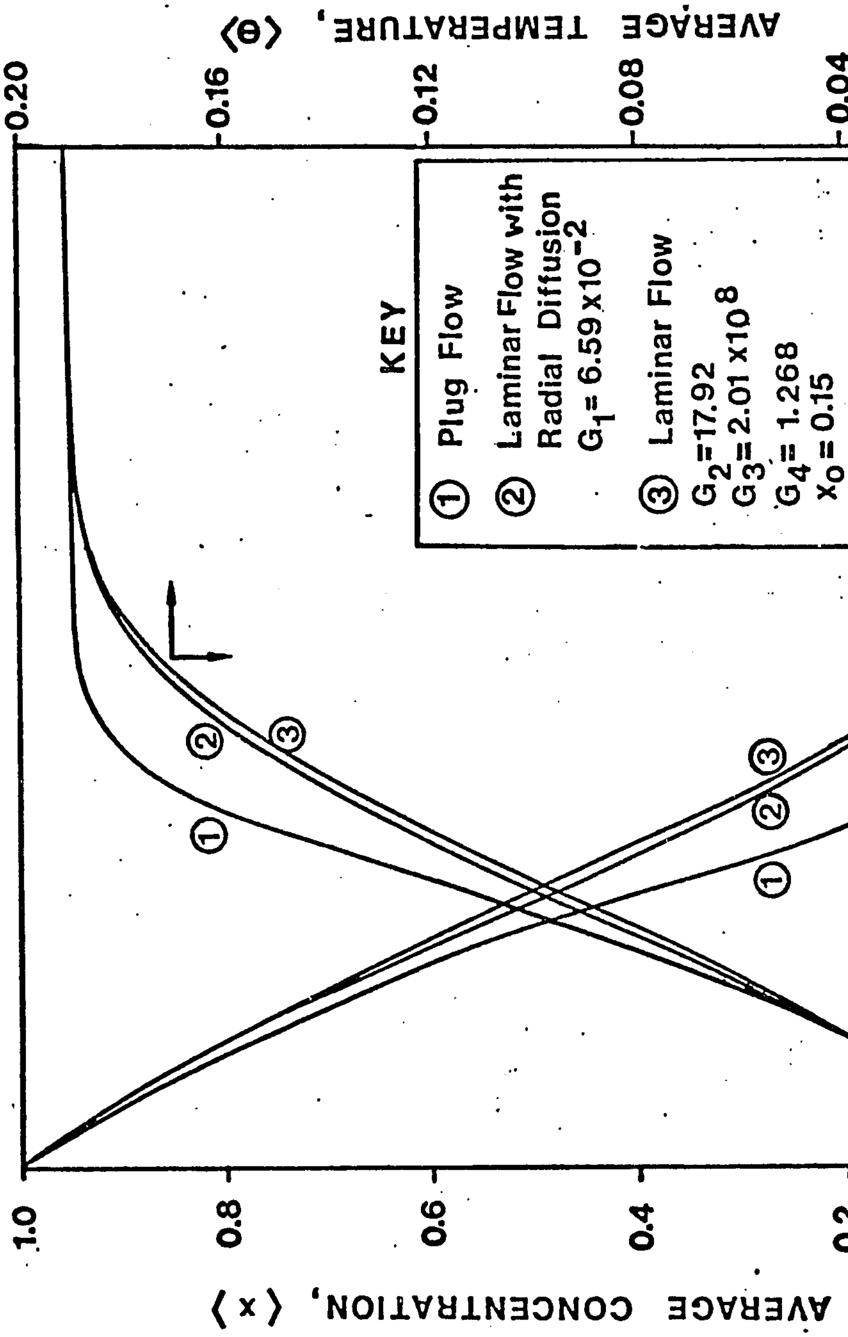

FIGURE IV-3 EFFECT OF FLOW MODEL. ADIABATIC REACTOR.

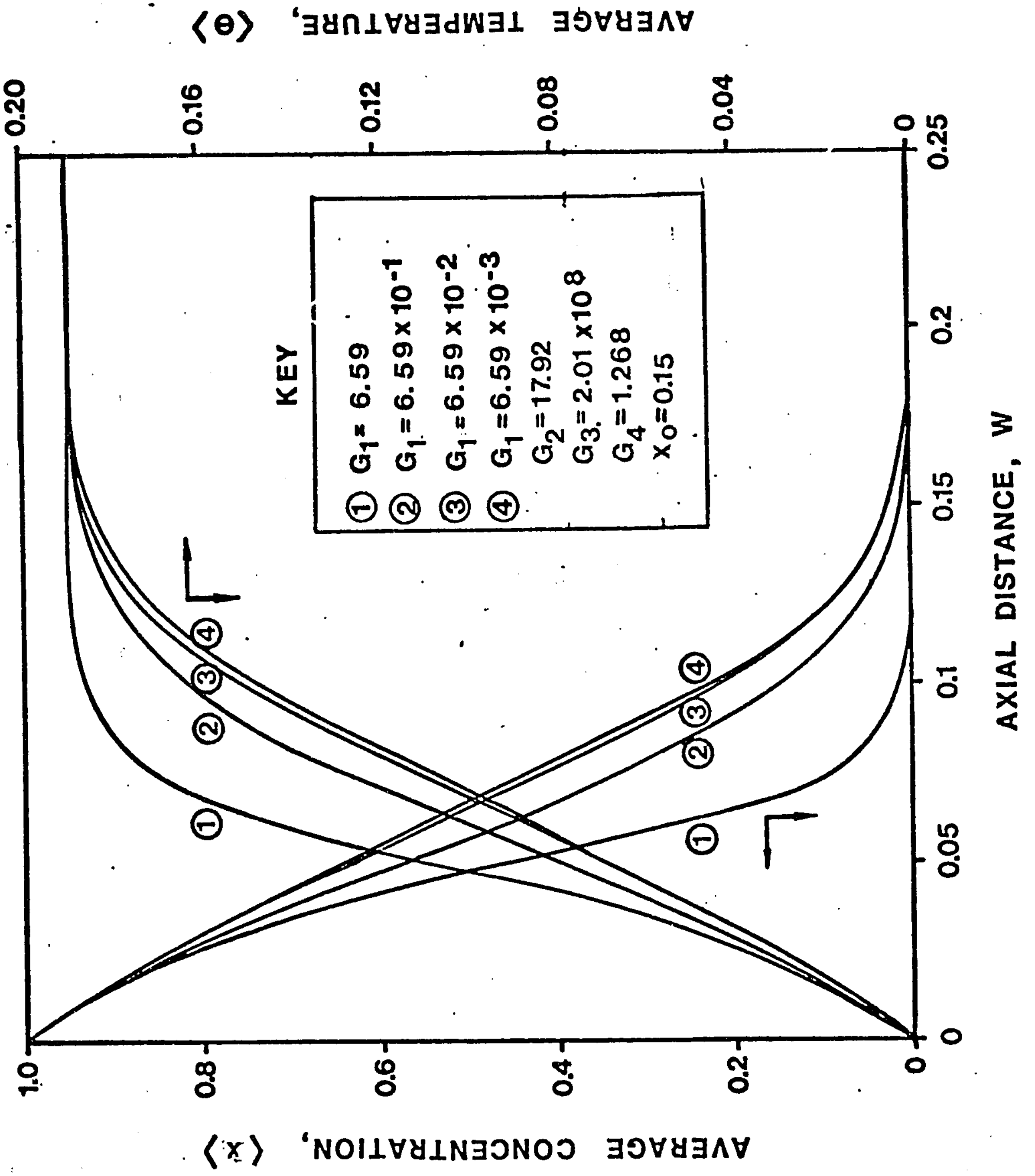

FIGURE IV-4 EFFECT OF LEWIS NUMBER, G_1.
ADIABATIC REACTOR.

IV-B-4 Effect of Heat of Reaction Group, G_4

In studying the effect of G_4 on the conversion and temperature profiles, a concentrated system was investigated so that the heat of reaction is of major importance in effect. G_4 was varied from 0.634 to 2.536. As can be seen from Figure IV-5, the maximum temperature attainable will be observed in a short reactor when G_4 values are high and a long reactor will be needed when a reaction exhibits low heat of reaction.

The temperature rises became steeper as G_4 was increased. When G_4 was doubled from 0.634 to 1.268, the maximum temperature changed from 0.093 to 0.190 and when doubled, from 1.268 to 2.536, $\langle\theta\rangle$ went from 0.190 to 0.380.

It was also possible to observe the effect of flow model as G_4 was varied. At a given value of G_4, the maximum temperature was reached sooner for the plug flow case than for the laminar flow models (Figure IV-5). It was also observed from Figure IV-5 that as G_4 was increased, conversions increased with the plug flow model predicting higher conversion than the laminar flow models.

IV-B-5 Effect of Concentration

Varying the inlet reactant concentration, ρ_{Ao}, affected the overall conversion and the final temperature. Conversions initially increased to a maximum and then decreased as ρ_{Ao}

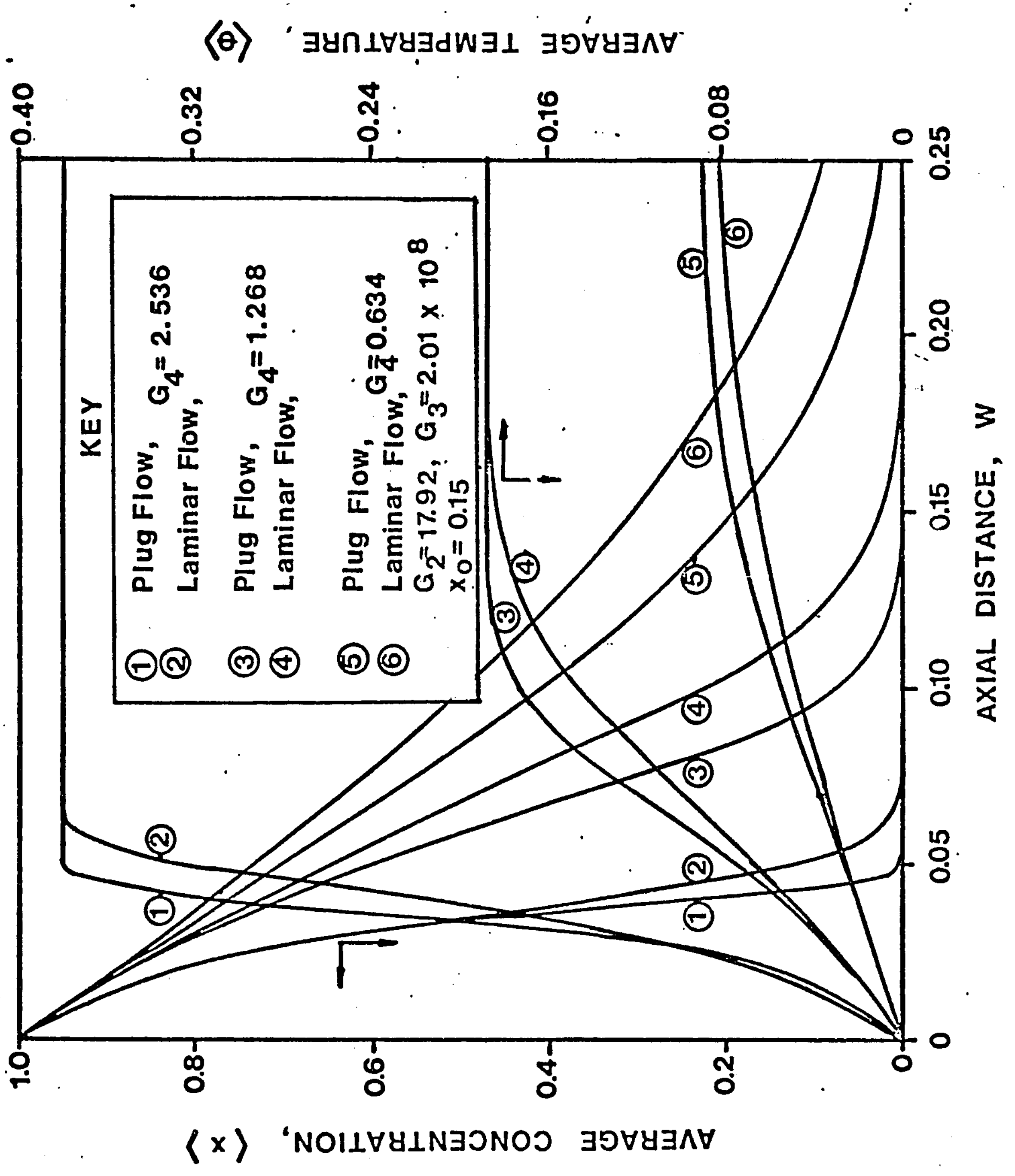

FIGURE IV-5 EFFECT OF HEAT OF REACTION GROUP, G_4.
ADIABATIC REACTOR.

was increased; this was the result of the accompanying decrease in ρ_{Bo}. As can be observed in Figure IV-6, this decrease in ρ_{Bo} was not always compensated for by the increase in reaction rate due to the temperature rise. Consequently, for a given length reactor, the percentage conversion could decrease as the concentration ρ_{Ao} was raised. This effect of concentration on percent conversion was also pronounced for a CWT reactor as discussed later in section IV-C-5.

IV-C CWT Reactor

In this section, a reactor with a wall temperature equal to the inlet temperature will be exclusively studied.

IV-C-1 Effect of Flow Model

In a CWT reactor, the cup-mixed temperatures were found to exhibit characteristic maxima as the reaction proceeded (Figure IV-7). In the same figure, the predicted maximum temperatures were observed to be appreciably smaller in plug flow than in laminar flow. It was also observed that due to the larger temperature rises taking place under laminar flow conditions, overall conversion rates were slightly higher in laminar flow than in plug flow.

IV-C-2 Effect of Lewis Number, G_1

When the effect of radial transport was studied by varying G_1, the maximum temperature decreased as G_1 increased

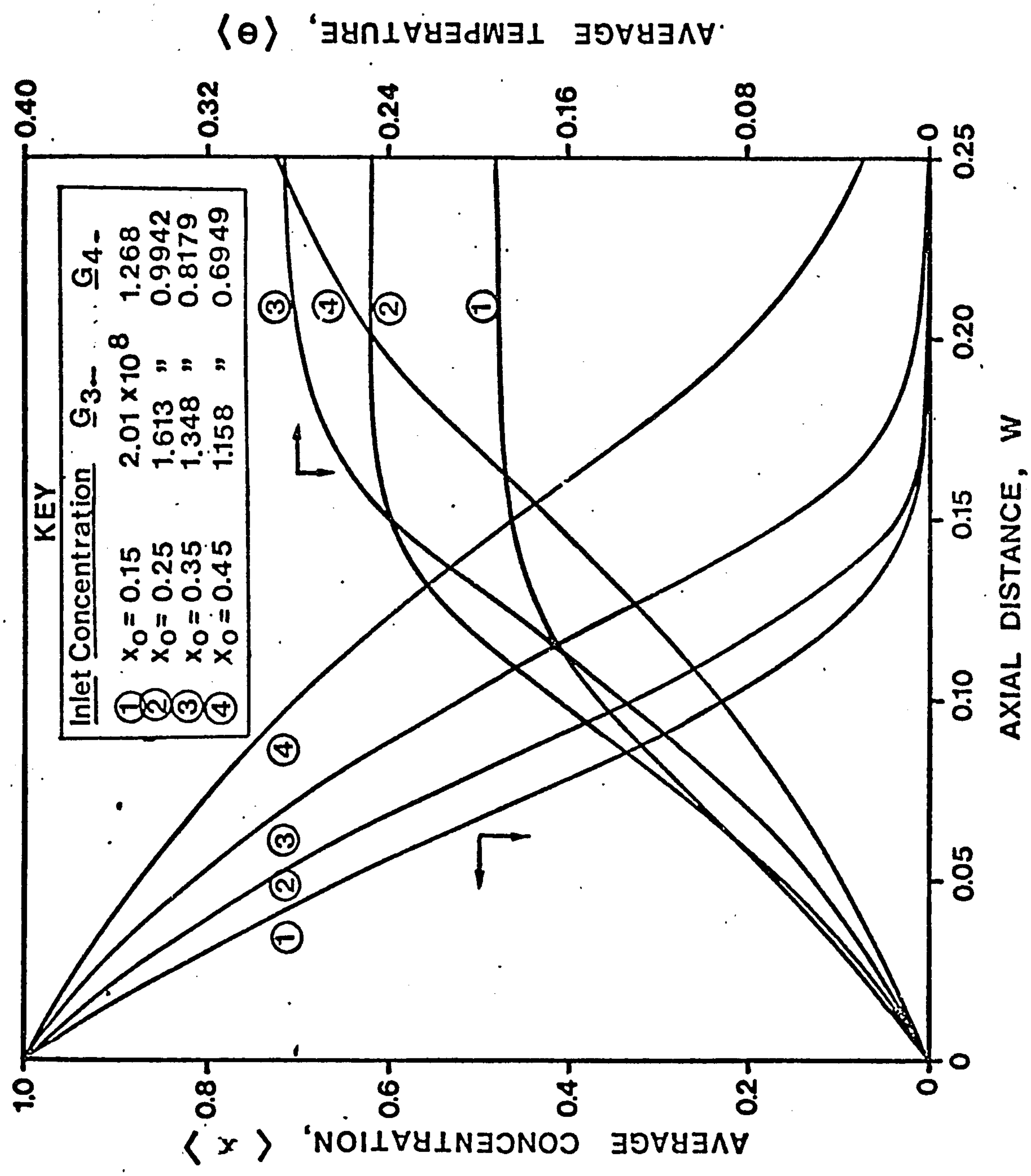

FIGURE IV-6 EFFECT OF REACTANT CONCENTRATION.
ADIABATIC REACTOR.

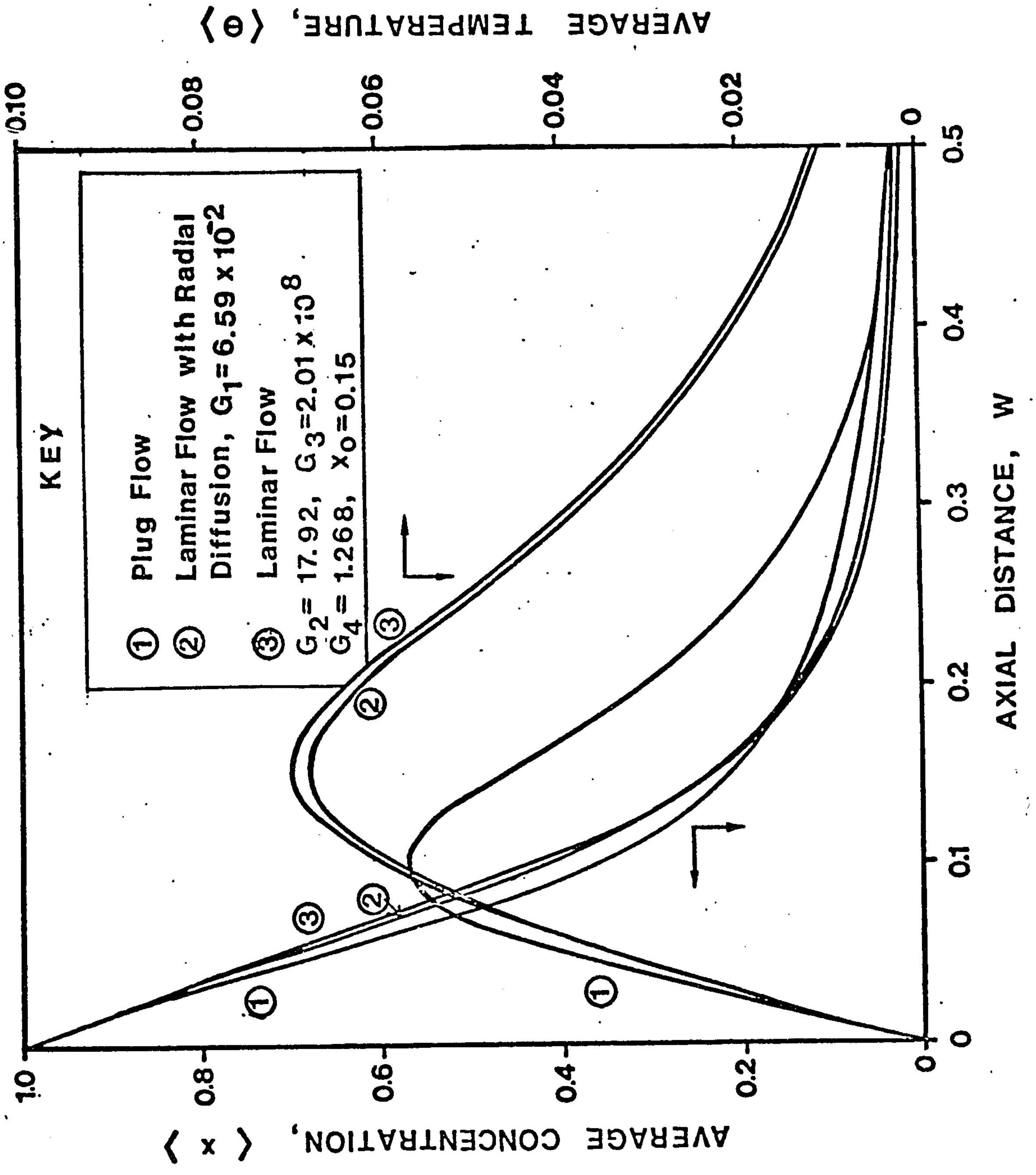

FIGURE IV-7 EFFECT OF FLOW MODEL. CWT REACTOR.

and the results tended towards those predicted for the plug flow reactor. Tabulated results appear in Appendix 1.

IV-C-3 Effect of Activation Energy Group, G_2 and Frequency Factor Group, G_3

Those results were similar to those calculated for the adiabatic reactor. The product $G_3e^{-G_2}$ was held constant at 3.316, and Figure IV-8 shows that the higher the frequency factor group, G_3, the higher the conversion.

IV-C-4 Effect of Heat of Reaction Group, G_4

When G_4 was varied, the calculations showed that as G_4 values were increased there was an accumulation of heat in the initial section of the reactor resulting in very high initial temperatures (Figure IV-9). These temperature rises resulted in acceleration of the reaction (Figure IV-10). This effect was the same for all flow models with the maximum temperature being reached faster in plug flow than in laminar flow.

The effect of G_4 on conversions is shown in Figure IV-10 where a varied effect of flow pattern on conversion was observed. Thus, for high values of G_4, overall conversion could be greater under laminar flow conditions than for plug flow conditions due to the large temperature rises. However, as heat effects became less important, the plug flow reactor

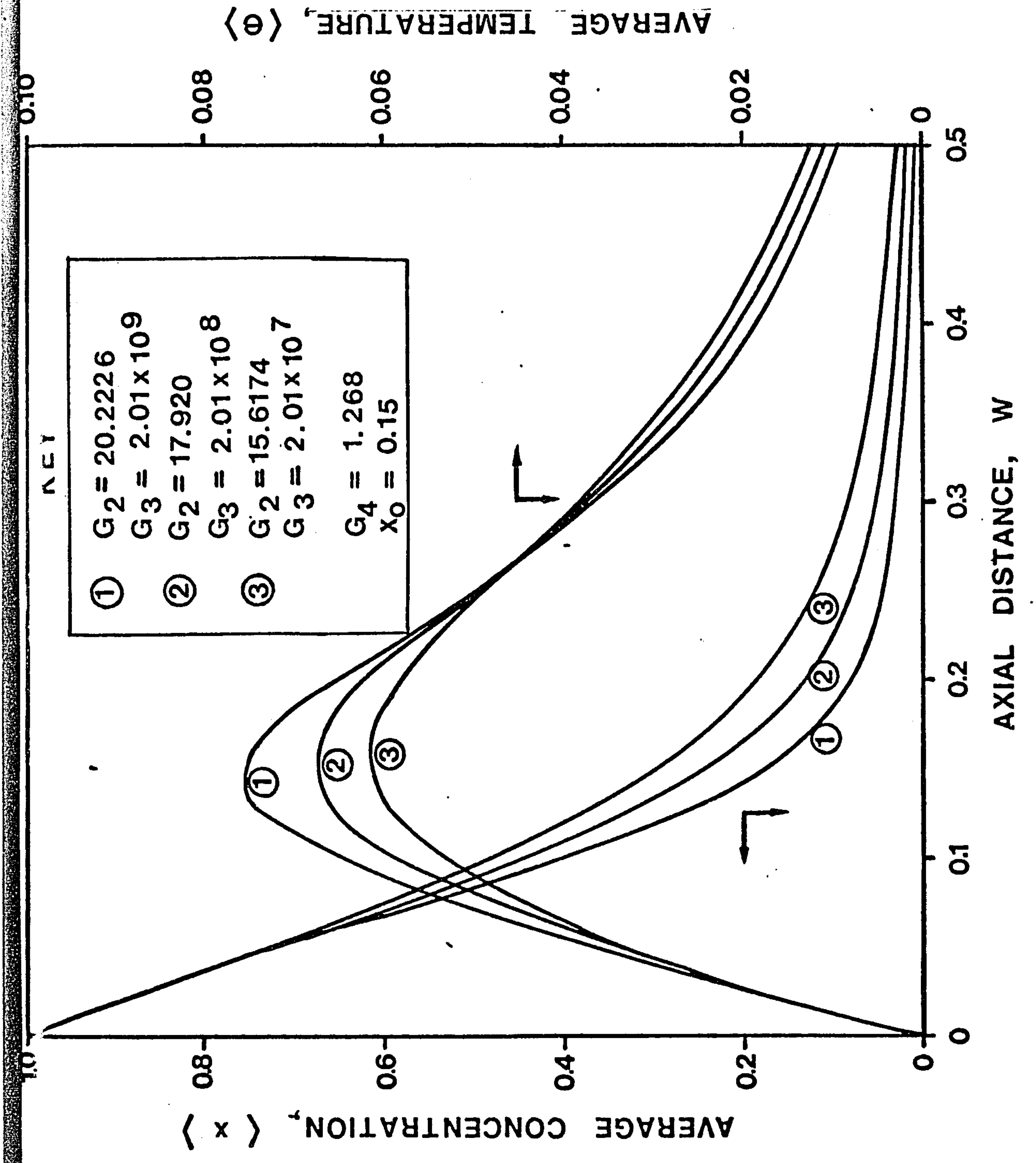

FIGURE IV-8 EFFECT OF ACTIVATION ENERGY GROUP, G_2, AND FREQUENCY FACTOR GROUP, G_3. CWT REACTOR.

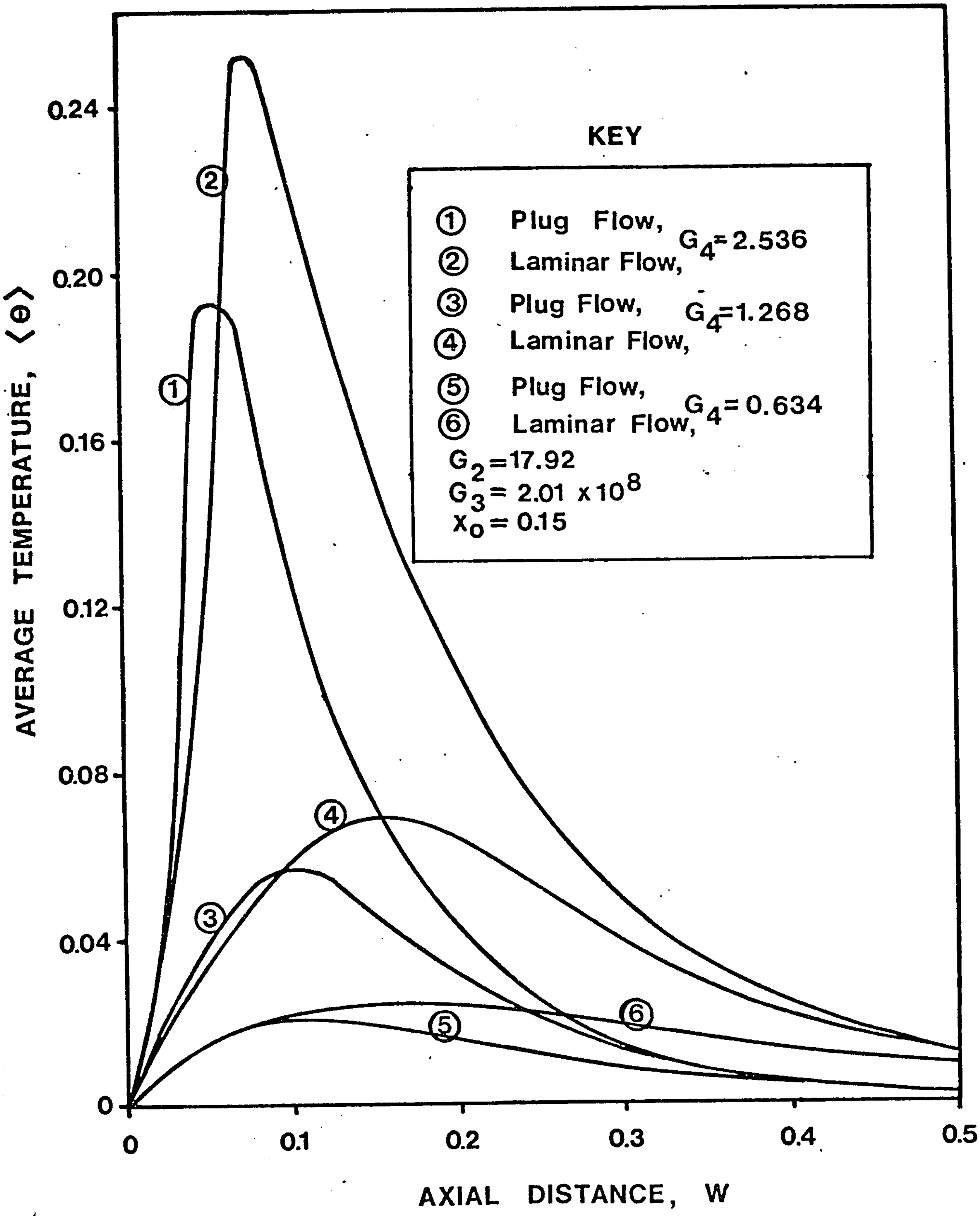

FIGURE IV-9 EFFECT OF HEAT OF REACTION GROUP, G_4.
CWT REACTOR.

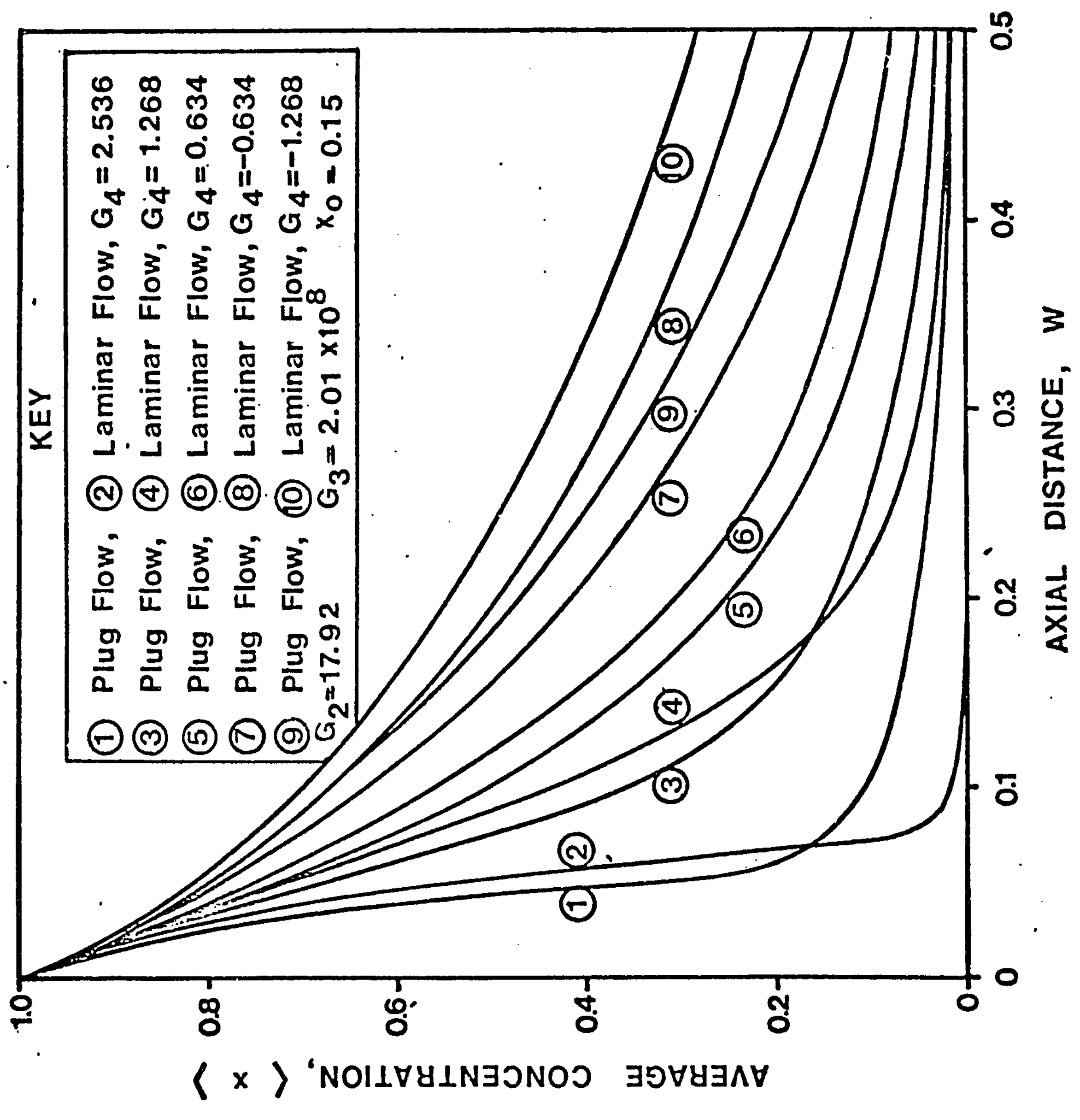

FIGURE IV-10 EFFECT OF HEAT OF REACTION GROUP, G_4. CWT REACTOR.

was observed to be more efficient. This latter effect has been predicted for an isothermal flow reactor(14) and was found in this study to be particularly pronounced for endothermic reactions (Figure IV-10). It should be noted that depending on the reaction, high temperature rises taking place in laminar flow could lead to undesirable product degradation rather than an increase in conversion.

IV-C-5 Effect of Concentration

The effect of inlet concentration was similar to the effects calculated for adiabatic reaction conditions. The maximum temperature initially rose as ρ_{Ao} was increased then decreased due to the decrease in ρ_{Bo} (Figure IV-11). This resulted in a decrease in the fractional conversion along the reactor as ρ_{Ao} was raised. Figure IV-11 shows the difference in conversion among various values of initial concentrations of reactants.

IV-D Radial Profiles

IV-D-1 Radial Profiles for Adiabatic Reactors

The radial profiles depended on both flow model and reaction conditions. Under plug flow conditions, concentration and temperature profiles were constant for an adiabatic reactor (Figures IV-12 and IV-13). Under laminar flow conditions, the profiles varied widely with the radial distance, a. The

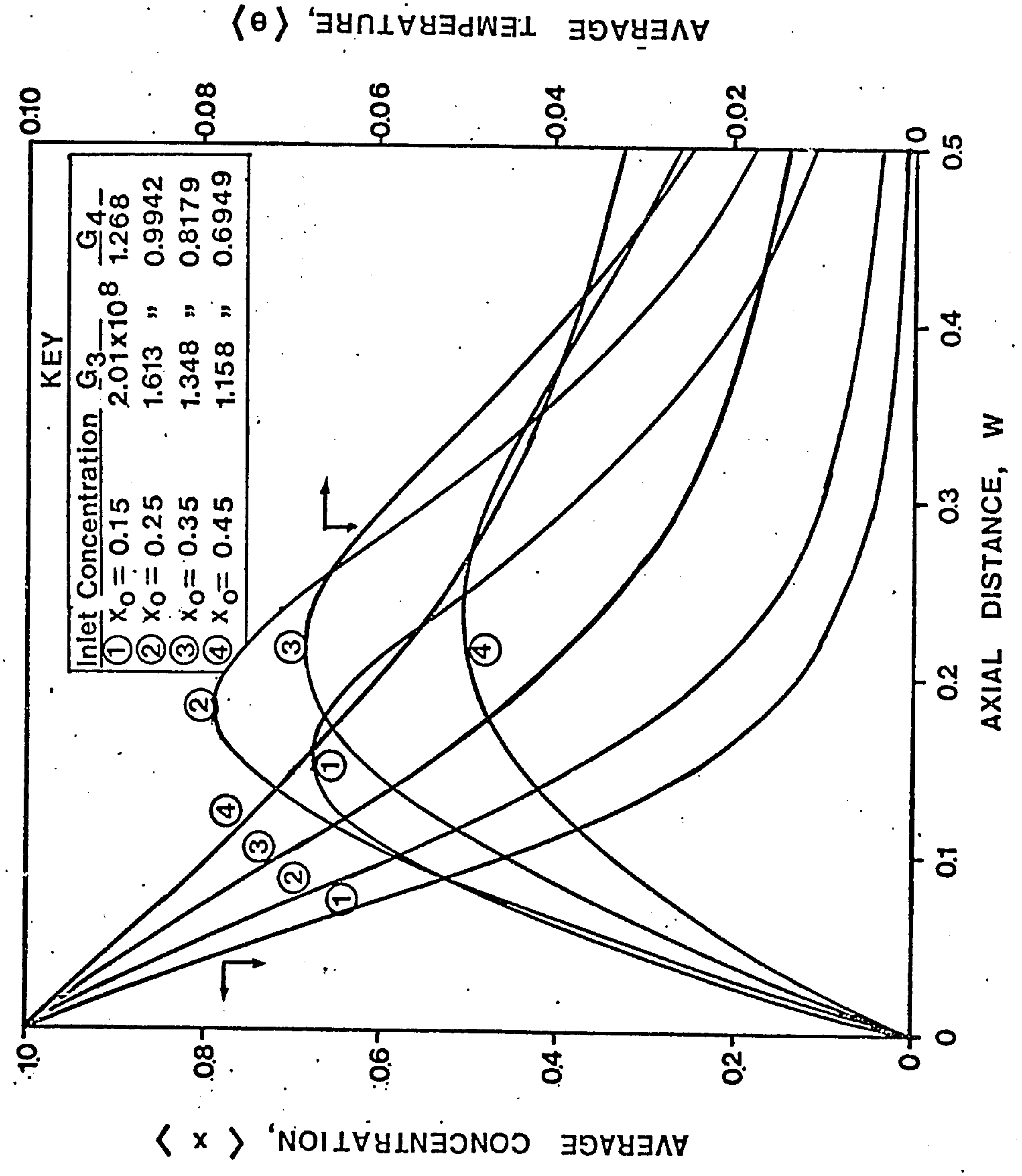

FIGURE IV-11 . EFFECT OF REACTANT CONCENTRATION.
CWT REACTOR.

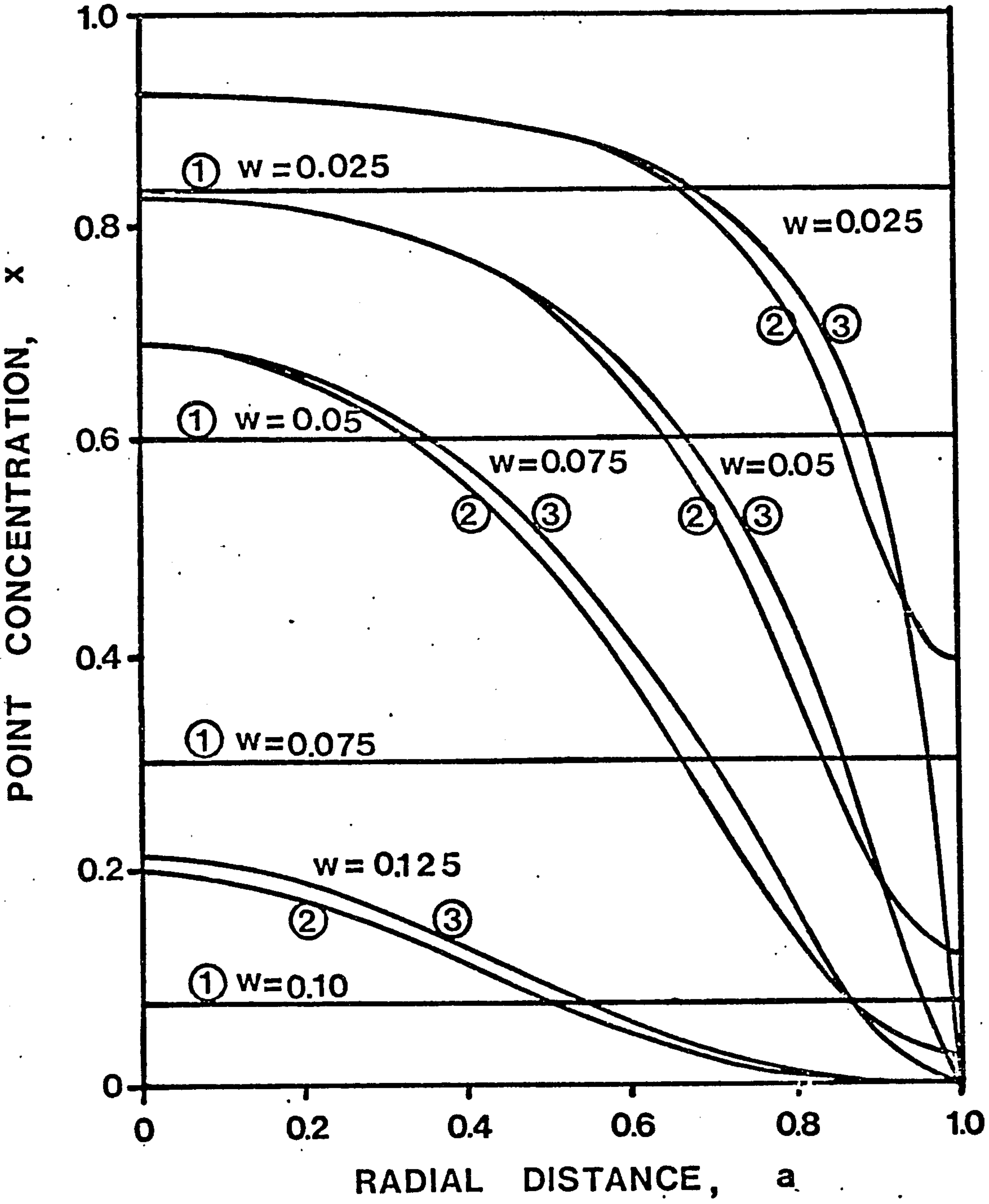

FIGURE IV-12 RADIAL CONCENTRATION PROFILES.
ADIABATIC REACTOR.

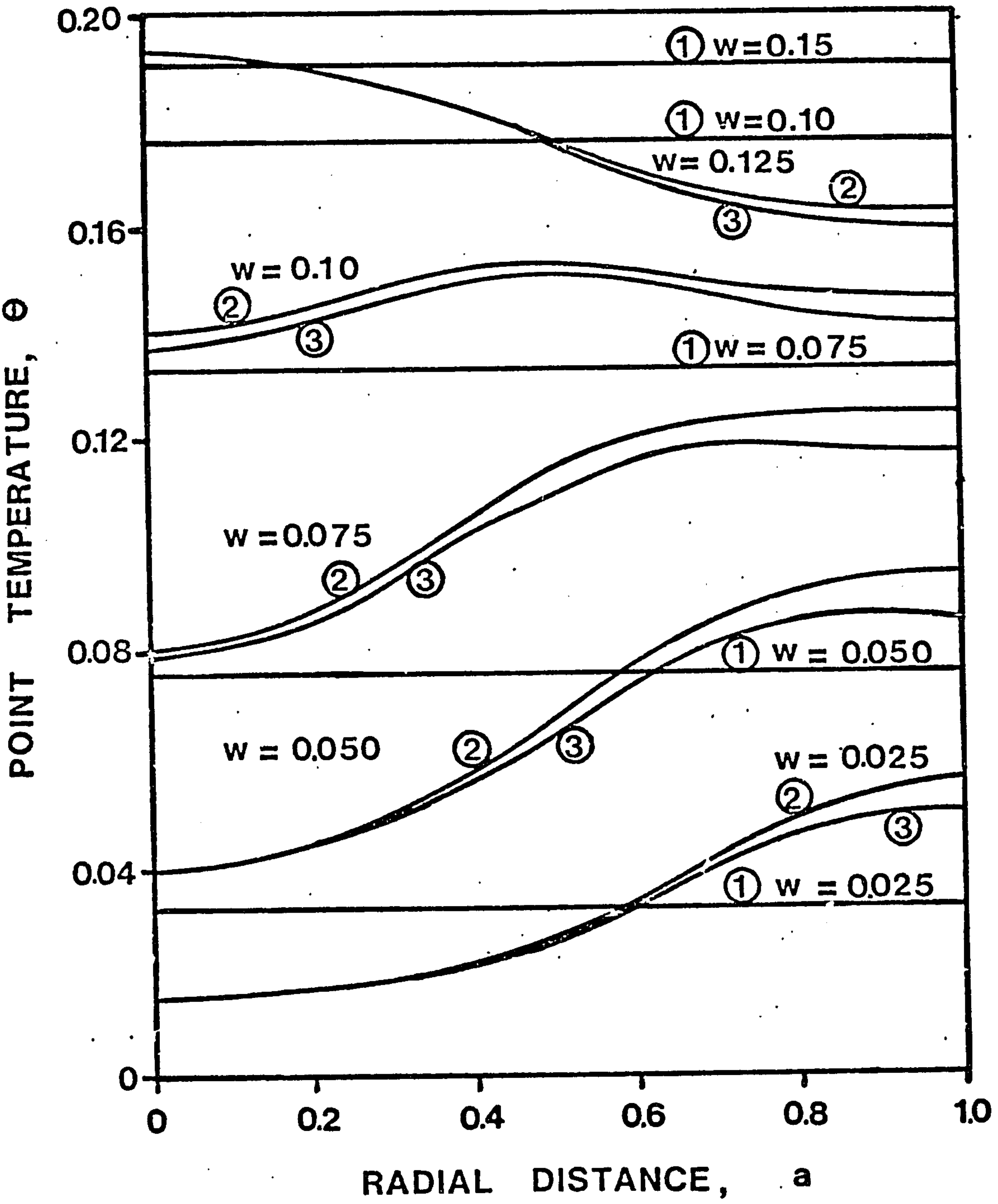

FIGURE IV-13 RADIAL TEMPERATURE PROFILES.
ADIABATIC REACTOR.

residence time of the material was higher at the wall and conversions were greater, resulting initially in a higher wall temperature (Figures IV-12 and IV-13). Figure IV-12 shows that the reactant concentration fell rapidly at the wall with a maximum reactant concentration being established at the centre of the reactor. Then, as the reaction proceeded and the reactant depleted, the profile gradually flattened.

The corresponding temperature profiles for the laminar flow reactor are shown in Figure IV-13. The maximum radial temperature occurred first near the reactor wall because of the small velocity there and then moved towards the centre of the reactor as the reaction proceeded. Point temperatures in excess of the theoretical adiabatic temperature were found due to radial transport of material. When the effect of G_1 was studied, radial transport of material tended to flatten the profiles.

IV-D-2 Radial Profiles for CWT Reactors

In contrast for the plug flow CWT reactor, the concentration profiles do not remain uniform as the reaction proceeds as observed in the adiabatic case (Figure IV-14). For the plug flow reactor, the model predicted a depletion of reactant concentration at the centre of the reactor opposite to that predicted for laminar flow. Heat was removed at the wall resulting in a decrease in reaction rates. Consequently, conversions were greater in the centre of the reactor than at the wall.

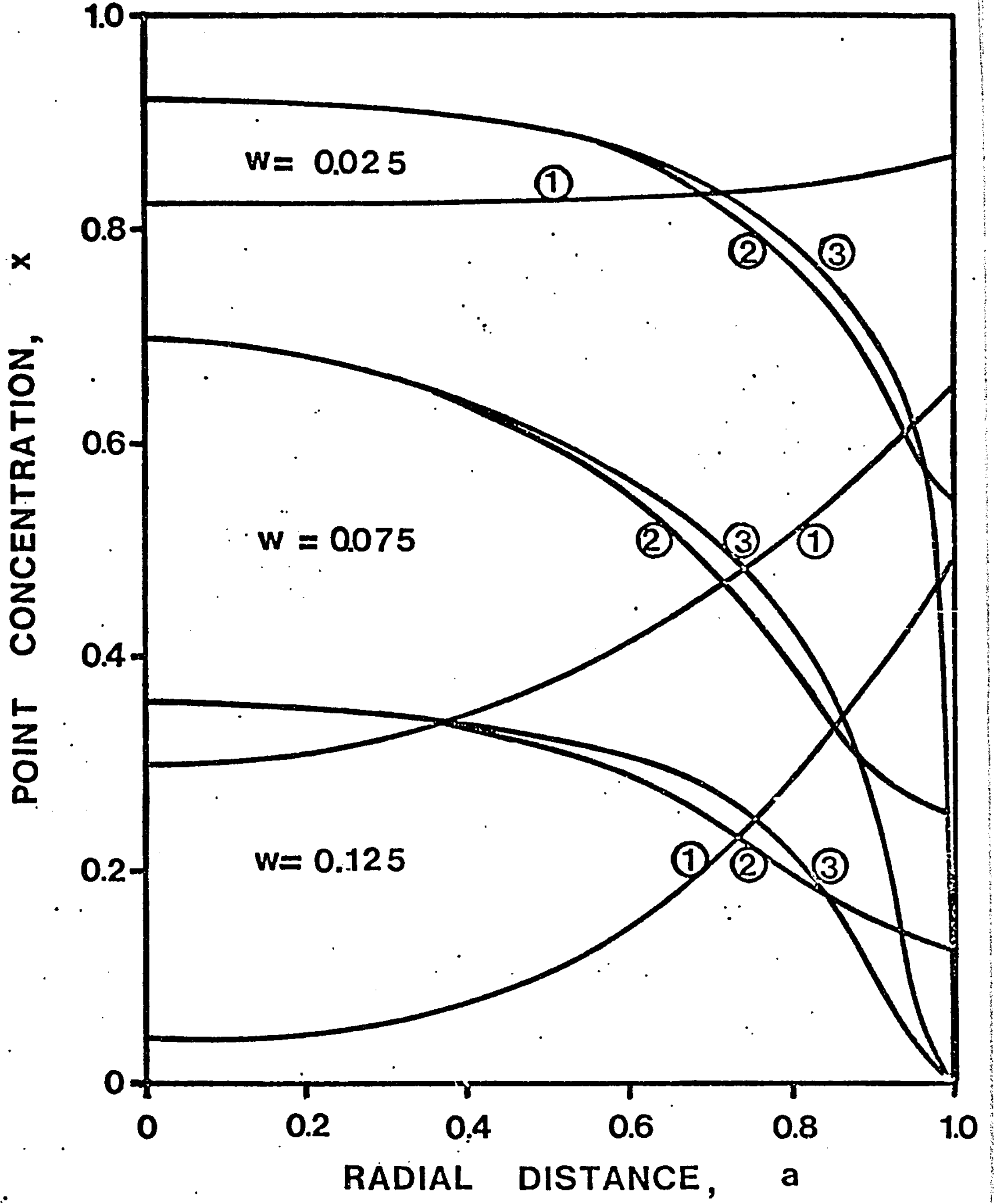

FIGURE IV-14 RADIAL CONCENTRATION PROFILES CWT REACTOR.

An opposite effect was observed for laminar flow. Due to the parabolic velocity profile, the residence time was larger at the wall and higher conversion took place, depleting the reactants (Figure IV-14). The concentration profiles were of approximately the same shape under laminar flow conditions as those found for the adiabatic reactor. As the reaction proceeded, the radial concentration profiles became more pronounced for plug flow but flattened for laminar flow.

In the case of the temperature profiles, the plug flow model always predicted a maximum at the centre of the reactor. Under laminar flow conditions, calculations showed that initially, the maximum temperature should appear at an intermediate radial position before being established at the centre of the reactor (Figure IV-15).

The calculations also showed that for all flow models, maximum point temperatures were much higher than the maximum cup-mixed temperatures. The calculations indicated, however, that there was very little effect of flow model on maximum point temperatures reached in a flow reactor even though maximum cup-mixed temperatures differed appreciably under laminar and plug flow conditions.

IV-E Comparisons between Adiabatic and CWT Reactors

Adiabatic reactors gave, as expected, greater conversions and temperature rises when compared to constant-wall-temperature reactors.

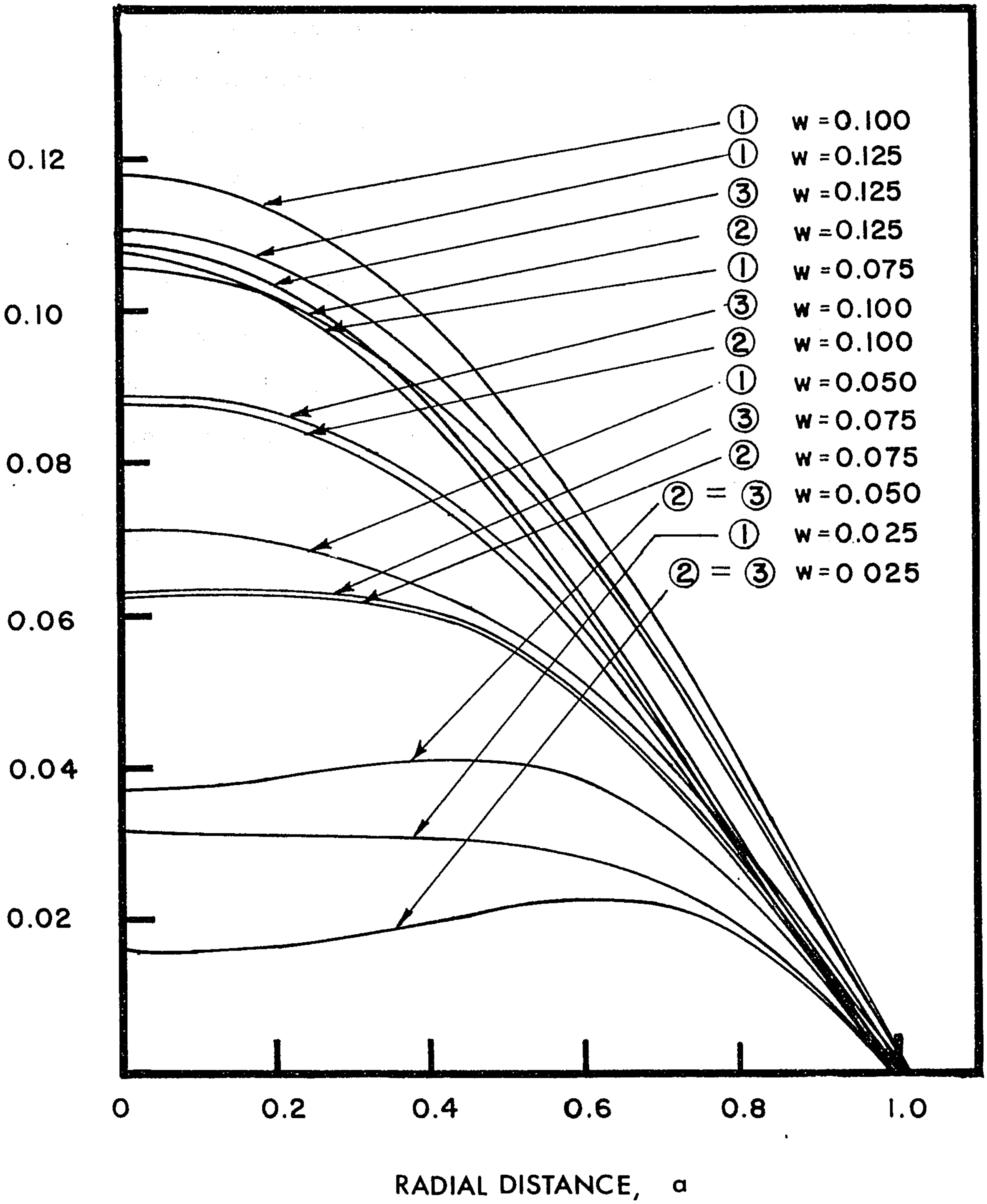

FIGURE IV-15 RADIAL TEMPERATURE PROFILES.
CWT REACTOR.

Although in the adiabatic reactor the plug flow model always gave higher conversions than the laminar flow assumption, in a CWT reactor and for highly exothermic reactions greater conversions can be obtained with the laminar flow conditions than with the plug flow assumption.

The radial concentration profiles for both the adiabatic and the CWT reactors predicted a maximum concentration at the centre of the reactor when laminar flow was assumed. However, with the plug flow assumption, the radial concentration profile for the adiabatic reactor was uniform and that for the CWT reactor was found to predict a minimum concentration at the centre of the reactor. The maximum radial point temperature reached the reactor centre at a shorter axial distance, w, in the CWT reactor than in the adiabatic reactor.

V. DETERMINATION OF REACTION RATE CONSTANT

Previous workers (4,23-26) concerned with the determination of the rate constant of the hydrolysis of acetic anhydride found that the pseudo-first-order rate constant is dependent on both the temperature and the initial acetic anhydride concentration.

Vles (26) published a summary of hydrolysis constants determined at temperatures between 0° and 25°C and a concentration range of 0.00324 to 1.1025 mole of acetic anhydride per liter of solution. The reaction rate constant, k, was found by Gold (27) to be a linear function of $(D - 1)/(2D + 1)$ where D is the dielectric constant. It was observed by Rivett and Sidgwick (23) and Vles (26) to decrease with increasing concentration of acetic anhydride. And finally it is reported by Orton and Jones (24) and Oshima (28) to be dependent on the presence of acetic acid. Koskikallio(29) observed that the activation energy, E, decreased as temperature increased. He also found that E was a function of the amount of acid present and concluded that the reaction was acid-catalyzed.

From data collected in the literature, it was found that the energy of activation was not a constant but depended strongly on the concentration of acetic anhydride. A wide range of activation energy values has been reported in the literature from 8.03 to 16.37 kcal/mole as concentration of acetic anhydride was varied from infinite dilution to equimolar concentration. For the concentration range (0.291 to 1.470 mole/ℓ) studied in this investigation no unique value of activation energy could be taken. Values of E at different temperatures and concentrations of acetic anhydride are summarized in Table V-1. The variation of E with concentration of acetic anhydride is shown in Figure V-1. In the same range of temperatures, the activation energy at a concentration of 10M was found to be twice that at infinite dilution. The activation energy was therefore assumed to be a function of concentration. The variation of E with acetic anhydride concentration, ρ_A, was approximated by

$$E = 5,270\ \rho_A^{.22} + 8,030 \text{ when } \rho_A < .2M \qquad \text{(V-1)}$$

$$\text{and} \quad E = 5,270\ \rho_A^{.24} + 8,030 \text{ when } \rho_A > .2M \qquad \text{(V-2)}$$

The effects of temperature and concentration on the frequency factor, A, were then investigated using previous workers' values of reaction rate constant, k (see Table V-2). Substituting E values from the above equations into the values of k reported in the literature, $\ell n\ A$ could be evaluated. These values were then plotted against ρ_A (Figure V-2). No significant effect of temperature on $\ell n\ A$ could be found but $\ell n\ A$ was shown to increase with increasing concentration. The following relationship was found.

$$\ell n\ A = 8.2689\ \rho_A^{.22} + 12.00 \qquad \text{(V-3)}$$

TABLE V-1

ACTIVATION ENERGY VALUES, E.

E (kcal/mole)	T (^oC)	ρ_A (gmole/ℓ.)	Authors
8.03	25	∞ dilution	Takashima (30)
10.61	15 to 35	0.02 to 0.06	Cleland & Wilhelm (4)
10.75	30 to 65	0.25	Glasser (31)
11.64	10 to 40	0.25	Takashima (32)
11.68	35 to 65	0.17	Dyne (33)
13.69	65 to 95	1.34	Marek (34)
13.75	25 to 50	1.24 to 2.59	Janssen (35)
16.0	20 to 60	9.7 to 10.5	Oshima (28)
16.37	-	8.85	Marmers (36)

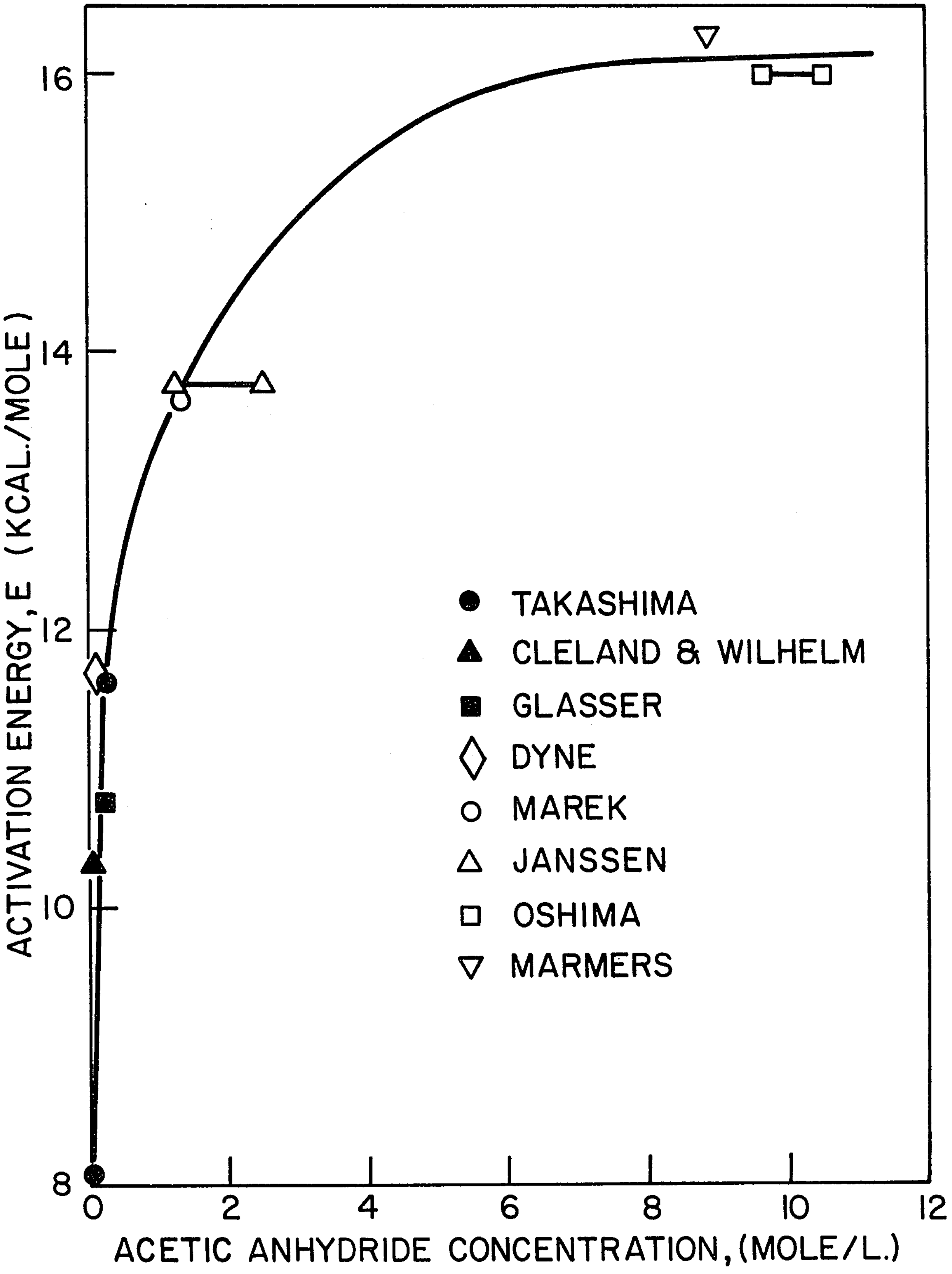

FIGURE V-1 VARIATION OF ACTIVATION ENERGY WITH ACETIC ANHYDRIDE CONCENTRATION.

TABLE V-2

VALUES OF REACTION RATE CONSTANT, k_I.

ρ_A (mole/)	Temperature (^oC)	E (Eqn. 3-1 or 3-2) (kcal /mole)	ℓnA (Eqn. 3-3)	k_I (Eqn. 3-4) (min^{-1})	k_I Literature (min^{-1})	Authors
0.02	25	10.26	15.50	.1621	.1620	Orton & Jones (24)
0.035	25	10.55	15.96	.1566	.1600	Vles (26)
0.075	15	11.01	16.68	.0778	.0817	Cleland & Wilhelm (4)
0.075	25	11.01	16.68	.1482	.1553	Cleland & Wilhelm (4)
0.075	25	11.01	16.68	.1482	.1596	Kusunoki (37)
0.075	35	11.01	16.68	.2710	.2733	Cleland & Wilhelm (4)
0.17	35	11.60	17.60	.2609	.2516	Dyne (33)
0.25	25	11.81	18.10	.1593	.12264	Glasser (31)
0.25	25	11.81	18.10	.1593	.1590	Takashima (32)
0.2650	25	11.86	18.17	.1575	.1485	Rivett & Sidgwick (23)
0.3389	18	12.09	18.52	.0917	.0916	Wilsdon & Sidgwick (25)
0.5353	25	12.57	19.21	.1347	.1328	Rivett & Sidgwick (23)
1.1	25	13.42	20.44	.1095	.1405	Kusunoki (37)
1.1025	18	13.42	20.45	.0635	.0634	Wilsdon & Sidgwick (25)

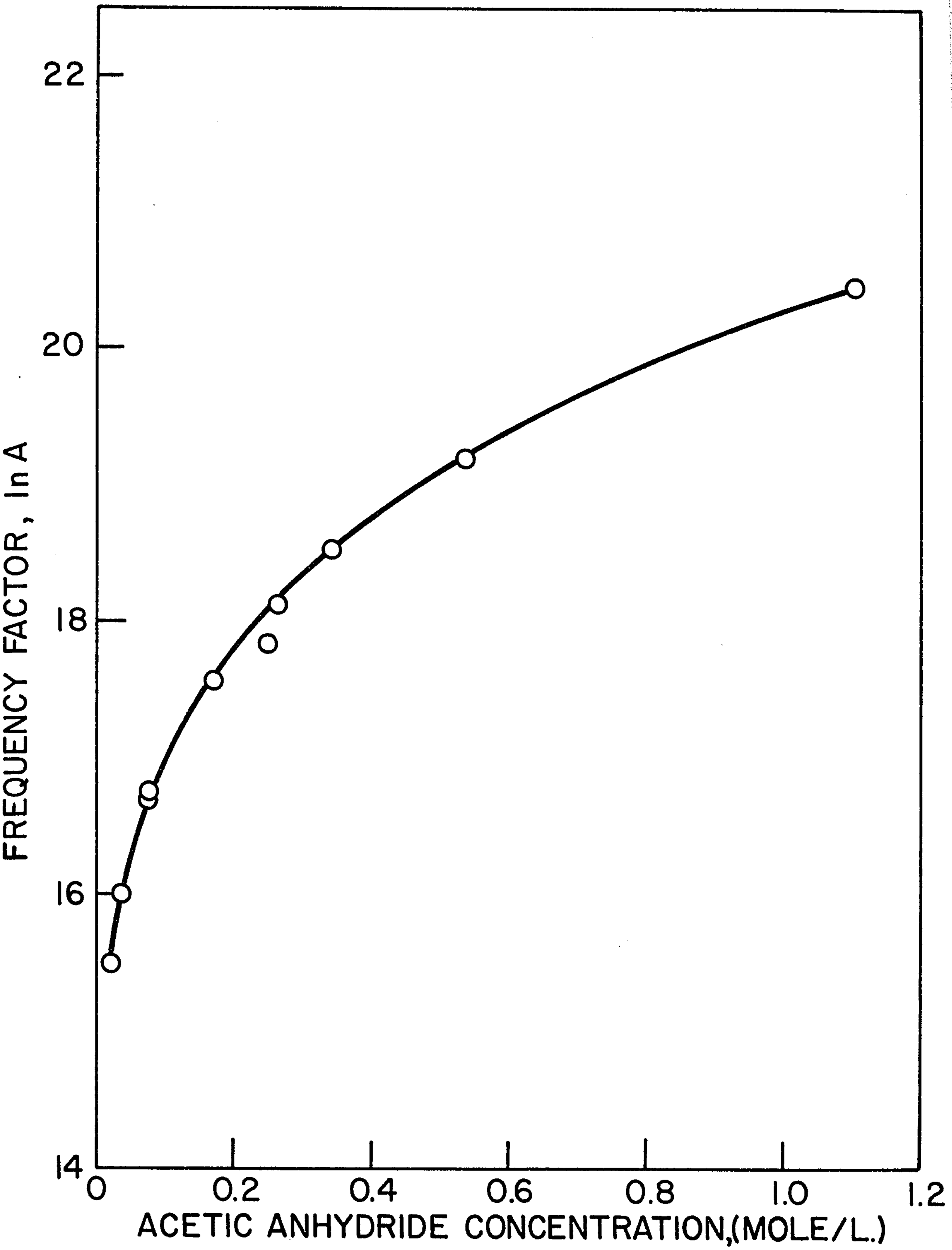

FIGURE V-2 VARIATION OF FREQUENCY FACTOR WITH ACETIC ANHYDRIDE CONCENTRATION.

The reaction rate constant was then evaluated at any value of temperature and concentration using the following derived relationship.

$$\ell n\ k = 8.2689\ \rho_A^{.22} + 12.00 - \frac{(5{,}270\rho_A^{.22\ \text{or}\ .24} + 8{,}030)}{RT} \qquad \text{(V-4)}$$

where k: min^{-1}

ρ_A: g mole/ℓ.solution

T: ^{o}K

Values of reaction rate constant calculated from equation (V-4) were found to be in good agreement with most literature values (Table V-2).

VI. EXPERIMENTAL - APPARATUS AND PROCEDURE

VI-A Apparatus

A schematic diagram of the apparatus is shown in Figure VI-1. Acetic anhydride and water were pumped by Milroyal duplex metering pump (B) to heating coils and to a mixing tank (D) where the two phases were mixed together. The coils and the mixing tank which also acted as a surge tank, were immersed in a water bath (C). The reactant mixture was then passed through the reactor (F) where acetic anhydride reacted with water to form acetic acid.

The reactor was made up of a stainless steel tube, I.D. = 1.87 cm. and overall length 250 cm. The inlet of the reactor comprised a conical section 4.25 in. long to minimize flow fluctuations as reactants entered the reactor. Water was circulated through the jacket (G) for operation of the reactor as a CWT reactor. When operating as an adiabatic reactor, walls were first covered out with an air jacket, but with later runs, the reactor was insulated with styrofoam.

Eight temperature probes (H) were placed in the reactor. The first seven ones were 25 cm. apart and the remaining ones 50 cm. apart. In order to obtain a radial profile, each thermocouple was placed on a traversing mechanism (Figure VI-2). During the runs, the thermocouples were recessed into the reactor wall so as to avoid disturbing the flow patterns. The millivolt readings were obtained with a Leeds and Northrup

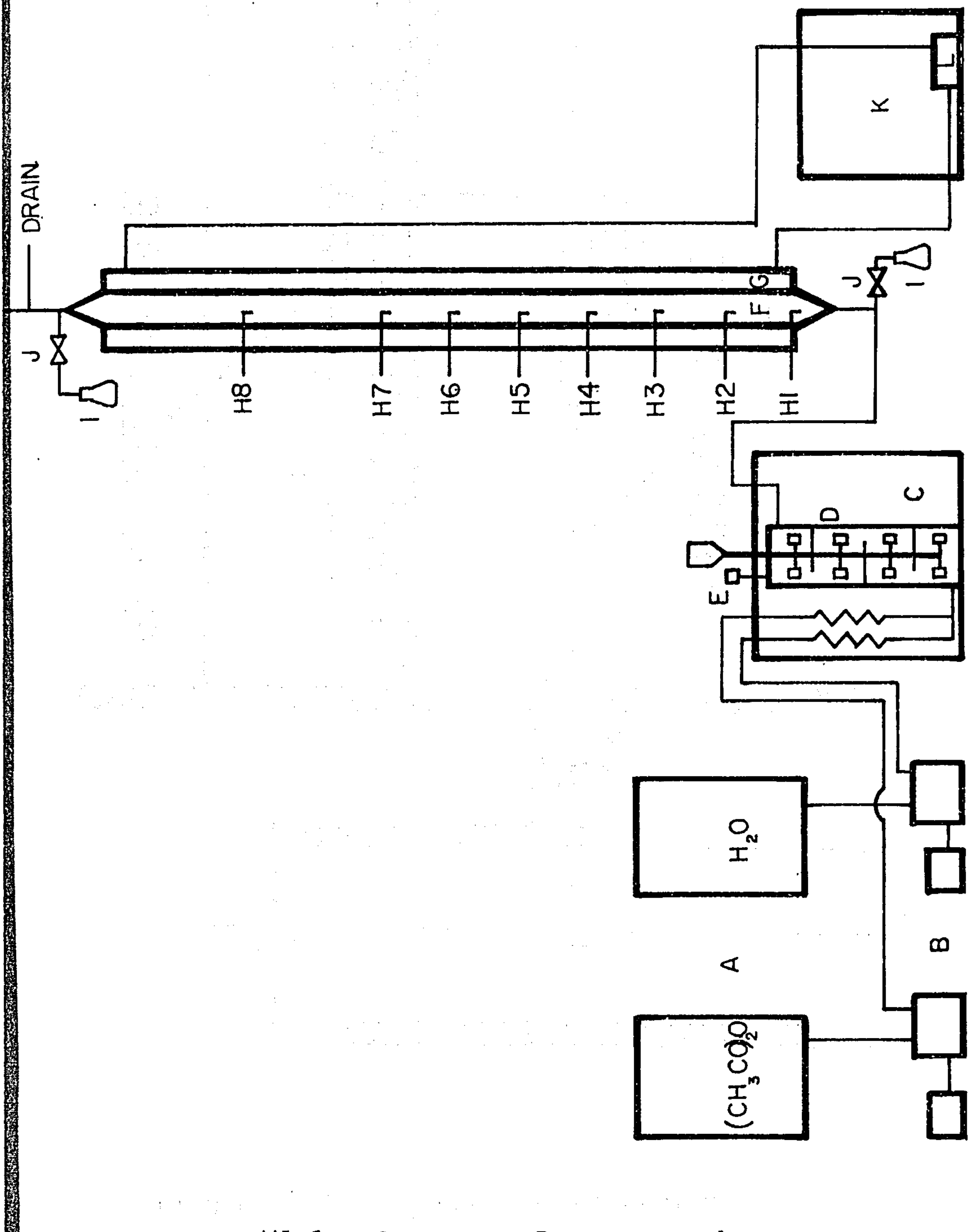

FIGURE VI-1 SCHEMATIC DIAGRAM OF APPARATUS

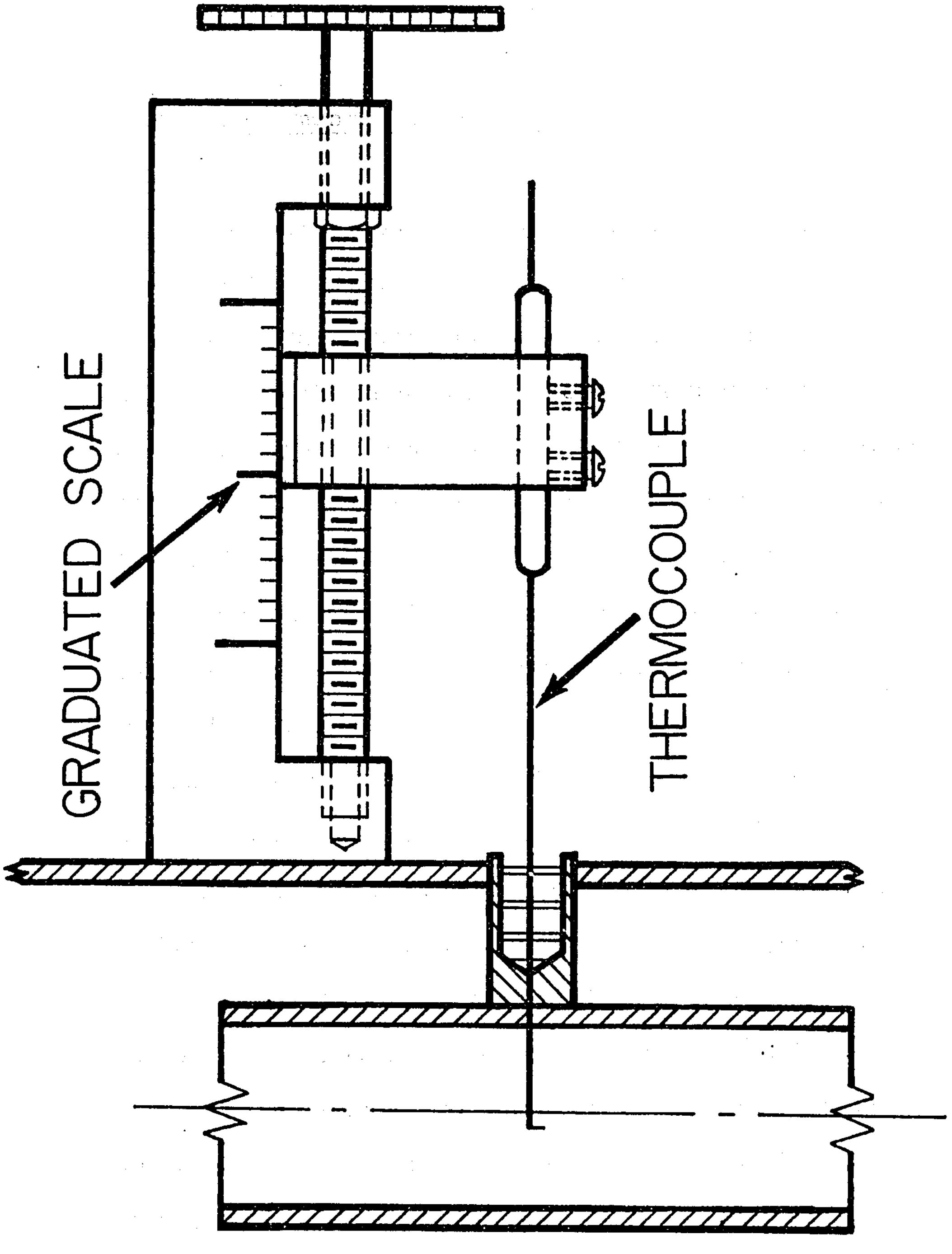

FIGURE VI-2 TRAVERSING MECHANISM

8686 Millivolt Potentiometer. Sample valves (J) were placed at the inlet and outlet of the reactor.

VI-B Experimental Procedure

The pumps were adjusted to give the desired flow rate. The reactants then passed in the heating coils, mixer and reactor. When CWT runs were being carried out, water was circulated through the jacket. Temperature and concentration measurements indicated when steady-state could be assumed. At this time, temperature profiles were taken down the reactor and the exit and inlet concentrations evaluated.

The values of the concentrations measured at the inlet of the reactor varied between 0.291 to 1.470 mole acetic anhydride per litre of solution. The range of inlet temperatures varied from 25.57° to 27.51°C and 35.45° to 38.91°C. The Reynolds number ranged from 88 to 346.

Acetic anhydride concentration was determined by the aniline-water method as described in Appendix 3. Two samples were taken at both the outlet and inlet of the reactor. One sample was analyzed for total acidity and the other was reacted with an excess of saturated aniline-water solution. The aniline reacted with the acetic anhydride to form acetanilide. Details and example of calculations appear in Appendix 3.

VII. EXPERIMENTAL RESULTS AND DISCUSSION

VII-A Introduction

Experiments were carried out at 25° and 35°C under adiabatic conditions and in a constant-wall-temperature (CWT) reactor. The effects of reaction conditions, inlet concentration and velocity on conversion and temperature were studied. The range of conditions investigated are shown in Table VII-1. The values of the physical properties, the dimensionless parameters characterizing each experiment and experimental results obtained are tabulated in full, Appendix 2.

Temperature rises were found to vary between 1.96 and 4.80°C in the air jacketed reactor and between 3.39 and 6.06°C in the insulated reactor. Typical radial and axial temperature profiles are shown in Figures VII-1 and VII-2, respectively. Conversions were between 30.6 and 56.4% in the CWT reactor, between 26.8 and 72.5% in the air jacketed reactor and between 24.0 and 75.6% in the insulated reactor.

VII-B Comparison of Experimental and Predicted Results

VII-B-1 Conversions

As water concentration was relatively constant simulated comparisons were based on a first-order reaction. The

TABLE VII-1

RANGE OF CONDITIONS

	CWT Reactor	Air Jacketed Reactor	Insulated Reactor
Temperature (°C)	26.70-38.91	26.68-36.55	25.57-36.96
ρ_{Ao}(mole AA/ℓ)	.291-1.282	.330-1.356	.582-1.470
ρ_{Bo}(mole H_2O/ℓ)	43.26-50.84	43.18-50.91	42.44-46.76
ρ_{Co}(mole CH_3COOH/ℓ)	.912-2.613	.840-2.502	1.370-2.458
$<u>$ (cm/sec)	.629-.856	.402-1.316	.629-1.316
Re	137-188	88-287	134-346
Temperature Rises (°C)	0.00-0.25	1.96-4.80	3.39-6.06
Conversion (%)	30.6-56.4	26.8-72.5	24.0-75.6

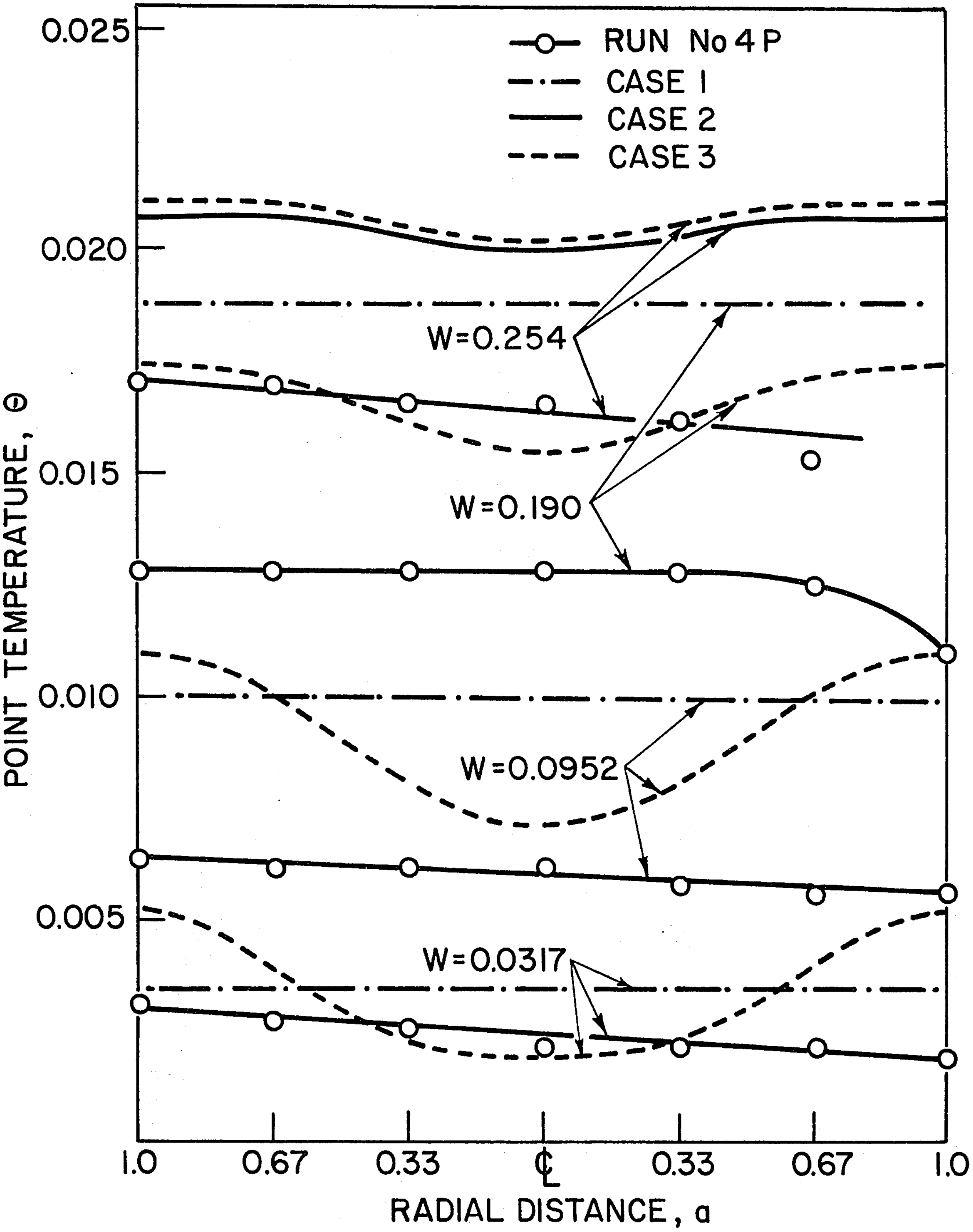

FIGURE VII-1 RADIAL TEMPERATURE PROFILES. INSULATED REACTOR.

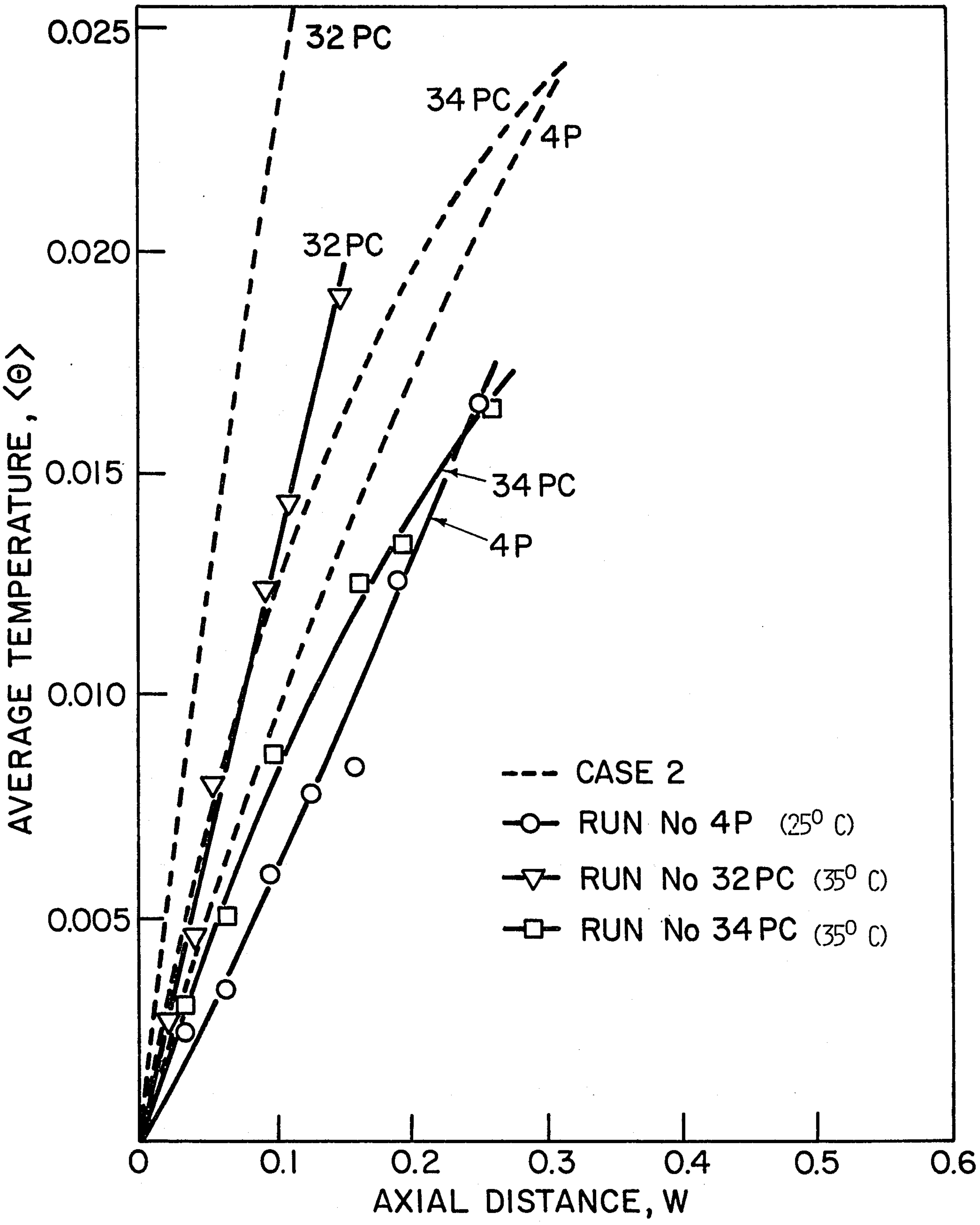

FIGURE VII-2 AXIAL TEMPERATURE PROFILES.
INSULATED REACTOR.

reaction rate constant, k, as discussed in Chapter V, was found to vary with acetic anhydride concentration and was calculated in the present investigation according to equation (V-4). The computed k values were found in good agreement with most literature values (Table V-2).

VII-B-1-a CWT Reactor

In the CWT reactor agreement between experimental and predicted conversions was very good (within 2% when laminar flow was assumed) at low initial acetic acid concentrations, ρ_{c_o} = 0.912 mole/ℓ, but larger differences were observed at higher ρ_{c_o} values (Table VII-2). The axial conversion profiles predicted by the plug flow (Case 1) and the laminar flow (Case 2) models and corresponding to reaction conditions of Run no. 15 are represented by the dashed lines in Figure VII-3 and show expected trends of conversions with axial distance, w. Experimental conversions obtained at 27°C for different Reynolds numbers were in general lower than those predicted by the three flow models and even lower than those computed for the constant-stirred-tank (CSTR) reactor (Table VII-2).

The acceleration of the reaction due to the presence of acetic acid has been reported by Oshima (28) at low (up to 0.8M) acetic acid concentrations (Section VII-C-1). On the other hand, the reaction has been observed by Orton and Jones (24) to be slowed down by the acid, the reaction taking place very slowly in glacial acetic acid. In the present study and at high acetic acid concentrations experimental conversions were found to be lower than

TABLE VII-2

EXPERIMENTAL AND COMPUTED ACETIC ANHYDRIDE CONCENTRATIONS. CWT REACTOR

			<x> Computed				Difference			
Run no.	ρ_{C_o} (mole/ℓ.)	<x> expt.	CSTR	Case 1	Case 2	Case 3	CSTR	Case 1	Case 2	Case 3
15	0.912	.436	.510	.382	.456	.450	-.074	+.054	-.020	-.014
17C	1.353	.601	.575	.477	.539	.532	+.026	+.124	+.062	+.069
17B	1.373	.610	.582	.487	.547	.541	+.028	+.123	+.063	+.069
13	1.648	.694	.621	.544	.596	.589	+.073	+.150	+.098	+.105
14	2.001	.630	.530	.412	.482	.475	+.100	+.218	+.148	+.155
24	2.613	.461	.308	.105	.185	.182	+.153	+.356	+.276	+.279

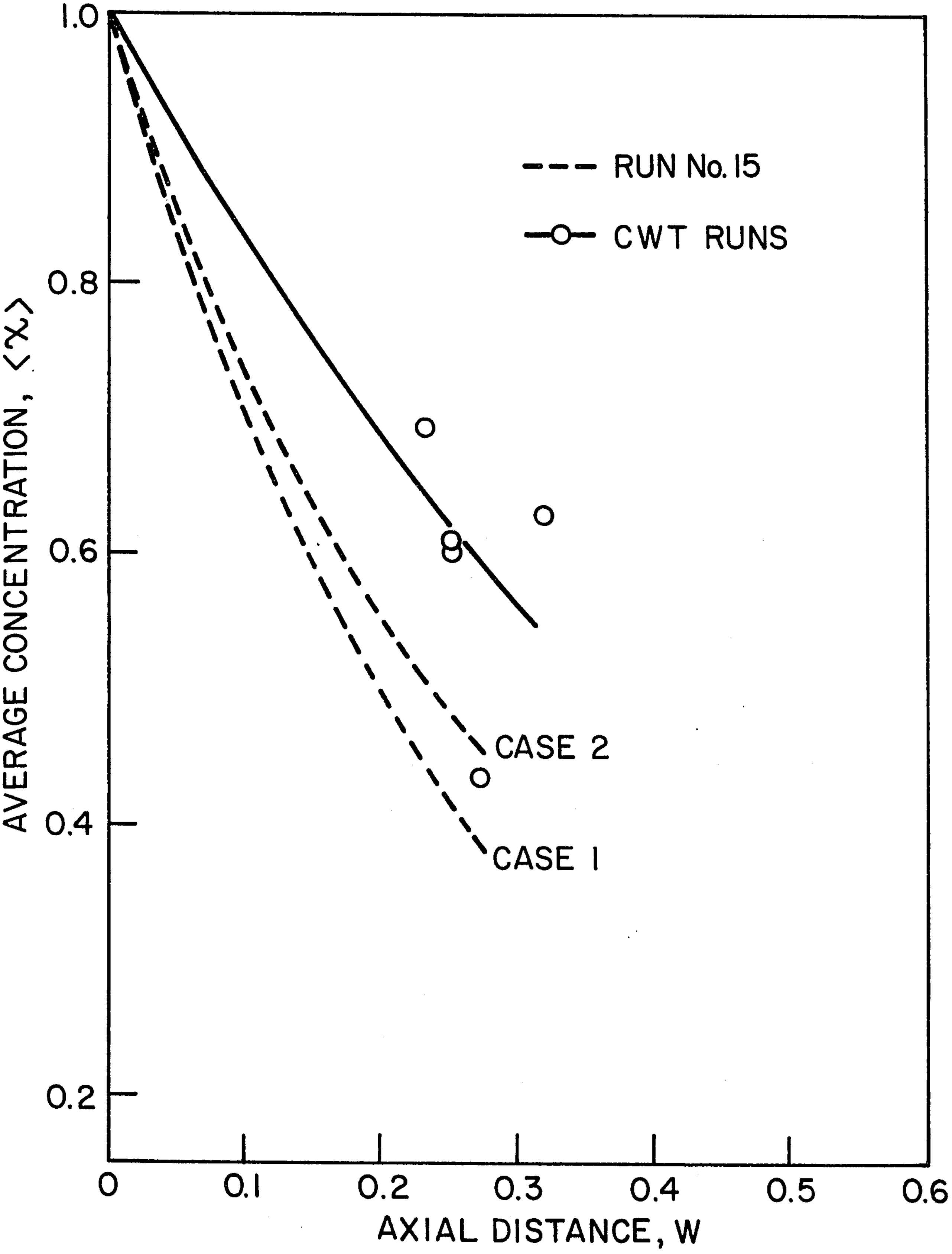

FIGURE VII-3 CONCENTRATION PROFILES, CWT REACTOR AT 25°C.

predicted and to differ more from the simulated results as the initial acetic acid concentrations increased (Table VII-2). The effect was found to be more pronounced at higher temperatures. When 2.6M acetic acid were present initially at 38.91°C, 28% less conversion than predicted was experimentally observed (Table VII-2). The acetic acid effect on conversion and temperature rise is discussed in greater detail in Section VII-C-1.

VII-B-1-b Air Jacketed and Insulated Reactors

Similar results as those observed in the CWT reactor were found in the air jacketed and insulated reactors (Table VII-3). Acetic acid concentration again tended to decrease conversion but its effect on conversion was not as evident as in the CWT reactor. An effect of the heat of reaction, ΔH, which is strongly concentration dependent (32) was also observed (Table VII-4). Discussion is reported to Section VII-C-2.

Observed and predicted conversions and temperature rises at different Reynolds numbers are tabulated in Table VII-5. The combined effect of Reynolds number and acetic acid concentration at 25°C is best visualized in Figure VII-4. It was observed that at a given Reynolds number conversion decreased as the initial acetic acid concentration increased showing the deceleration of the reaction at high acetic acid concentration. However at

TABLE VII-3

EFFECT OF THE PRESENCE OF ACETIC ACID ON CONVERSION AND TEMPERATURE RISE

Run No.	ρ_{c_o} (mole/ℓ)	$\left(\langle x\rangle_{expt} - \langle x\rangle_{Case\ 2}\right)$	$\left(T.Rise_{expt} - T.Rise_{Case\ 2}\right)$
CWT REACTOR			
15	.912	-.020	0
17C	1.353	+.062	0
17B	1.373	+.063	0
13	1.648	+.098	0
14	2.001	+.148	0
24	2.613	+.276	0
AIR JACKETED REACTOR			
5	.840	-.003	-0.07
1	1.046	-.049	+0.16
6	1.180	+.018	-0.17
7	1.450	+.112	-0.59
2	1.542	+.140	-2.92
3	1.742	+.184	-1.79
4	1.848	+.120	-1.53
8	2.046	+.089	-1.04
34	2.502	+.131	-2.66
INSULATED REACTOR			
7PC	1.370	+.010	-0.54
2P	1.380	+.105	-2.61
2PC	1.394	+.138	-1.57
3P	1.492	+.090	-2.08
3PC	1.662	+.082	-1.71
4P	1.872	+.124	-1.21
4PC	1.886	+.115	-1.05
31PC	1.664	+.219	-3.17
37PC	1.764	+.100	-1.59
32PC	1.938	+.186	-3.65
33PC	2.276	+.171	-2.86
34PC	2.458	+.091	-1.77

TABLE VII-4

EFFECT OF HEAT OF REACTION VALUE ON PREDICTED CONVERSION AND TEMPERATURE RISE

Run no.	ρ_{A_o} (mole/ℓ.)	ρ_{C_o} (mole/ℓ.)	Difference in Conversion		Difference in Temperature Rise (0°C)	
			ΔH = -8.9 kcal/mole	ΔH=-12.54 kcal/mole	ΔH = -8.9 kcal/mole	ΔH=-12.54 kcal/mole
7PC	.795	1.370	+.009	-.010	+.73	-.54
2P	1.470	1.380	-.078	-.105	-.62	-2.61
1	.880	1.046	+.061	+.049	+1.17	+.16

TABLE VII-5

EFFECT OF REYNOLDS NUMBER ON CONVERSION AND TEMPERATURE RISE

Run no.	Re	<x> expt.	<x> Case 2	T. Rise expt. (°C)	T. Rise Case 2 (°C)
CWT Reactor					
13	188	.694	.596	-0.15	0
17C	175	.601	.539	-0.06	0
17B	174	.610	.547	-0.25	0
15	163	.436	.456	-0.13	0
14	137	.630	.482	0.00	0
24	174	.461	.185	-0.02	0
Air Jacketed Reactor					
1	287	.595	.644	3.41	3.25
2	238	.732	.592	2.73	5.65
3	188	.676	.492	4.80	6.59
7	177	.575	.463	3.55	4.14
5	163	.433	.436	1.96	2.03
4	138	.497	.377	4.43	5.96
6	125	.360	.342	2.38	2.55
8	88	.301	.212	4.09	5.13
34	166	.275	.144	4.47	7.13
Insulated Reactor					
2P	237	.703	.598	3.39	6.00
2PC	232	.760	.622	3.91	5.48
3P	186	.599	.509	4.61	6.69
3PC	183	.609	.527	4.68	6.39
7PC	169	.526	.516	3.51	4.05
4P	136	.514	.390	4.95	6.16
4PC	134	.523	.408	5.19	6.24
31PC	346	.625	.406	5.14	8.31
32PC	289	.485	.299	5.90	9.55
33PC	227	.396	.225	6.06	8.92
37PC	208	.356	.256	3.42	5.01
34PC	165	.244	.153	5.11	6.88

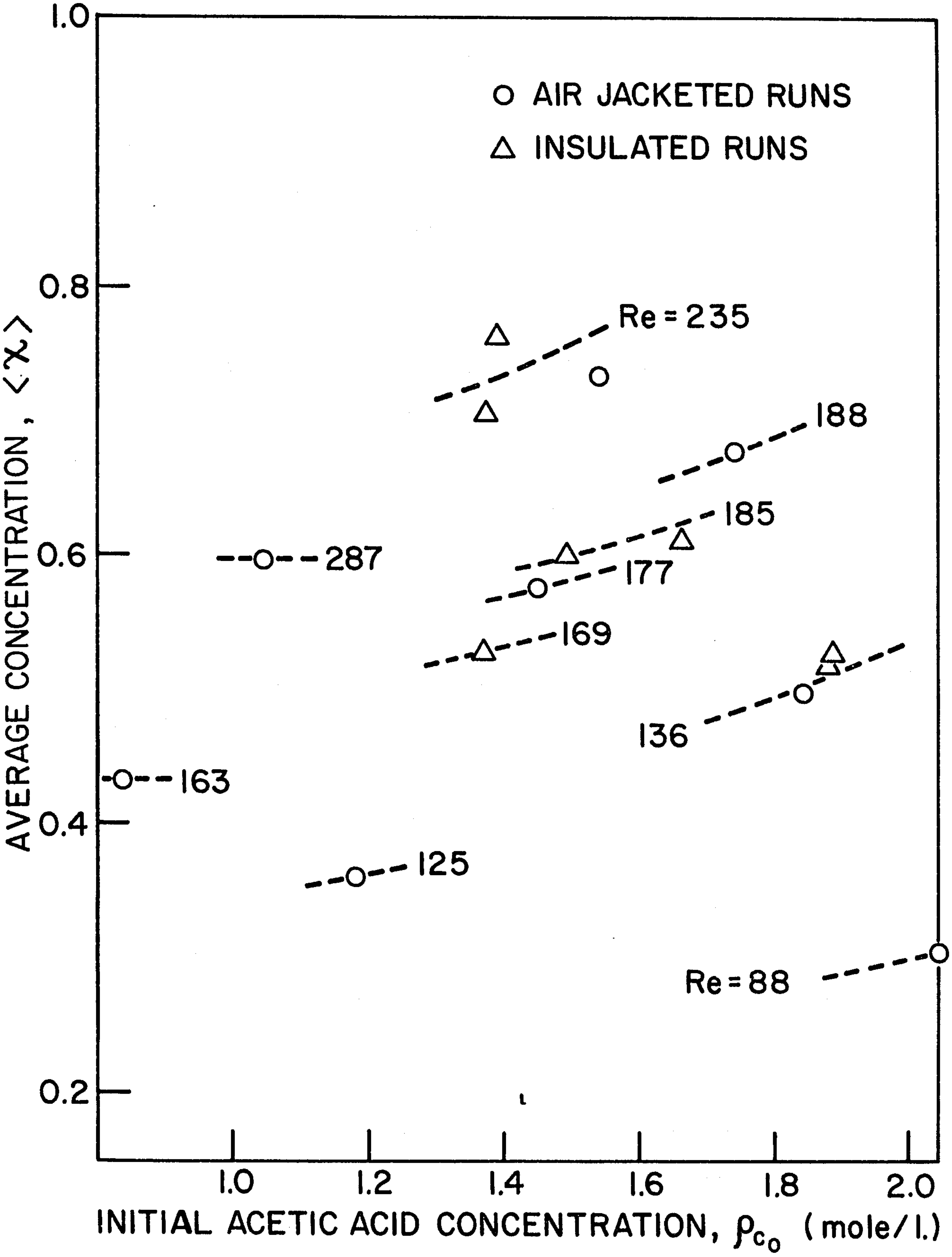

FIGURE VII-4 COMBINED EFFECT OF REYNOLDS NUMBER AND ACETIC ACID CONCENTRATION ON CONVERSION AT 25°C.

low acetic acid concentration higher conversion than predicted was always obtained in the three different types of reactor. This indicated that, as reported by Oshima (28), the reaction was accelerated by acetic acid when the acetic acid concentration is less than 1.05M. At higher acetic acid concentrations, the reaction was slowed down by the acid.

Conversion profiles for the air jacketed and insulated reactors are shown in Figure VII-5 for runs at 25°C and in Figure VII-6 for runs at 35°C. The simulated conversion profiles (dashed lines in both figures) were based on the reaction conditions for Run no. 4P (Figure VII-5) and Run no. 34PC (Figure VII-6). Experimental conversions were in most cases lower than predicted (Table 2-6).

The effect of reaction conditions is summarized in Table VII-6. Under similar conditions of temperature, initial acetic anhydride concentration and average velocity, more conversion was obtained in the insulated reactor (Run no. 3P) than in the air jacketed reactor (Run no. 3) and than in the CWT reactor (Run no. 13). The effect of reaction conditions was found to be less pronounced at low initial acetic anhydride concentration (Run nos. 15 and 5).

The greater differences observed between experimental and simulated values at 35° than at 25°C (Table 2-6) could be due to an error in estimating the activation energy. The error caused by approximating the kinetic constants is discussed in greater detail in Section VII-C-3.

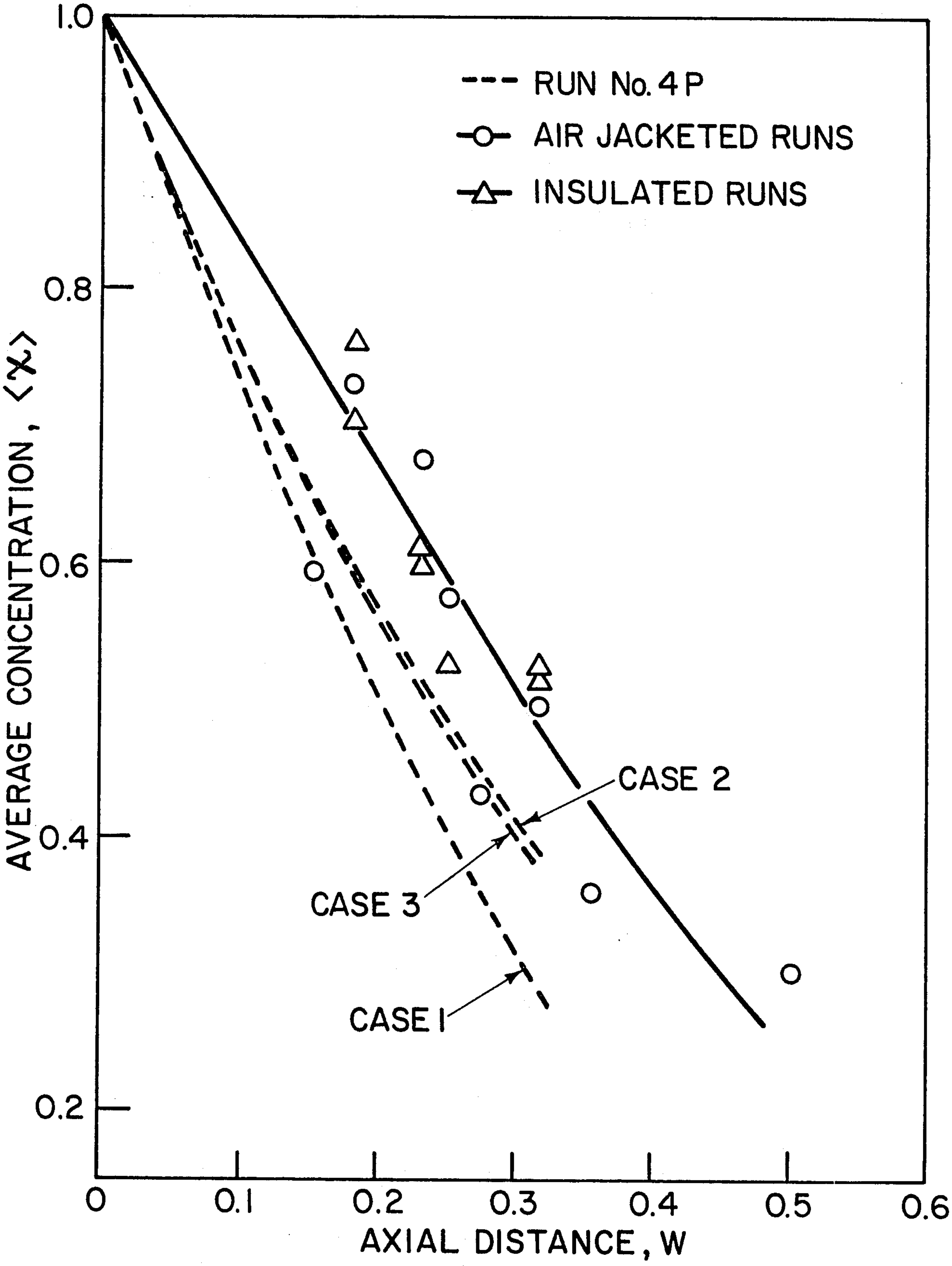

FIGURE VII-5 CONCENTRATION PROFILES, ADIABATIC REACTOR AT 25°C.

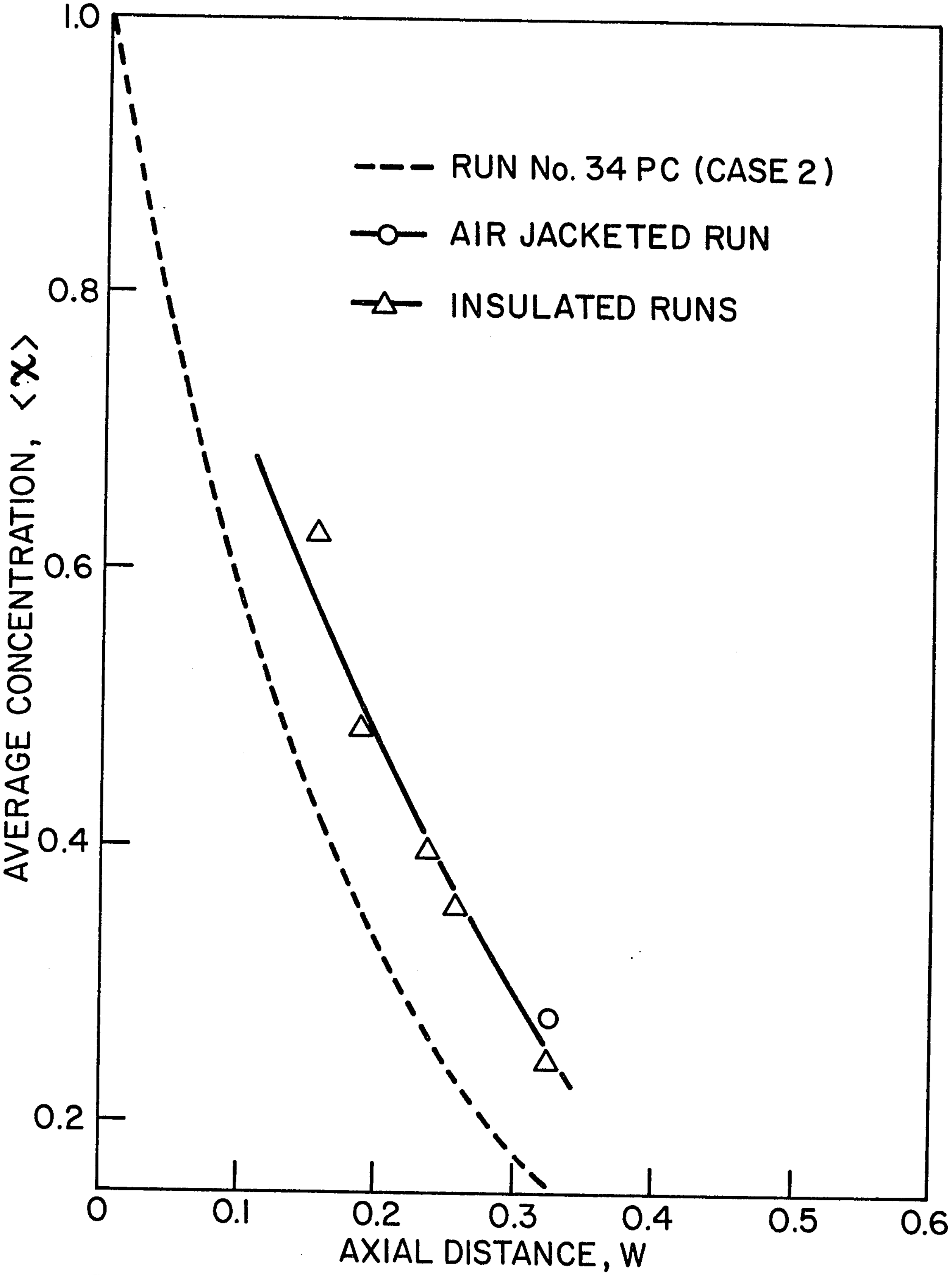

FIGURE VII-6 CONCENTRATION PROFILES, ADIABATIC REACTOR AT 350C.

TABLE VII-6

EFFECT OF REACTION CONDITIONS ON CONVERSION AND TEMPERATURE RISE

Run No	T_o (^oC)	ρ_{A_o} (mole/ℓ)	<x> expt.	Temperature Rise Exptal.(^oC)
1. CWT REACTOR				
13	27.42	1.282	.694	0
15	26.70	.291	.436	0
2. AIR JACKETED REACTOR				
3	27.48	1.252	.676	4.80
5	26.68	.330	.433	1.96
3. INSULATED REACTOR				
3P	27.03	1.325	.599	4.61
3PC	26.34	1.316	.609	4.68

VII-B-2 Temperature Rises

The temperature rises were based on a heat of reaction value of -12.54 kcal./mole at 25°C as given by Takashima (32) (Appendix 3). The results obtained were generally found to be lower than those predicted by laminar flow (Table 2-5) and were consistent with the observed conversion. The differences between experimental and predicted temperature rises are explained by the strong dependency of heat of reaction on concentration (Section VII-C-2) and were generally observed to be greater at high initial acetic anhydride concentrations or at high initial temperatures where the kinetics were not well-established.

The observed low and asymmetric radial temperature profiles (Figures VII-1 and VII-7) could be due to the heat lost through the temperature probe holders. The predicted lower temperature at the centre of the reactor could not be obserbed experimentally.

Figure VII-8 shows the variation of average temperature along the reactor. Measured values were lower than predicted and increasing with axial distance. The predicted higher average temperatures at 35°C than at 25°C were not observed (Run nos. 4 and 34). This was probably an error in estimating the activation energy at 35°C (Koskikallio(29)).

Air jacketed temperature rises were lower than those in the insulated reactor indicating heat lost through the reactor wall (Figures VII-2 and VII-8). In the insulated

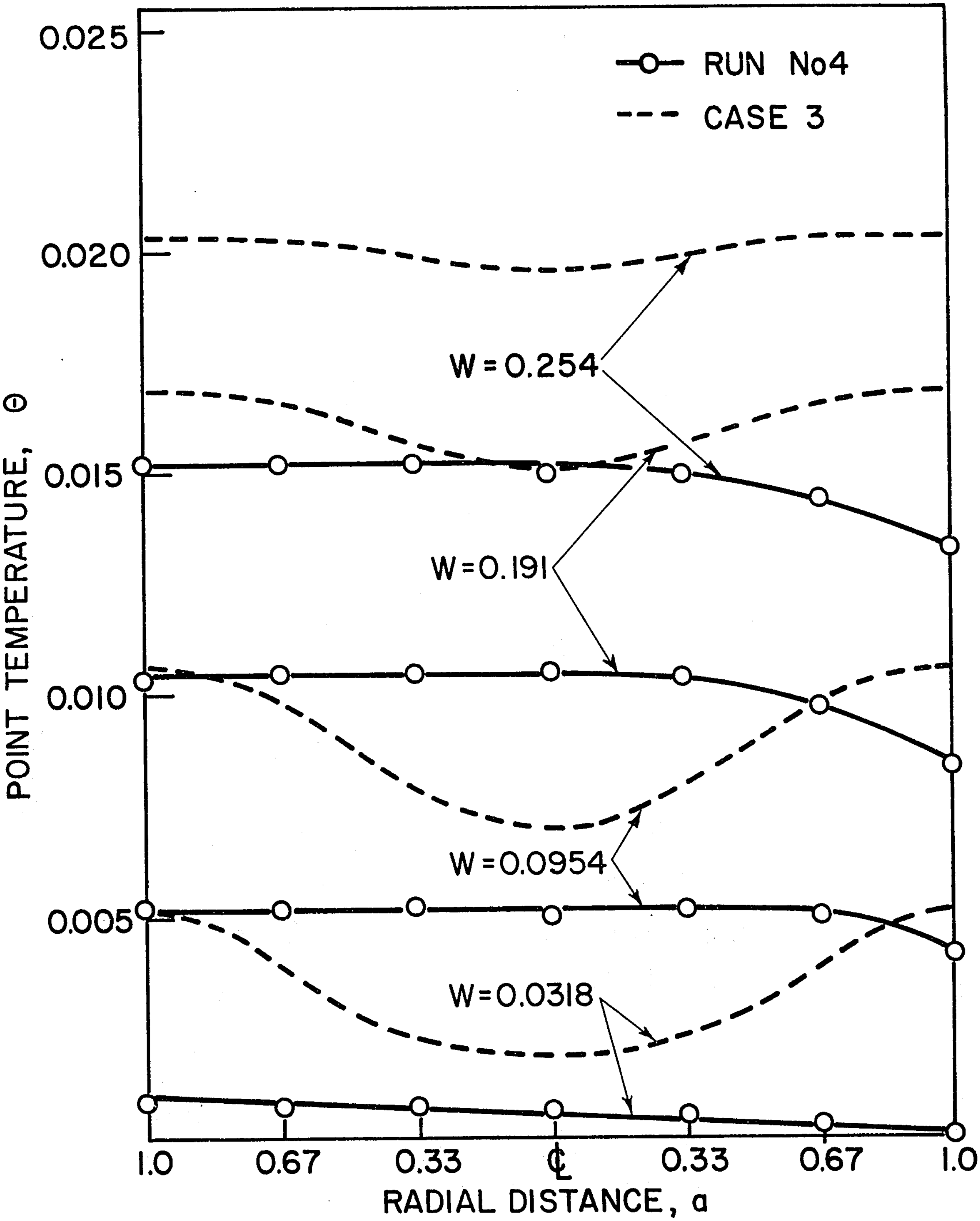

Figure VII-7 Radial Temperature Profiles. Air Jacketed Reactor.

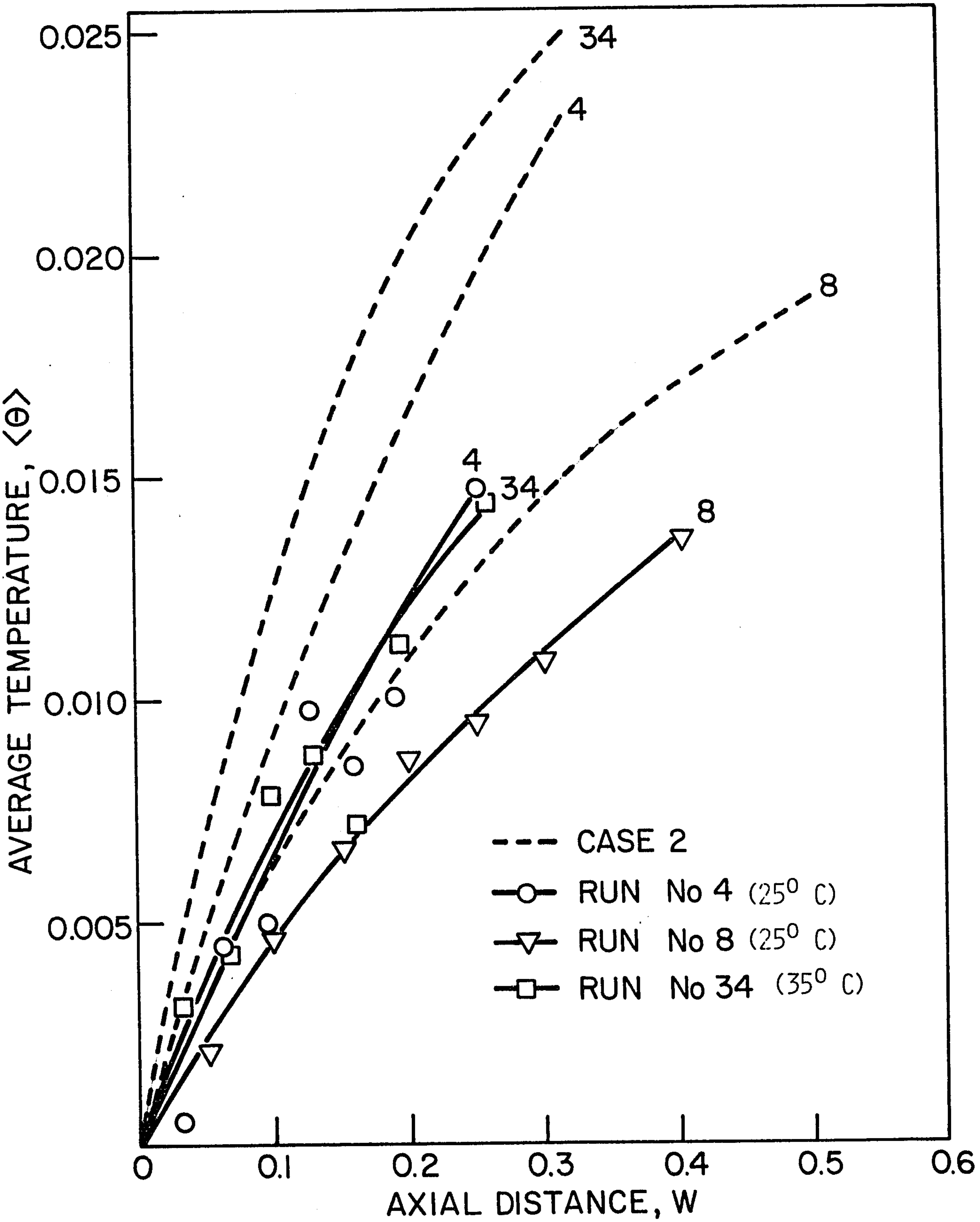

FIGURE VII-8 AXIAL TEMPERATURE PROFILES.
AIR JACKETED REACTOR.

reactor (Figure VII-2) the agreement was better than in the air jacketed reactor (Figure VII-8). In both reactors the axial temperature profiles were found to intersect at a shorter axial distance than predicted. This could be due to the presence of acetic acid. For example, in the insulated reactor, the larger initial acetic acid concentration in Run no. 34PC (ρ_{c_o} = 2.458M) than in Run no. 4P (ρ_{c_o} = 1.872M) caused the difference between the predicted and measured axial temperature profiles for Run no. 34PC to be greater at higher axial distance and more pronounced than that for Run no. 4P.

VII-C Discussion of Results

The mentioned differences between experimental and predicted results could be explained by the following effects:

1) Presence of acetic acid
2) Heat of reaction dependency on acetic anhydride concentration
3) Kinetics
4) Density and free convection
5) Entrance effect
6) Analytical errors.

VII-C-1 Presence of Acetic Acid

In his studies of the hydrolysis of acetic anhydride Oshima (28) observed that as the number of moles of acetic acid increased, the reaction was accelerated and developed an equation to evaluate the reaction rate constant as a function of acetic acid concentration. He showed that his equation held for acetic anhydride concentrations between 9.7 and 10.5M and for acetic acid concentrations of less than 0.8M. Consequently, Oshima's equation could not be used in the present study as acetic anhydride concentration at the reactor inlet ranged from 0.291 to 1.470M and acetic acid concentration from 0.84 to 2.61 moles/ℓ (Table VII-3). In the present investigation an acceleration of the reaction was also observed at low acetic acid concentrations however the opposite was consistently observed at higher acetic acid concentrations. This was in agreement with the deceleration of the reaction reported by Orton and Jones (24) at high acetic acid concentrations. In the CWT reactor, when 0.912M acetic acid was present at the inlet, 2.0% more conversions than predicted were observed (Run no. 15). But as the initial acetic acid concentration, ρ_{c_o}, increased from 1.3 to 2.0M conversion was found to be progressively decreased (6.2 to 14.8% lower than predicted). The effect was more pronounced at 35°C (Run no. 24).

This effect was also observed in the air jacketed and insulated reactors. In the air jacketed reactor and at low initial acetic acid concentration, ρ_{c_o} conversions were found to be slightly higher than predicted. At ρ_{C_O} greater than 1.05M experimental conversions were found to be lower than predicted indicating the deceleration effect of acetic acid. In the insulated reactor the lowest acetic acid concentration was 1.37M so that, as would be expected, conversions were always found to be lower than predicted at both 25° and 35° C.

In most runs, temperature rises were lower than predicted. The heat of reaction, ΔH, was taken as -12.54 kcal./mole. However, Takashima (32) showed that ΔH is a strong function of the acetic anhydride concentration.

VII-C-2 Heat of Reaction Dependency on Acetic Anhydride Concentration

The assumption that the heat of reaction, ΔH, was independent of acetic anhydride concentration was found to disagree with the present nonisothermal results (Table VII-4). Measured values of ΔH at different acetic anhydride concentrations are tabulated in Appendix 3. Heat of reaction effect on conversion and temperature rise can be shown by taking $\Delta H = -8.9$ kcal./mole as calculated from Perry (38) (Table VII-4). Accurate values of ΔH are necessary to correctly predict conversion and temperature rise in nonisothermal reactors.

VII-C-3 Kinetics

Lowering the reaction rate constant, k, calculated from equations (V-4) and based on Rivett and Sidgwick's(23) acetic anhydride concentration (ρ_A= 0.2650M), from 0.1575 to 0.1485 min^{-1} (Table V-2) would lower the predicted conversions by about 2%. Other approximations of k compared to measured literature values for the present range of concentration were found to be less significant.

The differences between experimental and predicted results at temperatures higher than 25°C could partially be due to the activation energy dependency on temperature measured by Koskikallio (29) and neglected in the present computations. This effect could be responsible for the larger differences observed between experimental and predicted results at 35°C than at 25°C.

VII-C-4 Density and Free Convection

Shiraishi,(11) studying the hydrolysis of acetic anhydride, measured the density of the reacting solution and found that it increased with increasing conversion. Also, in most of his isothermal runs, he observed lower conversion than predicted by laminar flow and even lower than predicted by a constant-stirred-tank reactor (CSTR). He explained that the discrepancies were caused by free convection decreasing conversion in an upward flow reactor.

The difference in density (due to a concentration difference) caused convective currents to take place in the reactor and disturbed the laminar flow. But since the reactor was in the vertical position, the convective currents were parallel to flow and the induced radial mixing due to free convection cannot cause conversion to become lower than that computed for a CSTR reactor. Another possible explanation for Shiraishi's observed discrepancies in conversion would be the reaction rate constant dependency on acetic anhydride and acetic acid concentrations.

Shinohara,(8) studying the saponification of ethyl acetate, observed that as Gr/4Re (parameter characterizing the magnitude of free convection and defined in Appendix 2) increased, in a nonisothermal reactor, the data differed more from the solutions for no free convection. Both, Shiraishi (11) and Shinohara,(8) reported that free convection in an upward flow reactor decreased conversion for exothermic reactions.

The present results agree with Shiraishi's and Shinohara's results since in most runs conversions were lower than predicted (Table VII-7). Due to the effect of acetic acid it is not possible, however, to evaluate the free convection effect. In the present investigation no definite conclusion can be drawn from Shinohara's work. Gr/4Re values are in the range where natural convection was reported. However, conversions are lower than those

TABLE VII-7

EFFECT OF Gr/4Re VALUES ON CONVERSION AND TEMPERATURE RISE

Run No.	Gr/4Re	$(\langle x\rangle_{\text{expt}} - \langle x\rangle_{\text{Case 2}})$	$(\text{T. Rise}_{\text{expt}} - \text{T. Rise}_{\text{Case 2}})$
1	11	-.049	+.16
5	12	-.003	-.07
6	18	+.018	-.17
2	20	+.140	-2.92
7	27	+.112	-.59
3	29	+.184	-1.79
4	33	+.120	-1.53
8	65	+.089	-1.04
34	104	+.131	-2.66
2P	10	+.105	-2.61
2PC	11	+.138	-1.57
3PC	15	+.082	-1.71
7PC	16	+.010	-.54
3P	20	+.090	-2.08
31PC	25	+.219	-3.17
4P	29	+.124	-1.21
4PC	34	+.115	-1.05
32PC	36	+.186	-3.65
33PC	56	+.171	-2.86
37PC	65	+.100	-1.59
34PC	73	+.091	-1.77

computed for a CSTR reactor and until the kinetics of the reaction are well-established no estimation of the magnitude of any free convection effect can be made.

VII-C-5 Entrance Effect

Assuming that the temperature in the conical zone is constant and equal to the temperature read by Probe 1 and that the rate of reaction is constant and equal to the rate at the inlet of the reactor, then the number of mole of acetic anhydride per litre of solution, reacted in the entrance section will be equal to the product of the reaction rate at the inlet of the reactor and the residence time of acetic anhydride in the entrance section. Therefore,

$$\rho_{Ao,\text{treated}} = \rho_{Ao,\text{untreated}} - \text{no. mole AA}/\ell \text{ reacted in entrance section.}$$

The inlet concentration of acetic anhydride was estimated about 42 cm. below the inlet point of the reactor where the initial temperature was read. This included two parts: the tubing part and the conical zone with a total volume of 23.37 cc.

Then the fraction of acetic anhydride unconverted was calculated.

$$\langle x \rangle_{\text{treated}} = \rho_{A,\text{outlet}} / \rho_{Ao,\text{ treated}}$$

$$\langle x \rangle_{\text{untreated}} = \rho_{A,\text{outlet}} / \rho_{Ao,\text{untreated}}$$

The maximum difference calculated between $\langle x \rangle_{treated}$ and $\langle x \rangle_{untreated}$ was 2.8%. Therefore, the entrance effect was only of minor importance.

VII-C-6 Analytical Errors

Calculations were performed on the lowest flow rate experiments in order to estimate the maximum possible error due to sampling. At an average velocity of 0.402 cm./sec., the time required to collect a ten cc. sample was about 9 seconds. If two more seconds are added for reading the exact volume collected and pouring it into a mixture of aniline-water, then the total time taken between the outlet of the reactor and the quenching of the reaction amounts to around 11 seconds.

The error, however, was found to be negligible and self-cancelling as the ratio of outlet to inlet fraction unconverted of acetic anhydride was the required measurement.

VIII. SUMMARY AND RECOMMENDATIONS

A theoretical study performed by computer and applicable to any homogeneous liquid-phase reaction has been carried out in order to determine the effects of varying parametric groups, reaction conditions, reaction kinetics, flow conditions and inlet reactant concentration on conversions and temperature rises. Radial and axial concentration and temperature profiles were obtained. Comparison of the CWT reactor with previous work showed good agreement. Some of the most important findings follow:

1) Although normally molecular diffusion would not be expected to influence profiles, conversions can be significantly affected if radial movement of material takes place.

2) At 25° C and when the reaction rate constant remained unchanged, an increase in activation energy showed that the reaction approached completion at a lower axial distance.

3) Higher overall conversions are usually obtained in plug flow, but for a constant-wall-temperature reactor, conversion rates can be enhanced under laminar flow conditions when large temperature effects are present.

4) Decreasing the inlet mole fraction of reactant A while increasing the total number of moles of reactants increased both the reaction rate constant (frequency factor group, G_3) and the heat of reaction group, G_4, and

consequently conversion was increased for both the adiabatic and the CWT reactors. Also as both G_3 and G_4 increased, the maximum temperature rises were approached at a faster rate and the maximum attainable temperature was reached at a shorter reactor length.

5) Under plug flow conditions, radial concentration and temperature profiles were constant for an adiabatic reaction. Under laminar flow conditions, maximum temperatures initially arose at an intermediate radial position before the maximum was established at the reactor centreline.

An equation based on data published by different authors was developed to compute the reaction rate constant as a function of the acetic anhydride concentration.

$$\ell n\ k = 8.2689\ \rho_A^{.22} + 12.00 - \frac{(5{,}270\rho_A^{.22\text{ or }.24} + 8{,}030)}{RT} \qquad \text{(V-4)}$$

This equation could cause a 2% error in predicting conversions at 25° C.

Experimental data for the hydrolysis of acetic anhydride in concentrated solutions were obtained at 25° and 35° C under adiabatic conditions and in a constant-wall-temperature reactor. Experimental conversions and temperature rises were in most cases lower than predicted. Conversions were predicted within 15% at 25° C and within 28% at 35° C in the CWT reactor, within 19% in the air jacketed reactor and within 22% in the insulated reactor. The best agreement between experimental and predicted results were generally observed at low acetic acid con centration and with the laminar flow model.

The reaction was found to be accelerated at initial acetic acid concentrations lower than 1.05M and slowed down at higher initial acetic acid concentrations.

The heat of reaction dependency on acetic anhydride was shown to affect both conversions and temperature rises. The effects or reaction conditions were found to be less pronounced at low initial acetic anhydride concentration.

Computation of Gr/4Re values indicated that free convection could be present but its effect on experimental results could not be estimated.

In carrying out the experimental runs, it is recommended that a different system be employed. The initial partial immiscibility of acetic anhydride into water made the system difficult to work with. A system with well-established kinetics would allow the effects of reaction conditions, inlet concentration, velocity and free convection on conversion and temperature rise to be evaluated.

The use of proper insulation around the temperature probe holders would improve data.

A computer programme taking into account the variation of the physical properties with temperature would be more accurate.

It would also be interesting to work with a larger diameter reactor where radial temperature, concentration and velocity profiles could be evaluated.

REFERENCES

1. Bosworth, R.C.L., Phil. Mag. 39, 847 (1948).
2. Denbigh, K.G., J. Appl. Chem. (London) 1, 227 (1951).
3. Denbigh, K.G., Chemical Reactor Theory, Vol. 1, Chap. 2, Cambridge University Press (1965).
4. Cleland, F.A. and Wilhelm, R.H., A.I.Ch.E. J. 2, 489 (1956).
5. Vignes, J.P. and Trambouze, P.J., Chem. Eng. Sci. 17, 73 (1962).
6. Rothenberg, R.I. and Smith, J.M., Can. J. Chem. Eng. 44, 67 (1966).
7. Rothenberg, R.I. and Smith, J.M., A.I.Ch.E. J. 12, 213 (1966).
8. Shinohara, T., Ph.D. Thesis, "An Experimental and Theoretical Study of a Laminar-flow Tubular Reactor", University of Utah (1972).
9. Lauwerier, H.A., Appl. Sci. Res. A8, 366 (1959).
10. Sandru, D. and Smith, J.M., A.I.Ch.E. J. 19, 558 (1973).
11. Shiraishi, H., Kagaku Kogaku 34, 414 (1970).
12. Chambré, P.L., Appl. Sci. Res. A9, 157 (1960).
13. Trombetta, M.L. and Happel, J., A.I.Ch.E. J. 11. 1041 (1965).
14. Andersen, T.S. and Coull, J., A.I.Ch.E. J. 16, 542 (1970).
15. Merrill, L.S., Jr. and Hamrin, C.E., Jr., A.I.Ch.E. J. 16, 194 (1970).
16. Lynn, S. and Huff, J.E., A.I.Ch.E. J. 17, 475 (1971).
17. Santarelli, F. and Foraboschi, F.P., Ing. Chim. Ital. 9, 37 (1973).
18. Bird, R.B., Stewart, W.E. and Lightfoot, E.N., Transport Phenomena, John Wiley & Sons, New York (1960).
19. Hayduk, W. and Laudie, H., A.I.Ch.E. J. 20, 611 (1974).
20. Lapidus, L., Digital Computation for Chemical Engineers, Chap. 4. McGraw-Hill, New York (1962).

REFERENCES

(continued)

21. Jensen, V.G. and Jeffreys, G.V., Mathematical Methods in Chemical Engineering, p. 420. Academic Press, New York (1963).

22. Lemay, R.J., B.A.Sc. Thesis, "Prediction of Concentration and Temperature Profiles in a Conical Flow Reactor", University of Ottawa, Ottawa (1974).

23. Rivett, A.C.D. and Sidgwick, N.V., J. Chem. Soc. (London) 97, 732 (1910).

24. Orton, K.J.P. and Jones, M., J. Chem. Soc. (London) 101, 1708 (1912).

25. Wilsdon, B.H. and Sidgwick, N.V., J. Chem. Soc. (London) 103, 1959 (1913).

26. Vles, S.E., Rec. trav. chim. 52, 809 (1933).

27. Gold, V., Trans. Far. Soc. 44, 506 (1948).

28. Oshima, T., Nippon Kagaku Zasshi, 89, 1036 (1968).

29. Koskikallio, J., Pouli, D. and Whalley, E., Can. J. Chem., 37, 1360 (1959).

30. Takashima, I., Nishida, A., Ogita, K. and Uchida, N., Kogyo Kagaku Zasshi, 74, 1293 (1971).

31. Glasser, D. and Williams, D.F., Ind. Eng. Chem. Fundam., 10, 516 (1971).

32. Takashima, I., Yoneyama, K. and Watanabe, K., Kogyo Kagaku Zasshi, 69, 1672 (1966).

33. Dyne, S.R., Glasser, D. and King, R.P., Rev. Sci. Instrum., 38, 209 (1967).

34. Marek, J., Chem. Listy, 48, 168 (1954); Collect. Czech. Chem. Commun., 19, 621 (1954).

35. Janssen, H.J., Haydel, C.H. and Greathouse, L.H., Ind. Eng. Chem., 49, 197 (1957).

36. Marmers, H., Ph.D. Thesis, University of Birmingham, Birmingham, England, 1965.

37. Kusunoki, K., Gondo, S. and Nakahara, S., Asahi Garasu Kogyo Gijutsu Shoreikai Kenkyu Hokoku. 16, 395 (1970).

REFERENCES

(continued)

38. Perry, J.H., (ed.), Chemical Engineers' Handbook, 4th Edit., p. 3-70, 3-123, 3-201, McGraw-Hill, New York (1963).

39. Caudri, J.F.M., Rec. trav. chim. 44, 1 (1930).

40. Gallant, R.W., Physical Properties of Hydrocarbons, Hydrocarbon Process. 47, 89, 142 (1968).

41. Timmermans, J., Physico-chemical Constants of Pure Organic Compounds, p. 375, Elsevier, New York (1950).

42. Weast, R.C., (ed.), Handbook of Chemistry and Physics, 52nd Edit., Chem. Rubber Co., Cleveland, Ohio (1971-72).

43. Smith, J.M. and Van Ness, H.C., Introduction to Chemical Engineering Thermodynamics, 2nd Edit., p. 128, McGraw-Hill, New York (1959).

44. Hsu, S.T., Engineering Heat Transfer, D. Van Nostrand Co., N.J. (1963).

45. Conn, J.B., Kistiakowsky, G.B., Roberts, R.M. and Smith, E.A., J. Amer. Chem. Soc., 64, 1747 (1942).

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APPENDICES

1. Theoretical Results and Previous Work
2. Experimental Data and Results
3. Analytical Method and Physical Properties
4. Equipment Details
5. Pump and Thermocouple Calibrations
6. Grid Spacings and Finite-Difference Equations
7. Computer Programme

APPENDIX 1

THEORETICAL RESULTS AND PREVIOUS WORK

1-A Theoretical Results

TABLE 1-1

EFFECT OF ACTIVATION ENERGY GROUP, G_2 AND FREQUENCY FACTOR GROUP, G_3. ADIABATIC REACTOR.

G_2	G_3	w = 0.10		w = 0.15		w = 0.20	
		<θ>	<x>	<θ>	<x>	<θ>	<x>
20.223	2.010 x 10^9	.1688	.1126	.1897	.0027	.1901	.0001
17.920	2.010 x 10^8	.1497	.2130	.1859	.0226	.1898	.0017
15.617	2.010 x 10^7	.1325	.3030	.1753	.0780	.1875	.0139

TABLE 1-2

EFFECT OF LEWIS NUMBER, G_1. CWT REACTOR.

G_1	w = 0.10		w = 0.15		w = 0.20		w = 0.50	
	<θ>	<x>	<θ>	<x>	<θ>	<x>	<θ>	<x>
0.00659	.05937	.4455	.06968	.2422	.06384	.1321	.01148	.0182
0.0659	.05850	.4413	.06810	.2405	.06219	.1316	.01115	.0171
0.659	.05602	.4343	.06281	.2432	.05661	.1385	.01040	.0173
6.59	.05371	.4261	.05826	.2445	.05215	.1441	.00992	.0183

1-B Previous Work

1-B-1 Hydration of Acetic Anhydride under Isothermal Conditions

A comparison was made with the data reported by Cleland and Wilhelm(4) for the hydration of acetic anhydride in dilute solutions (0.0222 to 0.0628 mole of acetic anhydride per litre of solution). The reaction conditions were approximated to an isothermal first-order reaction and experimental results were compared with predicted results of Cleland and Wilhelm and results calculated from the present theoretical study. These results are given in Tables 1-3 and 1-4. Agreement was very good. The calculations showed that Case 3 gave a very closed representation of experimental results with the plug flow model giving the poorest predictions, both at 25° and 35°C.

1-B-2 Saponification of Ethyl Acetate under Isothermal Conditions

A comparison was also made with the data reported by Vignes and Trambouze(5) for the saponification of ethyl acetate. The data were obtained for a second-order reaction with equimolar concentration of reactants taking place in a horizontal and isothermal (26°C) reactor. Results appear in Table 1-5. Good agreement between experimental results and

TABLE 1-3

COMPARISON OF CLELAND AND WILHELM'S EXPERIMENTAL AND THEORETICAL VALUES WITH PRESENT STUDY THEORETICAL VALUES AT 25°C

Run No.	Cleland & Wilhelm's		<x> Present Study			Differences			
	<x> Expt	<x> Theor	Case 1	Case 2	Case 3	C & W	Case 1	Case 2	Case 3
1	.592	.594	.560	.609	.593	-.002	+.032	-.017	-.001
1A	.697	.700	.678	.711	.699	-.003	+.019	-.014	-.002
1B	.587	.594	.560	.609	.593	-.007	+.027	-.022	-.006
1C	.468	.465	.418	.488	.466	+.003	+.050	-.020	+.002
2	.201	.172	.123	.205	.178	+.029	+.078	-.004	+.023
2B	.139	.172	.123	.205	.178	-.033	+.016	-.066	-.039
2D	.191	.172	.123	.205	.178	+.019	+.068	-.014	+.013
3	.623	.620	.591	.636	.621	+.003	+.032	-.013	+.002
8E	.282	.316	.240	.326	.315	-.034	+.042	-.044	-.033
3A	.629	.620	.592	.637	.621	+.009	+.037	-.008	+.008
3B	.622	.620	.591	.636	.621	+.002	+.031	-.014	+.001
4A	.160	.172	.123	.205	.178	-.012	+.037	-.045	-.018
4B	.179	.172	.123	.205	.178	+.007	+.056	-.026	+.001
7A	.712	.726	.701	.730	.724	-.014	+.011	-.018	-.012
7B	.714	.726	.701	.730	.724	-.012	+.013	-.016	-.010
8A	.285	.319	.242	.327	.316	-.034	+.043	-.042	-.031
8B	.289	.317	.241	.326	.315	-.028	+.048	-.037	-.026

TABLE 1-4

COMPARISON OF CLELAND AND WILHELM'S EXPERIMENTAL AND THEORETICAL VALUES WITH PRESENT STUDY THEORETICAL VALUES AT 35°C

Run No.	Cleland & Wilhelm's		<x> Present Study			Differences			
	<x> Expt	<x> Theor	Case 1	Case 2	Case 3	C & W	Case 1	Case 2	Case 3
9C	.571	.578	.536	.589	.574	-.007	+.035	-.018	-.003
11A	.441	.452	.394	.466	.446	-.011	+.047	-.025	-.005
11B	.439	.452	.394	.466	.446	-.013	+.045	-.027	-.007
5C	.435	.461	.390	.462	.454	-.026	+.045	-.027	-.019
5F	.428	.461	.390	.462	.454	-.033	+.038	-.034	-.026
9A	.571	.578	.536	.589	.574	-.007	+.035	-.018	-.003
9B	.578	.578	.536	.589	.574	0	+.042	-.011	+.004
10B	.147	.132	.083	.159	.137	+.015	+.064	-.012	+.010
10C	.155	.132	.083	.159	.137	+.023	+.072	-.004	+.018
5D	.422	.461	.390	.462	.454	-.039	+.032	-.040	-.032
5E	.423	.461	.390	.462	.454	-.038	+.033	-.039	-.031
6A	.043	.069	.023	.070	.065	-.026	+.020	-.027	-.022
6B	.042	.069	.023	.070	.065	-.027	+.019	-.028	-.023

TABLE 1-5

COMPARISON OF VIGNES AND TRAMBOUZE'S EXPERIMENTAL AND THEORETICAL VALUES WITH PRESENT STUDY THEORETICAL VALUES

Run No.	Vignes & Trambouze's		<x> Present Study		Differences		
	<x> Expt	<x> Theor $D_e = 10D_M$	Case 3 $D_e = D_M$	Case 3 $D_e = 10D_M$	V & T $D_e = 10D_M$	Present Study $D_e = D_M$	$D_e = 10D_M$
A1	.113	.107	.107	.094	+.006	+.006	+.019
B1	.126	.126	.131	.116	0	-.005	+.010
C1	.146	.145	.152	.136	+.001	-.006	+.010
D1	.180	.190	.199	.180	-.010	-.019	0
E1	.256	.262	.274	.254	-.006	-.018	+.002
F1	.340	.356	.364	.344	-.016	-.024	-.004
G1	.540	.557	.568	.554	-.017	-.028	-.014
A2	.129	.125	.128	.114	+.004	+.001	+.015
B2	.145	.144	.152	.137	+.001	-.007	+.008
C2	.188	.194	.201	.185	-.006	-.013	+.003
D2	.206	.205	.212	.195	+.001	-.006	+.011
E2	.228	.228	.236	.219	0	-.008	+.009
F2	.268	.257	.267	.250	+.011	+.001	+.018
G2	.290	.289	.291	.274	+.001	-.001	+.016
H2	.345	.350	.358	.342	-.005	-.013	+.003
I2	.388	.393	.402	.387	-.005	-.014	+.001
J2	.432	.447	.456	.442	-.015	-.024	-.010
K2	.472	.463	.498	.484	+.009	-.026	-.012
L2	.487	.508	.516	.503	-.021	-.029	-.016
M2	.580	.606	.612	.601	-.026	-.032	-.021
N2	.650	.655	.659	.650	-.005	-.009	0
O2	.676	.692	.696	.688	-.016	-.020	-.012
P2	.747	.749	.749	.743	-.002	-.002	+.004
A3	.135	.129	.132	.123	+.006	+.003	+.012
B3	.174	.165	.170	.160	+.009	+.004	+.014
C3	.175	.172	.176	.166	+.003	-.001	+.009
D3	.208	.208	.214	.204	0	-.006	+.004
E3	.291	.272	.292	.283	+.019	-.001	+.008
F3	.309	.315	.322	.313	-.006	-.013	-.004
G3	.385	.397	.413	.405	-.012	-.028	-.020
H3	.505	.526	.533	.526	-.021	-.028	-.021
I3	.600	.613	.612	.606	-.013	-.012	-.006

Case 3 flow conditions was obtained. Although the latter was always higher than the former, it was not considered necessary to enhance the diffusivity by a factor of ten as carried out by Vignes and Trambouze to improve their theoretical predictions.

1-B-3 Saponification of Ethyl Acetate Isothermal and Nonisothermal Conditions

Shinohara(8) investigated the saponification of ethyl acetate in dilute aqueous solutions. Experiments were performed under the following conditions:

Isothermal Reactor:

Temperature:	25° to 35°C
Average Velocity:	0.26 to 1.70 cm./sec.
Inlet Concentration:	0.023 to 0.048 mole ethyl acetate/ℓ

Nonisothermal Reactor:

Inlet Temperature:	20.95° to 34.50°C
Wall Temperature:	21.00° to 37.15°C
Average Velocity:	0.38 to 1.79 cm./sec.
Inlet Concentration:	0.036 to 0.050 mole ethyl acetate/ℓ

Results are given in Table 1-6.

TABLE 1-6

COMPARISON OF SHINOHARA'S EXPERIMENTAL RESULTS WITH PRESENT STUDY THEORETICAL RESULTS

Run No.	Shinohara's <x> Expt	<x> Present Study			Differences		
		Case 1	Case 2	Case 3	Case 1	Case 2	Case 3
758	.5290	.5141	.5620	.5554	+.0149	-.0330	-.0264
759	.5383	.4992	.5477	.5407	+.0391	-.0094	-.0024
760	.5285	.4900	.5390	.5320	+.0385	-.0105	-.0035
761	.4607	.4204	.4716	.4642	+.0403	-.0109	-.0035
762	.4312	.3808	.4326	.4247	+.0504	-.0014	+.0065
763	.4448	.4042	.4558	.4480	+.0406	-.0110	-.0032
764	.4706	.4359	.4871	.4799	+.0347	-.0165	-.0093
765	.4851	.4521	.5029	.4958	+.0330	-.0178	-.0107
766	.5042	.4782	.5308	.5232	+.0260	-.0266	-.0190
767	.4769	.4481	.5026	.4946	+.0288	-.0257	-.0177
768	.4704	.4398	.4947	.4866	+.0306	-.0243	-.0162
769	.4556	.4318	.4872	.4792	+.0238	-.0316	-.0236
770	.4410	.4141	.4705	.4625	+.0269	-.0295	-.0215
771	.4131	.3785	.4362	.4275	+.0346	-.0231	-.0144
772	.3991	.3639	.4222	.4136	+.0352	-.0231	-.0145
773	.3691	.3395	.3983	.3892	+.0296	-.0292	-.0201
774	.3360	.2938	.3526	.3434	+.0422	-.0166	-.0074
775	.3588	.3243	.3831	.3739	+.0345	-.0243	-.0151
776	.5152	.5013	.5523	.5443	+.0139	-.0371	-.0291
777	.5069	.4864	.5386	.5301	+.0205	-.0317	-.0232
780	.4673	.4467	.5016	.4928	+.0206	-.0343	-.0255
781	.4588	.4270	.4829	.4740	+.0318	-.0241	-.0152
782	.4329	.3996	.4570	.4478	+.0333	-.0241	-.0149
783	.3950	.3741	.4327	.4232	+.0209	-.0377	-.0282
784	.3813	.3536	.4126	.4030	+.0277	-.0313	-.0217
785	.3748	.3459	.4051	.3954	+.0289	-.0303	-.0206
786	.5612	.5205	.5699	.5620	+.0407	-.0087	-.0008
787	.5658	.5423	.5898	.5825	+.0235	-.0240	-.0167
788	.5645	.5387	.5865	.5791	+.0258	-.0220	-.0146
789	.5885	.5699	.6148	.6079	+.0186	-.0263	-.0194
790	.4943	.4671	.5180	.5110	+.0272	-.0237	-.0167
791	.4800	.4490	.5003	.4931	+.0310	-.0203	-.0131
792	.4790	.4435	.4948	.4876	+.0355	-.0158	-.0086

Continued

TABLE 1-6

(continued)

Run No.	Shinohara's <x> Expt	<x> Present Study			Differences		
		Case 1	Case 2	Case 3	Case 1	Case 2	Case 3
793	.4461	.4075	.4596	.4522	+.0386	-.0135	-.0061
794	.4561	.4212	.4733	.4661	+.0349	-.0172	-.0100
795	.4182	.3850	.4373	.4298	+.0332	-.0191	-.0116
796	.4093	.3701	.4225	.4149	+.0392	-.0132	-.0056
797	.4076	.3645	.4167	.4092	+.0431	-.0091	-.0016
798	.3940	.3509	.4028	.3953	+.0431	-.0088	-.0013
799	.3521	.3070	.3580	.3503	+.0451	-.0059	+.0018
629	.6860	.6923	.7237	.7150	-.0063	-.0377	-.0290
630	.6803	.6906	.7222	.7135	-.0103	-.0419	-.0332
631	.6664	.6556	.6913	.6815	+.0108	-.0249	-.0151
632	.6634	.6570	.6925	.6828	+.0064	-.0291	-.0194
633	.6102	.6076	.6484	.6370	+.0026	-.0382	-.0268
634	.6125	.6048	.6459	.6344	+.0077	-.0334	-.0219
635	.7868	.7691	.7912	.7850	+.0177	-.0044	+.0018
636	.7388	.7374	.7634	.7563	+.0014	-.0246	-.0175
637	.7136	.6977	.7285	.7201	+.0159	-.0149	-.0065
709	.6946	.6664	.7005	.6909	+.0282	-.0059	+.0037
710	.6672	.6408	.6783	.6679	+.0264	-.0111	-.0007
711	.6590	.6304	.6693	.6586	+.0286	-.0103	+.0004
712	.6033	.5894	.6337	.6217	+.0139	-.0304	-.0184
713	.5843	.5641	.6115	.5988	+.0202	-.0272	-.0145
714	.5540	.5342	.5854	.5716	+.0198	-.0314	-.0176
716	.4251	.4038	.4694	.4520	+.0213	-.0443	-.0269
717	.6980	.6936	.7244	.7156	+.0044	-.0264	-.0176
719	.6580	.6393	.6769	.6661	+.0187	-.0189	-.0081
720	.6596	.6395	.6770	.6665	+.0201	-.0174	-.0069
721	.6029	.5823	.6268	.6142	+.0206	-.0239	-.0113
722	.5747	.5570	.6043	.5911	+.0177	-.0296	-.0164
723	.5680	.5383	.5878	.5739	+.0297	-.0198	-.0059
724	.4532	.4494	.5080	.4916	+.0038	-.0548	-.0384
725	.4878	.4799	.5356	.5199	+.0079	-.0478	-.0321
726	.6022	.5735	.6193	.6071	+.0287	-.0171	-.0049
727	.5979	.5829	.6275	.6158	+.0150	-.0296	-.0179
728	.5784	.5370	.5872	.5740	+.0414	-.0088	+.0044
729	.5626	.5188	.5709	.5572	+.0438	-.0083	+.0054
730	.5620	.5150	.5677	.5538	+.0470	-.0057	+.0082
731	.5269	.4931	.5482	.5336	+.0338	-.0213	-.0067
732	.4986	.4755	.5323	.5171	+.0231	-.0337	-.0185
733	.4287	.3980	.4623	.4454	+.0307	-.0336	-.0167

APPENDIX 2

EXPERIMENTAL DATA AND RESULTS

2-A	Values of Physical Properties
2-B	Values of Dimensionless Parameters
2-C	Values of Gr/4Re
2-D	Experimental Data

2-A Values of Physical Properties

TABLE 2-1

VALUES OF PHYSICAL PROPERTIES

Run No.	T_o (°C)	ρ_{Ao} mole/ℓ	ρ_{Bo} mole/ℓ	ρ mole/ml	C_p cal/mole°K	$k_c(10^3)$ cal/cm.sec°K	$D_{AB}(10^5)$ cm^2/sec	<u> cm/sec
CWT REACTOR								
13	27.42	1.282	43.26	.05268	19.15	1.392	1.01	0.856
14	27.00	0.936	43.95	.05277	19.03	1.393	0.99	0.629
17B	26.72	0.770	46.84	.05352	18.74	1.413	0.99	0.804
17C	27.11	0.769	46.91	.05354	18.74	1.414	1.00	0.804
24	38.91	0.612	43.36	.05237	19.02	1.421	1.31	0.629
15	26.70	0.291	50.84	.05438	18.35	1.435	0.99	0.753
AIR JACKETED REACTOR								
2	27.29	1.356	43.27	.05271	19.17	1.394	1.00	1.086
3	27.48	1.252	43.18	.05265	19.16	1.391	1.01	0.856
4	27.26	0.890	44.74	.05298	18.95	1.399	1.00	0.629
1	27.16	0.880	47.36	.05369	18.72	1.419	1.00	1.316
7	27.51	0.722	46.90	.05351	18.73	1.413	1.01	0.804
34	36.55	0.694	43.35	.05242	19.05	1.422	1.25	0.629
8	27.17	0.575	45.76	.05316	18.80	1.402	1.00	0.402
6	26.79	0.350	49.72	.05412	18.44	1.428	0.99	0.578
5	26.68	0.330	50.91	.05441	18.35	1.436	0.99	0.753
INSULATED REACTOR								
2P	27.12	1.470	43.19	.05273	19.20	1.395	1.00	1.086
2PC	26.21	1.432	43.32	.05278	19.18	1.395	0.97	1.086
3P	27.03	1.325	43.59	.05281	19.13	1.396	0.99	0.856
3PC	26.34	1.316	43.07	.05266	19.18	1.392	0.98	0.856
31PC	36.23	1.285	42.94	.05251	19.20	1.427	1.24	1.316
32PC	36.96	1.210	42.44	.05232	19.23	1.422	1.26	1.086
33PC	36.73	0.995	42.49	.05226	19.19	1.419	1.25	0.856
4PC	26.21	0.994	44.05	.05284	19.03	1.395	0.97	0.629
4P	26.83	0.946	44.37	.05291	18.99	1.397	0.99	0.629
7PC	25.57	0.795	46.76	.05353	18.75	1.413	0.96	0.804
34PC	36.23	0.680	43.59	.05249	19.03	1.423	1.24	0.629
37PC	35.45	0.582	46.37	.05324	18.76	1.445	1.21	0.804

2-B Values of Dimensionless Parameters

TABLE 2-2

VALUES OF DIMENSIONLESS PARAMETERS

Run No.	$G_1 (\times 10^3)$	G_2	$G_3 (\times 10^{-9})$	$G_4 (\times 10^2)$	w	Re
CWT REACTOR						
13	7.32	22.81	10.610	0	.232	188
14	7.14	22.16	5.886	0	.317	137
17B	7.03	21.78	4.114	0	.252	174
17C	7.10	21.75	4.104	0	.252	175
24	9.18	20.50	2.766	0	.326	174
15	6.88	20.05	0.8954	0	.274	163
AIR JACKETED REACTOR						
2	7.25	22.95	11.830	5.619	.182	238
3	7.33	22.75	10.150	5.193	.231	188
4	7.18	22.04	5.357	3.712	.318	138
1	7.08	22.02	5.181	3.668	.154	287
7	7.16	21.60	3.684	3.014	.252	177
34	8.78	20.89	3.412	2.940	.325	166
8	7.13	21.19	2.542	2.408	.501	88
6	6.92	20.35	1.168	1.470	.356	125
5	6.88	20.26	1.068	1.386	.274	163
INSULATED REACTOR						
2P	7.26	23.15	13.880	6.083	.182	237
2PC	7.04	23.16	13.180	5.935	.182	232
3P	7.16	22.92	11.290	5.492	.232	186
3PC	7.11	22.95	11.170	5.464	.231	183
31PC	8.76	22.17	10.390	5.380	.154	346
32PC	8.92	21.98	9.276	5.104	.187	289
33PC	8.83	21.59	6.444	4.207	.237	227
4PC	6.99	22.35	6.560	4.147	.317	134
4P	7.12	22.20	5.985	3.945	.317	136
7PC	6.82	21.93	4.350	3.328	.251	169
34PC	8.70	20.88	3.296	2.878	.325	165
37PC	8.36	20.64	2.513	2.453	.258	208

2-C Values of Gr/4Re

The Grashof number, Gr is defined as

$$Gr = g\,\bar{\rho}^2\,\beta\,d^3\,\Delta T/\mu^2$$

where g = 980.665 cm./sec^2

$\bar{\rho}$ = density of the solution

= 1.00 gm./cm^3

β = thermal expansion coefficient

= 2.97×10^{-4} $^0C^{-1}$

d = diameter, cm.

ΔT = radial temperature difference, ^0C

μ = viscosity of water (g./cm. sec.)

The Grashof number was evaluated for all nonisothermal experiments. The viscosity of the solution was taken as the viscosity of water at the average temperature recorded by Probe 8. Values of Grashof numbers, Reynolds numbers and Gr/4Re appear in Table 2-3.

TABLE 2-3

VALUES OF Gr/4Re

Run No.	$\Delta T_{\text{Probe 8}}$ (^{o}C)	$\mu_{\text{Probe 8}}$ (x 10^{2}g./cm. sec)	Gr (x 10^{-3})	Re	Gr/4Re
2	0.65	.8004	19	238	20
3	0.69	.7635	22	188	29
4	0.56	.7729	18	138	33
1	0.43	.7912	13	287	11
7	0.63	.7830	19	177	27
34	1.52	.6437	69	166	104
8	0.73	.7798	23	88	65
6	0.32	.8151	9.1	125	18
5	0.27	.8245	7.5	163	12
2P	0.32	.7922	9.6	237	10
2PC	0.34	.7987	10	232	11
3P	0.48	.7737	15	186	20
3PC	0.36	.7837	11	183	15
31PC	0.76	.6395	35	346	25
32PC	0.86	.6223	42	289	36
33PC	1.05	.6231	51	227	56
4PC	0.59	.7776	18	134	34
4P	0.50	.7714	16	136	29
7PC	0.39	.8166	11	169	16
34PC	1.03	.6399	48	165	73
37PC	1.29	.6702	54	208	65

2-D Experimental Data

TABLE 2-4

RADIAL TEMPERATURES (°C)

CWT REACTOR

	Radial Position / Probe no.	1 a = 1	2	3	4 a = 0	5	6	7 a = 1
Run no. 13	1	27.48	27.40	27.50	27.50	27.50	27.43	26.99
	2	27.26	27.50	27.50	27.50	27.48	27.33	26.57
	3	27.28	27.50	27.52	27.52	27.52	27.40	26.77
	4	27.45	27.65	27.65	27.65	27.57	27.48	26.74
	5	27.43	27.67	27.70	27.70	27.67	27.55	27.04
	6	27.45	27.77	27.77	27.74	27.72	27.62	27.18
	7	27.58	27.70	27.73	27.68	27.51	27.07	26.80
	8	27.34	27.46	27.46	27.46	27.43	27.24	26.48
Run no. 14	1	27.16	27.09	27.26	27.26	27.26	27.21	27.04
	2	27.06	27.11	27.11	27.09	27.04	26.82	26.18
	3	26.94	27.06	27.06	27.06	27.06	26.91	26.33
	4	26.89	27.18	27.18	27.16	27.11	27.01	26.33
	5	26.91	27.18	27.21	27.21	27.11	26.99	26.57
	6	27.11	27.23	27.21	27.21	27.21	27.06	26.40
	7	27.07	27.19	27.19	27.17	26.97	26.68	26.24
	8	27.09	27.17	27.17	27.17	27.14	26.92	26.34
Run no. 15	1	27.21	27.38	27.38	27.38	27.33	27.11	26.77
	2	26.48	26.82	26.82	26.79	26.77	26.65	26.16
	3	26.48	26.74	26.82	26.82	26.77	26.60	26.23
	4	26.52	26.84	26.82	26.82	26.82	26.70	26.30
	5	26.57	26.82	26.82	26.82	26.72	26.48	26.26
	6	26.55	26.82	26.82	26.82	26.79	26.50	26.29
	7	26.68	26.75	26.75	26.73	26.60	26.36	26.14
	8	26.63	26.73	26.73	26.73	26.65	26.36	26.17
Run no. 17B	1	27.65	27.72	27.72	27.70	27.50	27.30	26.62
	2	26.33	26.67	26.67	26.67	26.67	26.57	25.74
	3	26.52	26.82	26.82	26.82	26.82	26.72	26.13
	4	26.62	26.89	26.89	26.89	26.89	26.72	26.11
	5	26.79	26.99	26.99	26.99	26.99	26.82	26.40
	6	26.65	26.79	26.72	26.72	26.72	26.60	25.94
	7	26.65	26.78	26.78	26.73	26.62	26.41	25.87
	8	26.53	26.65	26.70	26.60	26.46	26.46	25.87
Run no. 17C	1	27.70	27.84	27.84	27.79	27.62	27.28	26.79
	2	26.60	27.24	27.21	27.21	27.06	26.82	26.13
	3	26.74	27.24	27.28	27.28	27.33	27.06	26.30
	4	26.72	27.43	27.38	27.30	27.30	26.89	26.26
	5	26.92	27.35	27.35	27.39	27.33	27.00	26.50
	6	27.21	27.45	27.45	27.48	27.38	27.04	26.33
	7	27.17	27.29	27.31	27.24	27.07	26.60	26.24
	8	27.17	27.34	27.29	27.29	27.24	26.63	26.36

Continued

TABLE 2-4

(continued)

	Radial Position Probe no.	1 a = 1	2	3	4 a = 0	5	6	7 a = 1
Run no. 24	1	39.05	39.36	39.36	39.31	39.19	38.79	38.17
	2	38.63	39.04	39.04	39.04	38.97	38.83	38.17
	3	-	-	-	-	-	-	-
	4	38.78	38.33	39.11	39.11	39.11	39.11	38.56
	5	38.92	39.18	39.18	39.14	39.14	38.99	38.34
	6	-	-	-	-	-	-	-
	7	39.05	39.14	39.14	39.05	39.03	38.67	38.19
	8	39.98	39.07	39.05	39.05	39.00	38.69	38.36
AIR JACKETED REACTOR								
Run no. 1	1	27.23	27.21	27.13	27.23	27.09	27.13	27.09
	2	27.70	27.72	27.60	27.60	27.57	27.52	27.11
	3	28.11	28.11	28.04	28.04	28.04	28.06	27.77
	4	28.57	28.48	28.45	28.50	28.45	28.45	28.21
	5	28.94	28.87	28.91	28.99	28.94	28.89	28.52
	6	29.43	29.33	29.38	29.40	29.38	29.33	28.99
	7	29.75	29.75	29.70	29.78	29.68	29.39	28.87
	8	30.66	30.66	30.63	30.56	30.66	30.56	30.23
Run no. 2	1	27.26	27.26	27.28	27.30	27.38	27.28	27.28
	2	27.91	27.87	27.74	27.72	27.67	27.60	27.11
	3	28.09	28.06	28.06	28.06	28.06	28.16	27.84
	4	28.18	28.11	28.06	28.09	28.09	28.11	27.74
	5	29.40	29.40	29.40	29.43	29.43	29.57	29.21
	6	28.77	28.77	28.70	28.65	28.72	28.72	28.30
	7	29.19	29.19	29.21	29.21	29.21	29.07	28.41
	8	30.23	30.23	30.16	30.13	30.09	29.97	29.58
Run no. 3	1	27.41	27.41	27.41	27.41	27.50	27.65	27.60
	2	28.30	28.23	28.21	28.11	28.09	28.06	27.79
	3	28.91	28.91	28.94	29.01	29.01	28.91	28.72
	4	29.67	29.65	29.62	29.52	29.57	29.57	29.53
	5	30.23	30.23	30.28	30.30	30.55	30.48	30.13
	6	30.48	30.45	30.45	30.52	30.40	30.43	29.96
	7	30.87	30.87	30.97	30.97	31.02	30.78	30.28
	8	32.44	32.44	32.42	32.35	32.35	32.20	31.75
Run no. 4	1	27.23	27.23	27.26	27.26	27.30	27.28	27.23
	2	27.52	27.48	27.48	27.45	27.40	27.35	27.11
	3	28.65	28.65	28.65	28.67	28.67	28.60	28.35
	4	28.82	28.82	28.82	28.77	28.81	28.77	28.50
	5	30.23	30.23	30.26	30.28	30.28	30.13	29.99
	6	29.89	29.91	29.89	29.89	29.89	29.87	29.45
	7	30.37	30.42	30.42	30.42	30.40	30.18	29.78
	8	31.82	31.82	31.82	31.77	31.77	31.60	31.26

Continued

TABLE 2-4

(continued)

	Radial Position / Probe no.	1 a = 1	2	3	4 a = 0	5	6	7 a = 1
Run no. 5	1	26.67	26.67	26.67	26.67	26.67	26.70	26.70
	2	27.04	27.04	27.01	27.01	27.01	26.99	26.77
	3	27.28	27.28	27.28	27.30	27.23	27.23	27.06
	4	27.57	27.57	27.57	27.57	27.55	27.55	27.35
	5	27.77	27.77	27.77	27.82	27.82	27.74	27.72
	6	28.01	27.99	27.96	27.96	27.96	27.91	27.67
	7	28.24	28.21	28.26	28.26	28.26	28.12	27.95
	8	28.70	28.70	28.68	28.68	28.68	28.60	28.43
Run no. 6	1	26.79	26.79	26.79	26.79	26.79	26.79	26.82
	2	27.23	27.23	27.21	27.21	27.21	27.21	27.04
	3	27.65	27.65	27.65	27.65	27.62	27.62	27.43
	4	27.96	27.96	27.96	27.96	27.91	27.84	27.79
	5	28.16	28.16	28.16	28.16	28.21	28.13	28.04
	6	28.26	28.26	28.26	28.26	28.23	28.21	28.01
	7	28.65	28.65	28.65	28.63	28.63	28.41	28.31
	8	29.24	29.24	29.21	29.21	29.19	29.17	28.92
Run no. 7	1	27.48	27.48	27.48	27.48	27.60	27.60	27.48
	2	28.27	28.04	28.04	28.04	28.04	27.91	27.48
	3	28.48	28.48	28.48	28.48	28.62	28.57	28.13
	4	29.09	29.09	28.99	28.94	29.01	29.13	28.55
	5	29.45	29.47	29.47	29.52	29.62	29.62	29.30
	6	29.82	29.74	29.74	29.77	29.79	29.74	29.28
	7	30.28	30.35	30.35	30.35	30.37	30.01	29.53
	8	31.19	31.17	31.14	31.14	31.14	31.09	30.56
Run no. 8	1	27.21	27.21	27.21	27.18	27.18	27.18	27.04
	2	27.94	27.91	27.91	27.91	27.91	27.77	27.30
	3	28.65	28.65	28.65	28.67	28.67	28.52	28.21
	4	29.28	29.28	29.28	29.23	29.23	29.18	28.67
	5	29.89	29.89	29.89	29.89	29.87	29.65	29.30
	6	30.18	30.18	30.18	30.18	30.11	29.84	29.62
	7	30.73	30.75	30.70	30.63	30.51	30.09	29.70
	8	31.41	31.41	31.41	31.39	31.36	31.19	30.68
Run no. 34	1	36.81	36.91	36.91	36.91	36.72	36.17	35.43
	2	37.71	37.76	37.76	37.71	37.71	37.49	35.39
	3	38.36	38.36	38.34	38.19	38.00	37.53	36.50
	4	39.14	39.21	39.21	39.21	39.09	39.07	38.02
	5	39.59	39.61	39.61	39.59	39.51	39.11	37.78
	6	39.91	39.74	39.31	38.93	38.36	37.73	37.53
	7	40.55	40.55	40.55	40.48	40.12	39.55	38.43
	8	41.31	41.36	41.36	41.31	41.17	40.72	39.84
INSULATED REACTOR								
Run no. 2P	1	27.20	27.18	27.18	27.18	27.08	27.08	26.93
	2	27.90	27.90	27.88	27.88	27.88	27.88	27.76
	3	28.12	28.10	28.10	28.07	28.05	28.00	27.95
	4	28.73	28.73	28.80	28.75	28.75	28.75	28.66
	5	29.22	29.22	29.19	29.05	29.05	29.00	28.90
	6	29.61	29.56	29.39	29.37	29.32	29.22	29.12
	7	29.88	29.93	29.93	29.93	30.00	29.95	29.61
	8	30.56	30.54	30.59	30.54	30.54	30.51	30.27

Continued

TABLE 2-4

(continued)

	Radial Position / Probe no.	1 a = 1	2	3	4 a = 0	5	6	7 a = 1
Run no. 2PC	1	26.25	26.22	26.20	26.20	26.22	26.22	26.14
	2	26.88	26.85	26.80	26.75	26.75	26.75	26.75
	3	27.07	27.07	27.07	27.07	27.10	27.07	26.93
	4	27.53	27.53	27.56	27.56	27.56	27.56	27.48
	5	-	-	-	-	-	-	-
	6	28.42	28.37	28.34	28.25	28.25	28.20	28.12
	7	29.25	29.25	29.29	29.29	29.27	29.20	28.93
	8	30.24	30.24	30.17	30.12	30.12	30.07	29.90
Run no. 3P	1	27.10	27.10	27.00	26.98	27.05	27.05	26.93
	2	27.78	27.78	27.78	27.71	27.78	27.78	27.69
	3	28.05	28.00	27.95	28.07	28.10	28.00	27.93
	4	-	-	-	-	27.95	27.80	27.95
	5	29.41	29.39	29.32	29.14	29.12	29.07	28.95
	6	29.64	29.64	29.56	29.51	29.46	29.44	29.44
	7	30.44	30.54	30.54	30.49	30.49	30.44	30.17
	8	31.81	31.76	31.62	31.64	31.71	31.33	-
Run no. 3PC	1	26.44	26.32	26.40	26.40	26.32	26.27	26.22
	2	27.22	27.03	26.95	26.90	26.98	26.88	26.95
	3	27.32	27.34	27.34	27.34	27.34	27.34	27.29
	4	28.12	28.14	28.05	28.07	28.00	28.00	27.90
	5	-	-	-	-	-	-	-
	6	29.12	29.05	29.00	28.98	28.88	28.85	28.83
	7	29.93	29.93	30.05	30.05	30.03	29.95	29.71
	8	31.14	31.12	31.10	31.02	31.02	30.98	30.78
Run no. 4P	1	26.86	26.86	26.86	26.86	26.86	26.79	26.69
	2	27.76	27.64	27.59	27.47	27.47	27.47	27.42
	3	27.95	27.88	27.83	27.83	27.83	27.83	27.68
	4	28.73	28.68	28.68	28.68	28.56	28.51	28.51
	5	29.27	29.27	29.19	29.12	29.10	29.07	29.05
	6	29.44	29.37	29.34	29.34	29.29	29.27	29.25
	7	30.68	30.68	30.68	30.68	30.68	30.59	30.12
	8	31.95	31.93	31.81	31.79	31.69	31.45	-
Run no. 4PC	1	26.22	26.35	26.35	26.13	26.30	26.08	26.05
	2	27.00	26.88	26.88	26.88	26.78	26.88	26.88
	3	27.39	27.34	27.34	27.29	27.44	27.37	27.27
	4	28.17	28.24	28.17	28.17	28.14	28.14	28.00
	5	-	-	-	-	-	-	-
	6	29.32	29.22	29.12	29.07	29.03	28.98	28.88
	7	30.25	30.27	30.32	30.39	30.29	30.27	29.83
	8	31.57	31.57	31.50	31.52	31.40	31.24	30.98
Run no. 7PC	1	25.70	25.60	25.58	25.50	25.58	25.55	25.45
	2	-	-	-	-	-	-	-
	3	26.24	26.29	26.24	26.46	26.36	26.44	26.34
	4	27.05	27.05	26.97	26.97	26.80	26.90	26.83
	5	-	-	-	-	-	-	-
	6	27.46	27.42	27.39	27.34	27.27	27.27	27.22
	7	28.22	28.25	28.25	28.34	28.34	28.34	28.03
	8	29.17	29.17	29.07	29.07	29.15	29.15	28.78

Continued

TABLE 2-4

(continued)

	Radial Position Probe no.	1 a = 1	2	3	4 a = 0	5	6	7 a = 1
Run no. 31PC	1	36.39	36.39	36.39	36.39	36.39	36.15	35.53
	2	–	–	–	36.92	36.92	36.95	36.37
	3	37.58	37.51	37.56	37.56	37.44	37.44	36.83
	4	38.60	38.60	38.53	38.48	38.45	38.43	38.00
	5	–	–	–	–	–	–	–
	6	39.51	39.41	39.21	39.09	38.99	38.95	38.87
	7	40.14	40.12	40.16	40.16	40.16	39.88	39.42
	8	41.52	41.50	41.52	41.47	41.47	41.35	40.76
Run no. 32PC	1	37.10	37.15	37.08	37.12	37.08	36.86	36.34
	2	38.00	37.97	37.90	37.85	37.83	37.83	37.21
	3	38.62	38.55	38.57	38.55	38.40	38.36	37.66
	4	39.74	39.62	39.64	39.55	39.48	39.31	38.81
	5	–	–	–	40.42	40.23	40.04	39.85
	6	41.50	41.22	40.98	40.76	40.62	40.41	40.22
	7	41.50	41.50	41.57	41.57	41.57	41.33	40.62
	8	43.07	43.07	43.00	42.97	42.90	42.81	42.21
Run no. 33PC	1	37.03	36.93	36.86	36.77	36.89	36.60	36.05
	2	37.85	37.90	37.78	37.78	37.64	37.54	36.95
	3	38.45	38.45	38.48	38.40	38.36	38.26	37.70
	4	39.69	39.72	39.64	39.62	39.45	39.22	38.81
	5	–	–	–	–	–	–	–
	6	41.48	41.24	40.93	40.79	40.65	40.48	40.34
	7	41.59	41.66	41.59	41.59	41.54	41.35	40.66
	8	43.02	42.97	42.95	42.95	42.86	42.79	41.97
Run no. 34PC	1	36.50	36.48	36.50	36.43	36.29	36.00	35.43
	2	37.45	37.33	37.25	37.25	37.25	37.25	36.45
	3	38.05	38.00	38.00	37.90	37.90	37.68	37.05
	4	39.14	39.14	39.07	39.07	38.93	38.79	38.34
	5	–	–	–	–	–	–	–
	6	40.74	40.50	40.19	40.05	39.91	39.76	39.62
	7	40.56	40.66	40.64	40.62	40.52	40.28	39.40
	8	41.57	41.57	41.57	41.50	41.40	41.26	40.54
Run no. 37PC	1	35.65	35.67	35.67	35.58	35.53	35.31	34.71
	2	36.54	36.45	36.21	36.04	36.04	35.99	35.36
	3	36.50	36.59	36.59	36.59	36.52	36.33	35.74
	4	37.63	37.61	37.40	37.26	37.19	37.07	36.72
	5	–	–	–	–	–	–	–
	6	37.98	37.84	37.88	37.69	37.57	37.48	37.29
	7	38.21	38.29	38.28	38.31	38.31	38.02	37.19
	8	39.16	39.21	39.19	39.07	38.90	38.66	37.92

TABLE 2-5

AVERAGE TEMPERATURE RISES

Run No.	Experimental Temperature Rises at Probe 8	Temperature Rises at Outlet based on Experimental Conversion*	Computed Temperature Rises at Probe 8			Difference		
	(°C)	(°C)	Case 1 (°C)	Case 2 (°C)	Case 3 (°C)	Case 1 (°C)	Case 2 (°C)	Case 3 (°C)
<u>CWT REACTOR</u>								
13	-0.15	0	0	0	0	-0.15	-0.15	-0.15
14	0.00	0	0	0	0	0.00	0.00	0.00
17B	-0.25	0	0	0	0	-0.25	-0.25	-0.25
17C	-0.06	0	0	0	0	-0.06	-0.06	-0.06
24	-0.02	0	0	0	0	-0.02	-0.02	-0.02
15	-0.13	0	0	0	0	-0.13	-0.13	-0.13
<u>AIR JACKETED REACTOR</u>								
2	2.73	5.69	6.42	5.65	5.75	-3.69	-2.92	-3.02
3	4.80	6.37	7.60	6.59	6.69	-2.80	-1.79	-1.89
4	4.43	6.85	6.90	5.96	6.03	-2.47	-1.53	-1.60
1	3.41	5.16	3.64	3.25	3.30	-0.23	+0.16	+0.11
7	3.55	4.50	4.75	4.14	4.19	-1.20	-0.59	-0.64
34	4.47	8.30	8.00	7.13	7.17	-3.53	-2.66	-2.70
8	4.09	6.06	5.83	5.13	5.17	-1.74	-1.04	-1.08
6	2.38	3.12	2.91	2.55	2.58	-0.53	-0.17	-0.20
5	1.96	2.55	2.31	2.03	2.05	-0.35	-0.07	-0.09
<u>INSULATED REACTOR</u>								
2P	3.39	6.82	6.81	6.00	6.11	-3.42	-2.61	-2.72
2PC	3.91	5.35	6.19	5.48	5.59	-2.28	-1.57	-1.68
3P	4.61	8.26	7.72	6.69	6.81	-3.11	-2.08	-2.20
3PC	4.68	8.08	7.35	6.39	6.50	-2.67	-1.71	-1.82
31PC	5.14	7.90	9.69	8.31	8.40	-4.55	-3.17	-3.26
32PC	5.90	10.43	11.16	9.55	9.62	-5.26	-3.65	-3.72
33PC	6.06	10.08	10.30	8.92	8.98	-4.24	-2.86	-2.92
4PC	5.19	7.34	7.23	6.24	6.33	-2.04	-1.05	-1.14
4P	4.95	7.08	7.14	6.16	6.24	-2.19	-1.21	-1.29
7PC	3.51	5.52	4.63	4.05	4.11	-1.12	-0.54	-0.60
34PC	5.11	8.43	7.74	6.88	6.91	-2.63	-1.77	-1.80
37PC	3.42	5.75	5.73	5.01	5.04	-2.31	-1.59	-1.62

* Since conversion and temperature rises were evaluated at points 50 cm. apart, no comparison could be made between experimental temperature rises and temperature rises based on experimental conversions.

TABLE 2-6

COMPUTED AND EXPERIMENTAL ACETIC ANHYDRIDE CONCENTRATION, $\langle x \rangle = \rho_{A_{outlet}}/\rho_{A_o}$

Run No.	<x> Expt	<x> Computed			Difference		
		Case 1	Case 2	Case 3	Case 1	Case 2	Case 3
CWT REACTOR							
13	.694	.544	.596	.589	.150	.098	.105
14	.630	.412	.482	.475	.218	.148	.155
17B	.610	.487	.547	.541	.123	.063	.069
17C	.601	.477	.539	.532	.124	.062	.069
24	.461	.105	.185	.182	.356	.276	.279
15	.436	.382	.456	.450	.054	-.020	-.014
AIR JACKETED REACTOR							
2	.732	.529	.592	.585	.203	.140	.147
3	.676	.407	.492	.485	.269	.184	.191
4	.497	.279	.377	.370	.218	.120	.127
1	.595	.596	.644	.638	-.001	-.049	-.043
7	.575	.381	.463	.457	.194	.112	.118
34	.275	.064	.144	.141	.211	.131	.134
8	.301	.119	.212	.207	.182	.089	.094
6	.360	.252	.342	.337	.108	.018	.023
5	.433	.356	.436	.431	.077	-.003	.002
INSULATED REACTOR							
2P	.703	.535	.598	.591	.168	.105	.112
2PC	.760	.565	.622	.615	.195	.138	.145
3P	.599	.427	.509	.502	.172	.090	.097
3PC	.609	.449	.527	.519	.160	.082	.090
31PC	.625	.305	.406	.401	.320	.219	.224
32PC	.485	.188	.299	.295	.297	.186	.190
33PC	.396	.123	.225	.221	.273	.171	.175
4PC	.523	.312	.408	.401	.211	.115	.122
4P	.514	.293	.390	.383	.221	.124	.131
7PC	.526	.442	.516	.509	.084	.010	.017
34PC	.244	.070	.153	.150	.174	.091	.094
37PC	.356	.160	.256	.252	.196	.100	.104

APPENDIX 3

ANALYTICAL METHOD AND PHYSICAL PROPERTIES

3-A Determination of Acetic Anhydride Concentration

3-B Physical Properties of the System

3-A Determination of Acetic Anhydride Concentration. The Aniline-Water Method.

This method described earlier by Caudri(39) was used in the present study to determine the concentration of acetic anhydride at the inlet and outlet of the reactor. This method was also employed in the kinetics experiments.

Let us first consider the change in concentration occurring at the inlet of the reactor. Let us call a, the number of moles of acetic anhydride and b, the number of moles of water present at the entrance of the mixing chamber when the two reactants met. Assume that c moles of acetic anhydride have already been reacted when the solution arrives at the inlet of the reactor. So, the number of moles of reactants left and the number of moles of acetic acid produced are

$$\begin{array}{ccccc} (CH_3CO)_2O & + & H_2O & \rightarrow & 2CH_3COOH \\ (a-c) & & (b-c) & & 2c \end{array}$$

If the sample is allowed to go to completion, the concentrations will be

$$\begin{array}{ccccc} (CH_3CO)_2O & + & H_2O & \rightarrow & 2CH_3COOH \\ o & & (b-a) & & 2a \end{array}$$

If the reaction is quenched with a saturated aniline-water solution, the number of moles of acetic anhydride and acetic acid present in the inlet sample will be

$$\begin{array}{ccccccc} (CH_3CO)_2O & + & C_6H_5NH_2 & \rightarrow & CH_3COOH & + & CH_3CONHC_6H_5 \\ o & & & & (a+c) & & \end{array}$$

The same reasoning is applied at the outlet of the reactor assuming x moles of acetic anhydride have reacted in the reactor. Concentration values are summarized in Table 3-1.

Table 3-1

Concentration Values

Time	Total moles acid present when titrating sample	C_A (moles acetic anhydride unreacted with water)
initially	o	$a = C_{Ao}$
inlet	(a+c)	(a-c)
outlet	(a+c+x)	(a-c-x)
infinity	2a	o

(a+c) and (a+c+x), the total number of moles of acid present in the inlet and outlet samples after the addition of aniline-water, respectively, were determined by titration. By substracting the total number of moles of acid present in the sample at the reactor inlet (a+c) from that present at infinity (2a), the number of moles of acetic anhydride (a-c) present at the reactor inlet was obtained. Finally, by substracting the total number of moles of acid present in the sample at the reactor outlet (a+c+x) from that present at completion (2a), the number of moles of acetic anhydride (a-c-x) present at the reactor outlet was obtained. When calculating the ratio of (a-c-x) to (a-c), the experimental value of the dimensionless concentration, <x>, of unreacted acetic anhydride was estimated and compared with its corresponding simulated value obtained by computer.

3-B Physical Properties of the System Acetic anhydride-water-acetic acid

3-B-1 Inlet Concentrations

ρ_{Ao}, the number of moles of acetic anhydride per cm^3 of solution at the reactor inlet was obtained directly from titration of inlet solution together with titration of a completely reacted solution. In all runs, the calculations were based on a 10 ml. sample.

Sample Calculation

RUN NO. 3P

Time	Volume 1 N NaOH (ml)	C_A (mole/10 ml.)
initially	-	C_{Ao} = 0.02071
inlet	28.17	0.01325
outlet	33.48	0.00794
infinity	41.42	-

The dimensionless experimental concentration was calculated as the ratio of the outlet to the inlet concentration.

$$\langle x \rangle_{\text{expt.}} = \frac{C_{A_{\text{outlet}}}}{C_{A_{\text{inlet}}}} = \frac{0.00794}{0.01325} = 0.599$$

$$\rho_{A_o} = 0.01 \times C_{A_{\text{inlet}}} = 1.325 \times 10^{-3} \text{ mole/cm}^3$$

ρ_{Bo}, the number of moles of water per cm^3 of solution at the reactor inlet was obtained from the following equations:

$$\frac{C_{B_{inlet}} \cdot M_{water}}{\rho_{water}} + \frac{C_{A_{inlet}} \cdot M_A}{\rho_A} + \frac{C_{\substack{acid\\inlet}} \cdot M_{acid}}{\rho_{acid}} = 10$$

$$C_{\substack{acid\\inlet}} = 2(C_{Ao} - C_{A_{inlet}})$$

$$\rho_{Bo} = 0.01 \times C_{B_{inlet}}$$

3-B-2 Diffusivity, D_{AB}

The diffusivity of acetic anhydride into water was calculated according to the Hayduk-Laudie(19) equation.

$$D_{AB} = \frac{13.26 \times 10^{-5}}{V_A^{0.589}\ \mu_B^{1.14}}$$

where $$V_A = \frac{M_A}{\rho_{B.P._A}} = \frac{102.09}{0.925} = 110.4 \text{ ml./g.mole}$$

$$V_A^{0.589} = 15.97$$

M_A, the molecular weight of acetic anhydride and $\rho_{B.P._A}$, its density at normal boiling point, were obtained from Hydrocarbon Processing(40). The viscosity of water, μ_B, was determined at the inlet temperature and assumed to remain constant throughout the reactor. The values of water viscosity at different temperatures were obtained from Perry(38).

3-B-3 Density, ρ

The molal density of the mixture, ρ, was calculated according to the following equation:

$$\rho = \frac{mf_A \cdot \rho_A}{M_A} + \frac{mf_B \cdot \rho_B}{M_B} + \frac{mf_C \cdot \rho_C}{M_C}$$

ρ : mole/cm^3

ρ_A, the density of acetic anhydride, was obtained from Timmermans(41) and ρ_B, the density of water was taken from Handbook of Chemistry and Physics(42). ρ_C, the density of acetic acid, and M_A, the molecular weight of acetic anhydride, were obtained from Hydrocarbon Processing(40). M_B and M_C, the molecular weights of water and acetic acid were taken as 18.02 and 60.05, respectively. Since they are properties of the mixture, ρ and C_p were calculated per mole of mixture.

3-B-4 Heat Capacity, C_p

The molal heat capacity of the mixture, C_p, was calculated according to the equation(43).

$$C_p = mf_A \cdot C_{P_A} \cdot M_A + mf_B \cdot C_{P_B} \cdot M_B + mf_C \cdot C_{P_C} \cdot M_C$$

where C_p : cal/mole°C.

C_{P_A} and C_{P_C} were read from a graph of Hydrocarbon Processing(40) and C_{P_B} was obtained from the Handbook of Chemistry and Physics.(42)

3-B-5 Thermal Conductivity, k_c

The thermal conductivity of the mixture, k_c, was calculated from the following equation:

$$k_c = mf_A \cdot k_{c_A} + mf_B \cdot k_{c_B} + mf_C \cdot k_{c_C}$$

k_c : cal/sec. cm. °K.

k_{c_A} and k_{c_C} were read from Hydrocarbon Processing (40) and k_{c_B} was obtained from Hsu (44).

3-B-6 Heat of Reaction, ΔH

The heat of hydrolysis, ΔH, was taken as -12.54 kcal./mole at 25°C as given by Takashima (32). ΔH at temperatures higher than 25°C were obtained from the following equations (43):

$$\Delta H^o_T = \Delta H^o_{\text{reactants}} + \Delta H^o_{298} + \Delta H^o_{\text{products}}$$

$$\Delta H^o_T = \Delta H^o_{298} + \sum_{\text{products}} (n \int_{298}^{T} C^o_p \, dT) - \sum_{\text{reactants}} (n \int_{298}^{T} C^o_p dT)$$

Measured heat of reaction values at different temperatures and acetic anhydride concentrations appear in Table 3-2.

TABLE 3-2

HEAT OF REACTION VALUES

$-\Delta H$ (kcal/mole)	T (^oC)	ρ_A (mole/ℓ.)	Authors
9.34	-	8.85	Marmers (36)
12.54	25	0.2488	Takashima (32)
13.73	40	0.2488	Takashima (32)
13.96	30	-	Conn (45)
13.96	25	0.1507	Takashima (32)
14.3 ± .4	30,65	0.25	Glasser (31)
14.6 ± 2.8	35 to 65	0.17	Dyne (33)
14.97	10	0.2488	Takashima (32)
15.05	25	0.0759	Takashima (32)
16.1	25	∞ dilution	Takashima (32)

APPENDIX 4

EQUIPMENT DETAILS

1. Metering Pump:

Manufacturer: Milton Roy Co.

Model: Duplex D4 117 and Mo DO 117

Specifications: Both sides positive displacement

Rated pressure: 1,000 psi

Maximum flow rates: 1.5 and 5.0 cm^3/sec

2. Millivolt Potentiometer:

Manufacturer: Leeds and Northrup

Model: 8686 Millivolt Potentiometer

Specifications: Scale: 1 to 10 m.v. ± 0.00025 m.v.

3. Mixing Chamber:

Volume: 1 litre

Mounted with a one litre plastic surge tank

Mixing: 1.5 hp. motor

4 sets of blades and baffles

4. Thermometer:

Manufacturer: Fisher Scientific

Model: Total Immersion White Back Thermometer

Range: 0.1 to 51°C ± 0.05°C

5. Thermocouples:

Manufacturer: Thermo Electric

Nominal O.D.: 1/16 in.

Specifications: Metal sheathed, ceramic insulated thermocouple wire

APPENDIX 5

PUMP AND THERMOCOUPLE CALIBRATIONS

5-A	Pump Calibration
5-B	Thermocouple Calibration

5-A Calibration of Pump

The duplex stainless-steel positive-displacement pump used in the experiments to pump reactants through the vertical reactor was calibrated as follows. The pump was set at a fixed percent stroke and water allowed to flow in the mixing chamber installed in the heat bath and then through the reactor. A volume of water was collected at the outlet of the reactor and registered for an interval of time. The calibration of the pump appears in Figure 5-1.

5-B Calibration of Thermocouples

Thermocouples were calibrated at two temperatures; (1) at 25°C and then the experiments were carried out and (2) at 35°C followed by experiments. They were inserted in a constant-temperature bath and calibrated against an ASTM thermometer from the Bureau of Standards (U.S.A.).

The difference between the real temperature (temperature read from the Bureau of Standards thermometer) and the read temperature (temperature obtained through readings on the potentiometer) was added to the temperature read by the potentiometer during experiments.

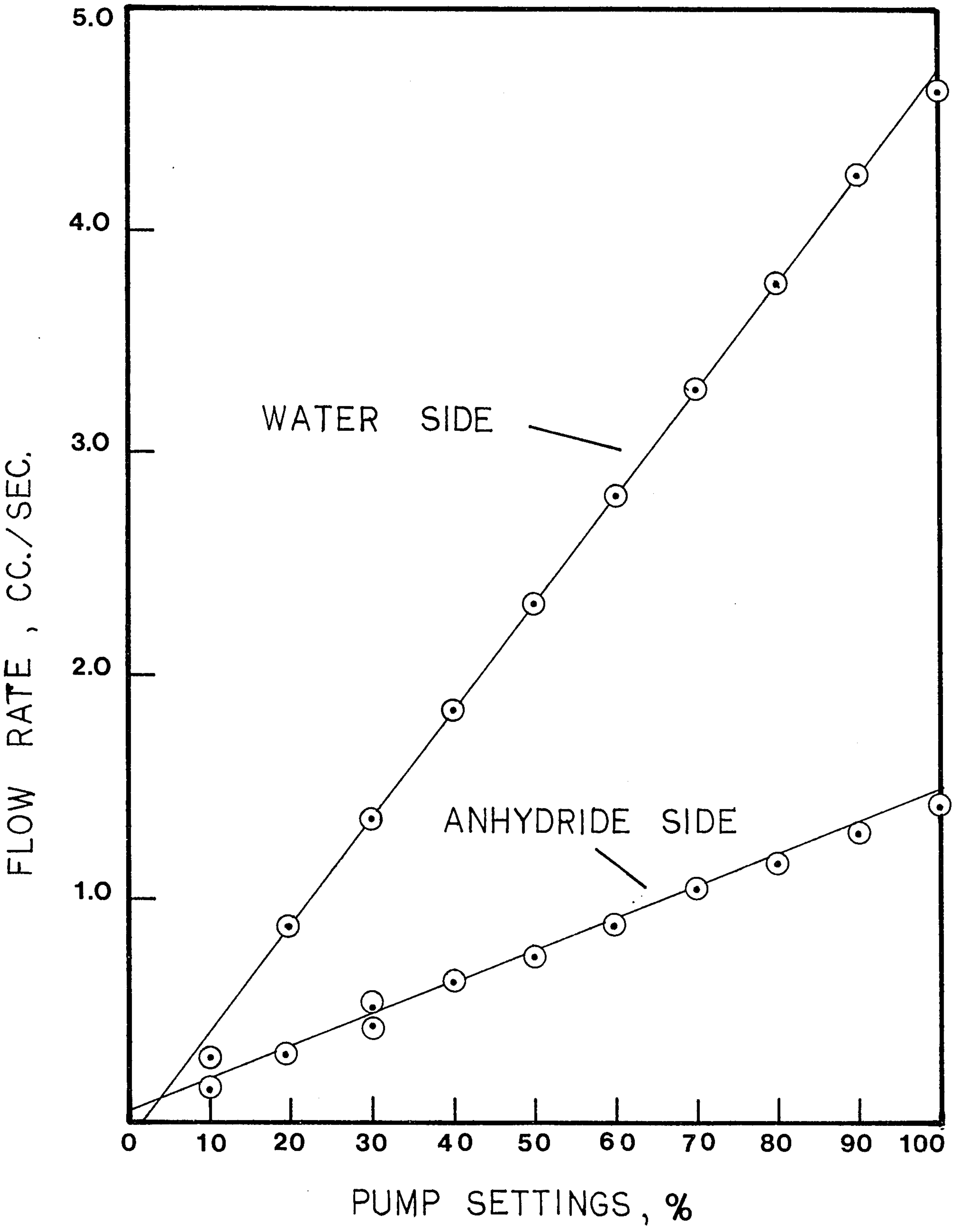

FIGURE 5-1 PUMP CALIBRATION CHART

TABLE 5-1

THERMOCOUPLES CALIBRATION

Calibration of Probes at 25°C

Probe#	Reading (mv)	T_{read} (°C)	T_{real} (°C)	Difference (°C)
1	.982	24.80	25.00	0.20
2	.945	23.90	25.00	1.10
3	.990	25.00	25.00	0.00
4	.987	24.93	25.00	0.07
5	.985	24.88	25.00	0.12*
6	.988	24.95	25.00	0.05*
7	.988	24.95	25.00	0.05
8	.990	25.00	25.00	0.00

Calibration of Probes at 35°C

Probe #	Reading (mv)	T_{read} (°C)	T_{real} (°C)	Difference (°C)
1	1.397	34.90	35.00	0.10
2	1.366	34.15	35.00	0.85
3	1.398	34.93	35.00	0.07
4	1.391	34.76	35.00	0.24
5	1.338	33.48	35.00	1.52*
6	1.345	33.64	35.00	1.36*
7	1.400	34.98	35.00	0.02
8	1.400	34.98	35.00	0.02

*N.B. Due to breakage of thermocouples, some thermocouples were changed between sets of experiments.

APPENDIX 6

GRID SPACINGS AND FINITE-DIFFERENCE EQUATIONS

6-A Determination of Grid Spacings

Limited numbers of radial and axial increments were used by previous workers(4,6) since computation time was the restricting parameter. In this study, the computer programme was written in the PLI language such that it could be compiled only once and executed many times. Compiling and execution were performed within less than 2 1/2 minutes computer time for the most complicated programme (Case 3). Programmes with different numbers of axial and radial increments were run and it was found that 100 radial and 500 axial increments could be run in less than 2 minutes execution time without yielding instability. This grid spacing was adopted in the theoretical survey.

In the experimental study, 120 radial and 300 axial increments were employed in order to minimize printing and get the computed values corresponding to a probe position. Since seven different radial temperatures were read, radial theoretical results were printed every 20 radial steps and since 8 probes (distant by the same length except the last two) were used, axial computed results were printed every 30 axial increments.

6-B Finite-Difference Equations

TABLE 6-1

FINITE-DIFFERENCE EQUATIONS

FIRST-ORDER REACTION

CWT CONDITIONS ($\theta_{wall} = 0$)

CASE 1

$0 \le a \le 1$	$A_1\ x_{m,n+1} = A_2\ x_{m,n}$
$0 < a < 1$	$A_3\ \theta_{m+1,n+1} + A_4\ \theta_{m,n+1} + A_5\ \theta_{m-1,n+1} = A_6$
$a = 0$	$A_7\ \theta_{2,n+1} + A_8\ \theta_{1,n+1} = A_9$

CASE 2

$0 \le a < 1$	$B_1\ x_{m,n+1} = B_2\ x_{m,n}$
$0 < a < 1$	$B_3\ \theta_{m+1,n+1} + B_4\ \theta_{m,n+1} + B_5\ \theta_{m-1,n+1} = B_6$
$a = 0$	$B_7\ \theta_{2,n+1} + B_8\ \theta_{1,n+1} = B_9$
$a = 1$	$x_{wall,n} = 0$ for $n \ge 2$

CASE 3

$0 < a < 1$	$C_1\ x_{m+1,n+1} + C_2\ x_{m,n+1} + C_3\ x_{m-1,n+1} = C_4$
$a = 0$	$C_5\ x_{2,n+1} + C_6\ x_{1,n+1} = C_7$
$a = 1$	$C_8\ x_{w,n+1} + C_9\ x_{w-1,n+1} + C_{10}\ x_{w-2,n+1} = C_{11}$
$0 < a < 1$	$C_{12}\ \theta_{m+1,n+1} + C_{13}\ \theta_{m,n+1} + C_{14}\ \theta_{m-1,n+1} = C_{15}$
$a = 0$	$C_{16}\ \theta_{2,n+1} + C_{17}\ \theta_{1,n+1} = C_{18}$

TABLE 6-2

FINITE-DIFFERENCE EQUATIONS

SECOND-ORDER REACTION

CWT CONDITIONS ($\theta_{wall} = 0$)

CASE 1

$$0 \leq a \leq 1 \qquad x_{m,n+1} = (-D_2 + \sqrt{D_2^2 - 4D_1D_3}\,) \,/\, 2D_1$$

$$0 < a < 1 \qquad D_4\ \theta_{m+1,n+1} + D_5\ \theta_{m,n+1} + D_6\ \theta_{m-1,n+1} = D_7$$

$$a = 0 \qquad D_8\ \theta_{2,n+1} + D_9\ \theta_{1,n+1} = D_{10}$$

CASE 2

$$0 \leq a < 1 \qquad x_{m,n+1} = (-E_2 + \sqrt{E_2^2 - 4E_1E_3}\,) \,/\, 2E_1$$

$$a = 1 \qquad x_{wall,n} = 0 \quad \text{for} \quad n \geq 2$$

$$0 < a < 1 \qquad E_4\ \theta_{m+1,n+1} + E_5\ \theta_{m,n+1} + E_6\ \theta_{m-1,n+1} = E_7$$

$$a = 0 \qquad E_8\ \theta_{2,n+1} + E_9\ \theta_{1,n+1} = E_{10}$$

CASE 3

$$0 < a < 1 \qquad F_1\ x_{m+1,n+1} + F_2\ x_{m,n+1} + F_3\ x_{m-1,n+1} = F_4$$

$$a = 0 \qquad F_5\ x_{2,n+1} + F_6\ x_{1,n+1} = F_7$$

$$a = 1 \qquad F_8\ x_{w,n+1} + F_9\ x_{w-1,n+1} + F_{10}\ x_{w-2,n+1} = F_{11}$$

$$0 < a < 1 \qquad F_{12}\ \theta_{m+1,n+1} + F_{13}\ \theta_{m,n+1} + F_{14}\ \theta_{m-1,n+1} = F_{15}$$

$$a = 0 \qquad F_{16}\ \theta_{2,n+1} + F_{17}\ \theta_{1,n+1} = F_{18}$$

TABLE 6-3

FINITE-DIFFERENCE EQUATIONS

FIRST-ORDER REACTION

ADIABATIC CONDITIONS

CASE 1

$$\theta_{n+1} = \theta_n + k\, G_3G_4 (x_{n+1} + x_n)\, e^{-G_2/(\theta_n + 1)}$$

CASE 2 (a = 1)

when n = 1

$$B_{10}\, \theta_{w,2} + B_{11}\, \theta_{w-1,2} + B_{12}\, \theta_{w-2,2} = B_{13}$$

when $n \geq 2$

$$B_{14}\, \theta_{w,n+1} + B_{15}\, \theta_{w-1,n+1} + B_{16}\, \theta_{w-2,n+1} = B_{17}$$

CASE 3 (a = 1)

$$C_{19}\, x_{w,n+1} + C_{20}\, x_{w-1,n+1} + C_{21}\, x_{w-2,n+1} = C_{22}$$

$$C_{23}\, \theta_{w,n+1} + C_{24}\, \theta_{w-1,n+1} + C_{25}\, \theta_{w-2,n+1} = C_{26}$$

TABLE 6-4

FINITE-DIFFERENCE EQUATIONS

SECOND-ORDER REACTION

ADIABATIC CONDITIONS

CASE 1

$$\theta_{n+1} = \theta_n + \frac{1}{2} k\ G_3 G_4 (x_n + x_{n+1})\ (x_n + x_{n+1} + 2\Delta x) e^{-G_2/(\theta_n + 1)}$$

CASE 2 (a = 1)

when n = 1

$$E_{11}\ \theta_{w,2} + E_{12}\ \theta_{w-1,2} + E_{13}\ \theta_{w-2,2} = E_{14}$$

when n > 1

$$E_{15}\ \theta_{w,n+1} + E_{16}\ \theta_{w-1,n+1} + E_{17}\ \theta_{w-2,n+1} = E_{18}$$

CASE 3 (a = 1)

$$F_{19}\ x_{w,n+1} + F_{20}\ x_{w-1,n+1} + F_{21}\ x_{w-2,n+1} = F_{22}$$

$$F_{23}\ \theta_{w,n+1} + F_{24}\ \theta_{w-1,n+1} + F_{25}\ \theta_{w-2,n+1} = F_{26}$$

TABLE 6-5

COEFFICIENTS VALUES

The coefficients A, B, C, D, E and F were known values and are defined as follows:

$$A_1 = 1 + k\ G_3\ e^{-G_2/(\theta_{m,n} + 1)}$$

$$A_2 = 1 - k\ G_3\ e^{-G_2/(\theta_{m,n} + 1)}$$

$$A_3 = -k\ (h + 2a_m)\ /\ 2a_m\ h^2$$

$$A_4 = 1 + (2k/h^2)$$

$$A_5 = k\ (h - 2a_m)\ /\ (2a_m\ h^2)$$

$$\begin{aligned} A_6 = {} & k\ (h + 2a_m)\ /\ (2a_m\ h^2)\ \theta_{m+1,n} + (1 + (2k/h^2))\ \theta_{m,n} \\ & + k\ (2a_m - h)\ /\ (2a_m\ h^2)\ \theta_{m-1,n} + k\ G_3 G_4 (x_{m,n+1} + x_{m,n}) \\ & \qquad e^{-G_2/(\theta_{m,n} + 1)} \end{aligned}$$

$$A_7 = -4k/h^2$$

$$A_8 = 1 + (4k/h^2)$$

$$\begin{aligned} A_9 = {} & (4k/h^2)\ \theta_{2,n} + (1 - 4\ k/h^2)\ \theta_{1,n} + k\ G_3 G_4 (x_{1,n+1} + x_{1,n}) \\ & \qquad e^{-G_2/(\theta_{1,n} + 1)} \end{aligned}$$

$$B_1 = 1 + [k\ G_3 e^{-G_2/(\theta_{m,n} + 1)}\ /\ 2(1 - a_m^2)]$$

$$B_2 = 1 - [k\ G_3 e^{-G_2/(\theta_{m,n} + 1)}\ /\ 2(1 - a_m^2)]$$

$$B_3 = -k\ (h + 2a_m)\ /\ 4(1 - a_m^2)\ a_m\ h^2$$

$$B_4 = 1 + k/h^2 (1 - a_m^2)$$

$$B_5 = k\ (h - 2a_m)\ /\ 4(1 - a_m^2)\ a_m\ h^2$$

TABLE 6-5

(continued)

$$B_6 = [k\ (h + 2a_m)/4(1 - a_m^2)a_m\ h^2]\ \theta_{m+1,n} + [1 - k/h^2(1 - a_m^2)]\ \theta_{m,n}$$

$$+ [k\ (2a_m - h)/4(1 - a_m^2)a_m\ h^2]\ \theta_{m-1,n} + k\ G_3G_4(x_{m,n+1} + x_{m,n})$$

$$e^{-G_2/(\theta_{m,n} + 1)}\ /2(1 - a_m^2)$$

$$B_7 = -2k/h^2$$

$$B_8 = 1 + 2k/h^2$$

$$B_9 = (2k/h^2)\ \theta_{2,n} + (1 - 2k/h^2)\ \theta_{1,n} + \frac{1}{2}k\ (x_{1,n+1} + x_{1,n})$$

$$G_3G_4e^{-G_2/(\theta_{1,n} + 1)}$$

$$B_{10} = B_{14} = 5/2h^2$$

$$B_{11} = B_{15} = -8/3h^2$$

$$B_{12} = B_{16} = 1/6h^2$$

$$B_{13} = \frac{1}{2}\ (x_{w,1} + x_{w,2})G_3G_4e^{-G_2}$$

$$B_{17} = 0$$

$$C_1 = -k\ G_1(h + 2a_m)/4(1 - a_m^2)\ a_m\ h^2$$

$$C_2 = 1 + k\ G_1/(1 - a_m^2)\ h^2 + k\ G_3e^{-G_2/(\theta_{m,n} + 1)}\ /\ 2(1 - a_m^2)$$

$$C_3 = k\ G_1(h - 2a_m)/4(1 - a_m^2)\ a_m\ h^2$$

$$C_4 = [k\ G_1(h + 2a_m)/4(1 - a_m^2)\ a_m\ h^2]\ x_{m+1,n}$$

$$+ [1 - k\ G_1(1 - a_m^2)\ h^2 - k\ G_3e^{-G_2/(\theta_{m,n} + 1)}\ /\ 2(1 - a_m^2)]\ x_{m,n}$$

$$+ [k\ G_1(2a_m - h)/4(1 - a_m^2)\ a_m\ h^2]\ x_{m-1,n}$$

TABLE 6-5

(continued)

$$C_5 = -2k\ G_1/h^2$$

$$C_6 = 1 + 2k\ G_1/h^2 + \frac{k\ G_3}{2}\ e^{-G_2/(\theta_{1,n} + 1)}$$

$$C_7 = (2k\ G_1/h^2)x_{2,n} + (1 - 2k\ G_1/h^2 - \frac{k\ G_3}{2}\ e^{-G_2/(\theta_{1,n} + 1)})x_{1,n}$$

$$C_8 = \frac{5\ G_1}{2h^2} + G_3\ e^{-G_2}$$

$$C_9 = -8G_1/3h^2$$

$$C_{10} = G_1/6h^2$$

$$C_{11} = 0$$

$$C_{12} = -k(h + 2a_m)\ /\ 4(1 - a_m^2)a_m\ h^2$$

$$C_{13} = 1 + k\ /\ (1 - a_m^2)h^2$$

$$C_{14} = k(h - 2a_m)\ /\ 4(1 - a_m^2)a_m\ h^2$$

$$C_{15} = [k(h + 2a_m)\ /\ 4(1 - a_m^2)a_m\ h^2]\ \theta_{m+1,n} + [1 - k\ /\ (1 - a_m^2)h^2]$$

$$\theta_{m,n} + [k(2a_m - h)\ /\ 4(1 - a_m^2)a_m\ h^2]\ \theta_{m-1,n}$$

$$+\ k(x_{m,n+1} + x_{m,n})\ G_3G_4e^{-G_2/(\theta_{m,n} + 1)}\ /\ 2(1 - a_m^2)$$

$$C_{16} = -2k/h^2$$

$$C_{17} = 1 + 2k/h^2$$

$$C_{18} = (2k/h^2)\ \theta_{2,n} + (1 - 2k/h^2)\ \theta_{1,n} + \frac{k}{2}(x_{1,n+1} + x_{1,n})$$

$$G_3G_4e^{-G_2/(\theta_{1,n} + 1)}$$

$$C_{19} = \frac{5\ G_1}{2h^2} + G_3e^{-G_2/(\theta_{w,n} + 1)}$$

$$C_{20} = -8G_1/3h^2$$

$$C_{21} = G_1/6h^2$$

$$C_{22} = 0$$

TABLE 6-5

(continued)

$$C_{23} = 5/2h^2$$

$$C_{24} = -8/3h^2$$

$$C_{25} = 1/6h^2$$

$$C_{26} = G_3G_4x_{w,n+1}\ e^{-G_2/(\theta_{w,n} + 1)}$$

$$D_1 = \frac{k\ G_3}{2}\ e^{-G_2/(\theta_{m,n} + 1)}$$

$$D_2 = 1 + (k\ G_3e^{-G_2/(\theta_{m,n} + 1)})\ (x_{m,n} + \Delta x)$$

$$D_3 = [-1 + (\frac{k\ G_3}{2}\ e^{-G_2/(\theta_{m,n} + 1)})\ (x_{m,n} + 2\Delta x)]\ x_{m,n}$$

$$D_4 = -k(h + 2a_m)\ /\ 2a_m\ h^2$$

$$D_5 = 1 + 2k/h^2$$

$$D_6 = k(h - 2a_m)\ /\ 2a_m\ h^2$$

$$\begin{aligned} D_7 = {} & [k(h + 2a_m)\ /\ 2a_m\ h^2]\ \theta_{m+1,n} + [1 - 2k/h^2]\ \theta_{m,n} \\ & + [k(2a_m - h)\ /\ 2a_m\ h^2]\ \theta_{m-1,n} \\ & + \frac{k}{2}\ G_3G_4(x_{m,n+1} + x_{m,n})\ (x_{m,n+1} + x_{m,n} + 2\Delta x)e^{-G_2/(\theta_{m,n} + 1)} \end{aligned}$$

$$D_8 = -4k/h^2$$

$$D_9 = (1 + 4k/h^2)$$

$$\begin{aligned} D_{10} = {} & (4k/h^2)\ \theta_{2,n} + (1 - 4k/h^2)\ \theta_{1,n} \\ & + \frac{k}{2}\ G_3G_4(x_{1,n+1} + x_{1,n})\ (x_{1,n+1} + x_{1,n} + 2\Delta x)e^{-G_2/(\theta_{1,n} + 1)} \end{aligned}$$

TABLE 6-5

(continued)

$$E_1 = \frac{k\ G_3}{4(1 - a_m^2)}\ e^{-G_2/(\theta_{m,n} + 1)}$$

$$E_2 = 1 + \frac{k\ G_3}{2(1 - a_m^2)}\ e^{-G_2/(\theta_{m,n} + 1)} .\ (x_{m,n} + \Delta x)$$

$$E_3 = [-1 + \frac{k\ G_3}{4(1 - a_m^2)}\ e^{-G_2/(\theta_{m,n} + 1)} .\ (x_{m,n} + 2\Delta x)]\ .\ x_{m,n}$$

$$E_4 = -k(h + 2a_m)/4(1 - a_m^2)a_m\ h^2$$

$$E_5 = 1 + k/(1 - a_m^2)h^2$$

$$E_6 = k(h - 2a_m)/4(1 - a_m^2)a_m\ h^2$$

$$\begin{aligned} E_7 = & [k(h + 2a_m)/4(1 - a_m^2)a_m\ h^2]\ \theta_{m+1,n} \\ & + [1 - k/(1 - a_m^2)h^2]\ \theta_{m,n} + [k(2a_m - h)/4(1 - a_m^2)a_m\ h^2]\ \theta_{m-1,n} \\ & + \frac{k\ G_3G_4}{4(1 - a_m^2)}\ (x_{m,n+1} + x_{m,n})(x_{m,n+1} + x_{m,n} + 2\Delta x).e^{-G_2/(\theta_{m,n} + 1)} \end{aligned}$$

$$E_8 = -2k/h^2$$

$$E_9 = 1 + 2k/h^2$$

$$\begin{aligned} E_{10} = & (2k/h^2)\ \theta_{2,n} + [1 - 2k/h^2]\ \theta_{1,n} \\ & + \frac{k\ G_3G_4}{4}\ (x_{1,n+1} + x_{1,n})(x_{1,n+1} + x_{1,n} + 2\Delta x).e^{-G_2/(\theta_{1,n} + 1)} \end{aligned}$$

$$E_{11} = E_{15} = 5/2h^2$$

$$E_{12} = E_{16} = -8/3h^2$$

$$E_{13} = E_{17} = 1/6h^2$$

$$E_{14} = (G_3G_4/4).(x_1 + x_2)(x_1 + x_2 + 2\Delta x)e^{-G_2}$$

$$E_{18} = 0$$

TABLE 6-5

(continued)

$$F_1 = -k\ G_1(h + 2a_m)\ /\ 4a_m\ h^2(1 - a_m^2)$$

$$F_2 = 1 + k\ G_1/h^2(1 - a_m^2) + \frac{k\ G_3}{4(1 - a_m^2)}\ (x_{m,n+1} + 2x_{m,n} + 2\Delta x)\ e^{-G_2/(\theta_{m,n} + 1)}$$

$$F_3 = k\ G_1(h - 2a_m)\ /\ 4a_m\ h^2(1 - a_m^2)$$

$$F_4 = [k\ G_1(h + 2a_m)\ /\ 4a_m\ h^2(1 - a_m^2)]\ x_{m+1,n} + [1 - k\ G_1/(1 - a_m^2)h^2 - \frac{k\ G_3}{4(1 - a_m^2)}\ (x_{m,n} + 2\Delta x)e^{-G_2/(\theta_{m,n} + 1)}] \cdot x_{m,n} + [k\ G_1(2a_m - h)\ /\ 4a_m\ h^2(1 - a_m^2)]\ x_{m-1,n}$$

$$F_5 = -2G_1k/h^2$$

$$F_6 = 1 + 2k\ G_1/h^2 + \frac{k\ G_3}{4}\ (x_{1,n+1} + 2x_{1,n} + 2\Delta x)e^{-G_2/(\theta_{1,n} + 1)}$$

$$F_7 = (2k\ G_1/h^2)\ x_{2,n} + \{1 - 2k\ G_1/h^2 - \frac{k\ G_3}{4}\ (x_{1,n} + 2\Delta x) \cdot e^{-G_2/(\theta_{1,n} + 1)}\} \cdot x_{1,n}$$

$$F_8 = 5G_1/2h^2 + G_3e^{-G_2}(x_{w,n+1} + \Delta x)$$

$$F_9 = F_{20} = -8G_1/3h^2$$

$$F_{10} = F_{21} = G_1/6h^2$$

$$F_{11} = F_{22} = 0$$

$$F_{12} = -k(h + 2a_m)\ /\ 4(1 - a_m^2)a_m\ h^2$$

$$F_{13} = 1 + k/(1 - a_m^2)h^2$$

$$F_{14} = k(h - 2a_m)\ /\ 4(1 - a_m^2)a_m\ h^2$$

TABLE 6-5

(continued)

$$
\begin{aligned}
F_{15} &= [k(h + 2a_m)/4(1 - a_m^2)a_m\ h^2]\ \theta_{m+1,n} \\
&\quad + [1 - k/(1 - a_m^2)h^2]\ \theta_{m,n} + [k(2a_m - h)/4(1 - a_m^2)a_m\ h^2]\ \theta_{m-1,n} \\
&\quad + \frac{k\ G_3G_4}{4(1 - a_m^2)}\ (x_{m,n+1} + x_{m,n}).(x_{m,n+1} + x_{m,n} + 2\Delta x).e^{-G_2/(\theta_{m,n} + 1)}
\end{aligned}
$$

$$F_{16} = -2k/h^2$$

$$F_{17} = 1 + 2k/h^2$$

$$
\begin{aligned}
F_{18} &= [2k/h^2]\ \theta_{2,n} + [1 - 2k/h^2]\ \theta_{1,n} + \frac{k\ G_3G_4}{4}\ e^{-G_2/(\theta_{1,n} + 1)} \\
&\quad .\ (x_{1,n+1} + x_{1,n}).(x_{1,n+1} + x_{1,n} + 2\Delta x)
\end{aligned}
$$

$$F_{19} = 5G_1/2h^2 + G_3e^{-G_2/(\theta_{w,n} + 1)}.\ (x_{w,n+1} + \Delta x)$$

$$F_{23} = 5/2h^2$$

$$F_{24} = -8/3h^2$$

$$F_{25} = 1/6h^2$$

$$F_{26} = G_3G_4x_{w,n+1}(x_{w,n+1} + \Delta x).e^{-G_2/(\theta_{w,n} + 1)}$$

APPENDIX 7

COMPUTER PROGRAMME

N.B.: THE REMARKS AT THE END OF EACH LINE INDICATE TO WHAT CASE THE LINE APPLIES. WHEN NOTHING APPEARS, THE LINE APPLIES TO ALL CASES.

REMARKS:

A : THE LINE APPLIES TO ADIABATIC CASES.
C : THE LINE APPLIES TO CWT REACTORS CASES.
E : EXAMPLE. THE LINE SHOULD BE CHANGED APPROPRIATELY FOR EACH CASE.
1 : (ALONE OR PRECEEDING A OR C) FIRST ORDER CASES.
2 : (ALONE OR PRECEEDING A OR C) SECOND ORDER CASES.
1,2,3 : (FOLLOWING A OR C) CASES 1,2, OR 3.
\- : THE LINE APPLIES TO ALL CASES EXCEPT THOSE PRECEEDED BY A MINUS SIGN.

```
                                                                                   REMARKS

                                        CASE_3:                                       E
 PROCEDURE OPTIONS (MAIN);


/*******************************************************************************

      PROGRAM TO SOLVE SIMULTANEOUS HEAT AND MASS TRANSFER IN A
      TUBULAR REACTOR BY NUMERICAL RELAXATION METHOD.

      CASE_3: LAMINAR FLOW WITH RADIAL DIFFUSION OF MATERIAL                         E
      ADIABATIC REACTOR                                                              E

      REFERENCE: R. DUSSAULT PH.D THESIS UNIVERSITY OF OTTAWA

*******************************************************************************/

1DECLARE
         RI FIXED BINARY(16),   /* RADIAL  ITERATIONS */                         -1A1,-2A1
         AI FIXED BINARY(16),   /* AXIAL   ITERATIONS */
         NRI FIXED BINARY(16), /* NUMBER OF RADIAL ITERATIONS PRINTED*/-1A1,-2A1
         NAI FIXED BINARY(16), /* NUMBER OF AXIAL  ITERATIONS PRINTED */
         LBND FIXED BINARY(16), /* LOWER PRINTING BOUND */

         UBND FIXED BINARY(16), /* UPPER PRINTING BOUND */

         (I,K,M,N,IC,IN,NC) FIXED BINARY(16) INITIAL(0),                         -1A1,-2A1
                                                                                 -2A3,-2C3
         (K,N,IC,IN,NC) FIXED BINARY(16) INITIAL(0),                             1A1,2A1
         (I,K,M,N,IC,IN,NC,ICOUNT) FIXED BINARY(16) INITIAL(0),                  2A3,2C3

         BACK LABEL,

         EXP BUILTIN,

         SYSIN FILE STREAM INPUT ENV(F(80)),
         SYSPRINT FILE STREAM PRINT ENV(F(121));


 START:

      OPEN FILE (SYSPRINT) PAGESIZE (100), FILE (SYSIN) INPUT;

      ON ENDFILE (SYSIN) GO TO EOP;


1NEW_DATA:

      GET FILE (SYSIN) LIST(RI,AI,NRI,NAI,LBND,UBND);                            -1A1,-2A1
      GET FILE (SYSIN) LIST(AI,NAI,LBND,UBND);                                   1A1,2A1

 BEGIN;

 DECLARE
         (X(0:RI,0:1),THETA(0:RI,0:1),A(RI+1,3),R(RI+1),                          E
         G1,G2,G3,G4,GK,W,AREA1,AREA2,DELTAX,                                     E
         AVCONS,AVTEMP,PART1,DIV,TNVCON,ROWAO,POWBO,AVSPEC,                       E
         B(RI+1,3),PART(0:RI,3),XX(0:RI),Y(0:RI),TOLERANCE,                       E
         TA(0:RI),AA(0:RI),FUNC1(0:RI),FUNC2(0:RI),                               E
         PART2,PART3,PART4,GH,TS,TS1,TS2,TEMP)                                    E
         FLOAT BINARY(53); /* DOUBLE PRECISION VERSION */


      ON ERROR SNAP BEGIN;
         ON ERROR SYSTEM;
         PUT PAGE FILE (SYSPRINT) DATA;
         END;
```

```
GET FILE (SYSIN) LIST(G1,G2,G3,G4,W);                                        1
GET FILE (SYSIN) LIST(G1,G2,G3,G4,W,ROWAO,ROWBO);                            2A1,2A2
GET FILE (SYSIN) LIST(TOLERANCE,G1,G2,G3,G4,W,ROWAO,ROWBO);                  2A3
GET FILE (SYSIN) LIST(CONST,G1,G2,G3,G4,W,ROWAO,ROWBO);                      2C1,2C2
GET FILE (SYSIN) LIST(CONST,TOLERANCE,G1,G2,G3,G4,W,ROWAO,ROWBO);  2C3


GH=1.0/RI;                                                                   -1A1,-2A1
GK=W/AI;
DELTAX = (ROWBO-RCWAO)/(ROWAO+RCWBO);                                        2
TNVCON = (ROWAO+ROWBO)/RCWAO;                                                2

/* AA IS THE DIMENSIONLESS RADIUS */                                         -1A1,-2A1
AA(0) = 0.0;                                                                 -1A1,-2A1
DO I=1 TO RI;                                                                -1A1,-2A1
    AA(I) = AA(I-1)+GH;                                                      -1A1,-2A1
    END;                                                                     -1A1,-2A1
TA(*) = 1.0-AA(*)*AA(*);                                                     -1A1,-2A1
                                                                             -1C1,-2C1
X(0) = 1.0;                                                                   1A1
X(*,0) = 1.0;                                                                1A2,1A3,1C1
                                                                             1C2,1C3
X(0) = RCWAO/(ROWAC+ROWBO);                                                  2A1
X(*,0) = ROWAO/(ROWAO+ROWBO);                                                2A2,2A3,2C1
                                                                             2C2,2C3
Y(0) = X(0)*TNVCON;                                                          1A1
Y(*,0) = X(*,0)*TNVCON;                                                      2A2,2C1,2C2
Y(*) = X(*,0)*TNVCON;                                                        2A3,2C3
THETA(*,0) = 0.0;                                                            -1A1,-2A1
THETA(0) = 0.0;                                                              1A1,2A1
FUNC1(*) = X(*,0)*AA(*)*TA(*);                                               1A2,1A3,1C2
                                                                             1C3,2A2,2A3
                                                                             2C2,2C3

FUNC1(*) = X(*,0)*AA(*);                                                     1C1,2C1
FUNC2(*) = THETA(*,0)*AA(*)*TA(*);                                           1A2,1A3,1C2
                                                                             1C3,2A2,2A3
                                                                             2C2,2C3
FUNC2(*) = THETA(*,0)*AA(*);                                                 1C1,2C1

/* INTEGRATION BY SIMPSONS RULE */                                           -1A1,-2A1
AREA1,AREA2=0.0;                                                             -1A1,-2A1
DO I=1 TO RI-1 BY 2;                                                         -1A1,-2A1
    AREA1=AREA1+((GH/3.0)*(FUNC1(I-1)+(4.0*FUNC1(I))+FUNC1(I+1)));-1A1,-2A1
    AREA2=AREA2+((GH/3.0)*(FUNC2(I-1)+(4.0*FUNC2(I))+FUNC2(I+1)));-1A1,-2A1
    END;                                                                     -1A1,-2A1


 X(*,1) = X(*,0);            /* CONCENTRATION PROFILE */                     -1A1,-2A1
 X(1) = X(0);                 /* CONCENTRATION PROFILE */                    1A1,2A1
 THETA(*,1) = THETA(*,0); /* TEMPERATURE PROFILE */                          -1A1,-2A1
 THETA(1) = THETA(0);        /* TEMPERATURE PROFILE */                       1A1,2A1

 AVCONS = 4.0*AREA1;                                                         1A2,1A3,1C2
                                                                             1C3,2A2,2A3
                                                                             2C2,2C3
 AVCONS = 2.0*AREA1;                                                         1C1,2C1

 AVTEMP = 4.0*AREA2;                                                         1A2,1A3,1C2
                                                                             1C3,2A2,2A3
                                                                             2C2,2C3
 AVTEMP = 2.0*AREA2;                                                         1C1,2C1

PUT FILE (SYSPRINT) EDIT
('SECOND ORDER ','CASE 3 ',' ADIABATIC REACTOR ',                            E
'THETA(WALL) ¬ 0.0 ','DOUBLE PRECISION')                                     E
    (PAGE,5(SKIP(4),COLUMN(40),A))
(' X(0) = ',X(0))                                                            1A1
    (PAGE,COLUMN(40),A,F(8,4))                                               1A1
('THE VALUES OF X(0,0) TO X(',RI,',0) INCLUSIVE ARE ',X(0,0))                1A2,1A3,1C1
                                                                             1C2,1C3
    ( PAGE, COLUMN(40), A, F(3,0), A, F(8,4) )                               1A2,1A3,1C1
                                                                             1C2,1C3
(' Y(0) = ',Y(0))                                                            2A1
    (PAGE,COLUMN(40),A,F(8,4))                                               2A1
('THE VALUES OF Y(0,0) TO Y(',RI,',0) INCLUSIVE ARE ',Y(0,0))                2A2,2C1,2C2
    ( PAGE, COLUMN(40), A, F(3,0), A, F(8,4) )                               2A2,2C1,2C2
('THE VALUES OF Y(0) TO Y(',RI,') INCLUSIVE ARE ',Y(0))                      2A3,2C3
    ( PAGE, COLUMN(40), A, F(3,0), A, F(8,4) )                               2A3,2C3
('THE VALUES OF THETA(0,0) TO THETA(',RI,',0) INCLUSIVE ARE ',               -1A1,-2A1
    THETA(0,0))                                                              -1A1,-2A1
    ( SKIP(4), COLUMN(40), A, F(3,0), A, F(8,4) )                            -1A1,-2A1
('THETA(0) = ',THETA(0))                                                     1A1,2A1
    ( SKIP(4),COLUMN(40),A,F(8,4))                                           1A1,2A1
('AVERAGE CONCENTRATION IS ',AVCONS)                                         -1A1,-2A1
    ( SKIP(4), COLUMN(40), A, F(10,5) )                                      -1A1,-2A1
('AVERAGE TEMPERATURE IS ',AVTEMP)                                           -1A1,-2A1
    ( SKIP(4), COLUMN(40), A, F(10,5) )                                      -1A1,-2A1
('NUMBER OF RADIAL ITERATIONS IS ',RI)                                       -1A1,-2A1
    ( SKIP(4), COLUMN(40), A, F(3,0) )                                       -1A1,-2A1
('NUMBER OF AXIAL ITERATIONS IS ',AI)
    ( SKIP(4), COLUMN(40), A, F(4,0) )
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 ('CONST OR THETA(WALL) IS ',CONST)                                       2C1,2C2,2C3
     ( SKIP(4), COLUMN(40), A, F(14,7) )                                  2C1,2C2,2C3
 ('THE TOLERANCE IS ',TOLERANCE)                                          2A3,2C3
     ( SKIP(4),COLUMN(40),A,F(14,7))                                      2A3,2C3
 ('  G1=',G1,'  G2=',G2,'  G3=',G3,'  G4=',G4,'  W=',W)
     (5(SKIP(4),COLUMN(38),A,E(12,4))));


  /* SET UP MATRIX B , B IS STORED IN COMPRESSED FORM */                  -1A1,-2A1
  B(1,1) = 1.0+((2.0*GK)/(GH*GH));                                        -1A1,-2A1,
                                                                          -1C1,-2C1
  B(1,1) = 1.0+((4.0*GK)/(GH*GH));                                        1C1,2C1
  B(1,2) = -(2.0*GK)/(GH*GH);                                             -1A1,-2A1,
                                                                          -1C1,-2C1
  B(1,2) = -(4.0*GK)/(GH*GH);                                             1C1,2C1
  B(1,3) = 0.0;                                                           -1A1,-2A1
  DO I = 1 TO RI-1;                                                       -1A1,-2A1
      TS = AA(I);                                                         -1A1,-2A1
      TS1 = TA(I);                                                        -1A1,-2A1,
                                                                          -1C1,-2C1
      TS2 = 4.0*AA(I)*GH*GH;                                              -1A1,-2A1,
                                                                          -1C1,-2C1
      TS2 = 2.0*AA(I)*GH*GH;                                              1C1,2C1
      B(I+1,1) = (GK*(GH-2.0*TS))/(TS2*TS1);                              -1A1,-2A1,
                                                                          -1C1,-2C1
      B(I+1,1) = (GK*(GH-2.0*TS))/TS2;                                    1C1,2C1
      B(I+1,2) = 1.0+(GK/(GH*GH*TS1));                                    -1A1,-2A1,
                                                                          -1C1,-2C1
      B(I+1,2) = 1.0+((2.0*GK)/(GH*GH));                                  1C1,2C1
      B(I+1,3) = -(GK*(GH+2.0*TS))/(TS2*TS1);                             -1A1,-2A1,
                                                                          -1C1,-2C1
      B(I+1,3) = -(GK*(GH+2.0*TS))/TS2;                                   1C1,2C1
      END;                                                                -1A1,-2A1
      B(RI+1,1) = 1.0/(6.0*GH*GH);                                        1A2,1A3,1C3
                                                                          2A2,2A3,2C3
  B(RI,3) = B(RI,2);                                                      1C1,2C1
      B(RI+1,2) = -8.0/(3.0*GH*GH);                                       1A2,1A3,1C3
                                                                          2A2,2A3,2C3
  B(RI,2) = B(RI,1);                                                      1C1,2C1
      B(RI+1,3) = 5.0/(2.0*GH*GH);                                        1A2,1A3,1C3
                                                                          2A2,2A3,2C3
  B(RI,1) = 0.0;                                                          1C1,2C1

  /* SET UP MATRIX PART WHICH IS USED IN CALCULATION OF R */              -1A1,-2A1
  DO I = 1 TO RI-1;                                                       -1A1,-2A1

      TS = 4.0*GH*GH*AA(I)*TA(I);                                         -1A1,-2A1,
                                                                          -1C1,-2C1
      TS = 2.0*GH*GH*AA(I);                                               1C1,2C1
      PART(I,1) = (GK*(GH+2.0*AA(I)))/TS;                                 -1A1,-2A1
      PART(I,2) = GK/(GH*GH*TA(I));                                       -1A1,-2A1,
                                                                          -1C1,-2C1
      PART(I,2) = (2.0*GK)/(GH*GH);                                       1C1,2C1
      PART(I,3) = (GK*(2.0*AA(I)-GH))/TS;                                 -1A1,-2A1
      END;                                                                -1A1,-2A1

  M = RI + 1;                                                             2A3
  N=0;
  IN = N+1;
  NC = 0;          /* COUNTER FOR AXIAL POSITION, AI */

LOOP_1:

  ICOUNT = 0;                                                             2A3,2C3
  K=K+1;
  IC=NC+1;

  X(*,N) = X(*,N+1);                                                      -1A1,-2A1
      X(N) = X(N+1);                                                      1A1,2A1
  XX(*) = X(*,N);                                                         2A3,2C3
      Y(*,N) = X(*,N)*TNVCON;                                             2A2,2C1,2C2
  THETA(*,N) = THETA(*,N+1);                                              -1A1,-2A1



   /* SOLVING FOR X(N+1) */                                               1A1,2A1
   /* SOLVING FOR X(*,N+1) */                                             1A2,1C1,1C2
                                                                          2A2,2C1,2C2
  DO I=0 TO RI-1;                                                         1A2,1C2,2A2
                                                                          2C2
  DO I=0 TO RI;                                                           1C1,2C1
      TS = GK*G3*EXP(-G2/(THETA(N)+1.0));                                 1A1,2A1
      TS = GK*G3*EXP(-G2/(THETA(I,N)+1.0))/(2.0*TA(I));                   1A2,1C2
      TS = GK*G3*EXP(-G2/(THETA(I,N)+1.0));                               1C1
      TS = GK*G3*EXP(-G2/(THETA(I,N)+1.0))/(4.0*TA(I));                   2A2,2C2
      X(IN) = X(N)*(1.0-TS)/(1.0+TS);                                     1A1
      X(I,IN) = X(I,N)*(1.0-TS)/(1.0+TS);                                 1A2,1C1,1C2
      D1 = TS/2.0;                                                        2A1
      D2 = 1.0+(TS*(X(N)+DELTAX));                                        2A1
```

```
        D3 = (-1.0+(0.5*TS*(X(N)+2.0*DELTAX)))*X(N);                2A1
        X(IN) = (-D2+SQRT(D2*D2-4.0*D1*D3))/(2.0*D1);               2A1
    Y(IN) = X(IN)*TNVCON;                                           2A1
        E1 = TS;                                                    2A2
        E2 = 1.0+(2.0*TS*(X(I,N)+DELTAX));                          2A2
        E3 = -X(I,N)+(TS*(X(I,N)+2.0*DELTAX)*X(I,N));               2A2
        X(I,IN) = (-E2+SQRT(E2*E2-4.0*E1*E3))/(2.0*E1);             2A2
        D1 = (GK*G3/2.0)*EXP(-G2/(THETA(I,N)+1.0));                 2C1
        D2 = 1.0+(GK*G3*EXP(-G2/(THETA(I,N)+1.0))*(X(I,N)+DELTAX)); 2C1
        D3 = (-1.0+(GK*G3*EXP(-G2/(THETA(I,N)+1.0))                 2C1
             *(X(I,N)+(2.0*DELTAX))/2.0))*X(I,N);                   2C1
        X(I,IN) = (-D2+SQRT(D2*D2-4.0*D1*D3))/(2.0*D1);             2C1
        E1 = TS;                                                    2C2
        E2 = 1.0+(2.0*TS*(X(I,N)+DELTAX));                          2C2
        E3 = -X(I,N)+(TS*(X(I,N)+2.0*DELTAX)*X(I,N));               2C2
        X(I,IN) = (-E2+SQRT(E2*E2-4.0*E1*E3))/(2.0*E1);             2C2
        Y(I,IN) = X(I,IN)*TNVCON;                                   2A2,2C1,2C2


      /* SET UP MATRIX A FOR CONCENTRATION IN COMPRESSED FORM */    1A3,1C3
        A(*,1) = G1*B(*,1);                                         1A3,1C3
     DO I = 2 TO RI;                                                1A3,1C3
        A(I,2) = G1*B(I,2)-G1+1.0+GK*G3*EXP(-G2/(THETA(I-1,N)+1.0)) 1A3,1C3
                 /(2.0*TA(I-1));                                    1A3,1C3
     END;                                                           1A3,1C3
        A(*,3) = G1*B(*,3);                                         1A3,1C3
     A(1,1) = G1*B(1,1)-G1+1.0+(GK*G3/2.0)*EXP(-G2/(THETA(0,N)+1.0)); 1A3,1C3
        A(1,2) = G1*B(1,2);                                         1A3,1C3
        A(RI+1,1) = G1*B(RI+1,1);                                   1A3,1C3
        A(RI+1,2) = G1*B(RI+1,2);                                   1A3,1C3
        A(RI+1,3) = G1*B(RI+1,3)+G3*EXP(-G2/(THETA(RI,N)+1.0));     1A3
     A(RI+1,3) = G1*B(RI+1,3)+G3*EXP(-G2);                          1C3


      /*SET UP MATRIX R FOR CONCENTRATION */                        1A3,1C3
        R(1) = ((2.0*GK*G1)/(GH*GH))*X(1,N)                         1A3,1C3
                  +X(0,N)*(1.0-((2.0*GK*G1)/(GH*GH))                1A3,1C3
              -((GK*G3/2.0)*EXP(-G2/(THETA(0,N)+1.0))));            1A3,1C3
     DO I=1 TO RI-1;                                                1A3,1C3
        PART1 = X(I+1,N)*G1*PART(I,1);                              1A3,1C3
        PART2 = X(I,N)*(1.0-G1*PART(I,2)                            1A3,1C3
             -((GK*G3*EXP(-G2/(THETA(I,N)+1.0)))/(2.0*TA(I))));     1A3,1C3
        PART3 = X(I-1,N)*G1*PART(I,3);                              1A3,1C3
        R(I+1) = PART1+PART2+PART3;                                 1A3,1C3
        END;                                                        1A3,1C3


        R(RI+1) = 0.0;                                              1A3,1C3

LOOP_2:                                                             2A3,2C3

     ICOUNT = ICOUNT+1;                                             2A3,2C3

     /* SET UP MATRIX A, A IS TO BE STORED IN COMPRESSED FORM */    2A3,2C3
     A(*,1) = G1*B(*,1);                                            2A3,2C3
     A(*,3) = G1*B(*,3);                                            2A3,2C3
     A(1,1)  = 1.0+((2.0*G1*GK)/(GH*GH))                            2A3,2C3
               +(((GK*G3)/4.0)*(XX(0)                               2A3,2C3
               +2.0*X(0,N)+2.0*DELTAX)                              2A3,2C3
               *EXP(-G2/(THETA(0,N)+1.0))));                        2A3,2C3
     A(1,2) = G1*B(1,2);                                            2A3,2C3
        TS = (G1*GK)/(GH*GH);                                       2A3,2C3
        TS2 = (GK*G3)/4.0;                                          2A3,2C3
     DO I=1 TO RI-1 BY 1;                                           2A3,2C3
        TS1 = TA(I);                                                2A3,2C3
        A(I+1,2) = 1.0+TS/TS1+(TS2/TS1                              2A3,2C3
                    *(XX(I)+2.0*X(I,N)+2.0*DELTAX)                  2A3,2C3
                    *EXP(-G2/(THETA(I,N)+1.0)));                    2A3,2C3
        END;                                                        2A3,2C3
     A(RI+1,1)     = G1/(6.0*GH*GH);                                2A3,2C3
     A(RI+1,2)   = -(8.0*G1)/(3.0*GH*GH);                           2A3,2C3
     A(RI+1,3)     = (5.0*G1)/(2.0*GH*GH)                           2A3,2C3
                  +G3*(XX(RI)+DELTAX)*EXP(-G2/(THETA(RI,N)+1.0));   2A3,2C3


     /* SET UP MATRIX R */                                          2A3,2C3
      R(1)    = (X(1,N)*((2.0*G1*GK)/(GH*GH)))                      2A3,2C3
                +X(0,N)*(1.0-((2.0*G1*GK)/                          2A3,2C3
                (GH*GH))-(GK*(G3/4.0)*(X(0,N)                       2A3,2C3
                +2.0*DELTAX)*EXP(-G2/(THETA(0,N)+1.0)))));          2A3,2C3
     DO I=1 TO RI-1 BY 1;                                           2A3,2C3
        PART1=X(I+1,N)*G1*PART(I,1);                                2A3,2C3
        PART2=X(I,N)*(1.0-(G1*PART(I,2))                            2A3,2C3
            -(((GK*G3)/(4.0*TA(I)))*                                2A3,2C3
             (X(I,N)+2.0*DELTAX)*                                   2A3,2C3
             EXP(-G2/(THETA(I,N)+1.0)))));                          2A3,2C3
        PART3=X(I-1,N)*G1*PART(I,3);                                2A3,2C3
        R(I+1)=PART1+PART2+PART3;                                   2A3,2C3
        END;                                                        2A3,2C3
     R(RI+1) = 0.0;                                                 2A3,2C3

     M=RI+1;                                                        1A3,1C3,2C3
```

```
      BACK=CONCENTRATION;                                                      1A3,1C3,2A3
                                                                               2C3
      GO TO SOLVE; /* SOLVE LINEAR EQUATIONS */                                1A3,1C3,2A3
                                                                               2C3

 CONCENTRATION:                                                                1A3,1C3,2A3
                                                                               2C3
      DO I=0 TO RI;                                                            1A3,1C3,2A3
                                                                               2C3
         X(I,IN) = R(I+1);                                                     1A3,1C3,2A3
                                                                               2C3
         END;                                                                  2A3,2C3
      IF ICOUNT = 1                                                            2A3,2C3
      THEN DO;                                                                 2A3,2C3
           XX(*) = X(*,IN);                                                    2A3,2C3
           GO TO LOOP_2;                                                       2A3,2C3
           END;                                                                2A3,2C3
      DO I =0 TO RI;                                                           2A3,2C3
         IF ABS(X(I,IN)-XX(I))>=TOLERANCE                                      2A3,2C3
         THEN DO;                                                              2A3,2C3
              XX(*) = X(*,IN);                                                 2A3,2C3
              IF ICOUNT>60                                                     2A3,2C3
              THEN DO;                                                         2A3,2C3
                   PUT FILE (SYSPRINT) EDIT                                    2A3,2C3
                   ('ICOUNT=',ICOUNT) (SKIP(2),A,F(4,0));                      2A3,2C3
                   PUT SKIP(2) FILE (SYSPRINT) DATA;                           2A3,2C3
                   IF ICOUNT>70 THEN GO TO NEXT;                               2A3,2C3
                   END;                                                        2A3,2C3
              ELSE GO TO LOOP_2;                                               2A3,2C3
              END;                                                             2A3,2C3
         END;                                                                  2A3,2C3
     NEXT:                                                                     2A3,2C3
      XX(*) = X(*,IN);                                                         2A3,2C3

         END;                                                                  -1A1,-2A1,
                                                                               -2A3,-2C3
      X(RI,IN) = 0.0;                                                          1A2,1C2,2A2
                                                                               2C2
      Y(RI,IN) = 0.0;                                                          2A2,2C2


     THETA(IN) = THETA(N)+GK*G3*G4*(X(IN)+X(N))*EXP(-G2/(THETA(N)+1.0));  1A1
         THETA(IN) = THETA(N)+0.5*GK*G3*G4*(X(N)+X(IN))                         2A1
                     *(X(N)+X(IN)+2.0*DELTAX)*EXP(-G2/(THETA(N)+1.0));          2A1
```

```
     /* SET UP MATRIX A FOR TEMPERATURE IN COMPRESSED FORM */                  -1A1,-2A1

        A=B;                                                                   -1A1,-2A1


        A(RI,3) = A(RI,2);                                                     1C2,1C3,2C2
                                                                               2C3
        A(RI,2) = A(RI,1);                                                     1C2,1C3,2C2
                                                                               2C3
        A(RI,1) = 0.0;                                                         1C2,1C3,2C2
                                                                               2C3

     /* SET UP MATRIX R FOR TEMPERATURE */                                     -1A1,-2A1
        R(1) = (((2.0*GK)/(GH*GH))*THETA(1,N))                                 -1A1,-2A1,
                                                                               -1C1,-2C1
        R(1) = (((4.0*GK)/(GH*GH))*THETA(1,N))                                 1C1,2C1
               +(THETA(0,N)*(1.0-((2.0*GK)/(GH*GH))))                          -1A1,-2A1,
                                                                               -1C1,-2C1
               +(THETA(0,N)*(1.0-((4.0*GK)/(GH*GH))))                          1C1,2C1
            +((GK/2.0)*(X(0,N)+X(0,IN))*G3*G4*EXP(-G2/(THETA(0,N)             1A2,1A3,1C2
                                                                               1C3
            +1.0)));                                                           1A2,1A3,1C2
                                                                               1C3
            +(GK*(X(0,N)+X(0,IN))*G3*G4                                        1C1
             *EXP(-G2/(THETA(0,N)+1.0)));                                      1C1
           +(((GK/4.0)*(X(0,N)+X(0,IN))*G3*G4*EXP(-G2/(THETA(0,N)              2A2,2C2
           +1.0)))*(X(0,N)+X(0,IN)+2.0*DELTAX));                               2A2,2C2
           +((GK*(X(0,N)+X(0,IN))*G3*G4                                        2C1
            *EXP(-G2/(THETA(0,N)+1.0)))                                        2C1
            *(X(0,N)+X(0,IN)+2.0*DELTAX)/2.0);                                 2C1
               +((GK/4.0)*(X(0,N)+X(0,IN))*(X(0,N)+X(0,IN)+2.0*DELTAX)  2A3,2C3
               *G3*G4*EXP(-G2/(THETA(0,N)+1.0)));                              2A3,2C3
     DO I = 1 TO RI-1;                                                         -1A1,-2A1
        PART1 = THETA(I+1,N)*PART(I,1);                                        -1A1,-2A1
        PART2 = THETA(I,N)* (1.0-PART(I,2));                                   -1A1,-2A1
        PART3 = THETA(I-1,N)*PART(I,3);                                        -1A1,-2A1
        PART4 = (GK*G3*G4*(X(I,N)+X(I,IN))*EXP(-G2/(THETA(I,N)+1.0)))  1A2,1A3,
                                                                                 1C2,1C3
                /(2.0*TA(I));                                                    1A2,1A3,
                                                                                 1C2,1C3
        PART4 = (GK*G3*G4*(X(I,N)+X(I,IN))*EXP(-G2/(THETA(I,N)+1.0))); 1C1
        PART4 = (GK*G3*G4*(X(I,N)+X(I,IN))*EXP(-G2/(THETA(I,N)+1.0))    2A2,2A3,
                                                                                 2C2,2C3
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```
                *(X(I,N)+X(I,IN)+2.0*DELTAX))/(4.0*TA(I));                       2A2,2A3,
                                                                                 2C2,2C3
        PARTA = (GK*G3*G4*(X(I,N)+X(I,IN))*EXP(-G2/(THETA(I,N)+1.0)))            2C1
                *(X(I,N)+X(I,IN)+2.0*DELTAX)/2.0;                                2C1

        R(I+1) = PART1+PART2+PART3+PART4;                                  -1A1,-2A1
        END;                                                               -1A1,-2A1
        R(RI+1) = 0.0;                                                     1A2,2A2
        R(RI+1) = G3*G4*X(RI,IN)*EXP(-G2/(THETA(RI,N)+1.0));               1A3
        R(RI+1) = G3*G4*X(RI,IN)*(X(RI,IN)+DELTAX)                         2A3
                  *EXP(-G2/(THETA(RI,N)+1.0));                             2A3
        IF N=0 THEN R(RI+1)=0.5*(X(RI,N)+X(RI,IN))*G3*G4*EXP(-G2);        1A2
        IF N=0 THEN R(RI+1)=0.25*(X(RI,N)+X(RI,IN))*G3*G4                  2A2
        *(X(RI,N)+X(RI,IN)+2.0*DELTAX)*EXP(-G2);                           2A2

     M = RI + 1;                                                           1A2,1A3,2A2
     M = RI;                                                               1C1,1C2,1C3
                                                                           2C1,2C2,2C3

     BACK = TEMPERATURE;                                                   -1A1,-2A1

     GO TO SOLVE; /* SOLVE LINEAR EQUATIONS */                             -1A1,-2A1

TEMPERATURE:                                                               -1A1,-2A1
     DO I = 0 TO RI;                                                       1A2,1A3,2A2
                                                                           2A3
     DO I = 0 TO RI-1;                                                     1C1,1C2,1C3
                                                                           2C1,2C2,2C3
        THETA(I,IN) = R(I+1);                                              -1A1,-2A1
        END;                                                               -1A1,-2A1
        THETA(RI,IN) = CONST;                                              1C1,1C2,1C3
                                                                           2C1,2C2,2C3


     IF K=NAI | (NC>=LBND & NC<=UBND)

     THEN DO ; /* PRINT OUT CALCULATIONS */

     K = 0;

     Y(*) = X(*,IN)*TNVCON;                                                2A3,2C3
     FUNC1(*) = X(*,IN)*AA(*)*TA(*);                                       -1A1,-2A1,
                                                                           -1C1,-2C1
     FUNC2(*) = THETA(*,IN)*AA(*)*TA(*);                                   -1A1,-2A1,
                                                                           -1C1,-2C1
```

```
     FUNC1(*) = X(*,IN)*AA(*);                                             1C1,2C1
     FUNC2(*) = THETA(*,IN)*AA(*);                                         1C1,2C1

     /* INTEGRATION BY SIMPSONS RULE */                                    -1A1,-2A1
     DO I = 1 TO RI-1 BY 2;                                                -1A1,-2A1
     AREA1,AREA2 = 0.0;                                                    -1A1,-2A1
        AREA1=AREA1+((GH/3.0)*(FUNC1(I-1)+(4.0*FUNC1(I))+FUNC1(I+1)));-1A1,-2A1
        AREA2=AREA2+((GH/3.0)*(FUNC2(I-1)+(4.0*FUNC2(I))+FUNC2(I+1)));-1A1,-2A1
        END;                                                               -1A1,-2A1


     PUT FILE (SYSPRINT) EDIT                                              -1A1,-2A1
         ('TEMPERATURE VALUES FROM THETA(0,',IC,') ')                      -1A1,-2A1
              ( PAGE, COLUMN(2), A, F(3,0), A)                             -1A1,-2A1
         ('TO THETA(',RI,',',IC,') ')                                      -1A1,-2A1
              ( A, F(3,0), A, F(3,0), A)                                   -1A1,-2A1
         ('CONCENTRATION VALUES FROM X(0,',IC,') ')                        1A2,1A3,1C1
                                                                           1C2,1C3
         ('CONCENTRATION VALUES FROM Y(0,',IC,') ')                        2A2,2A3,2C1
                                                                           2C2,2C3
              ( COLUMN(70), A, F(3,0), A)                                  -1A1,-2A1
         ('TO X(',RI,',',IC,') ')                                          1A2,1A3,1C1
                                                                           1C2,1C3
         ('TO Y(',RI,',',IC,') ')                                          2A2,2A3,2C1
                                                                           2C2,2C3
              ( A, F(3,0), A, F(3,0), A)                                   -1A1,-2A1
         ((THETA(I,IN),I,X(I,IN) DO I=0 TO RI BY NRI))                     1A2,1A3,1C1
                                                                           1C2,1C3
         ((THETA(I,IN),I,Y(I,IN) DO I=0 TO RI BY NRI))                     2A2,2C1,2C2
         ((THETA(I,IN),I,Y(I) DO I=0 TO RI BY NRI))                        2A3,2C3
              ( SKIP(1), 32( SKIP(2), COLUMN(25), F(11,7), COLUMN(60),-1A1,-2A1
              F(3,0), COLUMN(99), F(11,7)) );                              -1A1,-2A1


     AVCONS=4.0*AREA1;                                                     -1A1,-2A1,
                                                                           -1C1,-2C1
     AVCONS = 2.0*AREA1;                                                   1C1,2C1

     AVTEMP=4.0*AREA2;                                                     -1A1,-2A1,
                                                                           -1C1,-2C1
     AVTEMP = 2.0*AREA2;                                                   1C1,2C1

     AVSPEC = AVCONS*TNVCON;                                               2A2,2A3,2C1
                                                                           2C2,2C3
     DIV = THETA(IN)/(1.0-X(IN));                                          1A1
```

```
      DIV = AVTEMP/(1.0-AVCONS);                                              1A2,1A3
      DIV = THETA(IN)/(1.0-Y(IN));                                            2A1
      DIV = AVTEMP/(1.0-AVSPEC);                                              2A2,2A3


      PUT FILE (SYSPRINT) EDIT
         ('THETA(',IC,') = ',THETA(IN))                                       1A1,2A1
                   (COLUMN(2),A,F(3,0),A,F(11,7))                             1A1,2A1
          ('AVERAGE TEMPERATURE IS ', AVTEMP)                                 -1A1,-2A1
              ( SKIP(2), COLUMN(2), A, F(11,7) )                              -1A1,-2A1
         ('X(',IC,') = ',X(IN))                                               1A1
            ('Y(',IC,') = ',Y(IN))                                            2A1
              (COLUMN(40),A,F(3,0),A,F(11,7))                                 1A1,2A1
          ('AVERAGE CONCENTRATION IS ', AVCONS)                               1A2,1A3,1C1
                                                                              1C2,1C3
          ('AVERAGE SPECIFIC CONCENTRATION IS ',AVSPEC)                       2A2,2A3,2C1
                                                                              2C2,2C3
              ( COLUMN(74), A, F(11,7) )                                      1A2,1A3,2A2
                                                                              2A3,2C3
              ( COLUMN(74), A, F(11,7) );                                     1C1,1C2,1C3
                                                                              2C1,2C2
          ('DIV IS ',DIV)                                                     A
              (COLUMN(80),A,F(11,7));                                         1A1,2A1
              ( SKIP(2), COLUMN(2),A,F(11,7));                                1A2,1A3,2A2
              ( SKIP(2), COLUMN(2), A, F(11,7))                               2A3
        ('ICOUNT IS ',ICOUNT)                                                 2A3,2C3
              ( SKIP(2),COLUMN(2),A,F(5,0));                                  2A3,2C3

      END; /* END OF PRINTING SECTION */

      NC = NC+1;
      IF NC<A1 THEN GO TO LOOP_1;

      IF K>0                                                                  -1A1,-2A1
      THEN DO;                                                                -1A1,-2A1
           K=NA1;                                                             -1A1,-2A1
           GO TO TEMPERATURE;                                                 -1A1,-2A1
           END;                                                               -1A1,-2A1


      PUT FILE (SYSPRINT) EDIT
          ('NORMAL END OF PROGRAM')
          ( SKIP(6), A );
      GO TO END_BLOCK;



1SOLVE:                                                                       -1A1,-2A1

      /*

      THE FOLLOWING SUB-ROUTINE SHOULD BE USED IN ALL CASES EXCEPT
      CASES 1A1 AND 2A1

         MODIFICATION OF PROCEDURE 'TRIDIA' WHICH SOLVES SIMULTANEOUS
         LINEAR EQUATIONS IN WHICH THE COEFFICIENT MATRIX 'A' HAS THE
         TRI-DIAGONAL TERMS NON-ZERO AND OTHER OTHER ELEMENTS ARE ZERO.
         THE SOLUTIONS OF THE EQUATIONS ARE STORED IN THE DEPENDENT
         VARIABLE COEFFICIENT VECTOR 'R'.

         A(*,3)      MATRIX OF INDEPENDENT COEFFICIENTS
         R(*)        VECTOR OF DEPENDENT COEFFICIENTS, RETURNS SOLUTIONS
         M           NUMBER OF LINEAR EQUATIONS

         THIS MODIFICATION USES THE COMPRESSED STORAGE MODE OF THE
         MATRIX 'A', THAT IS USE A(M,3) INSTEAD OF A(M,M).
         FOR EXPLICIT USE SEE THE COMMENTS IN THE ORGINAL PROCEDURE.

      */


      /* MODIFICATION FOR THE A(M,1) TERM BEING NON-ZERO */
      TEMP = A(M,1)/A(M-1,1);
      DO I=2,3;
         A(M,I) = A(M,I)-TEMP*A(M-1,I);
         END;
      R(M) = R(M)-TEMP*R(M-1);

      /* MODIFY FIRST AND LAST ROWS FOR CALCULATION PURPOSES */
      A(1,3) = A(1,2);
      A(1,2) = A(1,1);
      A(M,1) = A(M,2);
      A(M,2) = A(M,3);

      /* MODIFY THE SECOND COLUMN WHICH NOW CONTAINS THE OLD DIAGONAL
         ELEMENTS */
      DO I=2 BY 1 TO M;
         TEMP = A(I,1)/A(I-1,2);
         A(I,2) = A(I,2)-TEMP*A(I-1,3);
         R(I) = R(I)-TEMP*R(I-1);
```

```
            END;

         /* BACK SOLUTION AND STORE ANSWERS IN R VECTOR */
         R(M) = R(M)/A(M,2);
         DO I = M-1 BY -1 TO 1;
            R(I) = (R(I)-A(I,3)*R(I+1))/A(I,2);
            END;

         GO TO BACK;  /* RETURNS TO EITHER CONCENTRATION OR TEMPFRATURE */


  END_BLOCK:
         END; /* END BEGIN BLOCK */

         GO TO NEW_DATA;

  EOP:
         END CASE_3; /* END OF PROCEDURE */                            E



 DATA CARDS :                                                          E

 120,300,20,30,501,502,.000001,.007039,17.181,1.6261E+07.1.9375,
 .1822,1.432E-03,43.32E-03,
```