A MATHEMATICAL STUDY OF THE TRANSIENT BEHAVIOR OF A FIXED-BED CATALYTIC REACTOR

Thesis by
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In Partial Fulfillment of the Requirements
For the Degree of
Doctor of Philosophy

California Institute of Technology
Pasadena, California
1965
(Submitted November 4, 1964)

ACKNOWLEDGEMENTS

My deepest gratitude is due to Professor Paul A. Longwell, who initiated and supervised the major part of this work. His teaching and encouragement are invaluable to the completion of the work. In the last phase of the work, Professor Richard C. Seagrave kindly supervised the work, and gave his priceless advice which helped to finish the thesis. He deserves my sincere thanks. My special appreciation is also due to Professor Bruce H. Sage for his constant encouragement and to Professor William H. Corcoran for the suggestion of the SO_2-oxidation system for this study. During my graduate residence, I was sponsored variously by an Institute Scholarship, a Special Fellowship, Teaching and Research Assistantships and a Woodrow-Wilson Fellowship, which are greatly appreciated. Many thanks to Mrs. June Gray for preparing the figures and Mrs. Joan Schuetz for typing the final script. Thank you very much Ming-Ing.

ABSTRACT

Partial differential equations describing the transient behavior of a non-adiabatic fixed-bed catalytic reactor are derived with a minimum of simplifying assumptions. These equations are applied to predict the transient behavior of a reactor for the oxidation of SO_2, taking into account the behavior of both the fluid stream and the associated catalyst pellets.

Stability analyses of the numerical methods of solving the equations are presented in great detail, as the methods of analyses available in the literature are inadequate for the complicated system of equations encountered. A special study is made of the effects on stability of various methods of handling the non-linear source terms in the equations. Some of the schemes proposed in the literature are found to be subject to severe stability criteria.

A method of obtaining a rigorous solution is devised. The method is always stable, and the use of varying time increment size is allowable. A rigorous solution takes only a few minutes of computer time with an IBM-7094 computer.

To investigate the effects of various limiting assumptions, three problems are studied using the rigorous method and also with methods employing various assumptions. These problems are the start-up, the loss of cooling with subsequent restoration, and the response of the exit concentration to a sinusoidal concentration forcing function at the entrance. For the system investigated, the effects of using an "effectiveness factor" model, neglecting radial changes, and neglecting the axial diffusion and axial velocity variations are found to be not large. The neglecting of reverse reactions, or the use of an average effectiveness factor throughout the whole reactor causes significant errors.

A simplified method, which for the system studied, gives a reasonably good approximation to the true solution, is used to investigate problems in the optimization and control of the reactor. The frequency response of the exit temperature to a sinusoidal forcing upon the optimum wall temperature is found to be equivalent to that of a phase lag network frequently used in regulating systems.

Limitations to the applicability of the simplified method are discussed.

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I. INTRODUCTION

This work is a mathematical study of the transient behavior of a non-adiabatic fixed-bed catalytic reactor.

A fixed-bed catalytic reactor consists of a large number of small porous catalyst pellets contained in a tube through which the reaction mixture is passed for conversion into the desired products. Some reactors are cooled or heated at the wall, while others depend on intermediate heat exchangers. The fixed-bed reactor, together with fluidized-bed reactors and moving-bed reactors belong to the class of reactors called heterogeneous reactors. In these reactors, reactions occur only at the exterior catalyst surface and at the interior surfaces of the catalyst. There are no reactions occurring in the stream.

In the chemical industry, fixed-bed reactors are quite popular. They are used, for instance, in petroleum cracking, in the oxidation of SO_2 to SO_3, and in the oxidation of naphthalene to phthalic anhydride.

The problems involved in the design of a fixed-bed reactor are very complicated. Temperature and concentration change not only in the axial direction, but also in the radial direction for the case in which there is cooling at the wall. The diffusional resistance in the interior of the catalyst gives rise to temperature and concentration gradients inside the catalyst. The film resistance between the stream and the catalyst surface is usually not negligible. This gives a total of three dimensional variations in properties. In addition, the reaction rate expression is usually a non-linear function of temperature and concentration. The stream velocity is a function of position due to the variations in fluid density and void fraction of the bed. Also, strictly speaking, all of the physical properties are variable. The result of all this is a gigantic problem which is complicated enough to challenge the solution even by the largest computers available, to say nothing of a solution by purely analytic methods.

As will be shown later, other investigators have solved reactor problems by making various assumptions in order to obtain a solution within a reasonable time. Since many of these assumptions have never been checked as to whether they are justifiable, it is both interesting and valuable to investigate their effects on the accuracy of the numerical solution obtained. To do this, a standard solution obtained by employing a minimum number of assumptions is required. An efficient way of obtaining such a solution has to be devised, as such a method has never been published, and has been considered to be impossible by some investigators. The main difficulty appears to be the lack of a stable method of solving the system of equations involved.

Stability analyses of numerical solutions as presented by many authors have been found to be inadequate for the complicated system of equations encountered. Therefore, a large part of this work is concerned with stability analyses.

An exothermic system of the oxidation of SO_2 to SO_3 is taken as an example to study the effects of various assumptions on the numerical solution obtained. After this, a short-cut method of solving a fixed-bed reactor problem is proposed. This method is then used in solving an optimization problem and a control problem in the reactor.

II. LITERATURE SURVEY

Reactor calculations published in the literature have been performed employing a large number of simplifying assumptions. The number of assumptions is so large that it seems most convenient for later reference to list them first before the works of various investigators are discussed. These assumptions are:

Assumption A. Diffusion in the interior of the catalyst can be accounted for by using an "effectiveness factor" model.

Assumption B. Radial changes in temperature and concentration can be neglected, with the transfer of heat between the stream and the wall approximated by the use of a heat transfer coefficient.

Assumption C. Reverse reactions are negligible.

Assumption D. Axial diffusion is negligible compared to the much larger transport due to convection.

Assumption E. The Peclet number for both heat and mass transfer is a constant.

Assumption F. The effectiveness factor may be taken as constant.

Assumption G. Radial velocity can be neglected and axial velocity is constant and uniform.

Assumption H. Film resistance between the stream and the catalyst surface is negligible.

Assumption I. The effectiveness factor is unity. This implies that the resistance to diffusion is negligible in the catalyst.

Assumption J. The specific heat of the catalyst and stream are constant.

Assumption K. Material balance for just one limiting component is needed.

Assumption L. The reaction rate is a function only of the temperature and concentration of the stream.

Barkelew(1) studied the stability of fixed-bed reactors with cooling at the wall, using assumptions B, C, D, G, K and L. The reactor behavior near the steady-state was investigated to determine the region where a reactor is unstable. A reactor is defined to be unstable if its highest local temperature is sensitive to slight changes in operating conditions.

Amundson, et al.,(2, 3, 4) also studied the stability of both adiabatic and non-adiabatic reactors, but from a completely different approach. A reactor is said to be unstable if the particle temperature at the steady-state is not unique, but can have two or three different values depending on the particle's previous history. For an unstable reactor, Amundson found that the stream temperature can jump abruptly from one axial location to another adjacent location. Assumptions B, C, G, I, J and K were employed. Both transient and steady-state solutions were obtained. The numerical method proposed by Crank and Nicolson was used with source terms iterated until convergence was assured.

Deans and Lapidus(5, 6) seem to be the first to account for radial changes in temperature and concentration. They proposed a finite mixing-stage model which automatically takes the axial and radial mixing into account. They used assumptions C, E, G, H, I, J, K and L, and obtained both transient and steady-state solutions. Using their model, a very large number of axial mixing-stages are needed, as the total number of axial stages needed should be equal to the length of the reactor divided by the diameter of the catalyst pellet.

Lapidus, et al.,(7) also used the above model to calculate the dynamic response of a three component system, using all the assumptions shown above except assumption K. They reported that three days of computation time were needed with an IBM-704 computer.

Richardson and Fahien(8) calculated the steady-state solution for the oxidation of sulfur dioxide, by using radial diffusivities estimated from assumption E and by using point values for diffusivities obtained experimentally. They used assumptions D, J, K and L, and a reaction rate expression correlated from a previous experiment. Both experimental velocity profiles and an average velocity were used. They found that the use of the experimental diffusivity and velocity profile gave the best solution, while the use of assumption E was found to be poor. These calculated solutions were compared with experimental results.

A steady-state solution for a system of the type $A \rightarrow B \rightarrow C$ was obtained by Carberry and Wendel(9). They employed assumptions A, B, C, J and K.

Froment(10) calculated a steady-state solution for a problem and showed that the radial variations in temperature and concentration are significant. He used assumptions C, D, G, J, K and L.

Both axial and radial mixing in packed beds have been investigated for various gases and liquids by a number of workers(11-18). These experimental results show that for gases the axial and the radial Peclet numbers approach 2 and 11 respectively at high Reynolds numbers. The Peclet number is defined as the ratio of the product of the particle diameter and fluid velocity to the diffusivity. Fahien and Smith(19) correlated the radial Peclet number for mass transfer to the diameter ratio of the packing to the reactor tube.

Numerical solutions of heat conduction problems in two and three dimensions were studied by Douglas and Rachford(20), and also by Brian(21). They used a non-iterative implicit scheme which consisted of integrating in each direction at one time so that the scheme proposed by Thomas(22) can be utilized to avoid the necessity of iterations.

Stone and Brian(23) studied the numerical solution of convective transport problems, and proposed a method of solving one-dimensional problems. Their method, however, does not seem to be applicable to the solution of multi-dimensional problems.

III. DERIVATION OF EQUATIONS

In this section, the differential equations describing the transient behavior of a fixed-bed reactor with wall-cooling will be derived with a minimum of assumptions as listed below:

Assumption M. Catalyst particles are assumed to be so small that, although actually discrete, they can be considered to serve as continuous sources (or sinks) of momentum, material, and heat for the stream. The material contained in the stagnant film around the catalyst is lumped into the stream. In other words, a property in the stream is the lumped average of that in the turbulent stream and that in the stagnant boundary film. Also, it is an average over a volume that is large compared to the particle size, so that the use of a continuous source is justified.

Assumption N. The radii of the catalyst pellets and the void fraction of the bed are constant.

Assumption O. Temperature and concentration in the interior of the catalyst are symmetric with respect to the center of a spherical pellet.

Assumption P. Knudsen diffusion prevails in the solid, and the diffusivity can be taken as a constant. The thermal conductivity of the solid is also constant.

Assumption Q. The same diffusivity for turbulent mass and energy diffusion is used.

In addition to the above assumptions, assumption J, that the specific heat of the catalyst and stream are constant, will be used.

A. EQUATIONS FOR THE STREAM

In the following, the stream equations are derived by applying the principal of conservation, which may be stated

$$\begin{matrix}\text{Rate of accumulation}\\ \text{of a quantity}\end{matrix} = \begin{matrix}\text{Net input of}\\ \text{the quantity}\end{matrix} + \begin{matrix}\text{Source}\\ \text{strength}\end{matrix} \qquad (1)$$

over the exterior void contained per unit volume of the bulk reactor fixed in space.

Total Continuity Equation

Rate of accumulation of material = $f \dfrac{\partial \sigma_f}{\partial \theta}$.

Net input of material = $-\nabla \cdot (f \sigma_f \vec{u})$.

Source of material should be the rate of mass transfer through the

catalyst surface = $f' a_i u_i \sigma'_{fi}$.

Note that primes are used to denote properties of the catalyst pellets. Applying equation (1), we obtain

$$f \frac{\partial \sigma_f}{\partial \theta} = -\nabla \cdot (f \sigma_f \vec{u}) + f' a_i u_i' \sigma_{fi}' . \qquad (2)$$

Making use of the substantial derivative, $\dfrac{D}{D\theta} = \dfrac{\partial}{\partial \theta} + \vec{u} \cdot \nabla$, this can be written as

$$f\,\frac{D\sigma_f}{D\theta} = -f\sigma_f\nabla\cdot\vec{u} + f'a_iu_i'\sigma_{fi}' \ . \qquad (2\text{-a})$$

Continuity Equation for the k-th Component

$$\text{Rate of accumulation of component } k = \frac{\partial(f\sigma_f n_k)}{\partial\theta} \ .$$

Net input of k-th component through diffusion and gross motion

$$= -\nabla\cdot(\vec{m}_k + f\sigma_f n_k\vec{u}) \ .$$

Source of the k-th component is the rate of transfer of the component through the catalyst surface due to diffusion and gross motion

$$= f'a_i\sigma_{fi}'u_i'n_{ki}' + a_i\sigma_{fi}'K_k(n_{ki}' - n_k) \ .$$

Substituting all these into equation (1),

$$\frac{\partial(f\sigma_f n_k)}{\partial\theta} = -\nabla\cdot(\vec{m}_k + f\sigma_f n_k\vec{u}) + f'a_i\sigma_{fi}'u_i'n_{ki}' + a_i\sigma_{fi}'K_k(n_{ki}' - n_k) \ . \qquad (3)$$

Removing the brackets, this becomes

$$f\sigma_f\frac{\partial n_k}{\partial\theta} + fn_k\frac{\partial\sigma_f}{\partial\theta} = -\nabla\cdot\vec{m}_k - n_k\nabla\cdot(f\sigma_f\vec{u}) - f\sigma_f\vec{u}\cdot\nabla n_k$$

$$+ f'a_i\sigma_{fi}'u_i'n_{ki}' + a_i\sigma_{fi}'K_k(n_{ki}' - n_k) \ . \qquad (4)$$

Multiplication of equation (2) by n_k gives

$$f n_k \frac{\partial \sigma_f}{\partial \theta} = -n_k \nabla \cdot (f \sigma_f \vec{u}) + f' a_i u_i' \sigma_{fi}' n_k \, . \tag{5}$$

Subtracting equation (5) from equation (4), and employing the substantial derivative, there results

$$f \sigma_f \frac{D n_k}{D \theta} = -\nabla \cdot \vec{m}_k + f' a_i \sigma_{fi}' u_i' (n_{k_i}' - n_k) + a_i \sigma_{fi}' K_k (n_{ki}' - n_k) . \tag{6}$$

Now, employing total diffusivities of $\underline{\varepsilon}_{dr}$ and $\underline{\varepsilon}_{dx}$ for the radial and the axial direction respectively, the diffusional flux of the component can be written as:

$$\vec{m}_k = -\sigma_f \underline{\varepsilon}_{dr} \frac{\partial n_k}{\partial r} \vec{e}_r - \sigma_f \underline{\varepsilon}_{dx} \frac{\partial n_k}{\partial x} \vec{e}_x \quad . \tag{7}$$

The divergence of this, with the sign changed, will be:

$$-\nabla \cdot \vec{m}_k = \frac{1}{r} \frac{\partial}{\partial r} \left(r \sigma_f \underline{\varepsilon}_{dr} \frac{\partial n_k}{\partial r} \right) + \frac{\partial}{\partial x} \left(\sigma_f \underline{\varepsilon}_{dx} \frac{\partial n_k}{\partial x} \right) . \tag{7-a}$$

Substituting equation (7-a) into equation (6), the continuity equation for the k-th component, is obtained:

$$\frac{Dn_k}{D\theta} = \frac{1}{f\sigma_f r} \frac{\partial}{\partial r} \left(r\sigma_f \underline{\epsilon}_{dr} \frac{\partial n_k}{\partial r} \right) + \frac{1}{f\sigma_f} \frac{\partial}{\partial x} \left(\sigma_f \underline{\epsilon}_{dx} \frac{\partial n_k}{\partial x} \right)$$

$$+ \frac{a_i \sigma_{fi}'}{f\sigma_f} (K_k + f'u_i')(n_{ki}' - n_k) \ . \tag{8}$$

For actual calculation, it is more convenient to rewrite this in the form:

$$\frac{\partial n_k}{\partial \theta} = \left(-u_r + \frac{1}{f} \frac{\partial \underline{\epsilon}_{dr}}{\partial r} + \frac{\underline{\epsilon}_{dr}}{f\sigma_f} \frac{\partial \sigma_f}{\partial r} + \frac{\underline{\epsilon}_{dr}}{fr} \right) \frac{\partial n_k}{\partial r}$$

$$+ \left(-u_x + \frac{1}{f} \frac{\partial \underline{\epsilon}_{dx}}{\partial x} + \frac{\underline{\epsilon}_{dx}}{f\sigma_f} \frac{\partial \sigma_f}{\partial x} \right) \frac{\partial n_x}{\partial x} + \frac{\underline{\epsilon}_{dr}}{f} \frac{\partial^2 n_k}{\partial r^2} + \frac{\underline{\epsilon}_{dr}}{f} \frac{\partial^2 n_k}{\partial x^2}$$

$$+ \frac{a_i \sigma_{fi}'}{f\sigma_f} (K_k + f'u_i')(n_{k_i}' - n_k) \ . \tag{8-a}$$

Momentum Balance

Using the vector and tensor notations employed by Bird, et al.(28).

Rate of accumulation of momentum $= \frac{\partial}{\partial\theta}\left(\frac{f\sigma_f\vec{u}}{g_o}\right)$.

Input of momentum due to gross motion $= -\nabla\cdot(f\sigma_f\vec{u}\,\vec{u}/g_o)$.

Input of momentum due to the pressure gradient $= -\nabla fP$.

Input of momentum due to shear forces $= -\nabla\cdot f\tau$.

Input of momentum due to gravitational force $= f\,\sigma_f\vec{g}$.

Source of momentum is the momentum through the catalyst surface

$$= \int_o^{a_i} \frac{f'\sigma_{fi}'\,\vec{u}_i'u_i'}{g_o}\,ds + \int_o^{a_i} \vec{F}_t\,ds = 0 + \vec{F}_d \ .$$

As is shown by this equation, the transport of momentum between the catalyst and the stream by gross motion is included in the drag force term shown on the right-hand side. However, this $\vec{F}_d$ for $u_i' \neq 0$ should be slightly different from $\vec{F}_d$ for the case $u_i' = 0$, which is available from the literature. This is so because of the influence of u_i' on $\frac{\partial u_t}{\partial r'}$, which will affect the local shear

$$\vec{F}_t = -\eta\left(\frac{\partial u_t}{\partial r'}\right)_i \vec{e}_t \ .$$

All the above expressions are substituted into the balance equation (1) and there results

$$\frac{\partial}{\partial\theta}\left(\frac{f\sigma_f\vec{u}}{g_o}\right) = -\nabla\cdot\frac{f\sigma_f\vec{u}\,\vec{u}}{g_o} - \nabla fP - \nabla\cdot f\tau + f\sigma_f\vec{g} + \vec{F}_d \quad . \tag{9}$$

Removing the brackets, equation (9) becomes

$$\frac{f\sigma_f}{g_o}\frac{\partial\vec{u}}{\partial\theta} + \frac{f\vec{u}}{g_o}\frac{\partial\sigma_f}{\partial\theta} = -\frac{\vec{u}}{g_o}\nabla\cdot(f\sigma_f\vec{u}) - \frac{f\sigma_f\vec{u}}{g_o}\cdot\nabla\vec{u} - \nabla fP - \nabla\cdot f\tau + f\sigma_f\vec{g} + \vec{F}_d \quad . \tag{10}$$

If equation (2) is multiplied by $\vec{u}/g_o$, there is obtained

$$\frac{f\vec{u}}{g_o}\frac{\partial\sigma_f}{\partial\theta} = -\frac{\vec{u}}{g_o}\nabla\cdot(f\sigma_f\vec{u}) + \frac{f'a_iu_i'\sigma_{fi}'\vec{u}}{g_o} \quad . \tag{11}$$

Equation (10) is now simplified by subtraction of equation (11) to become

$$\frac{f\sigma_f}{g_o}\frac{D\vec{u}}{D\theta} = -\nabla fP - \nabla\cdot f\tau + f\sigma_f\vec{g} + \vec{F}_d - \frac{f'a_iu_i'\sigma_{fi}'\vec{u}}{g_o} \quad . \tag{12}$$

Mechanical Energy Balance

For simplifying the energy equation to be derived later, a mechanical energy balance is required. A dot product of equation (12) with $\vec{u}$ is formed to obtain

$$f\sigma_f \frac{D}{D\theta}\left(\frac{1}{2g_o} u^2\right) = -\vec{u}\cdot \nabla fP - \vec{u}\cdot [\nabla\cdot f\tau] + f\sigma_f\vec{u}\cdot\vec{g} + \vec{F}_d\cdot\vec{u} - \frac{f'a_i u_i'\sigma_{fi}'u^2}{g_o} \quad . \tag{13}$$

This equation will be modified by using the following relationships which are written down without proof:

$$-\vec{u}\cdot \nabla fP = fP\nabla\cdot\vec{u} - \nabla\cdot fP\vec{u} \tag{14}$$

$$-\vec{u}\cdot[\nabla\cdot f\tau] = (\tau : \nabla f\vec{u}) - \nabla\cdot[\tau\cdot f\vec{u}] \quad . \tag{15}$$

Substituting the above two equations into equation (13), the mechanical energy balance is obtained:

$$f\sigma_f \frac{D\left(\frac{1}{2g_o} u^2\right)}{D\theta} = fP\nabla\cdot\vec{u} - \nabla\cdot fP\vec{u} + (\tau : \nabla f\vec{u}) - \nabla\cdot[\tau\cdot f\vec{u}] + f\sigma_f(\vec{u}\cdot\vec{g}) + \vec{F}_d\cdot\vec{u} - \frac{f'a_i u_i'\sigma_{fi}'u^2}{g_o} \quad . \tag{16}$$

Energy Balance

Rate of accumulation of internal and kinetic energy

$$= \frac{\partial}{\partial \theta} f\sigma_f \left(E + \frac{1}{2g_o} u^2\right) \quad .$$

Net input of internal and kinetic energy by the gross motion of fluid

$$= - \nabla \cdot f\sigma_f \vec{u} \left(E + \frac{1}{2g_o} u^2\right) \quad .$$

Net input of energy due to thermal and enthalpy diffusion

$$= - \nabla \cdot \vec{q} - \nabla \cdot \vec{H}_d \quad .$$

Net input of energy due to work done by the gravitational force

$$= f\sigma_f \vec{u} \cdot \vec{g} \quad .$$

Net input of energy due to work done by shear forces $= -\nabla \cdot [\tau \cdot f\vec{u}]$.

Net input of energy due to work done by pressure $= - \nabla \cdot fP\vec{u}$.

Source of energy due to transfer of heat and enthalpy through the

catalyst surface $= f' a_i \sigma_{fi}' u_i' H_i' + h_i a_i (T_i' - T)$

$$+ a_i \sigma_{fi}' \sum_k K_k (n_{k_i}' - n_k) \bar{H}_{k_i}' \quad .$$

The energy balance is now obtained by substituting all the above expressions into equation (1),

$$\frac{\partial}{\partial\theta} f\sigma_f \left(E + \frac{1}{2g_o} u^2\right) = - \nabla \cdot f\sigma_f\vec{u} \left(E + \frac{1}{2g_o} u^2\right) - \nabla \cdot \vec{q} - \nabla \cdot \vec{H}_d$$

$$+ f\sigma_f\vec{u} \cdot \vec{g} - \nabla \cdot fP\vec{u} - \nabla \cdot [\tau \cdot f\vec{u}] + h\, a_i (T_i' - T) + f' a_i \sigma_{fi}' u_i' H_i'$$

$$+ a_i \sigma_{fi}' \sum_k K_k (n_{k_i}' - n_k) \bar{H}_{k_i}' \quad . \qquad (17)$$

Removing the brackets this equation becomes

$$f\sigma_f \frac{\partial\left(E + \frac{1}{2g_o} u^2\right)}{\partial\theta} + f\left(E + \frac{1}{2g_o} u^2\right) \frac{\partial\sigma_f}{\partial\theta} = - \left(E + \frac{1}{2g_o} u^2\right) \nabla \cdot (f\sigma_f\vec{u})$$

$$- f\sigma_f\vec{u} \cdot \nabla\left(E + \frac{1}{2g_o} u^2\right) - \nabla \cdot \vec{q} - \nabla \cdot H_d + f\sigma_f\vec{u} \cdot \vec{g} - \nabla \cdot fP\vec{u}$$

$$- \nabla \cdot [\tau \cdot f\vec{u}] + h\, a_i (T_i' - T) + f' a_i \sigma_{fi}' u_i' H_i'$$

$$+ a_i \sigma_{fi}' \sum_k K_k (n_{k_i}' - n_k) \bar{H}_{k_i}' \quad . \qquad (18)$$

To remove the second term in the left-hand side of this equation, equation (2) is multiplied by $(E + \frac{1}{2g_o} u^2)$ to obtain

$$f(E + \frac{1}{2g_o} u^2) \frac{\partial \sigma_f}{\partial \theta} = -(E + \frac{1}{2g_o} u^2) \nabla \cdot (f\sigma_f \vec{u}) + f' a_i u_i' \sigma_{fi}' (E + \frac{1}{2g_o} u^2). \tag{19}$$

Subtracting equation (19) from equation (18) and rearranging the result by using a substantial derivative,

$$\begin{aligned} f\sigma_f \frac{D(E + \frac{1}{2g_o} u^2)}{D\theta} &= -\nabla \cdot \vec{q} - \nabla \cdot \vec{H}_d + f\sigma_f \vec{u} \cdot \vec{g} - \nabla \cdot fp\vec{u} - \nabla \cdot [\tau \cdot f\vec{u}] \\ &+ h\, a_i (T_i' - T) + f' a_i \sigma_{fi}' u_i' (H_i' - E - \frac{1}{2g_o} u^2) \\ &+ a_i \sigma_{fi}' \sum_k K_k (n_{k_i}' - n_k) \bar{H}_{k_i}' \quad . \end{aligned} \tag{20}$$

Now the mechanical energy balance derived previously can be used to remove the kinetic energy term from the left-hand side of this equation. Subtracting equation (16) from equation (20) and representing the viscous dissipation term $-f\tau : \nabla \vec{u}$ by Φ, there results

$$f\sigma_f \frac{DE}{D\theta} = - \nabla\cdot \vec{q} - \nabla\cdot \vec{H}_d - fP\nabla\cdot \vec{u} + \Phi + h_i a_i (T_i' - T)$$

$$+ f' a_i \sigma_{fi}' u_i' (H_i' - E + \frac{1}{2g_o} u^2) + a_i \sigma_{fi}' \sum_k K_k (n_{k_i}' - n_k) \bar{H}_{k_i}' - \vec{F}_d \cdot \vec{u} \quad . \tag{21}$$

From the thermodynamic relation

$$dE = dH - d(PV) = C_p d_T + \sum_k \bar{H}_k dn_k + [(\frac{\partial H}{\partial P})_{T,n} - V]dP - PdV, \tag{22}$$

there follows

$$\frac{DE}{D\theta} = C_p \frac{DT}{D\theta} + \sum_k \bar{H}_k \frac{Dn_k}{D\theta} + [(\frac{\partial H}{\partial P})_{T,n} - V] \frac{DP}{D\theta} - P \frac{DV}{D\theta} \quad . \tag{22-a}$$

This equation is now substituted into equation (21), and there is obtained:

$$f\sigma_f C_p \frac{DT}{D\theta} = - f\sigma_f \sum_k \bar{H}_k \frac{Dn_k}{D\theta} - f\sigma_f (\frac{\partial H}{\partial P})_{T,n} \frac{DP}{D\theta} + f \frac{DP}{D\theta} + f\sigma_f P \frac{DV}{D\theta}$$

$$- \nabla \cdot \vec{q} - \nabla \cdot \vec{H}_d - fP\nabla \cdot \vec{u} + \Phi + h_i a_i (T_i' - T) - \vec{F}_d \cdot \vec{u}$$

$$+ f' a_i \sigma_{fi}' u_i' (H_i' - E + \frac{1}{2g_o} u^2) + a_i \sigma_{fi}' \sum_k K_k (n_{k_i}' - n_k) \bar{H}_{k_i}' \quad . \tag{23}$$

Equation (23) will be simplified by the use of the following relationships:

$$f\sigma_f P \frac{DV}{D\theta} = f\sigma_f P \frac{D(\frac{1}{\sigma_f})}{D\theta} = -\frac{fP}{\sigma_f}\frac{D\sigma_f}{D\theta} = fP\nabla\cdot\vec{u} - \frac{Pf'a_i u_i'\sigma_{fi}'}{\sigma_f} \quad . \qquad (24)$$

From equation (28):

$$\vec{F}_d \cdot \vec{u} = -\nabla(fP)\cdot\vec{u} \quad . \qquad (24\text{-a})$$

By definition:

$$f\frac{DP}{D\theta} = f\frac{\partial P}{\partial\theta} + \vec{u}\cdot\nabla(fP) \quad . \qquad (24\text{-b})$$

Substituting equations (24), (24-a), and (24-b) into equation (23), there results

$$f\sigma_f C_p \frac{DT}{D\theta} = -f\sigma_f \sum_k \bar{H}_k \frac{Dn_k}{D\theta} - f\sigma_f \left(\frac{\partial H}{\partial P}\right)_{T,n} \frac{DP}{D\theta} + f\frac{\partial P}{\partial\theta} - \nabla\cdot\vec{q}$$

$$-\nabla\cdot\vec{H}_d + \Phi + h_i a_i (T_i' - T) + f'a_i\sigma_{fi}'u_i'(H_i' - H + \frac{1}{2g_o}u^2)$$

$$+ a_i\sigma_{fi}' \sum_k K_k (n_{k_i}' - n_k)\bar{H}_{k_i}' \quad . \qquad (25)$$

Now the turbulent enthalpy flux is represented by

$$\vec{H}_d = -\sigma_f \epsilon_{dr} \frac{\partial H}{\partial r} \vec{e}_r - \sigma_f \epsilon_{dx} \frac{\partial H}{\partial x} \vec{e}_x \quad . \tag{25-a}$$

Since

$$dH = C_p dT + \sum_k \bar{H}_k \, dn_k + \left(\frac{\partial H}{\partial P}\right)_{T,n} dP \;, \tag{25-b}$$

if molecular diffusion is neglected, i. e., $\underline{\epsilon}_d = \epsilon_d$, by combining equations (7-a), (25-a), and (25-b), the expression for the enthalpy flux can be written as:

$$\begin{aligned} \vec{H}_d = & -\sigma_f \epsilon_{dr} C_p \frac{\partial T}{\partial r} \vec{e}_r - \sigma_f \epsilon_{dx} C_p \frac{\partial T}{\partial x} \vec{e}_x + \sum_k \bar{H}_k \vec{m}_k \\ & - \sigma_f \epsilon_{dr} \left(\frac{\partial H}{\partial P}\right)_{T,n} \left(\frac{\partial P}{\partial r}\right)_{\theta, x} \vec{e}_r - \sigma_f \epsilon_{dx} \left(\frac{\partial H}{\partial P}\right)_{T,n} \left(\frac{\partial P}{\partial x}\right)_{\theta, r} \vec{e}_x \quad . \end{aligned} \tag{25-c}$$

Using this,

$$\begin{aligned} - \nabla \cdot \vec{H}_d = & \frac{1}{r} \frac{\partial}{\partial r} \left(r \sigma_f C_p \epsilon_{dr} \frac{\partial T}{\partial r}\right) + \frac{\partial}{\partial x} \left(\sigma_f C_p \epsilon_{dx} \frac{\partial T}{\partial x}\right) - \sum_k \bar{H}_k \nabla \cdot \vec{m}_k \\ & - \sum_k \vec{m}_k \cdot \nabla \bar{H}_k + \frac{1}{r} \frac{\partial}{\partial r} \left[\sigma_f \epsilon_{dr} \left(\frac{\partial H}{\partial P}\right)_{T,n} \left(\frac{\partial P}{\partial r}\right)\right] \\ & + \frac{\partial}{\partial x} \left[\sigma_f \epsilon_{dx} \left(\frac{\partial H}{\partial P}\right)_{T,n} \left(\frac{\partial P}{\partial x}\right)\right] \quad . \end{aligned} \tag{26}$$

Equations (6) and (26) are then substituted into equation (25), and the energy equation for the stream becomes

$$f\sigma_f C_p \frac{DT}{D\theta} = \frac{1}{r}\frac{\partial}{\partial r}\left(r\sigma_f C_p \epsilon_{dr} \frac{\partial T}{\partial r}\right) + \frac{\partial}{\partial x}\left(\sigma_f C_p \epsilon_{dx} \frac{\partial T}{\partial x}\right) + h_i a_i (T_i' - T)$$

$$- \nabla \cdot \vec{q} + \Phi - f\sigma_f \left(\frac{\partial H}{\partial P}\right)_{T,n} \frac{DP}{D\theta} + f \frac{\partial P}{\partial \theta} - \sum_k \vec{m}_k \cdot \nabla \bar{H}_k$$

$$+ \frac{1}{r}\frac{\partial}{\partial r}\left[\sigma_f \epsilon_{dr} \left(\frac{\partial H}{\partial P}\right)_{T,n} \left(\frac{\partial P}{\partial r}\right)\right] + \frac{\partial}{\partial x}\left[\sigma_f \epsilon_{dx} \left(\frac{\partial H}{\partial P}\right)_{T,n} \left(\frac{\partial P}{\partial x}\right)\right]$$

$$+ f' a_i \sigma_{fi}' u_i' \left[H_i' - H + \frac{u^2}{2g_o} - \sum_k (n_{ki}' - n_k) \bar{H}_k\right]$$

$$+ a_i \sigma_{fi}' \sum_k K_k (n_{ki}' - n_k)(\bar{H}_{ki}' - \bar{H}_k) \quad . \qquad (27)$$

Equation (27) can be written in an alternate form:

$$\frac{\partial T}{\partial \theta} = \left[-u_r + \frac{1}{f}\frac{\partial \epsilon_{dr}}{\partial r} + \frac{\epsilon_{dr}}{f\sigma_f C_p}\frac{\partial(\sigma_f C_p)}{\partial r} + \frac{\epsilon_{dr}}{fr}\right]\frac{\partial T}{\partial r}$$

$$+ \left[-u_x + \frac{1}{f}\frac{\partial \epsilon_{dx}}{\partial x} + \frac{\epsilon_{dx}}{f\sigma_f C_p}\frac{\partial(\sigma_f C_p)}{\partial x}\right]\frac{\partial T}{\partial x} + \frac{\epsilon_{dr}}{f}\frac{\partial^2 T}{\partial r^2}$$

$$+ \frac{1}{f} \epsilon_{dx} \frac{\partial^2 T}{\partial x^2} + \frac{h_i a_i}{f \sigma_f C_p} (T_i' - T) + \frac{1}{f \sigma_f C_p} \Big\{ -\nabla \cdot \vec{q} + \Phi$$

$$- f \sigma_f \left(\frac{\partial H}{\partial P} \right)_{T,n} \frac{DP}{D\theta} + f \frac{\partial P}{\partial \theta} - \sum_k \vec{m}_k \cdot \nabla \bar{H}_k + \frac{1}{r} \frac{\partial}{\partial r} \left[\sigma_f \epsilon_{dr} \left(\frac{\partial H}{\partial P} \right)_{T,n} \left(\frac{\partial P}{\partial r} \right) \right]$$

$$+ \frac{\partial}{\partial x} \left[\sigma_f \epsilon_{dx} \left(\frac{\partial H}{\partial P} \right)_{T,n} \frac{\partial P}{\partial x} \right] + f' a_i \sigma_{fi}' u_i' \left[H_i' - H + \frac{u^2}{2 g_o} - \sum_k (n_{ki}' - n_k) \bar{H}_k \right]$$

$$+ a_i \sigma_{fi}' \sum_k K_k (n_{ki}' - n_k)(\bar{H}_{ki}' - \bar{H}_k) \Big\} \quad . \qquad (27\text{-a})$$

Equation for Pressure

The momentum equation as given in equation (12) is much too complicated to be used in deriving an equation for pressure. Fortunately, only the pressure gradient term and the drag force term in that equation are important. If only those two terms are retained, equation (12) becomes

$$\vec{F}_d = \nabla f P \quad . \qquad (28)$$

If the drag force is put in the form

$$\vec{F}_d = - F' \vec{u} \quad . \qquad (29)$$

equation (28) will become

$$\vec{u} = - \frac{f}{F'} \nabla P = - \frac{1}{F} \nabla P \ . \tag{30}$$

Compared with the Ergun equation$^{(24)}$, the factor F should take the form:

$$F = \frac{(1 - f)}{f^2 D_p g_o} \left[\frac{150 \mu (1 - f)}{D_p} + 1.75 \sigma_f f \, |u| \right] \ . \tag{31}$$

Substituting equation (30) into equation (2) with the last term neglected and dividing through by f,

$$\frac{\partial \sigma_f}{\partial \theta} = \frac{\sigma_f}{F} \nabla^2 P + \nabla P \cdot \nabla \left(\frac{\sigma_f}{F} \right) \ . \tag{32}$$

Assuming a perfect gas,

$$MP = \sigma_f RT \ . \tag{33}$$

Differentiating with respect to time, this becomes

$$M \frac{\partial P}{\partial \theta} + P \frac{\partial M}{\partial \theta} = \sigma_f R \frac{\partial T}{\partial \theta} + RT \frac{\partial \sigma_f}{\partial \theta} \ . \tag{34}$$

Dividing through by RT and rearranging

$$\frac{\partial \sigma_f}{\partial \theta} = \frac{M}{RT} \frac{\partial P}{\partial \theta} - \frac{\sigma_f}{T} \frac{\partial T}{\partial \theta} + \frac{P}{RT} \frac{\partial M}{\partial \theta} \quad . \tag{35}$$

Substituting equation (35) into equation (32), and dividing through by M/(RT), there is obtained

$$\frac{\partial P}{\partial \theta} = \frac{P}{\bar{F}} \nabla^2 P + \frac{P}{\sigma_f} \nabla P \cdot \nabla \left(\frac{\sigma_f}{F} \right) + \frac{P}{T} \frac{\partial T}{\partial \theta} - \frac{P}{M} \frac{\partial M}{\partial \theta} \quad . \tag{36}$$

This equation can be rewritten in a more convenient form:

$$\begin{aligned} \frac{\partial P}{\partial \theta} = & \left[\frac{P}{rF} + \frac{P}{\sigma_f} \frac{\partial}{\partial r} \left(\frac{\sigma_f}{F} \right) \right] \frac{\partial P}{\partial r} + \left[\frac{P}{\sigma_f} \frac{\partial}{\partial x} \left(\frac{\sigma_f}{F} \right) \right] \frac{\partial P}{\partial x} + \frac{P}{\bar{F}} \frac{\partial^2 P}{\partial r^2} \\ & + \frac{P}{\bar{F}} \frac{\partial^2 P}{\partial x^2} + \left[\frac{P}{T} \frac{\partial T}{\partial \theta} - \frac{P}{M} \frac{\partial M}{\partial \theta} \right] \quad . \end{aligned} \tag{37}$$

B. EQUATIONS FOR THE INTERIOR OF THE CATALYST PELLET

For the interior of the catalyst, the partial pressures of various components rather than their weight fractions, are used. This is more convenient because the reaction rate is usually expressed as a function of temperature and the partial pressures of the components. Also, the amount of a component adsorbed in the solid is a function of temperature and its partial pressure.

Continuity Equation for the k-th Component

Rate of accumulation of component k in lb-moles/sec per unit volume of the catalyst

$$= \frac{\partial}{\partial \theta} \left[\left(\frac{f' P_k'}{RT'} \right) + \underline{K}_k \, P_k'^{\gamma_k} \right] . \tag{38}$$

If it is assumed that the molal flux of component k in the radial direction of the catalyst can be represented by

$$f' u' \frac{P_k'}{RT'} - \frac{D_k'}{RT'} \frac{\partial P_k'}{\partial r'} ,$$

then, the rate of input of component k due to gross motion and diffusion is

$$= \frac{1}{r'^2}\frac{\partial}{\partial r'}\left[-f'r'^2u'\frac{P_k'}{RT'} + \frac{r'^2D_k'}{RT'}\frac{\partial P_k'}{\partial r'}\right]. \qquad (39)$$

Source of component k, lb-moles/(sec)(cu ft) = R_k .

Substitution of all these into equation (1) gives

$$\frac{\partial}{\partial\theta}\left(\frac{f'P_k'}{RT'} + \underline{K}_k P_k'^{\gamma_k}\right) = \frac{1}{r'^2}\frac{\partial}{\partial r'}\left[-f'r'^2u'\frac{P_k'}{RT'} + \frac{r'^2D_k'}{RT'}\frac{\partial P_k'}{\partial r'}\right] + R_k \quad . \qquad (40)$$

Carrying out the differentiation, multiplying through by RT'/(f' + RT' $\gamma_k \underline{K}_k P_k^{\gamma_k-1}$), and rearranging,

$$\frac{\partial P_k'}{\partial\theta} = \frac{2D_k'}{(f' + RT'\gamma_k\underline{K}_kP_k^{\gamma_k-1})r'}\frac{\partial P_k'}{\partial r'} + \frac{D_k'}{(f' + RT'\gamma_k\underline{K}_kP_k^{\gamma_k-1})}\frac{\partial^2 P_k'}{\partial r'^2}$$

$$+ \frac{RT \; R_k}{(f' + RT' \gamma_k \underset{\sim}{K}_k P_k^{\gamma_k - 1})} + \frac{1}{(f' + RT' \gamma_k \underset{\sim}{K}_k P_k^{\gamma_k - 1})} \left(\frac{f' \, P_k'}{T'} \frac{\partial T'}{\partial \theta} \right.$$

$$\left. + \frac{RT'}{r'^2} \frac{\partial}{\partial r'} \left(- f' r'^2 u' \frac{P_k'}{RT'} \right) \right) \quad . \qquad (41)$$

Energy Balance

Rate of accumulation of internal energy per unit volume of catalyst

$$= \frac{\partial}{\partial \theta} \left(\sum_k \frac{f' P_k'}{RT'} \underset{\sim}{\bar{E}}_k' + \sum_k \underset{\sim}{K}_k P_k'^{\gamma_k} \underset{\sim}{\bar{E}}_k + \sigma_s E_s \right) .$$

Rate of input of energy due to gross motion and conduction

$$= \frac{1}{r'^2} \frac{\partial}{\partial r'} \left(- f' r'^2 u' \sum_k \frac{P_k'}{RT'} \underset{\sim}{\bar{H}}_k' + r'^2 k_s \frac{\partial T'}{\partial r'} \right) .$$

Rate of input of enthalpy due to diffusion of material

$$= - \nabla \cdot \sum_k \underset{\sim}{\vec{m}}_k \underset{\sim}{\bar{H}}_k = \frac{1}{r'^2} \sum_k \frac{\partial}{\partial r'} \left(\frac{r'^2 D_k' \underset{\sim}{\bar{H}}_k}{RT'} \frac{\partial P_k'}{\partial r'} \right) .$$

Using equation (1),

$$\frac{\partial}{\partial\theta}\left(\sum_k f'\frac{P_k'}{RT'}\underset{\sim}{\bar{\bar{E}}}_k' + \sum_k \underline{K}_k P_k'^{\gamma_k}\underset{\sim}{\bar{\bar{E}}}_{ks} + \sigma_s E_s\right) = \frac{1}{r'^2}\frac{\partial}{\partial r'}\left(r'^2 k_s \frac{\partial T'}{\partial r'}\right)$$

$$+\frac{1}{r'^2}\frac{\partial}{\partial r'}\left(- f' r'^2 u' \sum_k \frac{P_k'}{RT'}\underset{\sim}{\bar{\bar{H}}}_k' + \frac{r'^2 D_k' \underset{\sim}{\bar{\bar{H}}}_k'}{RT'}\frac{\partial P_k'}{\partial r'}\right) . \qquad (42)$$

If it is assumed that $\underset{\sim}{\bar{\bar{E}}}_{ks} = \underset{\sim}{\bar{\bar{E}}}_k' - \Delta \underset{\sim}{\underline{E}}\, ad_k$, (43)

the left-hand side of equation (42) becomes

$$\frac{\partial}{\partial\theta}\left(\sum_k f'\frac{P_k'}{RT'}\underset{\sim}{\bar{\bar{E}}}_k' + \sum_k \underline{K}_k P_k'^{\gamma_k}\underset{\sim}{\bar{\bar{E}}}_{ks} + \sigma_s E_s\right) = C\frac{\partial T'}{\partial\theta}$$

$$+ \sum_k \underset{\sim}{\bar{\bar{E}}}_k' \frac{\partial}{\partial\theta}\left(f'\frac{P_k'}{RT'} + \underline{K}_k P_k'^{\gamma_k}\right) - \sum_k \Delta\underset{\sim}{\underline{E}}\, ad_k \frac{\partial}{\partial\theta}\left(\underline{K}_k P_k'^{\gamma_k}\right), \qquad (44)$$

$$\text{where } C = \sum_k \left(f'\frac{P_k'}{RT'} + \underline{K}_k P_k'^{\gamma_k}\right)\underset{\sim}{C}_{vk} + \sigma_s C_s \quad . \qquad (45)$$

When equation (40) and equation (44) are substituted into equation (42),

$$C \frac{\partial T'}{\partial \theta} + \frac{1}{r'^2} \sum_k \underset{\sim}{\bar{E}}_k' \frac{\partial}{\partial r'} \Bigg(- f' r'^2 u' \frac{P_k'}{RT'} + \frac{r'^2 D_k'}{RT'} \frac{\partial P_k'}{\partial r'} \Bigg) + \sum_k \underset{\sim}{\bar{E}}_k' R_k$$

$$- \sum_k \Delta \underset{\sim}{E}\, ad_k \left(\underline{K}_k P_k'^{\gamma_k} \right) = \frac{1}{r'^2} \frac{\partial}{\partial r'} \left(r'^2 k_s \frac{\partial T'}{\partial r'} \right)$$

$$+ \frac{1}{r'^2} \frac{\partial}{\partial r'} \Bigg[- f' r'^2 u' \sum_k \frac{P_k'}{RT'} \underset{\sim}{\bar{H}}_k' + \frac{r'^2 D_k' \underset{\sim}{\bar{H}}_k'}{RT'} \frac{\partial P_k'}{\partial r'} \Bigg] . \qquad (46)$$

Rearranging this, an energy equation is obtained:

$$\frac{\partial T'}{\partial \theta} = \frac{2k_s}{C r'} \frac{\partial T'}{\partial r'} + \frac{k_s}{C} \frac{\partial^2 T'}{\partial r'^2} - \frac{1}{C} \sum_k \underset{\sim}{\bar{E}}_k' R_k$$

$$+ \frac{1}{C} \sum_k \Bigg\{ \Delta \underset{\sim}{E}\, ad_k \frac{\partial}{\partial \theta} \left(\underline{K}_k P_k'^{\gamma_k} \right) + \frac{\underset{\sim}{\bar{V}}_k'}{r'^2} \frac{\partial}{\partial r'} \left(- f' r'^2 u' \frac{P_k'}{RT'} + \frac{r'^2 D_k'}{RT'} \frac{\partial P_k'}{\partial r'} \right)$$

$$- f'u' \frac{P_k'}{RT'} \frac{\partial \underset{\sim}{\bar{H}}_k'}{\partial r'} + \frac{D_k'}{RT'} \left(\frac{\partial \underset{\sim}{\bar{H}}_k'}{\partial r'} \right) \left(\frac{\partial P_k'}{\partial r'} \right) \Bigg\} \qquad (47)$$

C. SUMMARY OF EQUATIONS TO BE SOLVED

The equations which have been derived so far are further simplified by neglecting the velocity in the catalyst pellet, the molecular diffusivities in the stream, the space derivatives of diffusivities, the space derivatives of the specific weight of the stream, viscous dissipation, the pressure dependence of enthalpy, the changes in partial volumes, the amount of material adsorbed by the catalyst, and the coupled derivative terms in the catalyst equations. These are neglected not only because it is impossible to include in calculation all the terms in the equations derived before, but also because the terms neglected are believed to be much less significant than the terms retained. For instance, in the original energy equation, i. e., equation (27-a), molecular energy transport and viscous dissipation terms are apparently much smaller than turbulent diffusion or heat generation terms.

The equations to be used in the rigorous solution are listed below with the appropriate boundary conditions:

Continuity Equation for the k-th Component

$$\frac{\partial n_k}{\partial \theta} = \left(-u_r + \frac{\epsilon_{dr}}{fr}\right) \frac{\partial n_k}{\partial r} - u_x \frac{\partial n_k}{\partial x} + \frac{\epsilon_{dr}}{f} \frac{\partial^2 n_k}{\partial r^2} + \frac{\epsilon_{dx}}{f} \frac{\partial^2 n_k}{\partial x^2}$$

$$+ DM1_k \, P_{ki}' + D_k n_k \ . \qquad (48)$$

Assuming a constant viscosity of 0.032 c.p. and solving the Ergun$^{(24)}$ equation for the axial velocity, there results

$$u_x = \frac{-0.01112 + \sqrt{0.0001144 + 0.0674\sigma\left(-\frac{\partial P}{\partial x}\right)}}{0.0674\sigma} \ . \quad u_r = \frac{\left(-\frac{\partial P}{\partial r}\right)}{\left(-\frac{\partial P}{\partial x}\right)} u_x \ .$$

The correlation given by Fahien and Smith(19) for turbulent diffusivity in a packed-bed is used to obtain, for $D_p = 0.25$ in.,

$$\frac{\epsilon_{dr}}{f} = 0.00188\, u_x$$

$$\frac{\epsilon_{dx}}{f} = 0.0104\, u_x \quad .$$

Where $f = 0.35$.

The correlation for mass transfer between the catalyst surface and the stream is used to obtain the following expressions for the coefficients used in equation (48)(29).

$$DM1_1 = 483 \left(\frac{T}{1247} \right)^{1.5} \left(\frac{u_x}{13.45} \right)^{0.49}$$

$$DM1_2 = 610 \left(\frac{T}{1247} \right)^{1.5} \left(\frac{u_x}{13.45} \right)^{0.49}$$

$$DM1_3 = 334 \left(\frac{T}{1247} \right)^{1.5} \left(\frac{u_x}{13.45} \right)^{0.49}$$

$$D_1 = -0.0114 \times DM1_1 \times \sigma T \quad .$$

$$D_2 = -0.00912 \times DM1_2 \times \sigma T \ .$$

$$D_3 = -0.0228 \times DM1_3 \times \sigma T \ .$$

Boundary conditions are:

$$\theta = 0, \quad n_k = n_k^o, \quad k = 1, 2, 3 \ .$$

$$\theta > 0 \ .$$

$$r = 0, \quad \frac{\partial n_k}{\partial r} = 0 \ . \tag{49}$$

$$r = R, \quad \frac{\partial n_k}{\partial r} = 0 \ . \tag{50}$$

$$x = 0, \quad \frac{\partial n_k}{\partial x} = \frac{u_x}{\epsilon_{dx}} (n_k - n_{ke}) \ . \tag{51}$$

$$x = X, \quad \frac{\partial n_k}{\partial x} = 0^* \ . \tag{52}$$

<u>Energy Equation:</u>

$$\frac{\partial T}{\partial \theta} = \left(-u_r + \frac{\epsilon_{dr}}{fr}\right) \frac{\partial T}{\partial r} - u_x \frac{\partial T}{\partial x} + \frac{\epsilon_{dr}}{f} \frac{\partial^2 T}{\partial r^2} + \frac{\epsilon_{dx}}{f} \frac{\partial^2 T}{\partial x^2}$$

$$+ DM1_4 T_i' + D_4 T \ . \tag{53}$$

*See footnote on next page.

The correlation for heat transfer between the catalyst and the surrounding stream is used to obtain:

$$DM1_4 = -D_4 = 390 \left(\frac{T}{1247}\right)^{0.26} \left(\frac{u_x}{13.45}\right)^{0.45} \left(\frac{0.0354}{\sigma}\right)^{0.51} .$$

Boundary conditions are:

Initial Condition $\theta = 0, \quad T = T^0 .$ (54)

Symmetry $r = 0, \quad \frac{\partial T}{\partial r} = 0 .$ (55)

Wall Condition $r = R, \quad T = T_w .$ (56)

Entrance Condition $x = 0, \quad \frac{\partial T}{\partial x} = \frac{u_x}{\epsilon_{dx}} (T - T_e) .$ (57)

Exit Condition $x = X, \quad \frac{\partial T}{\partial x} = 0^* .$

Pressure Equation:

$$\frac{\partial P}{\partial \theta} = P\left\{\left[\frac{1}{rF} + \frac{1}{\sigma_f} \frac{\partial}{\partial r} \left(\frac{\sigma_f}{F}\right)\right] \frac{\partial P}{\partial r} + \frac{1}{\sigma_f} \frac{\partial}{\partial x} \left(\frac{\sigma_f}{F}\right) \frac{\partial P}{\partial x} + \frac{1}{F} \frac{\partial^2 P}{\partial r^2}\right.$$

*This boundary condition was found to be unpractical for a numerical solution. The subject will be discussed later.

$$+ \frac{1}{F} \frac{\partial^2 P}{\partial x^2} + \left\{ \left[\frac{1}{T} \frac{\partial T}{\partial \theta} - \frac{1}{M} \frac{\partial M}{\partial \theta} \right] \right\} . \tag{58}$$

Substituting f, D_p, g_o, μ with numerical values, equation (31) becomes

$$F = 0.055 \left(0.404 + 1.224 \times \sigma_f u_x \right) \quad . \tag{59}$$

Boundary conditions are:

$$\theta = 0, \quad P = P^o \quad . \tag{60}$$

$$r = 0, \quad \frac{\partial P}{\partial r} = 0 \quad . \tag{61}$$

$$r = R, \quad u_r = 0, \text{ so } \frac{\partial P}{\partial r} = 0 \quad . \tag{62}$$

$$x = 0, \quad P = P_e \quad . \tag{63}$$

$$x = X, \quad P = P_1 \quad . \tag{64}$$

Continuity Equation for the k-th Component in Catalyst

$$\frac{\partial P_k'}{\partial \theta} = \frac{2D_k'}{f'r'}\frac{\partial P_k'}{\partial r'} + \frac{D_k'}{f'}\frac{\partial^2 P_k'}{\partial r'^2} + R_k' \ . \qquad (65)$$

$$f' = 0.6 \ .$$

Knudsen diffusivities are evaluated for each component. Estimating the surface area as 1.71 x 10^6 ft^2/lb, and the pore volume of 0.0078 ft^3/lb, and using the equations given in Smith's(30) textbook, the results are

$$D_1' = (0.034/3600)ft^2/sec.$$

$$D_2' = (0.0031/3600)ft^2/sec.$$

$$D_3' = (0.031/3600)ft^2/sec.$$

The reaction rate expression given by Hougen and Watson(29) for the catalytic oxidation of SO_2 is to be used. With conversion factors included, the source terms become:

$$R_1' = -\frac{RT'}{f} \times \frac{0.0257\, e^{14.154 - 14400/T'}}{(1 + \sqrt{Po_2}\, e^{-5.78 + 9224/T'} + Pso_3\, e^{-8.82 + 15220/T'})^2}$$

$$\times \left(Pso_2 \sqrt{Po_2} - Pso_3\, e^{10.1 - 20800/T'} \right) \ .$$

$$R_2' = - R_1' \ .$$

$$R_3' = 0.5\, R_1' \ .$$

Boundary conditions:

$$\theta = 0, \quad P_k' = P_k'^{o} \ . \tag{66}$$

$$r' = 0, \quad \frac{\partial P_k'}{\partial r'} = 0 \ . \tag{67}$$

$$r = r_i, \quad \frac{M_k D_k'}{RT_i'} \frac{\partial P_k'}{\partial r'} = K_k \left(\sigma n_k - \frac{M_k P_{ki}'}{RT_i'} \right) \ . \tag{68}$$

Energy Equation in Catalyst:

$$\frac{\partial T'}{\partial \theta} = \frac{2k_s}{Cr'} \frac{\partial T'}{\partial r'} + \frac{k_s}{C} \frac{\partial^2 T'}{\partial r'^2} + R_T \tag{69}$$

k_s = 0.52 Btu/(sq. ft.) (hr.) (^{o}F/ft.) .

C = 18.5 Btu/ (cu. ft.) (^{o}F) .

$$R_T = \frac{2237.8 \times 0.0257\, e^{+\,14.154\,-\,14400/T'}}{(1 + \sqrt{Po_2}\, e^{-5.78\,+\,9224/T'} + Pso_3\, e^{-8.84\,+\,15220/T'})^2} \qquad (70)$$

$$\times\, (Pso_2 \sqrt{Po_2} - Pso_3\, e^{10.1\,-\,\frac{20800}{T'}})$$

Boundary conditions are:

$$\theta = 0, \quad T' = T'^{o} \qquad (71)$$

$$r' = 0, \quad \frac{\partial T'}{\partial r'} = 0 \qquad (72)$$

$$r' = r_i', \quad k_s \frac{\partial T'}{\partial r'} = h_i\,(T - T_i') \qquad (73)$$

D. COMMENTS ON THE BOUNDARY CONDITION AT EXIT OF REACTOR

At the exit of reactor, the mass flux of the k-th component toward the boundary is

$$(\vec{\underline{m}}_k)_x = f\sigma_f u_x n_k - \sigma_f \epsilon_{dx} \frac{\partial n_k}{\partial x} \quad . \qquad \text{(73-a)}$$

If diffusivity is assumed to be zero outside the packed-bed, the flux away from the boundary is

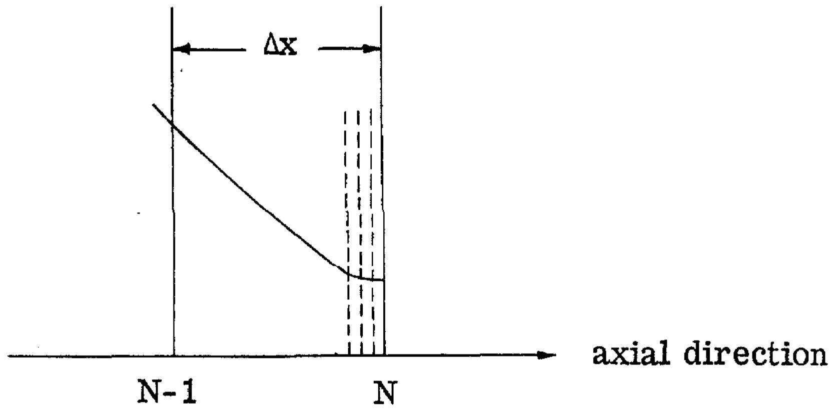
$$(\vec{\underline{m}}_k)_x = u_x'' \sigma_f n_k \quad . \qquad \text{(73-b)}$$

Since $f\sigma_f u_x = \sigma_f u_x''$

by combination of these three equations, there results

$$\frac{\partial n_k}{\partial x} = 0 \quad . \qquad \text{(73-c)}$$

This condition is mathematically applicable, but is hardly usable in practice. The axial concentration profile near the boundary presumably should look like:



So, unless extremely fine meshes are chosen, as is shown with dotted lines, the results would be too inaccurate to be acceptable. For the finite difference method, it is more reasonable to use the following approximations:

$$\frac{\partial}{\partial x}\left(\epsilon_{dx}\frac{\partial n_k}{\partial x}\right) = \frac{1}{\Delta x}\left\{ 0 \times \frac{n_{k_{N+1}} - n_{k_N}}{\Delta x} - \frac{\epsilon_{dx}\left(n_{k_N} - n_{k_{N-1}}\right)}{\Delta x}\right.$$

$$= \frac{\epsilon_{dx}\left(n_{k_{N-1}} - n_{k_N}\right)}{\Delta x^2} \qquad (73\text{-d})$$

$$\frac{\partial n_k}{\partial x} = \frac{n_{k_N} - n_{k_{N-1}}}{\Delta x} \qquad (73\text{-e})$$

The use of equation (73-d) is based on the fact that the turbulent mass diffusivity may be taken as zero outside the reactor. One may tend to think that the condition $n_{k_{N+1}} = n_{k_N}$ is equally logical to use, but in fact such a condition is valid only at the steady-state.

The choice of a backward difference approximation as shown by equation (73-e), rather than a more accurate approximation such as the one in which $n_{k_{N-2}}$ is involved, is to make the scheme proposed by Thomas(22) applicable. Otherwise, an iterative scheme would be required.

IV. NUMERICAL SOLUTION OF THE SYSTEM OF DIFFERENTIAL EQUATIONS

A. GENERAL DISCUSSION

Difficulties Involved in Solving the Equations:

In a numerical method of solving partial differential equations, finite difference approximations are used for time and space derivatives, using finite time and space increments. The solution at the end of a time increment is obtained from that at the beginning of the time increment, and the process is repeated until enough solution is obtained.

Numerous difficulties are encountered in the numerical solution of the system of partial differential equations which is derived above. In the following, these difficulties are listed and the proposals of various workers concerning the methods of handling these difficulties are discussed.

(a). Non-linear source terms in the differential equations. Three methods are available for handling the source terms: They can be evaluated at the beginning of each time increment; the technique used in Runge-Kutta Method for ordinary differential equations can be applied (25); or an iterative method such as that suggested by Crank and Nicolson (26) can be employed. The first two methods are subject to severe stability criteria, while the last one presents a convergence problem. If a convergent scheme is devised, the last method is always stable as will be shown later, but such a method is quite time consuming.

(b). Predominance of convection over diffusion. This has been reported to give an oscillatory solution to a two-dimensional problem when an alternating-direction implicit method is used. If there were no diffusion, the profiles of temperature and concentration in the axial direction would be discontinuous for the transient situation, following an applied step-change in entrance conditions. At a particular location, the change in a property with time would undergo a discontinuous change at a particular instant. It is not surprising that a numerical method cannot handle this convection problem as well as the diffusion problem is handled. Stone and Brian(23) proposed a method of solving the convection problem with improved accuracy over the Crank-Nicolson's method. However, their method is applicable to a one-dimensional problem only.

(c). The coupling between the properties at the surface of the catalyst and those in the stream present a multi-dimensional problem which requires new solution techniques. This will be discussed later.

(d). A stupendous amount of computation time would be required if a method based on published techniques were used. If the source terms are evaluated at the beginning of a time increment, for the problems to be studied, stability of the numerical scheme requires that the time increments be less than 1/200 sec. Stability criteria for such a scheme will be derived later. Total computation time for one transient solution up to steady-state would be about 300 hours with an IBM-7094 computer. Alternatively, an iterative method can be used to avoid the stability problem, but as Lapidus(6, 7) and others have pointed out, the rate of convergence of such a scheme is hard to estimate.

An Ideal Method:

To attain the same order of accuracy, it is much more efficient to use a method in which the time increment is changed from time to time to keep the increase of any property, within one time increment, of the same order of magnitude rather than to use a method in which time increments are kept constant. For the former scheme to be applicable, a method is required which is stable no matter how large the time increment is. Also, to save computation time, it is desirable to avoid the necessity of relying on iterations. Such a method will be suitable not only for a transient problem, but also for a steady-state problem, as in the latter case much larger time increments can be used, and the steady-state solution will be obtainable in ten or fifteen time increments, which is competitive against any iterative methods for solving an elliptic problem.

B. LINEARIZATION OF THE SYSTEM OF NON-LINEAR PARTIAL DIFFERENTIAL EQUATIONS

In the present study, the exothermic oxidation of sulfur dioxide, SO_2, to sulfur trioxide, SO_3, by air is selected for actual calculation.

As a non-linear system is difficult to study, it is desirable to linearize the non-linear source terms in the equations derived previously for the reactor problem. Then, by focusing study on the behavior of the system in the neighborhood of a fixed time, a linear system which is amenable to a reasonably simple analysis is obtained.

For instance, equation (65) can be rewritten as

$$\frac{\partial P_k'}{\partial \theta} = \frac{2D_k'}{f'r'} \frac{\partial P_k'}{\partial r'} + \frac{D'k}{f'} \frac{\partial^2 P_k'}{\partial r'^2} + R_{k_o}' + \sum_k \left(\frac{\partial R_k'}{\partial P_k'} \right) \left(P_k' - P_{k_o}' \right)$$

$$+ \frac{\partial R_k'}{\partial T'} \left(T' - T_o' \right) \quad . \tag{74}$$

Where R_{k_o}' is evaluated with P_{k_o}'s and T_o'. In this way, the equations for the interior of the catalyst, namely, equation (65) for $k = 1$ to 3, and equation (69), can be combined in vector form as

$$\frac{\partial \vec{\Phi}_c}{\partial \theta} = (D_1)\,\frac{\partial \vec{\Phi}_c}{\partial r'} + (D_2)\,\frac{\partial^2 \vec{\Phi}_c}{\partial r'^2} + (S_c)\,\vec{\Phi}_c + \vec{C}_c{}' \quad . \tag{75-a}$$

Where $\vec{\Phi}_c = \text{col}\,(P_1', P_2', P_3', T')$. (76)

$$(D_1) = \begin{pmatrix} \frac{2D_1'}{f'r'} & & & 0 \\ & \frac{2D_2'}{f'r'} & & \\ & & \frac{2D_3'}{f'r'} & \\ 0 & & & \frac{2k_s}{Cr'} \end{pmatrix} \tag{77}$$

$$(D_2) = \begin{pmatrix} \frac{D_1'}{f'} & & & 0 \\ & \frac{D_2'}{f'} & & \\ & & \frac{D_3'}{f'} & \\ 0 & & & \frac{k_s}{C} \end{pmatrix} \tag{78}$$

$$(S_c) = \begin{pmatrix} \frac{\partial R_1'}{\partial P_1'} & \frac{\partial R_1'}{\partial P_2'} & \frac{\partial R_1'}{\partial P_3'} & \frac{\partial R_1'}{\partial T'} \\ \frac{\partial R_2'}{\partial P_1'} & \frac{\partial R_2'}{\partial P_2'} & \frac{\partial R_2'}{\partial P_3'} & \frac{\partial R_2'}{\partial T'} \\ \frac{\partial R_3'}{\partial P_1'} & \frac{\partial R_3'}{\partial P_2'} & \frac{\partial R_3'}{\partial P_3'} & \frac{\partial R_3'}{\partial T'} \\ \frac{\partial R_T'}{\partial P_1'} & \frac{\partial R_T'}{\partial P_2'} & \frac{\partial R_T'}{\partial P_3'} & \frac{\partial R_T'}{\partial T'} \end{pmatrix} . \qquad (79\text{-a})$$

$$\vec{C}_c' = \begin{pmatrix} R_{1_o}' \\ R_{2_o}' \\ R_{3_o}' \\ R_T' \end{pmatrix} - (S_c)\, \vec{\Phi}_{c_o} \qquad (79\text{-b})$$

Since (S_c) as shown by equation (79-a) is not diagonal, the solution of equation (75-a) by an implicit method will require an iterative scheme. To avoid this, equation (79-a) is replaced by

$$(S_c) = \lambda_{(S_c)}\,(I) + [(S_c) - \lambda_{(S_c)}\,(I)] \tag{79}$$

where $\lambda_{(S_c)}$ is the only non-zero eigen-value of (S_c), and is equal to

$$\lambda_{(S_c)} = \left(\frac{\partial R_1{}'}{\partial P_1{}'}\right) + \left(\frac{\partial R_2{}'}{\partial P_2{}'}\right) + \left(\frac{\partial R_3{}'}{\partial P_3{}'}\right) + \left(\frac{\partial R_T{}'}{\partial T'}\right) \quad ,$$

which is always negative for the problems to be studied.

It is obvious that the eigen-values of $[(S_c) - \lambda_{(S_c)}(I)]$ are zero and $-\lambda_{(S_c)}$, which is always positive.

Replacing equation (79-a) by equation (79), equation (75-a) becomes

$$\frac{\partial \vec{\Phi}_c}{\partial \theta} = (D_1)\,\frac{\partial \vec{\Phi}_c}{\partial r'} + (D_2)\,\frac{\partial^2 \vec{\Phi}_c}{\partial r'^2} + \lambda_{(S_c)}\,\vec{\Phi}_c + \vec{C}_c \ . \tag{75}$$

Where $\vec{C}_c = \vec{C}_c{}' + [(S_c) - \lambda_{(S_c)}\,(I)]\,\vec{\Phi}_{c_o}$

$$= \begin{pmatrix} R_{1_o}{}' \\ R_{2_o}{}' \\ R_{3_o}{}' \\ R_{T_o}{}' \end{pmatrix} - \lambda_{(S_c)}\,\vec{\Phi}_{c_o} \ . \tag{80}$$

In the following, it will be shown that the operation just performed for transforming equation (75-a) into equation (75) corresponds to employing the stoichiometry of the reaction to account for the dependence upon the other variables of the source term in the equation for one variable.

If the effect of diffusion is temporarily neglected, it is apparent that

$$P_i' - P_{i_o}' = (P_k' - P_{k_o}') \times \frac{R_i'}{R_k'} \quad . \tag{80-a}$$

$$\frac{\partial R_k'}{\partial P_i'} = \frac{R_k'}{R_i} \frac{\partial R_i'}{\partial P_i'} \quad . \tag{80-b}$$

where i, k = 1 to 4; P_4' denotes T'; and R_4' denotes R_T'.

Substituting these equations into equation (74), there is obtained

$$\frac{\partial P_k'}{\partial \theta} = \frac{2D_k'}{f'r'} \frac{\partial P_k'}{\partial r'} + \frac{D_k'}{f'} \frac{\partial^2 P_k'}{\partial r'^2}$$

$$+ R_{k_o}' + (P_k' - P_{k_o}') \lambda_{(S_c)} \quad . \tag{80-c}$$

It should be noted that the diffusion terms have been included in this equation.

The combined equation corresponding to equation (75-a) will be:

$$\frac{\partial \vec{\Phi}_c}{\partial \theta} = (D_1) \frac{\partial \vec{\Phi}_c}{\partial r'} + (D_2) \frac{\partial \vec{\Phi}_c}{\partial r'^2} + \lambda_{(S_c)} \vec{\Phi}_c + \vec{C}_c \quad , \qquad (80\text{-d})$$

where

$$\vec{C}_c = \begin{pmatrix} R_{1_o}' \\ R_{2_o}' \\ R_{3_o}' \\ R_{T_o}' \end{pmatrix} - \lambda_{(S_c)} \vec{\Phi}_{c_o} \qquad (80\text{-e})$$

Equation (80-d) is identical to equation (75), and the physical meaning of using equation (75) instead of equation (75-a) has been established.

Within a short period of time, the terms for the stream equations can be simplified by removal of the terms containing the properties at the catalyst surface. For instance, in equation (48), if P_{ki}' is considered as a function of θ and n_k,

$$P_{ki}'(\theta, n_k) = P_{ki}'(\theta, {}_o n_k) + \left(\frac{\partial P_{ki}'}{\partial n_k}\right)_\theta (n_k - {}_o n_k)$$

$$= {}_o P_{ki}' - \left(\frac{\partial P_{ki}'}{\partial n_k}\right)_\theta {}_o n_k + \left(\frac{\partial P_{ki}'}{\partial n_k}\right)_\theta n_k \; . \quad (81)$$

Where ${}_o P_{ki}'$ is P_{ki}' obtained at time θ if the stream concentration remained at ${}_o n_k$, which is the value at time θ_o.

Equation (81) allows equation (48) to be rewritten as:

$$\frac{\partial n_k}{\partial \theta} = (-u_r + \frac{\epsilon_{dr}}{f}) \frac{\partial n_k}{\partial r} - u_x \frac{\partial n_k}{\partial x} + \frac{\epsilon_{dr}}{f} \frac{\partial^2 n_k}{\partial r^2} + \frac{\epsilon_{dx}}{f} \frac{\partial^2 n_k}{\partial x^2}$$

$$+ \left[DM1_k \text{ x } \left(\frac{\partial P_{ki}'}{\partial n_k}\right)_\theta + D_k \right] n_k + DM1_k \left[{}_o P_{ki}' - \left(\frac{\partial P_{ki}'}{\partial n_k}\right)_\theta {}_o n_k \right] \; . \quad (82)$$

Repeating this procedure with equation (53), all the stream equations can be combined to give the vector equation:

$$\frac{\partial\vec{\Phi}_f}{\partial\theta} = (D_3)\,\frac{\partial\vec{\Phi}_f}{\partial r} + (D_4)\,\frac{\partial\vec{\Phi}_f}{\partial x} + (D_5)\,\frac{\partial^2\vec{\Phi}_f}{\partial r^2}$$

$$+ (D_6)\,\frac{\partial^2\vec{\Phi}_f}{\partial x^2} + (S_f)\,\vec{\Phi}_f + \vec{C}_f \quad . \qquad (83)$$

where

$$\vec{\Phi}_f = \mathrm{col}\ (n_1,\ n_2,\ n_3,\ T,\ P) \ ,$$

$$(D_3) = \begin{pmatrix} (-u_r + \frac{\epsilon_{dr}}{f}) & & & & 0 \\ & (-u_r + \frac{\epsilon_{dr}}{f}) & & & \\ & & (-u_r + \frac{\epsilon_{dr}}{f}) & & \\ & & & (-u_r + \frac{\epsilon_{dr}}{f}) & \\ 0 & & & & P\left[\frac{1}{rF} + \frac{1}{\sigma_f}\frac{\partial}{\partial r}\left(\frac{\delta_f}{F}\right)\right] \end{pmatrix} . \qquad (84)$$

$$(D_4) = \begin{pmatrix} -u_x & & & & 0 \\ & -u_x & & & \\ & & -u_x & & \\ & & & -u_x & \\ 0 & & & & \frac{P}{\sigma_f}\,\frac{\partial}{\partial x}\left(\frac{\sigma_f}{F}\right)\frac{\partial P}{\partial x} \end{pmatrix} . \qquad (85)$$

$$(D_5) = \begin{pmatrix} \frac{\epsilon_{dr}}{f} & & & & 0 \\ & \frac{\epsilon_{dr}}{f} & & & \\ & & \frac{\epsilon_{dr}}{f} & & \\ & & & \frac{\epsilon_{dr}}{f} & \\ 0 & & & & \frac{P}{\bar{F}} \end{pmatrix} . \qquad (86)$$

$$(D_6) = \begin{pmatrix} \frac{\epsilon_{dx}}{f} & & & & 0 \\ & \frac{\epsilon_{dx}}{f} & & & \\ & & \frac{\epsilon_{dx}}{f} & & \\ & & & \frac{\epsilon_{dx}}{f} & \\ 0 & & & & \frac{P}{\bar{F}} \end{pmatrix} . \qquad (87)$$

$$(S_f) = \begin{pmatrix} \left[DM1_1 \cdot \left(\frac{\partial P_{1_i}{}'}{\partial n_1}\right)_\theta + D_1\right] & & & & 0 \\ & \left[DM1_2 \cdot \left(\frac{\partial P_{2_i}{}'}{\partial n_2}\right)_\theta + D_2\right] & & & \\ & & \left[DM1_3 \cdot \left(\frac{\partial P_{3_i}{}'}{\partial n_3}\right)_\theta + D_3\right] & & \\ & & & \left[DM1_4 \cdot \left(\frac{\partial T_i{}'}{\partial T}\right)_\theta + D_4\right] & \\ 0 & & & & \left(\frac{1}{T}\,\frac{\partial T}{\partial \theta} - \frac{1}{M}\,\frac{\partial M}{\partial \theta}\right) \end{pmatrix} . \tag{88}$$

$$\vec{C}_f = \begin{pmatrix} DM1_1\left[{}_oP_{1_i} - \frac{\partial P_{1_i}{}'}{\partial n_1}{}_\theta\ {}_on_1\right] \\ DM1_2\left[{}_oP_{2_i} - \frac{\partial P_{2_i}{}'}{\partial n_2}{}_\theta\ {}_on_2\right] \\ DM1_3\left[{}_oP_{3_i} - \frac{\partial P_{3_i}{}'}{\partial n_3}{}_\theta\ {}_on_3\right] \\ DM1_4\left[{}_oT_i{}' - \left(\frac{\partial T_i{}'}{\partial T}\right)_\theta {}_oT\right] \\ 0 \end{pmatrix} . \tag{89}$$

C. TRANSFORMATION OF THE SYSTEM OF LINEAR PARTIAL DIFFERENTIAL EQUATIONS INTO A SYSTEM OF ORDINARY DIFFERENTIAL EQUATIONS

Thus far, the linear partial differential equations (75) and (83) have been obtained. These equations are valid over a short period of time after a certain fixed time around which the behavior of the system is of interest. However, the stability analysis of partial differential equations is not generally known. However, the analysis of the stability of a system of ordinary differential equations is well-established. For this reason, before carrying out a stability analysis, it is desirable to transform the system of partial differential equations into a system of ordinary differential equations, which are applicable at a particular location in space. This can be accomplished by assuming that the solution to the system of partial differential equations can be expanded into a complex Fourier series over the space (27). Thus, for the stream:

$$\vec{\Phi}_f = \sum_{\vec{k}} \vec{G}_f(\vec{k})\, e^{i\vec{k}\cdot\vec{y}} = \sum_{\vec{k}} \vec{\Phi}_f(\vec{k}) \quad , \tag{90}$$

where $\vec{k} = \begin{pmatrix} 2\pi j_r/L_r \\ 2\pi j_x/L_x \end{pmatrix}$. (91)

$$y = \begin{bmatrix} r \\ x \end{bmatrix} . \tag{92}$$

j_r and j_x are integers from $-\infty$ to $+\infty$.

L_r and L_x are periods in the r and x directions respectively.

The space derivatives in equation (83) are usually approximated by central difference formulae. For example

$$\left(\frac{\partial \vec{\Phi}_f}{\partial r}\right)_{\text{at } \vec{y}} = \frac{\vec{\Phi}_f\,(r + \Delta r,\ x) - \vec{\Phi}_f\,(r - \Delta r,\ x)}{2\Delta r} . \tag{93}$$

Using the expansion expressed in equation (90), this derivative becomes

$$\left(\frac{\partial \vec{\Phi}_f}{\partial r}\right)_{\text{at } \vec{y}} = \frac{1}{2\Delta r}\left[\sum_{\vec{k}} \vec{G}_f\,(\vec{k})\,\left(e^{i\vec{k}\cdot\vec{y}}\right)\left(e^{ik_r\Delta r}\right)\right.$$

$$\left.-\sum_{\vec{k}} \vec{G}_f\,(\vec{k})\left(e^{i\vec{k}\cdot\vec{y}}\right)\left(e^{-ik_r\Delta r}\right)\right] = \sum_{\vec{k}} \vec{G}_f\,(\vec{k})\left(e^{i\vec{k}\cdot\vec{y}}\right)\frac{i\sin(k_r\Delta r)}{\Delta r} .$$

$$= \sum_{\vec{k}} \vec{\Phi}_f (\vec{k}) \frac{i \sin(k_r \Delta r)}{\Delta r} \quad . \tag{94}$$

Taking the limit as $\Delta r \rightarrow 0$, equation (94) gives

$$\left(\frac{\partial \vec{\Phi}_f}{\partial r} \right)_{\text{at } \vec{y}} = \sum_{\vec{k}} i\, k_r\, \vec{\Phi}_f (\vec{k}) \quad . \tag{95}$$

Similarly, for the x-derivative,

$$\left(\frac{\partial \vec{\Phi}_f}{\partial x} \right)_{\text{at } \vec{y}} \doteqdot \sum_{\vec{k}} \vec{\Phi}_f (\vec{k}) \frac{i \sin(k_x \Delta x)}{\Delta x} \quad . \tag{96}$$

and as a limiting value when Δx goes to 0 :

$$\left(\frac{\partial \vec{\Phi}_f}{\partial x} \right)_{\text{at } \vec{y}} = \sum_{\vec{k}} i\, k_x\, \vec{\Phi}_f (\vec{k}) \quad . \tag{97}$$

For the second derivative:

$$\left(\frac{\partial^2 \vec{\Phi}_f}{\partial r^2} \right)_{\text{at } \vec{y}} \doteqdot \frac{1}{\Delta r^2} \left[\vec{\Phi}_f (r + \Delta r,\ x) - 2\vec{\Phi}_f (r,\ x) + \vec{\Phi}_f (r - \Delta r,\ x) \right]$$

$$= \frac{1}{\Delta r^2} \sum_{\vec{k}} \vec{G}(\vec{k}) e^{i\vec{k} \cdot \vec{y}} \left(e^{i k_r \Delta r} - 2 + e^{-i k_r \Delta r}\right)$$

$$= \sum_{\vec{k}} \vec{\Phi}_f(\vec{k}) \, \frac{-4 \sin^2\left(\frac{k_r \Delta r}{2}\right)}{\Delta r^2} \quad . \tag{98}$$

Taking a limit as $\Delta r \to 0$, there is obtained the differential value:

$$\left(\frac{\partial^2 \vec{\Phi}_f}{\partial r^2}\right)_{\text{at } \vec{y}} = \sum_{\vec{k}} (-k_r^{\,2}) \, \vec{\Phi}_f(\vec{k}) \quad . \tag{99}$$

Similarly:

$$\left(\frac{\partial^2 \vec{\Phi}_f}{\partial x^2}\right)_{\text{at } \vec{y}} \doteq \sum_{\vec{k}} \vec{\Phi}_f(\vec{k}) \, \frac{-4 \sin^2\left(\frac{k_x \Delta x}{2}\right)}{\Delta x^2} \quad . \tag{100}$$

$$\frac{\partial^2 \vec{\Phi}_f}{\partial x^2}_{\text{at } \vec{y}} = \sum_{\vec{k}} (-k_x^{\,2}) \, \vec{\Phi}_f(\vec{k}) \quad . \tag{101}$$

If equations (90), (95), (97), (99) and (101) are substituted into equation (83), there is obtained:

$$\frac{d \sum_{\vec{k}} \vec{\Phi}_f(\vec{k})}{d\theta} = (D_3) \sum_{\vec{k}} i\, k_r\, \vec{\Phi}_f(\vec{k}) + (D_4) \sum_{\vec{k}} i\, k_x\, \vec{\Phi}_f(\vec{k}) + (D_5) \sum_{\vec{k}} (-k_r^2)\, \vec{\Phi}_f(\vec{k})$$

$$+ (D_6) \sum_{\vec{k}} (-k_x^2)\, \vec{\Phi}_f(\vec{k}) + (S_f) \sum_{\vec{k}} \vec{\Phi}_f(\vec{k}) + \vec{C}_f \quad , \qquad (102)$$

Or one can write this for just one harmonic of the Fourier series:

$$\frac{d \vec{\Phi}_f(\vec{k})}{d\theta} = [\, i\, k_r (D_3) + i\, k_x (D_4) - k_r^2 (D_5) - k_x^2 (D_6) + (S_f) \,]\, \vec{\Phi}_f(\vec{k})$$

$$+ \vec{C}_f(\vec{k}) = (A_f)\, \vec{\Phi}_f(\vec{k}) + \vec{C}_f(\vec{k}) \quad , \qquad (103)$$

where $(A_f) = [\, i\, k_r (D_3) + i\, k_x (D_4) - k_r^2 (D_5) - k_x^2 (D_6) + (S_f) \,]$. (104)

If finite difference approximations are used for the space derivatives, instead of equation (103), the following equation is obtained by substituting equations (90), (94), (96), (98) and (100) into equation (83) and retaining just one harmonic:

$$\begin{aligned} \frac{d\,\vec{\Phi}_f(\vec{k})}{d\theta} &= \left[\frac{i \sin(k_r \Delta r)}{\Delta r} (D_3) + \frac{i \sin(k_x \Delta x)}{\Delta x} (D_4) - \frac{4 \sin^2(\frac{k_r \Delta r}{2})}{\Delta r^2} (D_5) \right. \\ &\quad \left. - \frac{4 \sin^2(\frac{k_x \Delta x}{2})}{\Delta x^2} (D_6) + (S_f) \right] \vec{\Phi}_f(\vec{k}) + \vec{C}_f(\vec{k}) \\ &= (B_f)\, \vec{\Phi}_f(\vec{k}) + \vec{C}_f(\vec{k}) \quad , \end{aligned} \tag{105}$$

where

$$\begin{aligned} (B_f) &= \left[\frac{i \sin(k_r \Delta r)}{\Delta r} (D_3) + \frac{i \sin(k_x \Delta x)}{\Delta x} (D_4) \right. \\ &\quad \left. - \frac{4 \sin^2(\frac{k_r \Delta r}{2})}{\Delta r^2} - \frac{4 \sin(\frac{k_x \Delta x}{2})}{\Delta x^2} (D_6) + (S_f) \right] \quad . \end{aligned} \tag{106}$$

For the interior of the catalyst, the expansion

$$\vec{\Phi}_c = \sum_{k_{r'}} \vec{\Phi}_c (k_{r'}) = \sum_{k_{r'}} \vec{G}_c (k_{r'}) e^{i k_{r'} r'} \quad , \tag{107}$$

where $k_r = 2\pi j_{r'}/L_{r'}$ (108)

$j_{r'}$ = integers from $-\infty$ to $+\infty$,

$L_{r'}$ = period in r' direction

is employed.

Using the above expansion, equation (75) can be transformed into the following, if only one harmonic is written:

$$\frac{d \vec{\Phi}_c (k_{r'})}{d\theta} = [i k_{r'} (D_1) - k_{r'}^{2} (D_2) + \lambda_{(S_c)} (I)] \vec{\Phi}_c (k_{r'}) + \vec{C}_c (k_{r'})$$

$$= (A_c) \vec{\Phi}_c (k_{r'}) + \vec{C}_c (k_{r'}) \quad , \tag{109}$$

where $(A_c) = [i k_r{}' (D_1) - k_{r'}^{2} (D_2) + \lambda_{(S_c)} (I)]$. (110)

And if finite difference approximations are used for space derivatives:

$$\frac{d\vec{\Phi}_c(k_{r'})}{d\theta} = \left[\frac{i \sin(k_{r'}\Delta r')}{\Delta r'}(D_1) - \frac{4\sin^2\left(\frac{k_{r'}\Delta r'}{2}\right)}{\Delta r'^2}(D_2) + \lambda_{(S_c)}(I)\right]\vec{\Phi}_c(k_{r'})$$

$$+ \vec{C}_c(k_{r'}) = (B_c)\,\vec{\Phi}_c(k_{r'}) + \vec{C}_c(k_{r'}) \quad , \qquad (111)$$

$$\text{where } (B_c) = \left[\frac{i \sin(k_{r'}\Delta r')}{\Delta r'}(D_1) - \frac{4\sin^2\left(\frac{k_{r'}\Delta r'}{2}\right)}{\Delta r'^2}(D_2) + \lambda_{(S_c)}(I)\right]. \qquad (112)$$

It has been shown that at a particular location in space, the system of partial differential equations for the stream as represented by equation (83) can be expanded into an infinite number of systems of ordinary differential equations represented by equation (103) for one particular harmonic; and similarly, equation (75) can be expanded into an infinite number of systems like that shown by equation (109). If space derivatives are approximated by finite difference methods, in place of the above mentioned equations, equations (105) and (111) are obtained. Note that the use of finite difference approximations for the space derivatives simply reduces the absolute values of the diagonal elements in matrices (A_f) and (A_c). As will be shown later, this will have the effect of rendering the stability criteria slightly less severe for an unstable method, such as the forward difference method.

D. STABILITY ANALYSIS

Definition of Stability

For the system of partial differential equations (83) to be stable, it is required that the system of ordinary differential equations (103) be stable for all $\vec{k}$, i.e., for all harmonics of the Fourier series. By being stable it is meant that the solution is bounded as time goes to infinity. So, in order to study the stability of the original system of partial differential equations, one can alternatively investigate the stability of the deduced system of ordinary differential equations.

For simplicity, $\vec{k}$ is dropped in equation (103) to obtain:

$$\frac{d\vec{\Phi}_f}{d\theta} = (A_f)\,\vec{\Phi}_f + \vec{C}_f \quad . \tag{113}$$

It must be noted that (A_f) and $\vec{C}_f$ can be considered to be constant only for a short duration of time, and that they are functions of $\vec{k}$.

The behavior of this system of equations and the behavior of various numerical solutions to this system can now be investigated.

If all eigenvalues of (A_f) are distinct, the analytic solution of equation (113) is

$$\vec{\Phi}_f = \sum_j \xi_j\, e^{\lambda_j \theta}\, \vec{\beta}_j - A^{-1}\vec{C} \quad , \tag{114}$$

with ξ_j's satisfying the initial condition

$$\vec{\Phi}_f^{\,o} = \sum_j \xi_j \vec{\beta}_j \quad . \tag{115}$$

It is obvious that if all λ_j's have negative real parts, $\vec{\Phi}_f$ will be bounded and reach the steady-state solution $-A^{-1}\vec{C}$ as $\theta \to \infty$, no matter what the initial condition is. A matrix having eigenvalues with all negative real parts will be called a stable matrix in this study.

A numerical solution to equation (113) can be put in the form:

$$(\vec{\Phi}_f)_N = \sum_j \omega_j q_j^{\theta/h} \vec{b}_j - A^{-1}\vec{C} \quad , \tag{116}$$

with ω_j's satisfying the initial conditions

$$\vec{\Phi}_f^{\,o} = \sum_j \omega_j \vec{b}_j \quad . \tag{117}$$

For the numerical solution (116) to be stable, it is required that all q_j's be less than one in absolute value. A stable numerical scheme should therefore generate a q (or q's for a multilevel method) of modulus less than one if its (or their) corresponding eigenvalue of the original matrix has a negative real part.

In case there is one (or maybe more than one) eigenvalue, say λ_j, which has a positive real part, then there exists corresponding to this λ_j a q_j with modulus greater than one. In this case, both the analytical and the numerical solutions will grow without bound as time increases, and the system is said to be unstable. If one is using a three or more level method, corresponding to the λ_j, there would exist one or more parasitic roots q_j', q_j'', etc. The absolute values of these must be smaller than one, or the numerical solution will be unsatisfactory as some spurious solutions will grow in magnitude as time goes on.

Solutions (114) and (116) show that only the complimentary solution is related to the stability of the system. Therefore, in the following it is appropriate to investigate only the homogeneous equation:

$$\frac{d\vec{\Phi}}{d\theta} = (A)\,\vec{\Phi} \quad . \tag{118}$$

In the above equation, all the subscripts have been dropped for simplicity. The stability of a numerical method for solving equation (118) will be analyzed by finding the relationship between an eigenvalue of (A) and the corresponding q for the numerical method. A mapping of one upon the other will be shown on two complex planes to indicate the region of stability.

Forward-Difference Method

This is the simplest of all methods and is easily applicable to a non-linear problem. In this method, the right-hand-side of equation (118) is evaluated at the beginning of each time increment. Thus:

$$\vec{\Phi}_{\ell+1} - \vec{\Phi}_{\ell} = h\,(A)\,\vec{\Phi}_{\ell} \quad . \tag{119}$$

$$\text{If} \quad \vec{\Phi}_{\ell} = q^{\ell}\,\vec{b} \quad , \tag{120}$$

then equation (119) becomes

$$\left[(I)(q-1) - h\,(A)\right] q^{\ell}\,\vec{b} = 0 \quad . \tag{121}$$

For equation (121) to have a non-trivial solution, it is necessary that

$$\left|(I)(q-1) - h\,(A)\right| = 0 \quad . \tag{122}$$

And from this the relationship:

$$\lambda h = q - 1 \tag{123}$$

is obtained.

This relationship is shown in Figure 1. The shaded area on the λh-plane corresponds to the shaded area on the q-plane, and these are unstable regions. This plot shows that the applicability of this method is very limited because of the small stability region. If λh is a pure imaginary number, (which corresponds to a pure convection problem), the plot tells that the corresponding $|q|$ is always greater than one, and, therefore, the method is unstable no matter how small a time increment is taken.

Crank-Nicolson's Method(26)

In this method, the right-hand-side of equation (118) is the average of that evaluated at the beginning and that evaluated at the end of a time increment:

$$\vec{\Phi}_{\ell+1} - \vec{\Phi}_{\ell} = 0.5h\,(A)\,(\vec{\Phi}_{\ell+1} + \vec{\Phi}_{\ell}) \quad . \tag{124}$$

Substituting equation (120) and rearranging

$$\left[(I)\,(q - 1) - 0.5h\;(q + 1)\,(A) \right] q^{\ell} \vec{b} = 0 \quad . \tag{125}$$

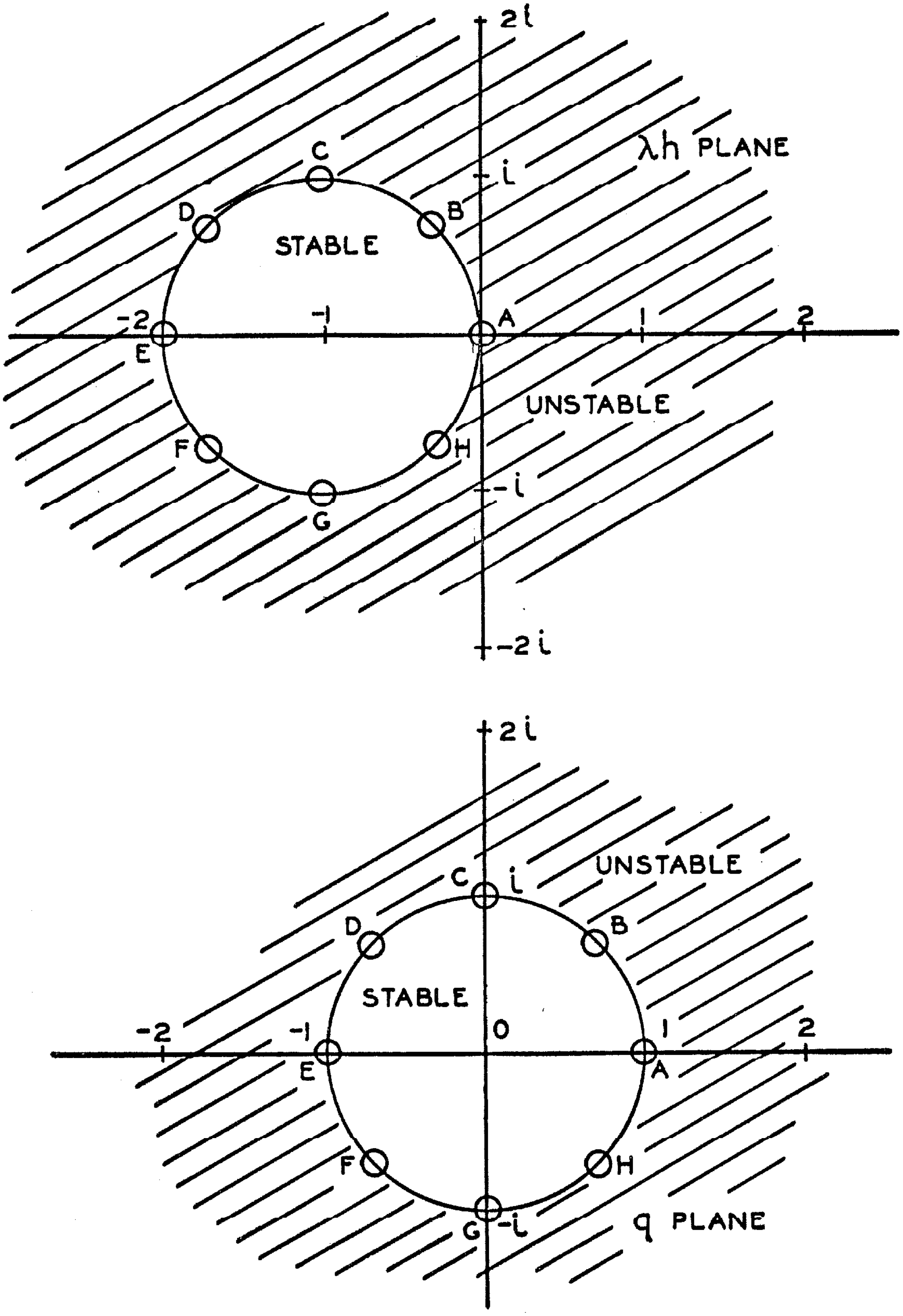


Figure 1. Stability Region of Forward Difference Method.

For existence of a non-trivial solution, it is necessary that

$$\left| (I)\,(q - 1) \;-\; 0.5h\,(q + 1)\,(A) \right| = 0 \;. \qquad (126)$$

From this,

$$\lambda h = \frac{2\,(q - 1)}{q + 1} \;. \qquad (127)$$

Equation (127) is plotted in Figure 2. For λh with negative real parts, the corresponding q's are always within the unit circle on the q-plane. Hence, the method is unconditionally stable. However, for the case where λh lies on the imaginary axis -- this is the case of pure convective transfer without diffusion and sources -- the corresponding q will have an absolute value of one. In this case, once an error is introduced in the solution, it will never decay but will oscillate with the same amplitude from then on. This explains why for a pure convection problem, or for a problem where diffusion is much smaller than convection, it has been necessary to use artificially larger diffusivities to smooth out the oscillations inherent to the numerical solution. In Figure 2, this is equivalent to the shifting of the λh to the left, so that the corresponding $|q|$ will be less than one, and whatever errors introduced in the process of computations will decay.

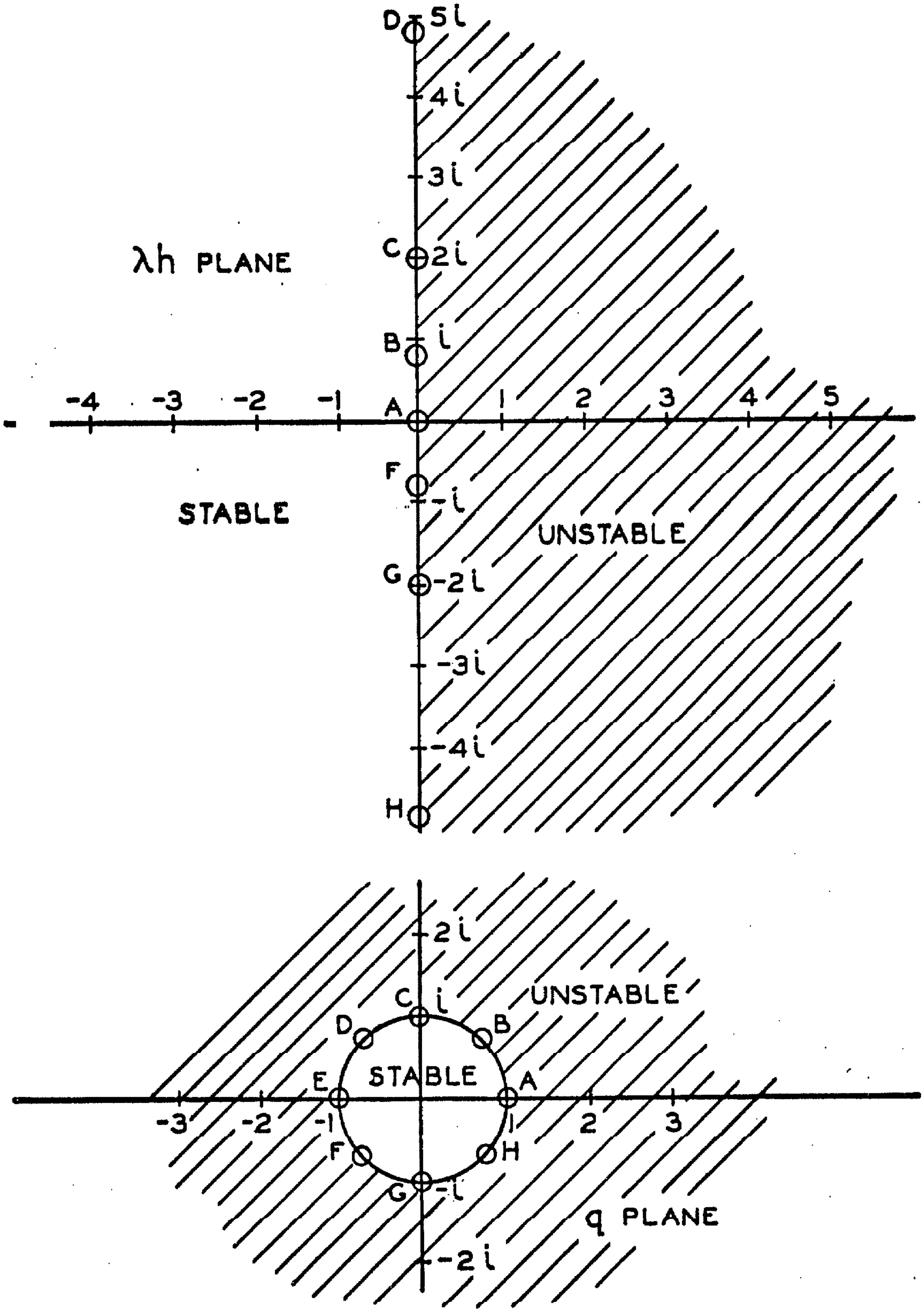


Figure 2. Stability Region of Crank-Nicolson Method.

Backward-Difference Method

In this method, the right-hand-side of equation (118) is evaluated at the end of each time increment:

$$\vec{\Phi}_{\ell+1} - \vec{\Phi}_{\ell} = h\,(A)\,\vec{\Phi}_{\ell+1} \quad . \tag{128}$$

Substituting equation (120), this becomes

$$\left[(I)\,(q-1) - hq\,(A)\right] q^{\ell}\vec{b} = 0 \quad . \tag{129}$$

If a non-trivial solution exists for this equation, it is required that

$$\left|(I)\,(q-1) - hq\,(A)\right| = 0 \ , \tag{130}$$

and consequently

$$\lambda h = \frac{q-1}{q} \quad . \tag{131}$$

This is plotted in Figure 3. The method is seen to be always stable as is the Crank-Nicolson method. In addition, it is noted that this method should give a smoother solution than the latter method for solving a convection problem. An imaginary eigen-value of (A) generates a q of modulus less than one, and the result is that errors will tend to decay, as is the case where there is diffusion.

Method W

This method is best explained by the following equation:

$$\vec{\Phi}_{\ell+1} - \vec{\Phi}_{\ell} = h\,(A)\,[w\vec{\Phi}_{\ell+1} + (1 - w)\,\vec{\Phi}_{\ell}\,] \ . \qquad (132)$$

The Crank-Nicolson method and the backward-difference method discussed previously are merely two particular cases of this method employing w = 0.5 and 1 respectively.

It can be easily shown, as for the previous three methods, that q and λh are related by the relationship:

$$\lambda h = \frac{q - 1}{wq + (1 - w)} \ . \qquad (133)$$

For $w \geqq 0.5$, the method is always stable. As w approaches 1, the solution will become smoother and smoother, but with an inevitable sacrifice in accuracy. A good combination of accuracy

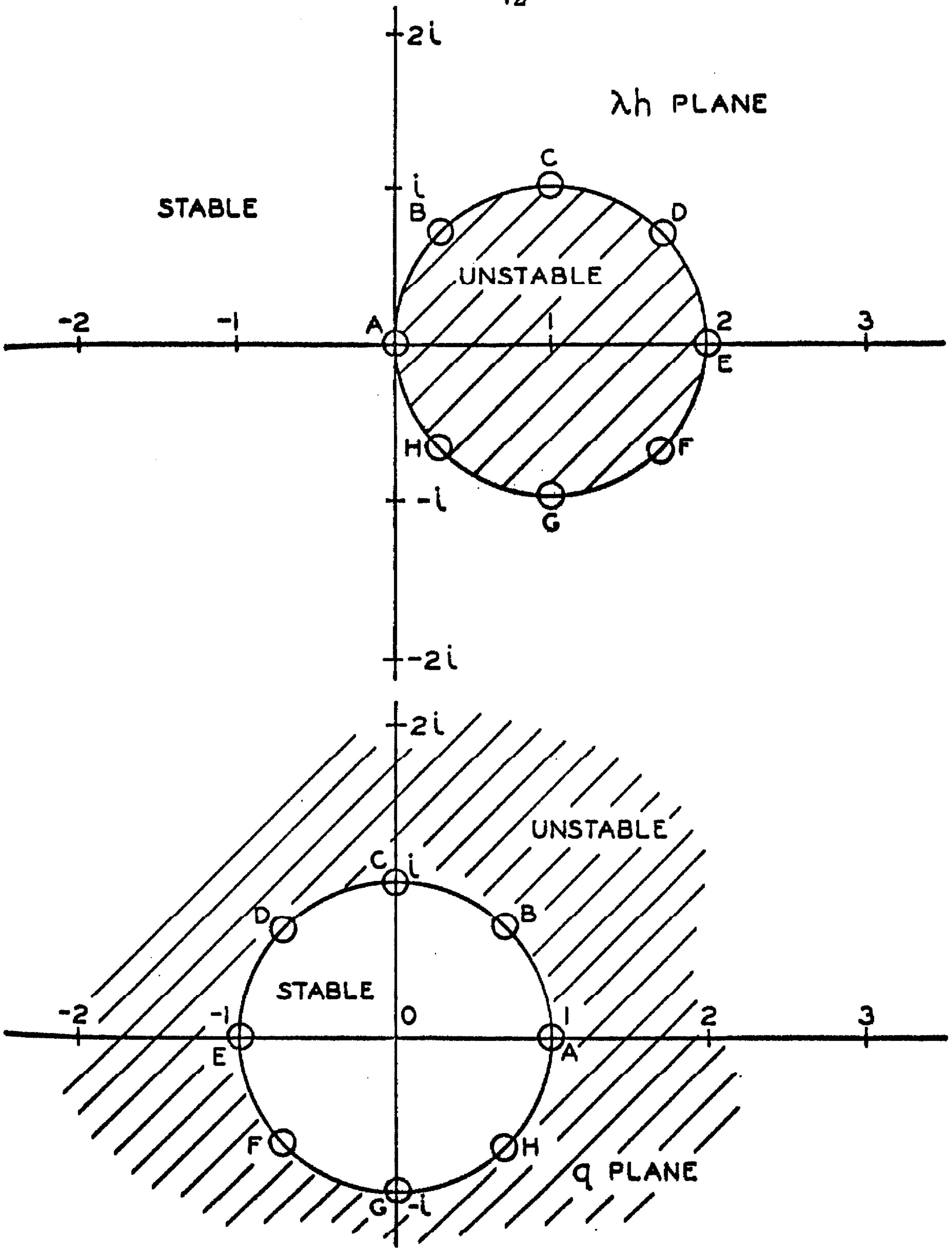


Figure 3. Stability Region of Backward-Difference Method.

and smoothness should be obtained by a suitable choice of w.

Method E

This method is represented by:

$$\vec{\Phi}_{\ell + w} - \vec{\Phi}_{\ell} = wh\,(A)\,\vec{\Phi}_{\ell + w} \quad , \tag{134}$$

$$\vec{\Phi}_{\ell + 1} - \vec{\Phi}_{\ell} = h\,(A)\,\vec{\Phi}_{\ell + w} \quad . \tag{135}$$

This two-step method will be shown to be equivalent to the one-step method w just discussed.

Combining equations (134) and (135),

$$\vec{\Phi}_{\ell + w} = w\,\vec{\Phi}_{\ell + 1} + (1 - w)\,\vec{\Phi}_{\ell} \quad . \tag{136}$$

Substitution of this equation into equation (135) results in

$$\vec{\Phi}_{\ell + 1} - \vec{\Phi}_{\ell} = h\,(A)\,[w\vec{\Phi}_{\ell + 1} + (1 - w)\,\vec{\Phi}_{\ell}\,] \quad . \tag{137}$$

Thus, the two-step method represented by equations (134) and (135) has been shown to be equivalent to the one-step method expressed by equation (137), which is identical to equation (132) for method w.

Method E is important because, as will be shown later, it can be modified for the solution of multidimensional problems.

Method F

In the previous section, method E was shown to be identical to method w, which is unconditionally stable if $w \geq 0.5$. Nevertheless, method E must rely on an iterative scheme to solve a two-dimensional problem, such as the one presented by the system of differential equations for the stream. Method F is a modification of method E, and is suitable for solving a two-dimensional problem. The method is expressed by:

$$\vec{\Phi}_{\ell+w}{}^{*} - \vec{\Phi}_{\ell} = wh\,(A_1)\,\vec{\Phi}_{\ell+w}{}^{*} + wh\,(A_2)\,\vec{\Phi}_{\ell} \quad . \qquad (138)$$

$$\vec{\Phi}_{\ell+w}{}^{**} - \vec{\Phi}_{\ell} = wh\,(A_1)\,\vec{\Phi}_{\ell+w}{}^{*} + wh\,(A_2)\,\vec{\Phi}_{\ell+w}{}^{**} \quad . \qquad (139)$$

$$\vec{\Phi}_{\ell+1} - \vec{\Phi}_{\ell} = h\,(A_1)\,\vec{\Phi}_{\ell+w}{}^{*} + h\,(A_2)\,\vec{\Phi}_{\ell+w}{}^{**} \quad . \qquad (140)$$

$$\text{where } (A_1) = \left[\frac{i \sin (k_r \Delta r)}{\Delta r} (D_3) - \frac{4 \sin^2 \left(\frac{k_r \Delta r}{2} \right)}{\Delta r^2} (D_5) \right] , \tag{141}$$

$$(A_2) = \left[\frac{i \sin (k_x \Delta x)}{\Delta x} (D_4) - \frac{4 \sin^2 \left(\frac{k_x \Delta x}{2} \right)}{\Delta x^2} (D_6) + (S_f) \right] . \tag{142}$$

This three-step method shown by the above equations is in fact equivalent to a one-step method, as will be demonstrated below:

Multiplying equation (140) by w and subtracting the product from equation (139),

$$\vec{\Phi}_{\ell + w}^{**} = w \vec{\Phi}_{\ell + 1} + (1 - w) \vec{\Phi}_{\ell} \quad . \tag{143}$$

Subtracting equation (139) from equation (138) and rearranging result in

$$\vec{\Phi}_{\ell + w}^{*} = \vec{\Phi}_{\ell + w}^{**} - w^2 h (A_2)(\vec{\Phi}_{\ell + 1} - \vec{\Phi}_{\ell}) \quad . \tag{144}$$

Then, substituting equations (143) and (144) into equation (140), one obtains:

$$\Phi_{\ell+1} - \Phi_{\ell} = [(I) + w^2h^2(A_1)(A_2)]^{-1} h(A) [w\vec{\Phi}_{\ell+1} + (1-w)\vec{\Phi}_{\ell}] \; . \tag{145}$$

This is the one-step method equivalent to the three-step method shown by equations (138), (139) and (140). This method is always stablc, no matter how large h may be, if $w \geqq 0.5$, and also if, for a stable system, the matrix

$$(A_N) = [(I) + w^2h^2 (A_1)(A_2)]^{-1} (A) \quad , \tag{146}$$

is stable for all $\vec{k}$'s.

In the stream equations, (S_f) is diagonal, and so both (A_1) and (A_2) are diagonal. Let the diagonal elements in a certain row be $a_1 = \alpha_1 + i\beta_1$, $a_2 = \alpha_2 + i\beta_2$ for (A_1) and (A_2) respectively. Then the corresponding element for (A) should be $a = (\alpha_1 + \alpha_2) + i(\beta_1 + \beta_2)$. By substituting these into equation (146), the corresponding element for (A_N) is found to be

$$a_N = \alpha_N + i\beta_N$$

$$= \frac{(\alpha_1 + \alpha_2) + i(\beta_1 + \beta_2)}{1 + w^2h^2(\alpha_1 + i\beta_1)(\alpha_2 + i\beta_2)}$$

$$= \frac{(\alpha_1 + \alpha_2) + i\,(\beta_1 + \beta_2)}{1 + w^2h^2(\alpha_1\alpha_2 - \beta_1\beta_2) + i\,w^2h^2(\alpha_1\beta_2 + \alpha_2\beta_1)} \quad . \tag{147}$$

Therefore, taking the real part alone

$$\alpha_N = \frac{(\alpha_1 + \alpha_2) + w^2h^2\,[\alpha_2\,(\alpha_1{}^2 + \beta_1{}^2) + \alpha_1\,(\alpha_2{}^2 + \beta_2{}^2)]}{[1 + w^2h^2\,(\alpha_1\alpha_2 - \beta_1\beta_2)]^2 + w^4h^4\,(\alpha_1\beta_2 + \alpha_2\beta_1)^2} \quad . \tag{148}$$

From equation (141), it is obvious that

$$\alpha_1 < 0 \quad . \tag{149}$$

So, for the case $\alpha_2 < 0$, it follows from equation (148) that

$$\alpha_N < 0 \quad . \tag{149-a}$$

If this is true for all rows of the matrices, the method should be stable.

The case $\alpha_2 > 0$ is trivial because in this case, as will be shown next, the source terms can be evaluated at the beginning of each time increment without affecting the stability of a numerical method. However, if method F is still used in such a case, stability requires that

$$\alpha_1 [1 + w^2h^2 (\alpha_2{}^2 + \beta_2{}^2)] + \alpha_2 [1 + w^2h^2 (\alpha_1{}^2 + \beta_1{}^2)] < 0 , \quad (150)$$

which can be rewritten as

$$\alpha_2 [1 + w^2h^2 |a_1|^2] < - \alpha_1 [1 + w^2h^2 |a_2|^2] . \quad (151)$$

For a stable system

$$\alpha_1 + \alpha_2 < 0 ,$$

or

$$\alpha_2 < - \alpha_1 . \quad (152)$$

So, if $$|a_1| < |a_2| \quad , \tag{153}$$

equation (151) will be satisfied, and the method should be stable.

Methods in Which the Source Terms are Evaluated Explicitly

The simplest case is the one in which the source terms are evaluated at the beginning of each time increment. If the Crank-Nicolson method is employed for the space derivatives, such a method can be expressed by:

$$\vec{\Phi}_{\ell+1} - \vec{\Phi}_{\ell} = 0.5h(D)(\vec{\Phi}_{\ell+1} + \vec{\Phi}_{\ell}) + h(S)\vec{\Phi}_{\ell} \quad . \tag{154}$$

Because of increased complexities, a different approach will be taken to investigate the stability of this scheme.

Rearranging equation (154), there is obtained:

$$\vec{\Phi}_{\ell+1} = [(I) - 0.5h\,(D)]^{-1}\,[(I) + 0.5h\,(D) + h(S)]\,\vec{\Phi}_{\ell} \, . \tag{155}$$

If the maximum eigenvalue of matrix

$$(E) = [(I) - 0.5h\,(D)]^{-1}\,\Big[(I) + 0.5h\,(D) + h\,(S)\Big] \;, \tag{156}$$

is of modulus less than one, the recurrence formula (155) will lead to a bounded solution as ℓ is indefinitely increased. The analysis for a general case is too difficult and a special case in which matrix (S) is also diagonal will be investigated. For a diagonal matrix, the diagonal elements are its eigen-values. The inverse of a diagonal matrix is another diagonal matrix in which the diagonal elements are the inverses of the diagonal elements of the first matrix. Let e_k, d_k and s_k be k-th diagonal elements of (E), (D) and (S) respectively. Then:

$$e_k = \frac{1 + 0.5h\,d_k + h\,s_k}{1 - 0.5h\,d_k} \quad . \tag{157}$$

If s_k is real and positive, for a stable system

$$\mathrm{Re}(d_k) + s_k < 0 \quad ,$$

or

$$s_k < -\,\mathrm{Re}(d_k) \quad . \tag{158}$$

The following relationship follows immediately

$$|e_k| < \left| \frac{1 + 0.5h\, d_k - h\,\mathrm{Re}\,(d_k)}{1 - 0.5h\, d_k} \right|$$

$$= \left| \frac{1 - 0.5h\,\mathrm{Re}\,(d_k) + 0.5h\,\mathrm{Im}\,(d_k)}{1 - 0.5h\,\mathrm{Re}\,(d_k) - 0.5h\,\mathrm{Im}(d_k)} \right| = 1 \ . \qquad (159)$$

So, the scheme is always stable.

If s_k is real and negative,

$$|e_k| = \left| \frac{1 + 0.5h\,\mathrm{Re}\,(d_k) + h\, s_k + 0.5h\,\mathrm{Im}\,(d_k)}{1 - 0.5h\,\mathrm{Re}\,(d_k) - 0.5h\,\mathrm{Im}\,(d_k)} \right| , \qquad (160)$$

and for $|e_k|$ to be smaller than unity, it is required that

$$|\ 1 + 0.5h\,\mathrm{Re}\,(d_k) + h\, s_k\ | < 1 - 0.5h\,\mathrm{Re}\,(d_k) \quad , \qquad (161)$$

or

$$-2 < h\, s_k < -h\,\mathrm{Re}\,(d_k) \ . \qquad (162)$$

The right-hand inequality is automatically satisfied and the criterion becomes

$$-2 < h\,s_k \quad . \tag{163}$$

It is interesting to note that the relationship shown by equation (163) is identical to the stability criterion for the forward-difference method of solving equation (118) for the case where (A) = (S).

For the problems which will be investigated later, s_k can be as small as - 400, and for such a case, h should be smaller than 1/200 sec.

Now, the method proposed by Brian will be investigated$^{(21)}$. The method can be expressed by:

$$\vec{\Phi}_{\ell+1/2} - \vec{\Phi}_{\ell} = 0.5h\,(D)\,\vec{\Phi}_{\ell+1/2} + 0.5h\,(S)\,\vec{\Phi}_{\ell} \tag{164}$$

$$\vec{\Phi}_{\ell+1} - \vec{\Phi}_{\ell} = h\,(D+S)\,\vec{\Phi}_{\ell+1/2} \quad . \tag{165}$$

From equation (164) can be obtained

$$\vec{\Phi}_{\ell+1/2} = [(I) - 0.5h\,(D)]^{-1}[(I) + 0.5h\,(S)]\,\vec{\Phi}_{\ell} \quad , \tag{166}$$

and substituting this equation into equation (165) results in

$$\vec{\Phi}_{\ell+1} - \vec{\Phi}_{\ell} = h\,(D + S)\ [(I) - 0.5h\,(D)]^{-1}\,[(I) + 0.5h\,(S)]\,\vec{\Phi}_{\ell} \quad . \tag{167}$$

It is very difficult to find the region of stability for this scheme. However, some important conclusions can be drawn by comparing equation (167) with equation (119). First, even for the case where (S) is diagonal and positive, there is no guarantee that the scheme is stable. And for the case where the diagonal elements of (S) are negative, it is required that

$$1 + 0.5h\,s_k > 0 \quad , \tag{168}$$

which is identical to equation (163) for the previous method.

If

$$1 + 0.5h\,s_k < 0 \quad , \tag{169}$$

then, the corresponding eigen-value of matrix

$$(D + S)\ [(I) - 0.5h\,(D)]^{-1}\ [(I) + 0.5h\,(D)] \quad ,$$

will have a positive real part, and the scheme will undoubtedly be unstable.

The methods using one of the Runge-Kutta's schemes are more complicated, but are similar to the one just mentioned in that the source terms are first evaluated at the beginning of a time increment, and similar stability restrictions should exist. Fox(25) gives the stability requirement of the Runge-Kutta method for solving ordinary differential equations.

E. VARIOUS METHODS OF SOLUTION USED IN THIS STUDY

Method G

This is the method used to obtain the rigorous solution. The equations derived are solved as they are except that two more assumptions are introduced. These are assumptions E and J, which assume that the Peclet number for both heat and mass transfer, and the specific heat of the catalyst and stream are constant.

Central difference approximations for all the space derivatives are employed. Method F and method W are used for the stream and for the catalyst interior respectively, and $w = 1$ is chosen to make the solution smoother. The linearization shown by equation (74) is carried out for each time increment and the coefficients in equation (75) and (83) are evaluated at the beginning of the time increment. The properties within the catalyst at the end of each time increment are expressed as functions of corresponding stream properties and substituted into the stream equations to obtain $\vec{C}_f$ and (S_f). After the stream equations have been integrated in both radial and axial directions, the results are used in the boundary conditions for equation (75), which is integrated to obtain the solution at the end of the time increment. In each of these integrations, the scheme proposed by Thomas and described in most textbooks on numerical solution of partial differential equations is utilized to avoid the necessity of iterations$^{(22)}$.

It should be emphasized that the success of method G in solving a reactor problem lies in the elimination of catalyst surface properties in the stream equations, so that, in effect, the integration in the catalyst interior and that in the stream can be carried out simultaneously.

Method H

In order to save the lengthy calculations for the catalyst interior, an additional assumption -- assumption A -- to simplify method G, which is described above, is employed. The concept of an effectiveness factor which is frequently used in a steady-state case is assumed to hold even in a transient case. If the reaction rate is expressed in an apparent first order form with respect to P_{SO_2}', and it is assumed that temperature is uniform throughout the same catalyst pellet and that a quasi-steady-state is always reached, the effectiveness factor will be^(28)

$$\text{E. F.} = \frac{3\,[\psi \coth \psi - 1]}{\psi^2} , \tag{170}$$

where

$$\psi = r_i' \sqrt{\frac{-C_1 f'}{D_1'}} , \tag{171}$$

and C_1 is the coefficient in the rate expression

$$R_1' = - C_1 P_{SO_2}' + C_2 \quad . \qquad (172)$$

As C_1 is not constant, the effectiveness factor shown in equation (170) is calculated at the beginning of each time increment.

The accumulation of material in the catalyst is neglected, and the amount of a component reacted or produced by the reaction as calculated by using the effectiveness factor is equated to the amount transferred from the stream. The accumulation of heat in the catalyst, however, is taken into account.

As in method G, a property at the catalyst surface is expressed as a function of its corresponding property in the stream. Substituting this into the stream equation; integrating to get the stream property at the end of a time increment; the surface property from the obtained stream property can be calculated.

Method P

To further simplify the calculations, a method involving two more assumptions was tested. They are assumptions B and G. This is the same as the plug-flow model commonly used in reactor calculations except that axial mixing is still taken into account, whereas the plug-flow assumption usually neglects the existence of any kind of mixing. The same effectiveness factor model used in method H is used in this method.

Method G'

This method differs from method G only in the way the properties in the catalyst interior are calculated. Instead of solving equation (65), the substitution

$$r'' = \left(\frac{r'}{r_i'}\right)^4 , \tag{173}$$

is used

to transform equation (65) into

$$\frac{\partial P_k'}{\partial \theta} = \frac{16\ D_k'}{f'\ r_i'^2}\ (r'')^{1.5}\ \frac{\partial^2 P_k'}{\partial r''^2} + \frac{20\ D_k'}{f' r_i'^2}\ (r'')^{0.5}\ \frac{\partial P_k'}{\partial r''} + R_k' \ , \tag{174}$$

and the boundary condition (68) into

$$\frac{4}{r_i'} \times \frac{M_k D_k'}{RT_i'}\ \frac{\partial P_k'}{\partial r''} = K_k \left(\sigma_f n_k - \frac{M_k P_{ki}'}{RT_i'}\right) \ . \tag{175}$$

By making this transformation, the accuracy of solution is greatly increased, as smaller radial increment sizes are used toward the surface of catalyst, where the changes in properties are more rapid, than toward the center of catalyst. A half increment is used at the center of the catalyst pellet.

V. RESULTS

Various problems involved in the reactor for the oxidation of SO_2 were solved by using the four methods described before. An IBM-7094 computer was used, and the programs were written in Fortran. For methods G and G', a total of 13 subroutines were employed, and about 700 Fortran cards are needed.* For method P there are only about 300 Fortran cards in the program.

Because the coefficients in the pressure equation, i.e., equation (37), are extremely large, the equation is integrated by using a double precision arithmetic in order to prevent the accumulation of errors which has been found to be serious enough to give a useless solution, when a single precision arithmetic is employed.

Unless otherwise stated, the number of space increments taken in each direction is 5, except that, for method G', 5.5 increments are taken in the direction of the radius of the catalyst.

Parameters for the Reactor Selected for this Study

The following are the parameters of the reactor studied:

Radius of reactor = 1 in.
Radius of catalyst pellets = 1/8 in.
Entrance composition = 7.1% SO_2, 11% O_2, 81.9% N_2

---

*The program for method G' is given in Appendix II.

Entrance temperature = $1200^{o}R$
Entrance pressure = 15.0 psia
Exit pressure = 14.7 psia

A sketch of this reactor is shown in Figure 4.

Problem (a)

To see whether method G' with 5.5 increments in the catalyst is adequate in predicting the behavior inside the catalyst, a dependable solution is needed. Such a solution can be obtained only by employing a large number of increments. To do this for the entire reactor would cause both storage and time problems in a computer. For this reason, the behavior of a single catalyst pellet which is subjected to a step-change in the surroundings will be studied.

A single spherical catalyst pellet initially filled with air at $1200^{o}R$ is subjected to a step-change in the surrounding stream composition and temperature. The stream concentration and temperature is then held constant at $n_{SO_2} = 0.03068$, $n_{SO_3} = 0.1443$, $n_{O_2} = 0.08487$ and $T = 1419.6^{o}R$, which is the steady-state solution obtained by method G for problem (b), at the center of stream and 0.6 ft. from the entrance.

The concentration profiles within the catalyst as obtained by methods G and G' are plotted in Figure 5. Two different radial increment sizes were used for method G', but no significant difference is noticed from the figure for the use of 5.5 increments and 23.5 increments. The result obtained by method G, however, shows a large deviation.

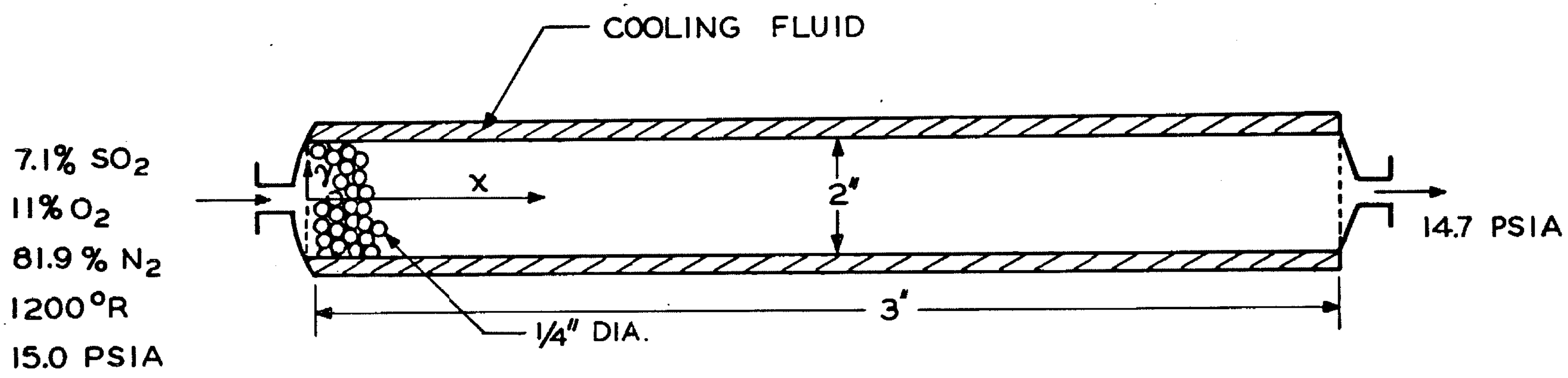


Figure 4. A Fixed-Bed Reactor for Oxidation of SO_2 by Air.

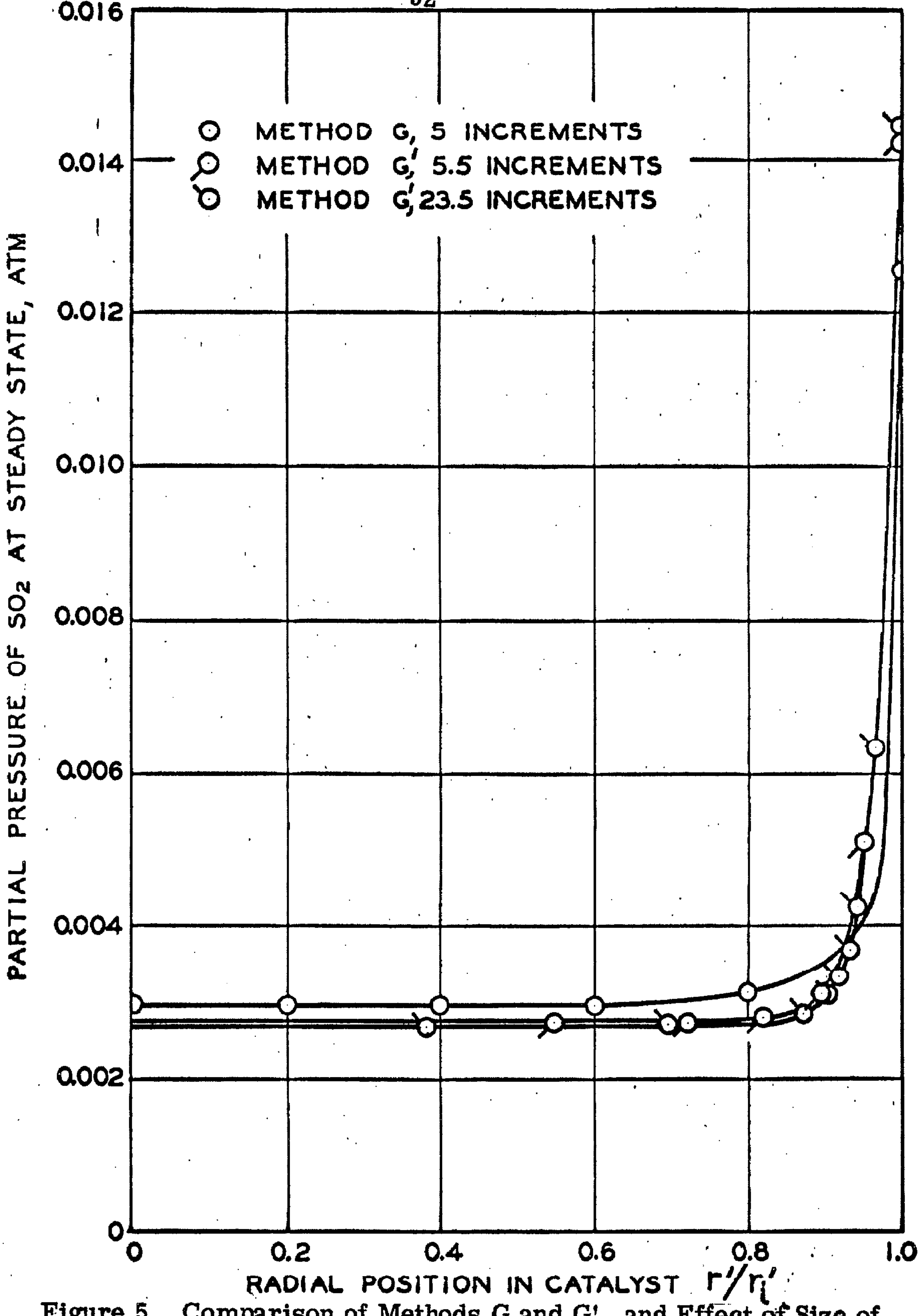


Figure 5. Comparison of Methods G and G', and Effect of Size of Catalyst Radial Increments; Problem (a).

In Figure 6 the effectiveness factor is shown as a function of time. This was obtained by method G' by dividing the rate of SO_2-transfer from the stream to the catalyst by the rate of reaction of SO_2 calculated from the surface composition and temperature, and also estimated by the use of equation (148). The effectiveness factor obtained by method G is only shown at the steady-state. The plot shows that method G is very inaccurate, and that the estimation of the effectiveness factor by equation (148) is poor at the very beginning, but is about as good as the one obtained by method G' with 5.5 radial increments.

Problem (b)

The start-up of the reactor is studied. The reactor is initially filled up with pure air at $1200^{o}R$. The composition of the entrance stream is suddenly switched to the operating one, and the wall is kept at $1200^{o}R$.

Axial profiles in stream composition and temperature were obtained by methods G and G' and are shown in Figures 7 and 8 respectively. As already pointed out in the study of problem (a), method G is found to be very poor.

Figure 9 is a plot of the steady-state concentration profile within the catalyst, calculated by method G' at the center of the reactor and 1.2 ft. from the entrance.

P_{O_2}'-profiles in a catalyst located at the hottest spot in the reactor are shown in Figure 10 for various times.

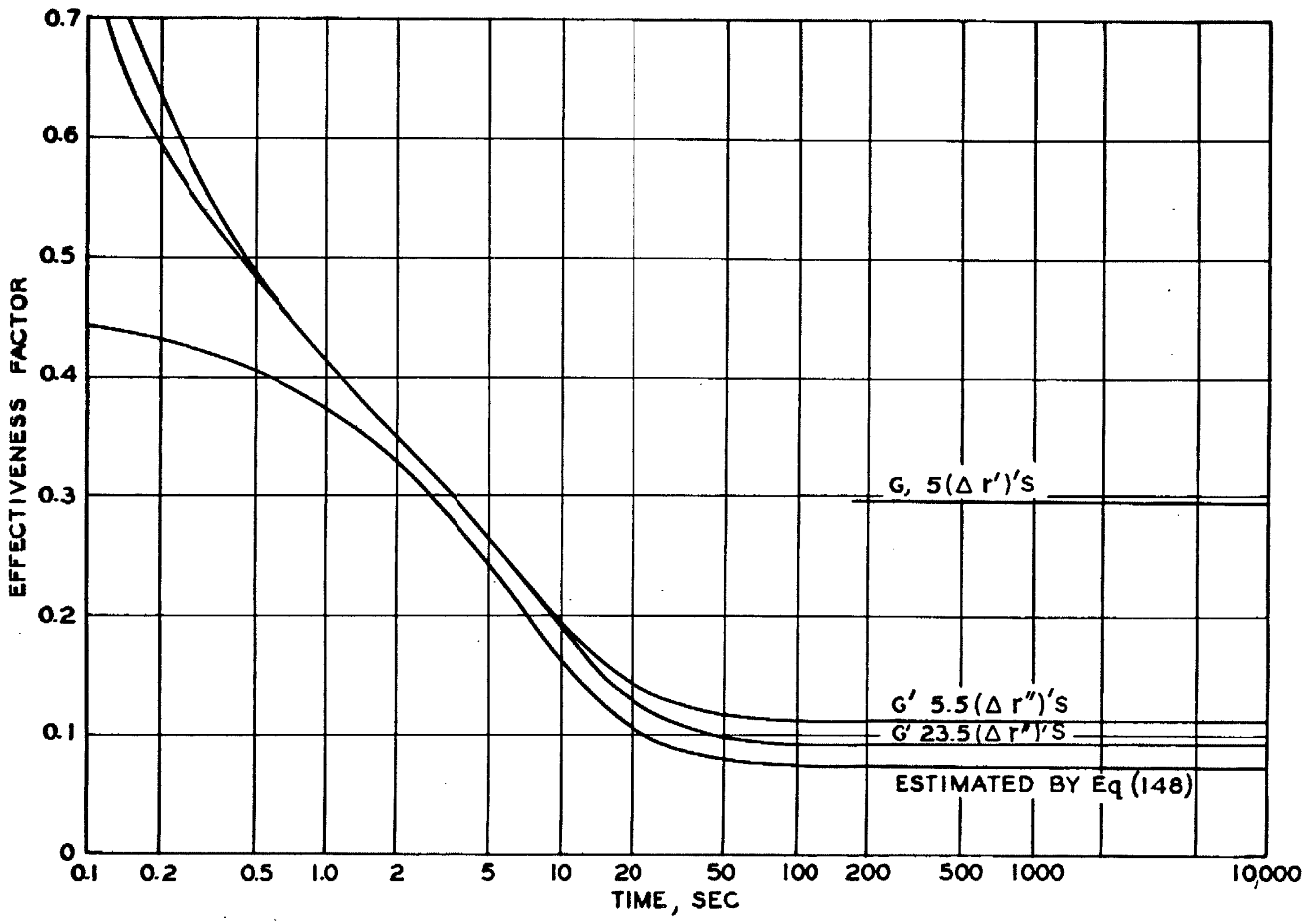


Figure 6. Changes of Effectiveness Factor with Time.

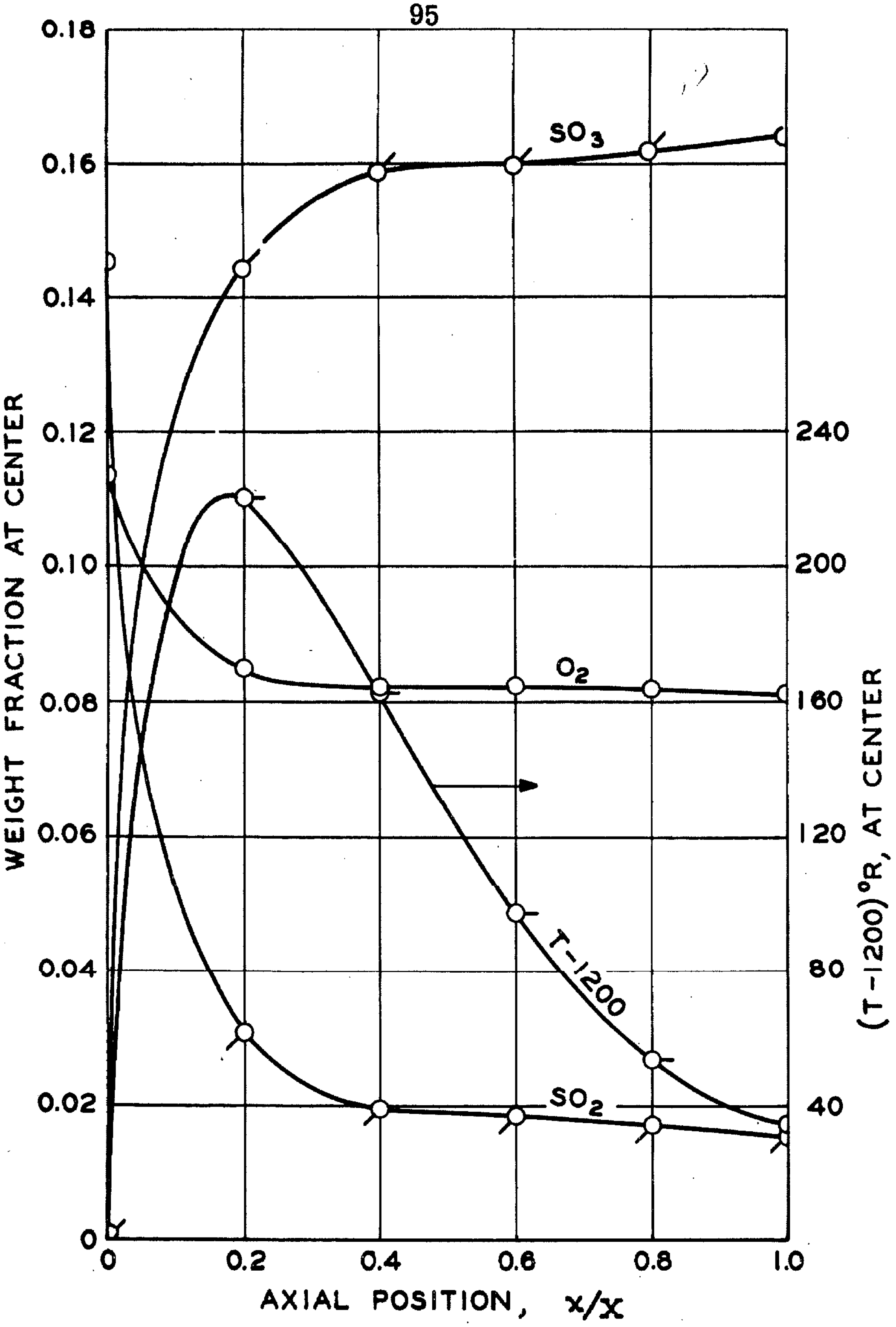


Figure 7. Steady-State Solution Obtained by Method G; Problem (b).

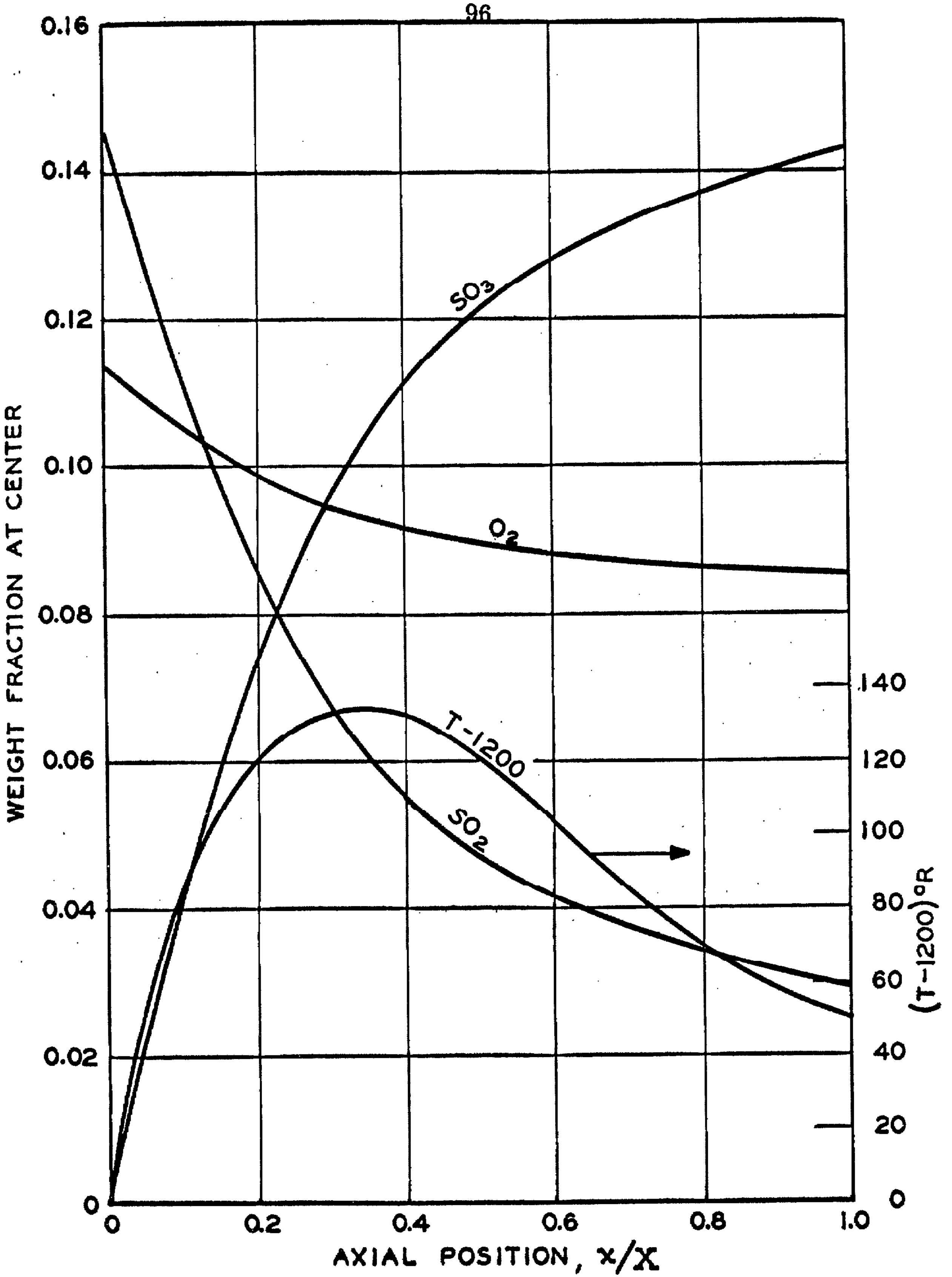


Figure 8. Steady-State Solution for Stream; Problem (b); Method G'.

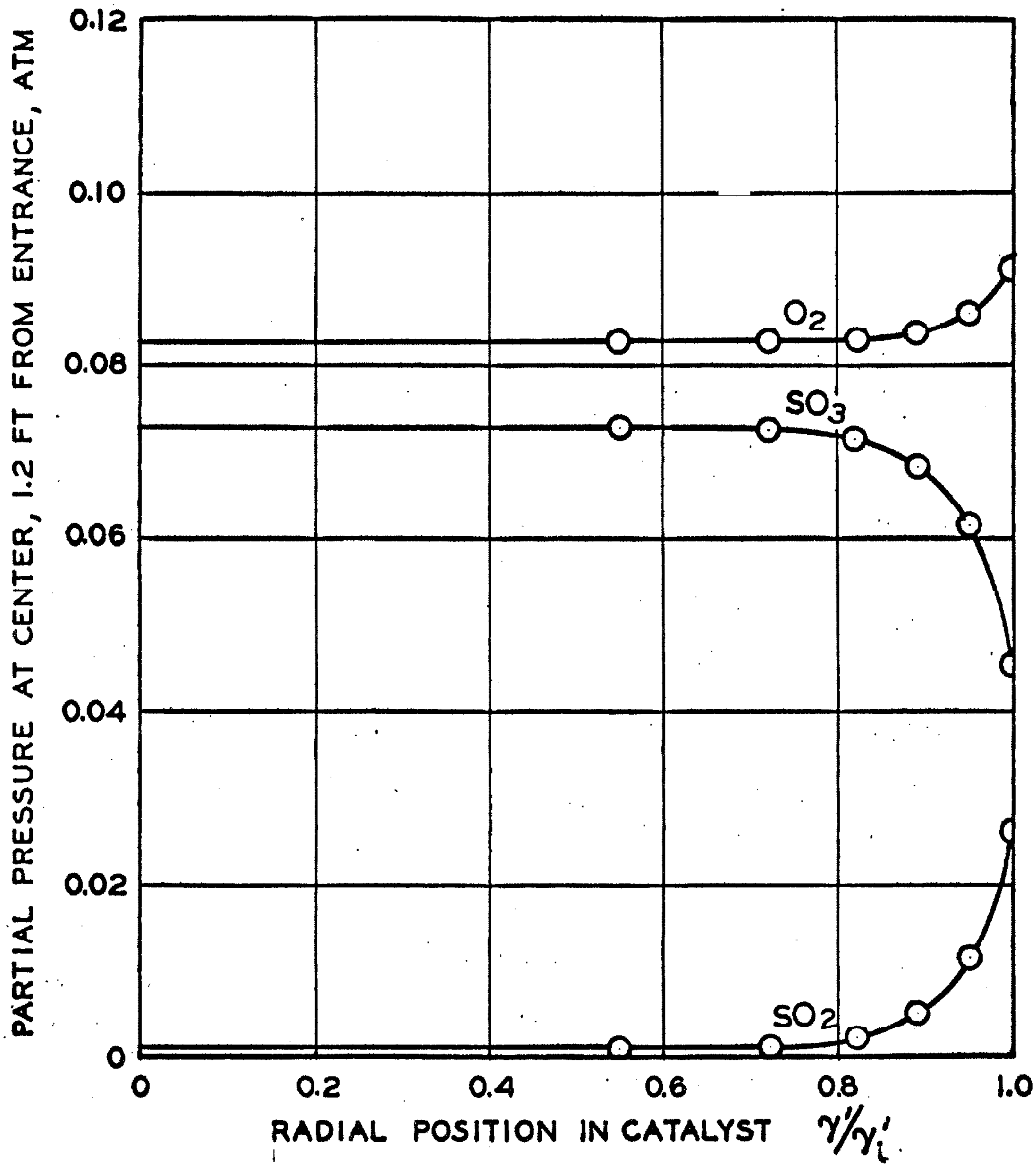


Figure 9. Concentration Profile Within Catalyst; Problem (b); Method G'.

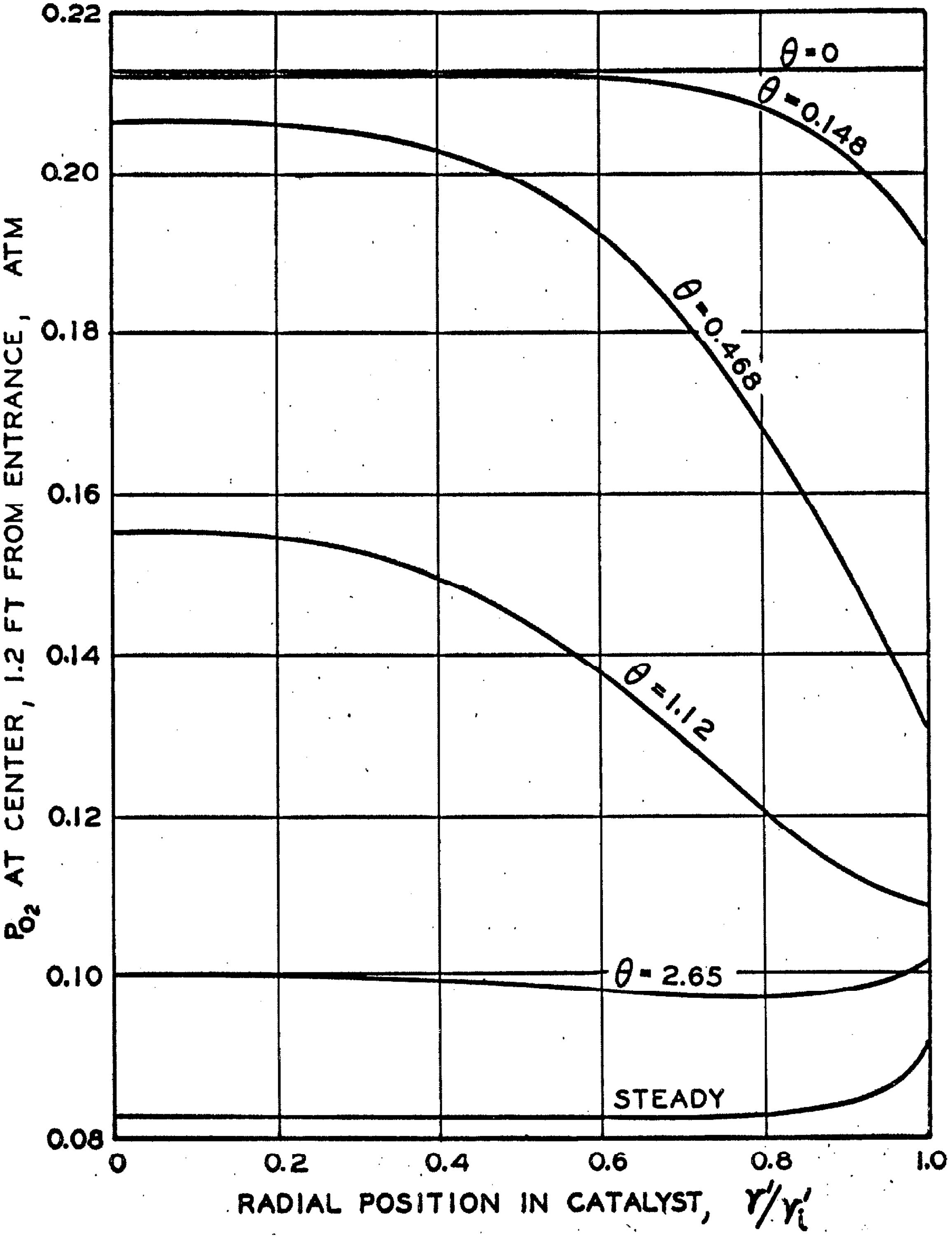


Figure 10. Partial Pressure of Oxygen in Catalyst at Various Time; Problem (b); Method G'.

Figure 11 shows the axial velocity at various axial locations, and at various times. To check the accuracy of method H, the steady-state solution obtained by method H is shown with that obtained by method G' in Figures 12 and 13. Maximum difference in the quantity n_{SO_2} is only 5% and that in temperature is 7.5%.

The steady-state radial profiles in n_{SO_2} and temperature are shown in Figures 14 and 15. The results of both method G' and method H are plotted. Maximum difference of 8.5% is observed for the temperature, while the difference in n_{SO_2} is much less.

In Figure 16 the transient changes in exit n_{SO_2} at the center of stream are shown. Both methods G' and H were used, and two different time increment sizes were used. The total times needed by each method to reach a steady-state are shown on the plot. The maximum difference between the solutions obtained by methods G' and H with the use of approximately the same time increment size is about 20%. The steady-state solutions are much closer - less than 5% difference.

The transient response of the stream temperature at the hottest spot in the reactor is shown in Figure 17. Methods G' and H gave a maximum difference of only 7.5%. The effect of the size of time increment is found to be much less in this case than the case of concentration response.

In method P radial variations in properties are neglected and we have only bulk mean properties at each axial location. So, the solutions by methods G' and H will be compared with that of method P on the basis of bulk mean properties.

The bulk mean temperature and SO_2 distributions at the steady-state are shown in Figures 18 and 19 for methods G', H and

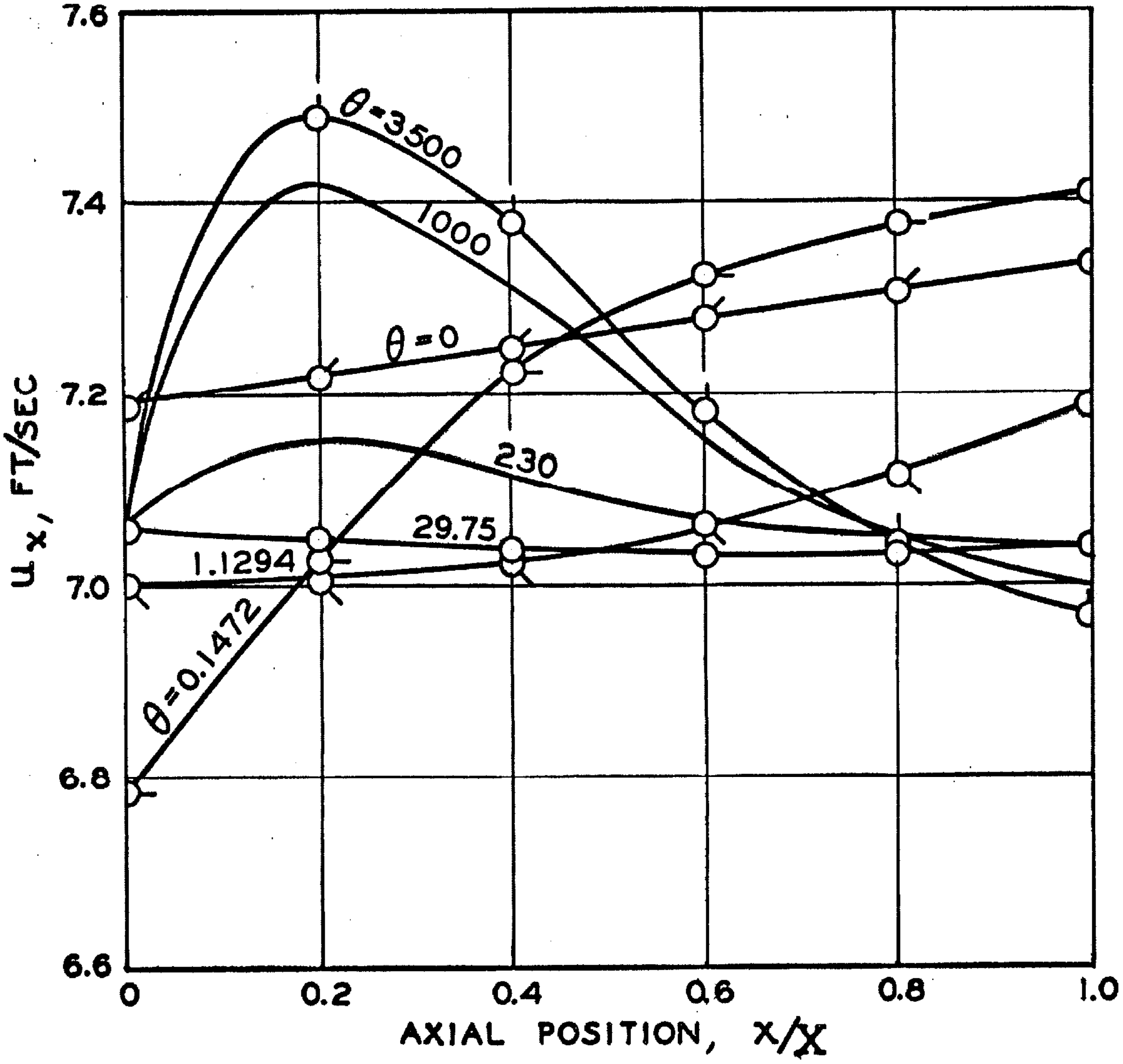


Figure 11. Axial Velocity at Various Times and Locations.

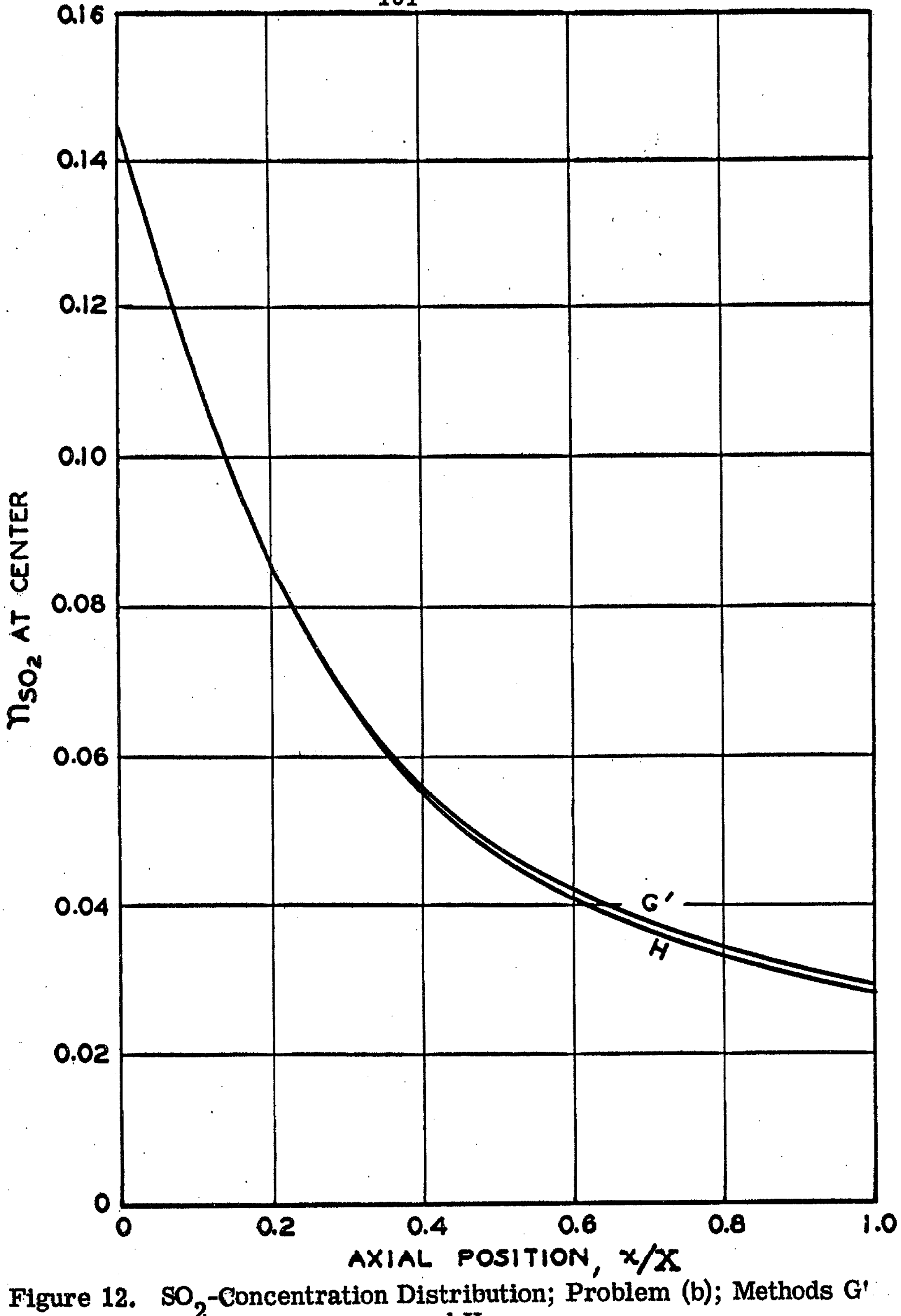


Figure 12. SO_2-Concentration Distribution; Problem (b); Methods G' and H.

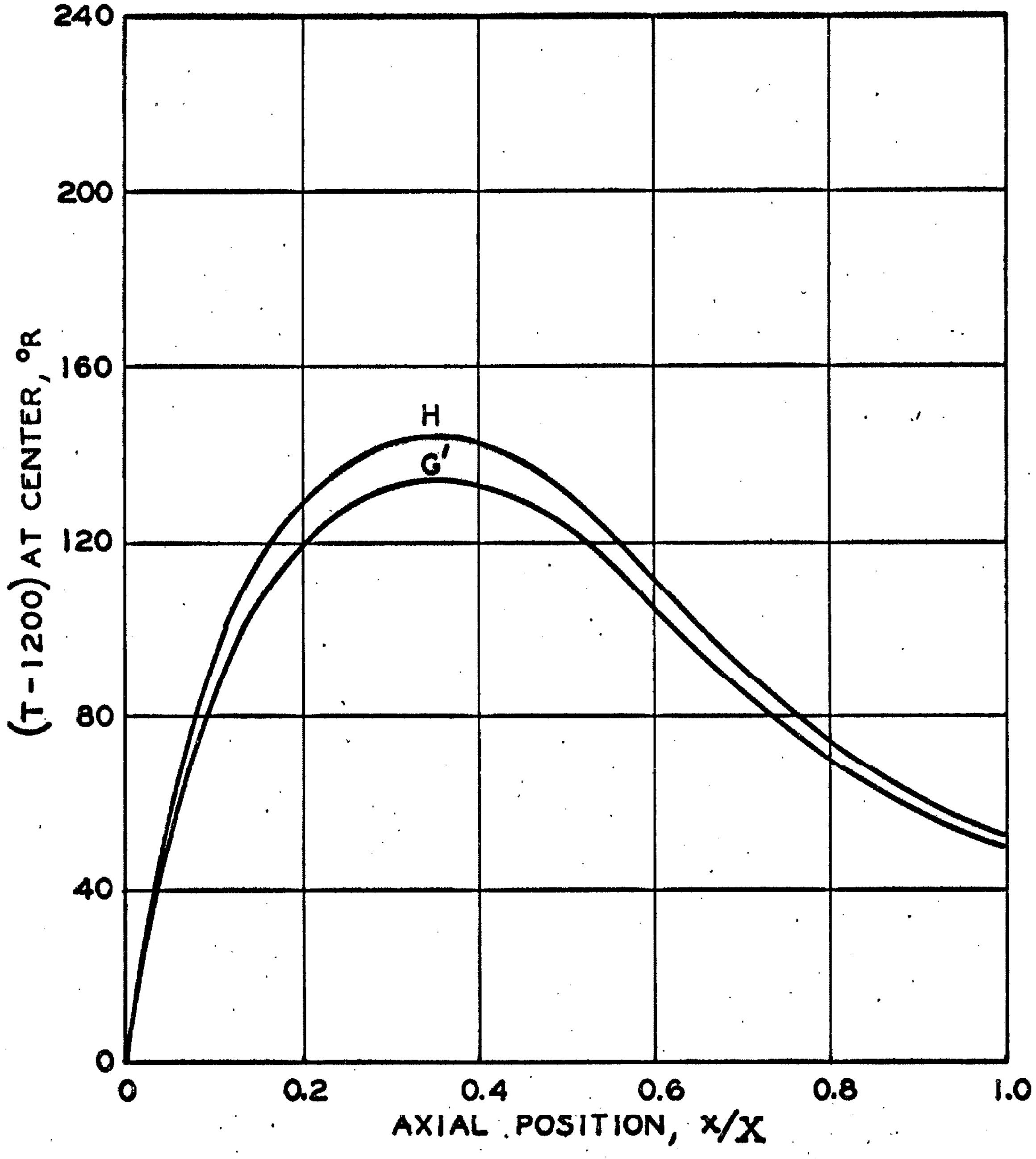


Figure 13. Steady-State Temperature Distribution; Problem (b); Methods G' and H.

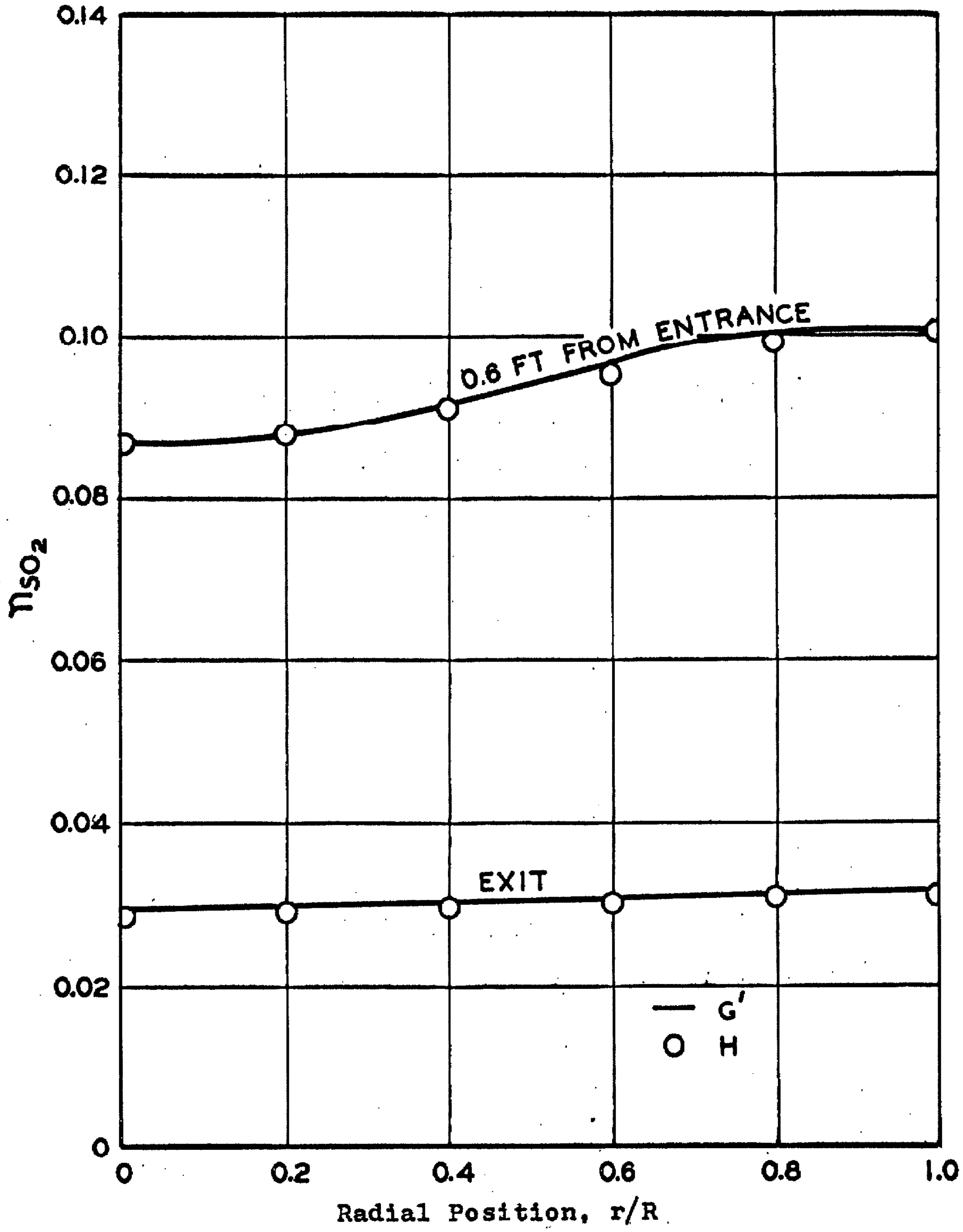


Figure 14. Radial Profile in SO_2-Concentration at Steady-State; Problem (b); Methods G' and H.

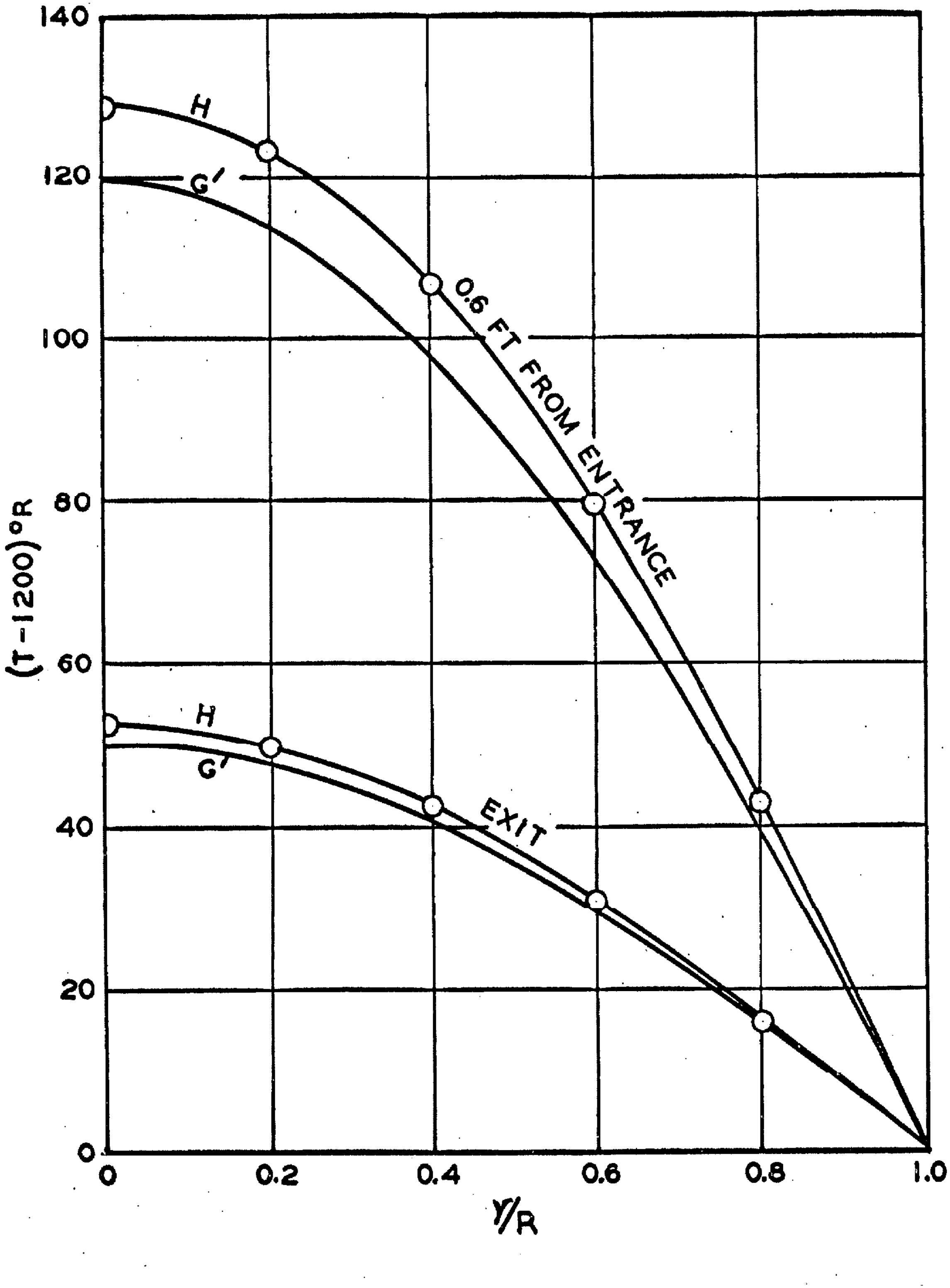


Figure 15. Radial Profile in Temperature at Steady-State; Problem (b); Methods G' and H.

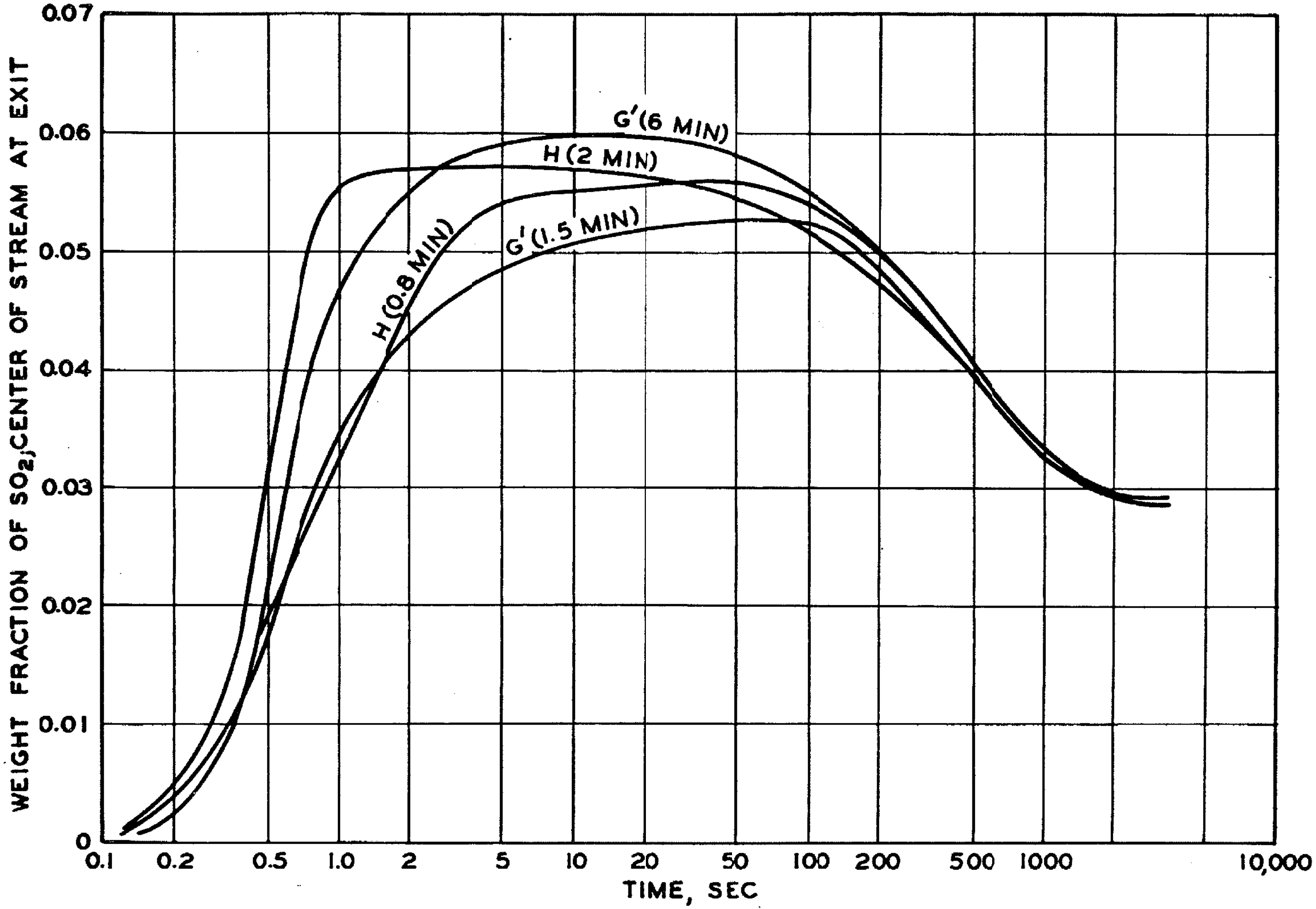


Figure 16. Transient Changes in Exit n_{SO_2}; Problem (b).

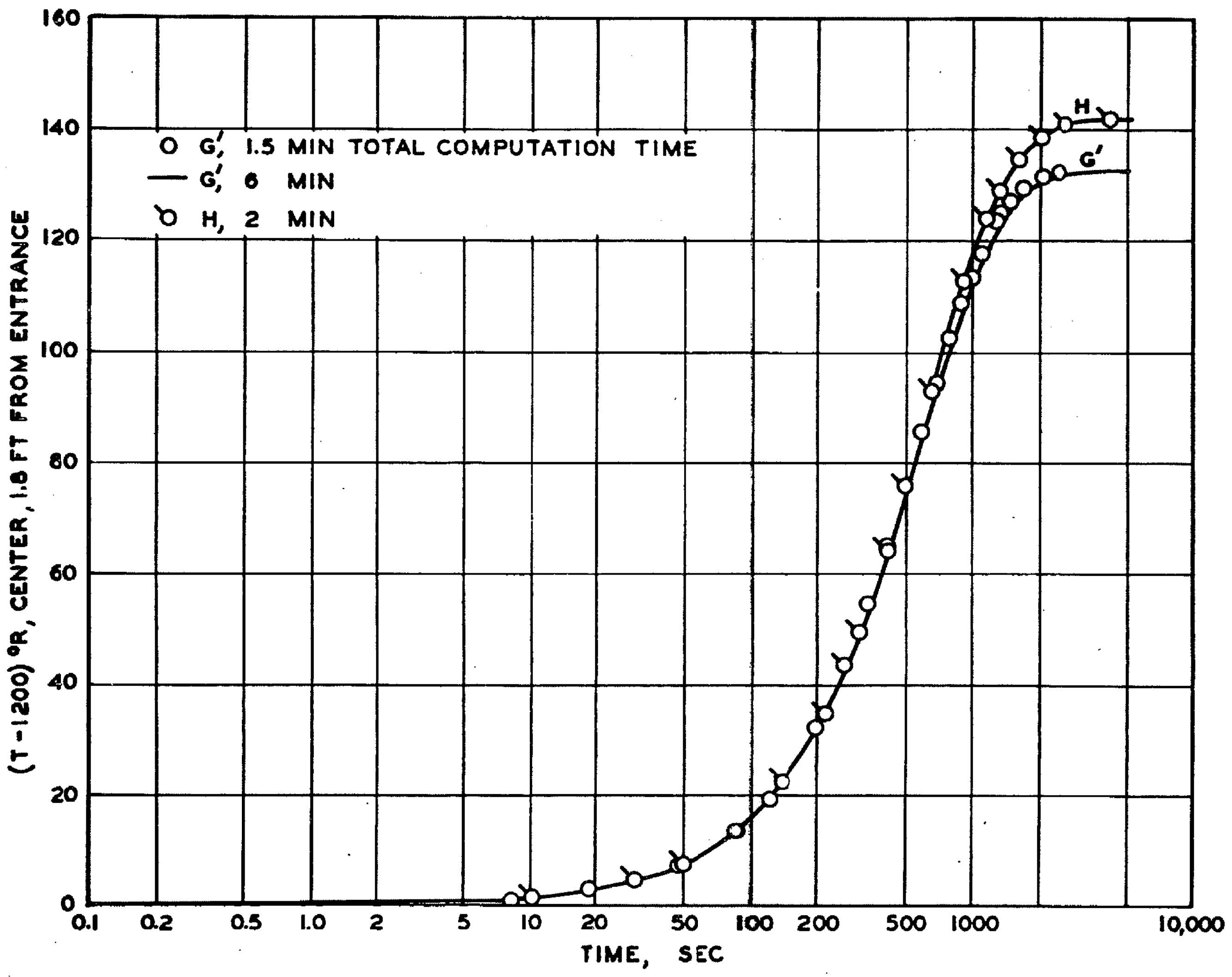


Figure 17. Transient Response of Temperature; Problem (b).

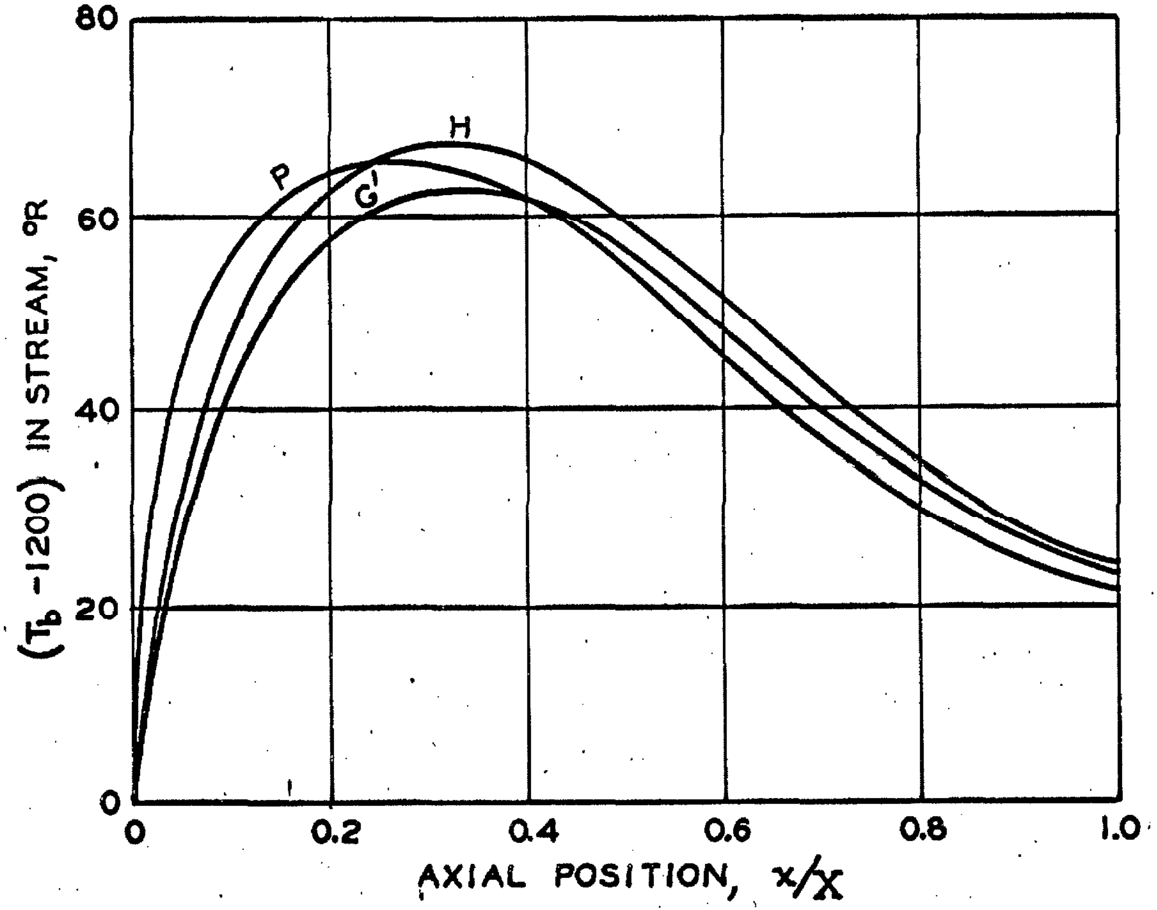


Figure 18. Steady-State Bulk Mean Temperature Distribution; Problem (b).

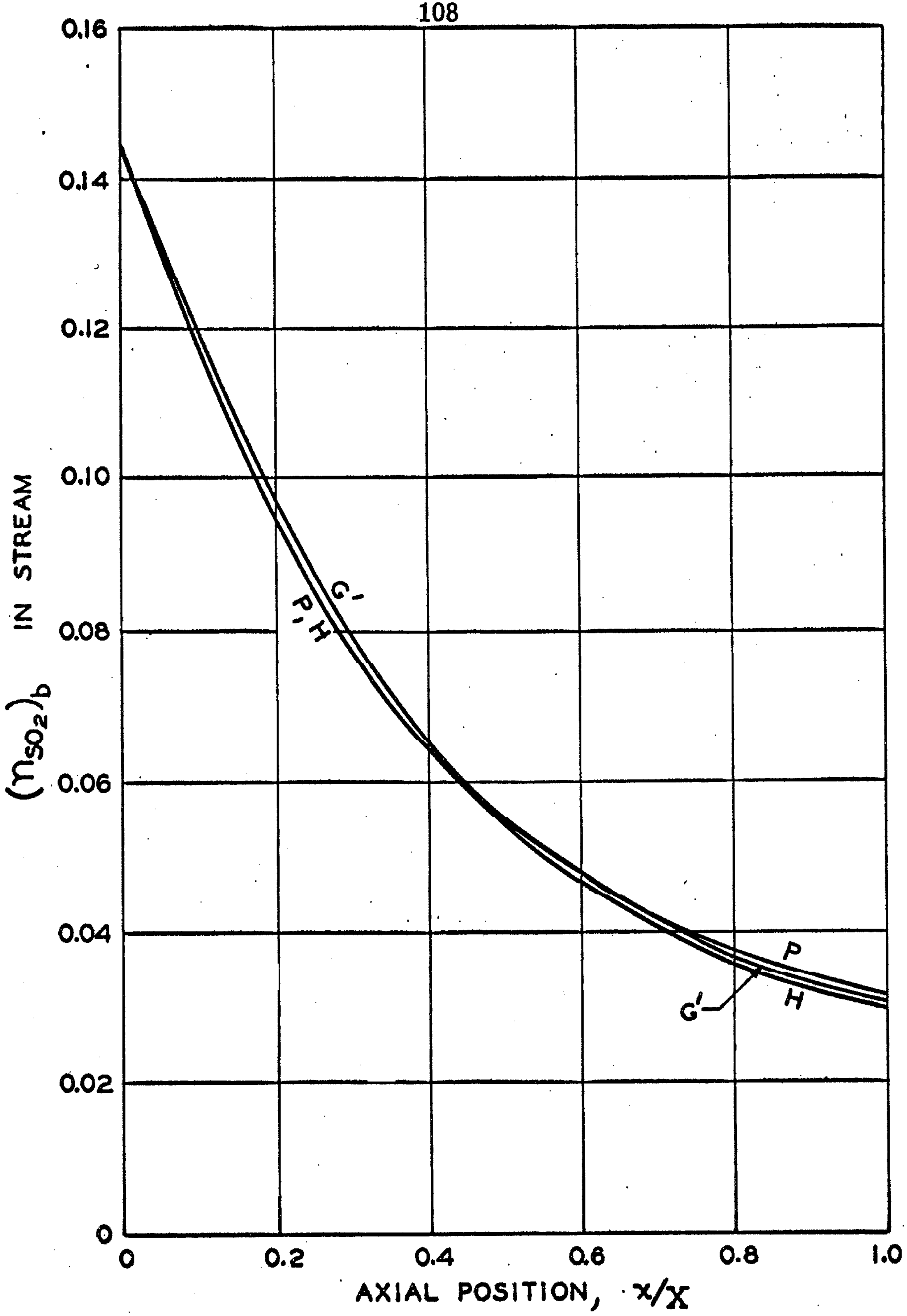


Figure 19. Steady-State SO_2-Concentration Distribution; Problem (b); Methods G', H and P.

P. A maximum of only about 12% difference between these methods is noticed for the temperature distributions, while the n_{SO_2}-distribution is pretty much the same for all the methods.

Transient temperature changes in the stream 0.6 ft. from the entrance are plotted in Figure 20. The result of method H is not much different from that of method G'. But the result of method P is quite different, the maximum error being about 30%.

Figure 21 shows the transient changes in n_{SO_2} at the exit. Method H and method P gave about the same results, which deviate from that of method G' by a maximum of 25%.

For method P, the solutions obtained by using 5, 10 and 20 axial increments are shown in Figures 22, 23 and 24. It appears that the use of 10 axial increments does somewhat improve the solution over that obtained by the use of 5 increments -- about 12% difference -- but the use of more than 10 increments does not materially improve the accuracy.

The effect of using different time increment sizes in method P is depicted in Figure 25. The total time needed in each case to reach a steady-state is indicated. Note that the use of larger time increments only affects the transient solution, and has no effect on the steady-state solution.

In Figure 26, the steady-state temperature distributions obtained by method P are shown with or without the use of assumption F - constant effectiveness factor. The maximum error caused by using assumption F is about 70%.

The effect of using assumption D, which neglects axial diffusion, is shown to be negligible in Figure 27.

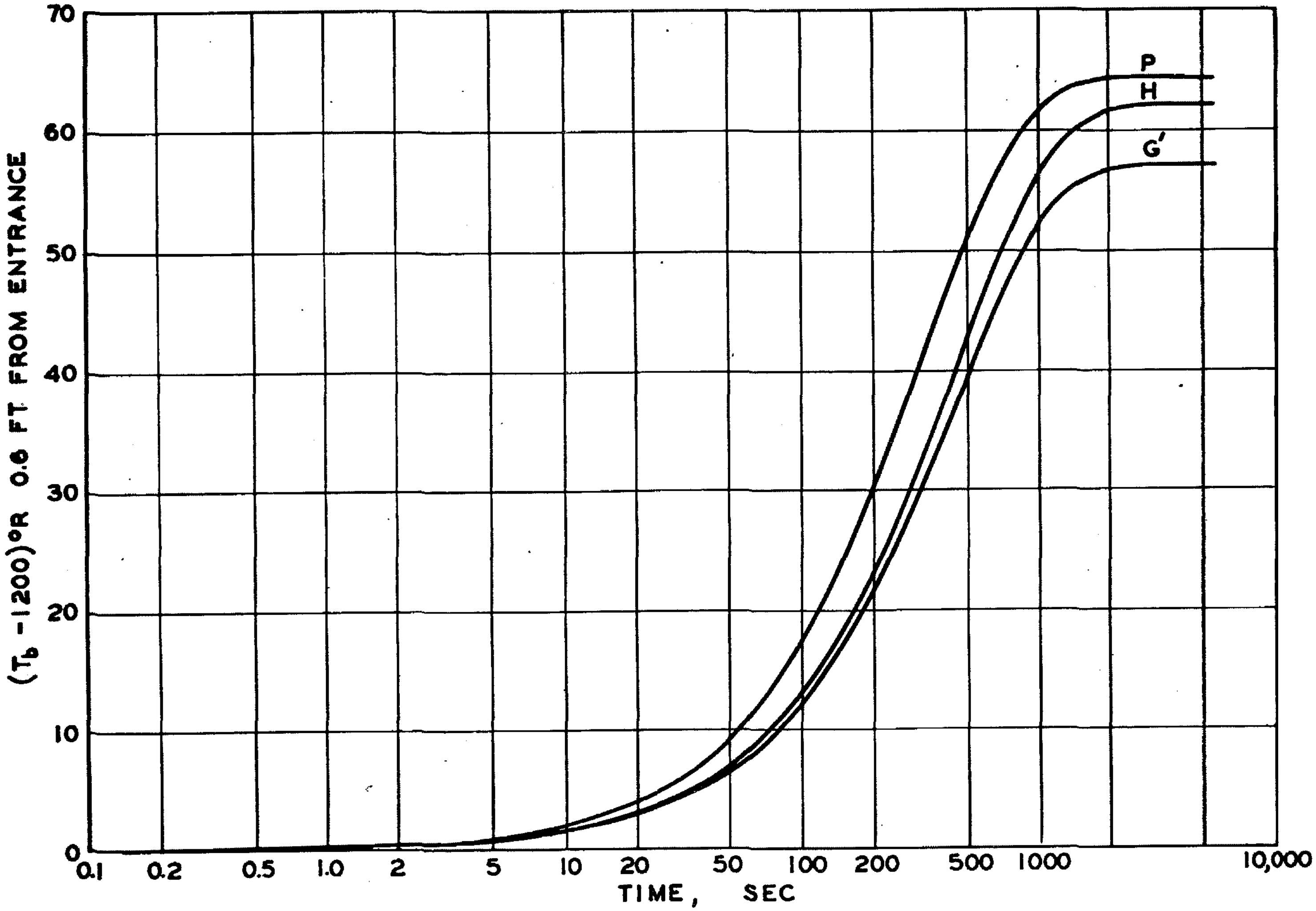


Figure 20. Transient Changes in Temperature; Problem (b).

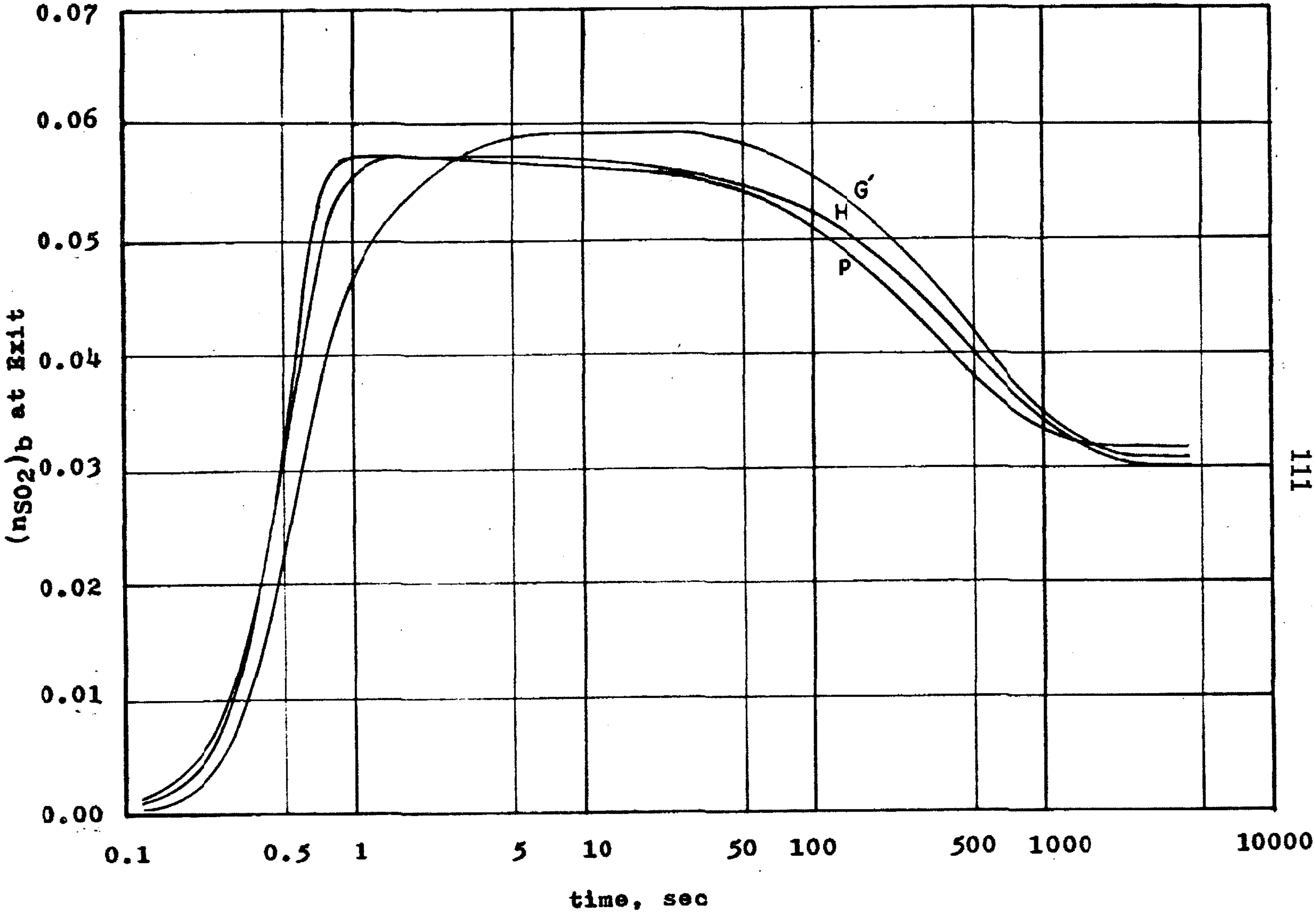


Figure 21. Transient Changes in SO_2-Concentration at Exit; Problem (b).

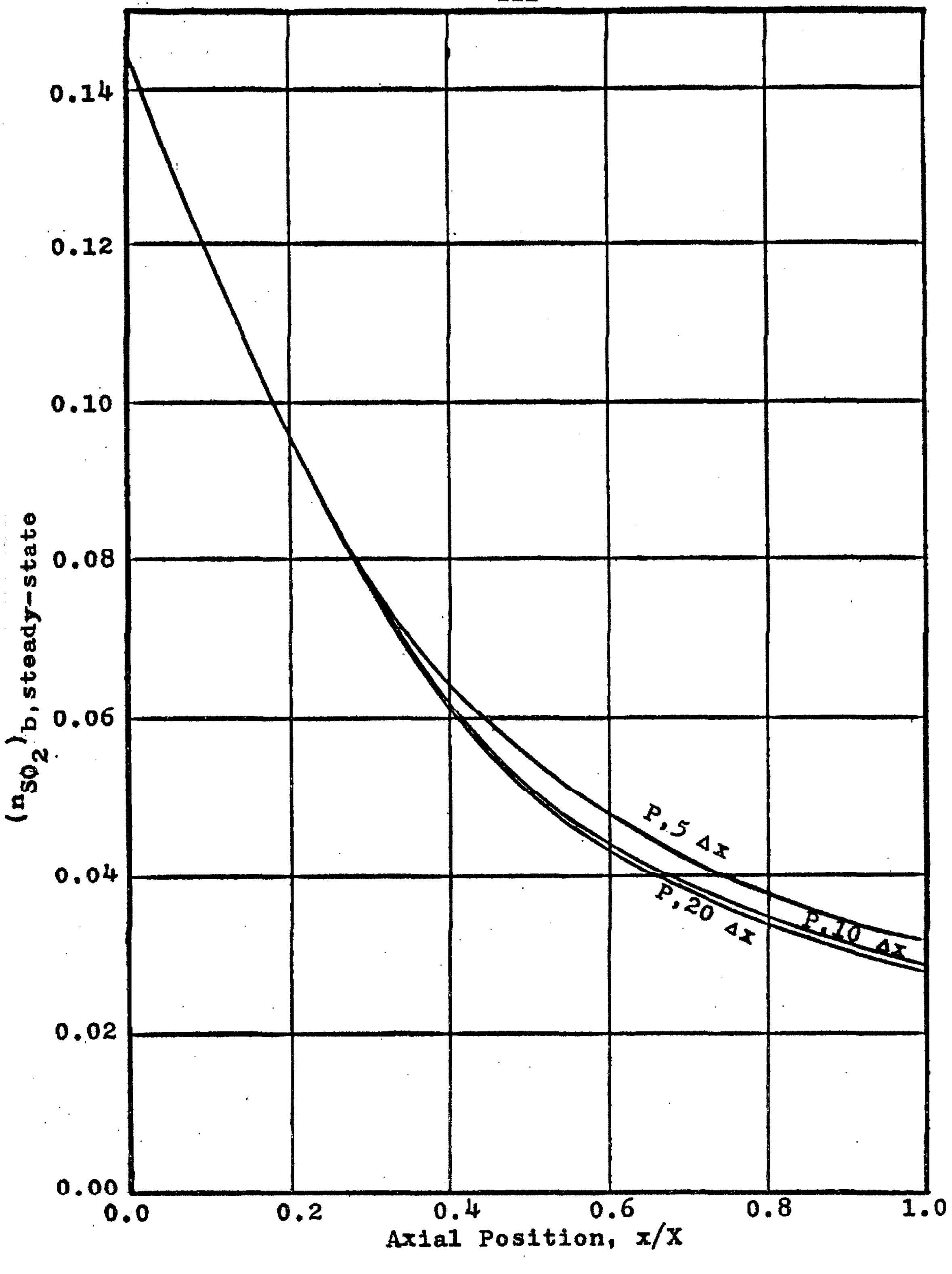


Figure 22. Effect of Size of Axial Increments on SO_2-Concentration Profile; Problem (b); Method P.

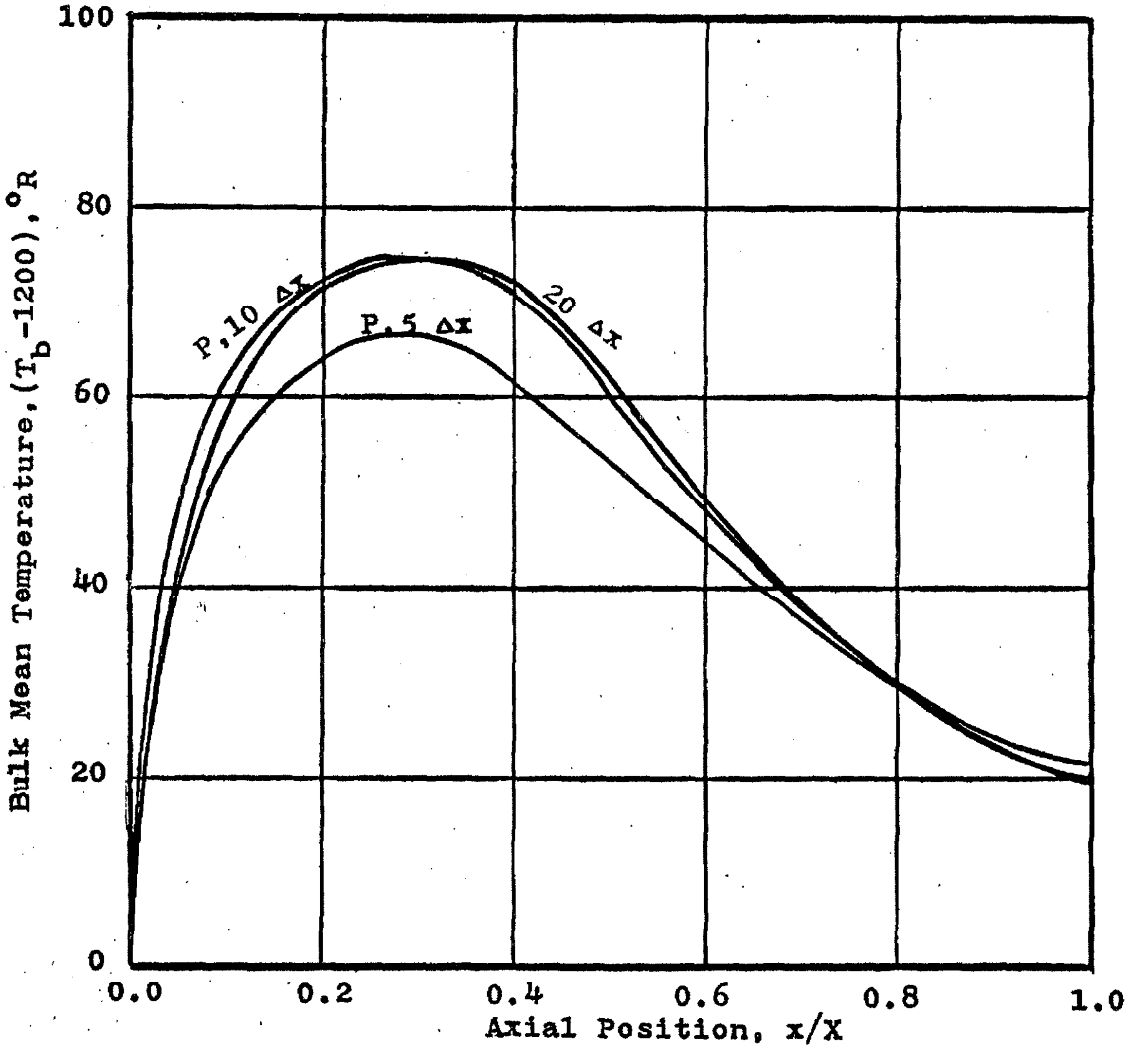


Figure 23. Effect of Size of Axial Increments on Temperature Profile; Problem (b); Method P.

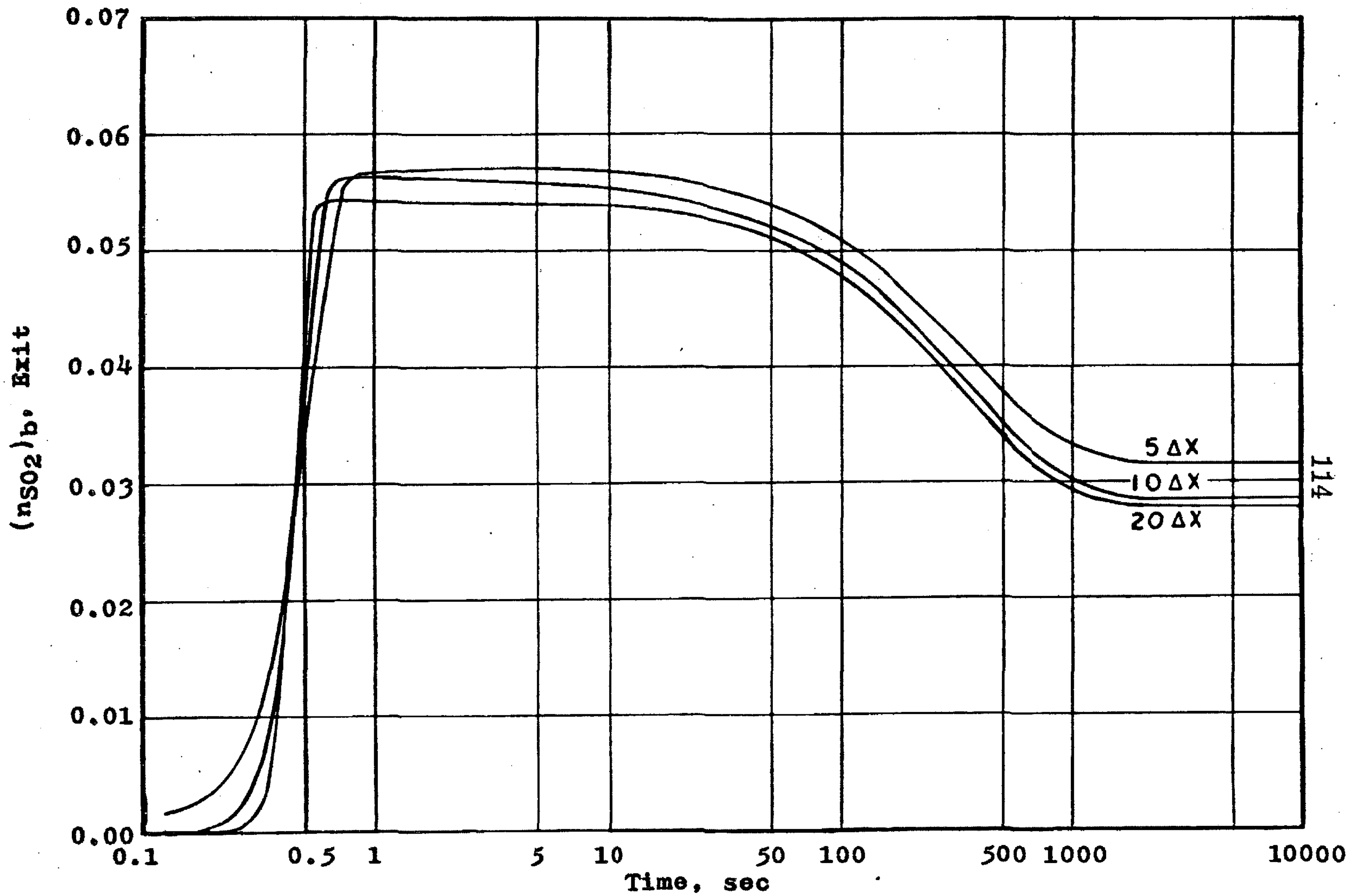


Figure 24. Effect of Axial Increment Size on Transient Changes in SO_2-Concentration at Exit; Problem (b); Method P.

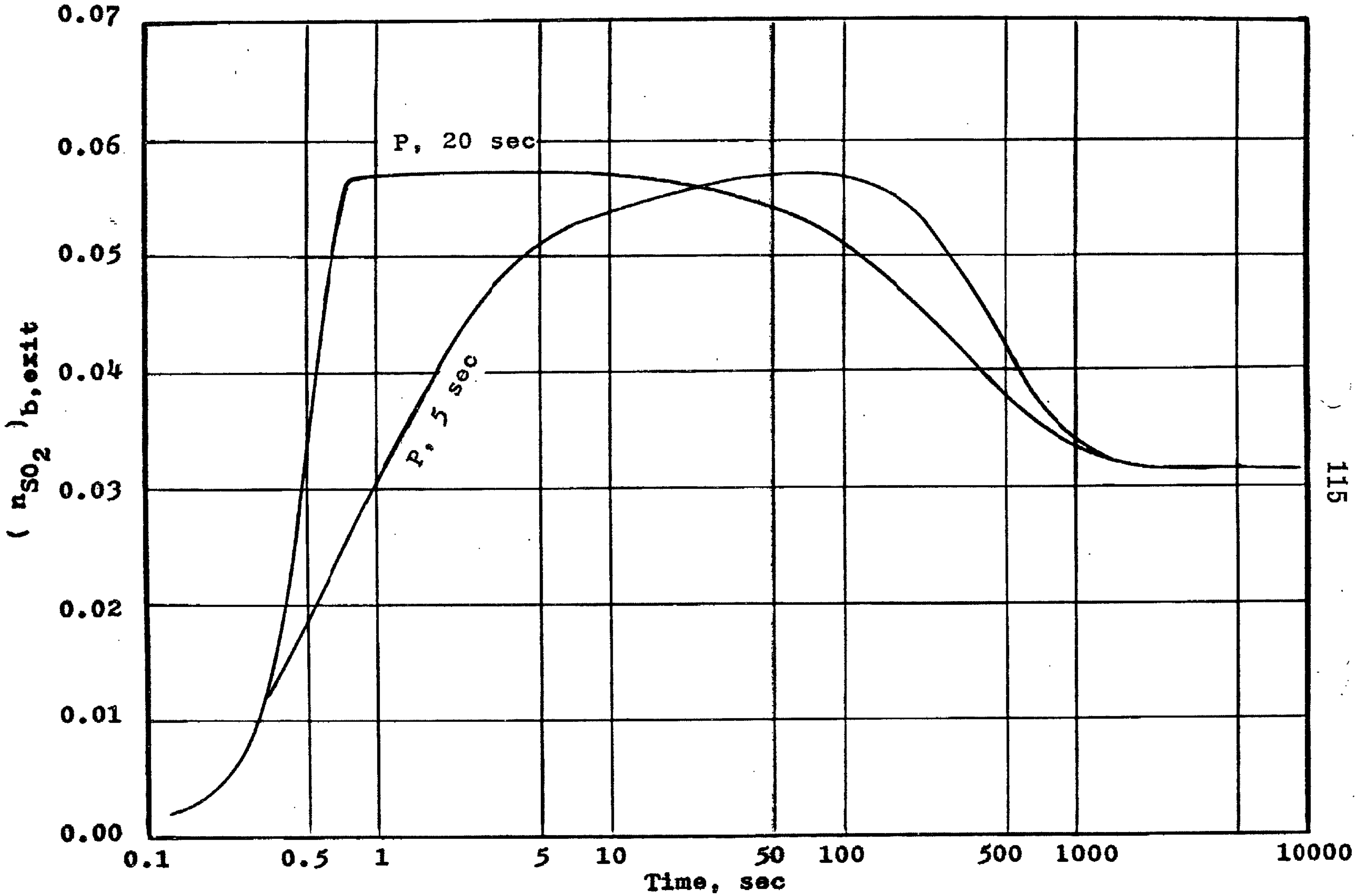


Figure 25. Effect of Size of Time Increment on Transient Solution; Problem (b); Method P.

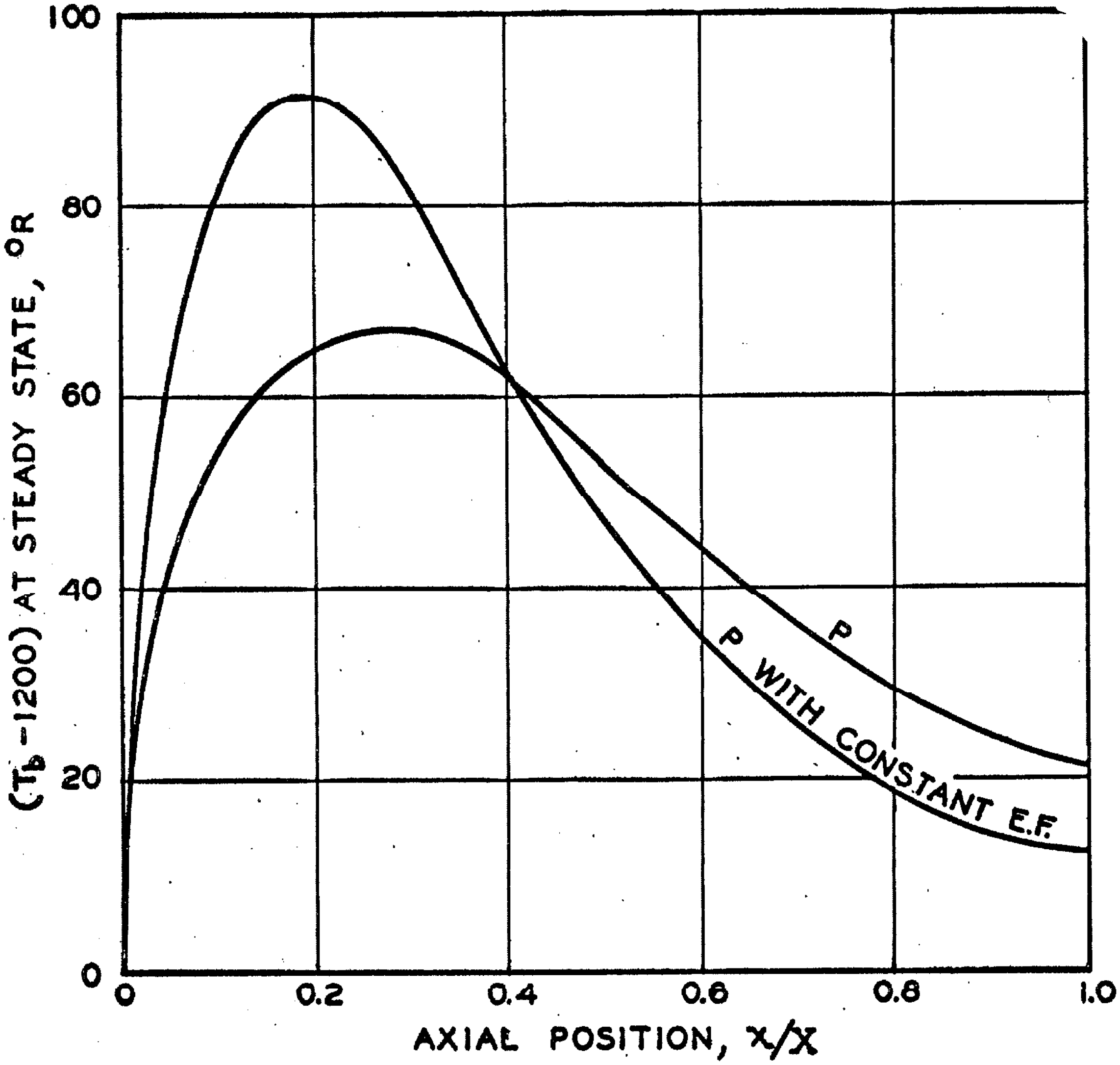


Figure 26. Effect of Using a Constant Average Effectiveness Factor; Problem (b); Method P.

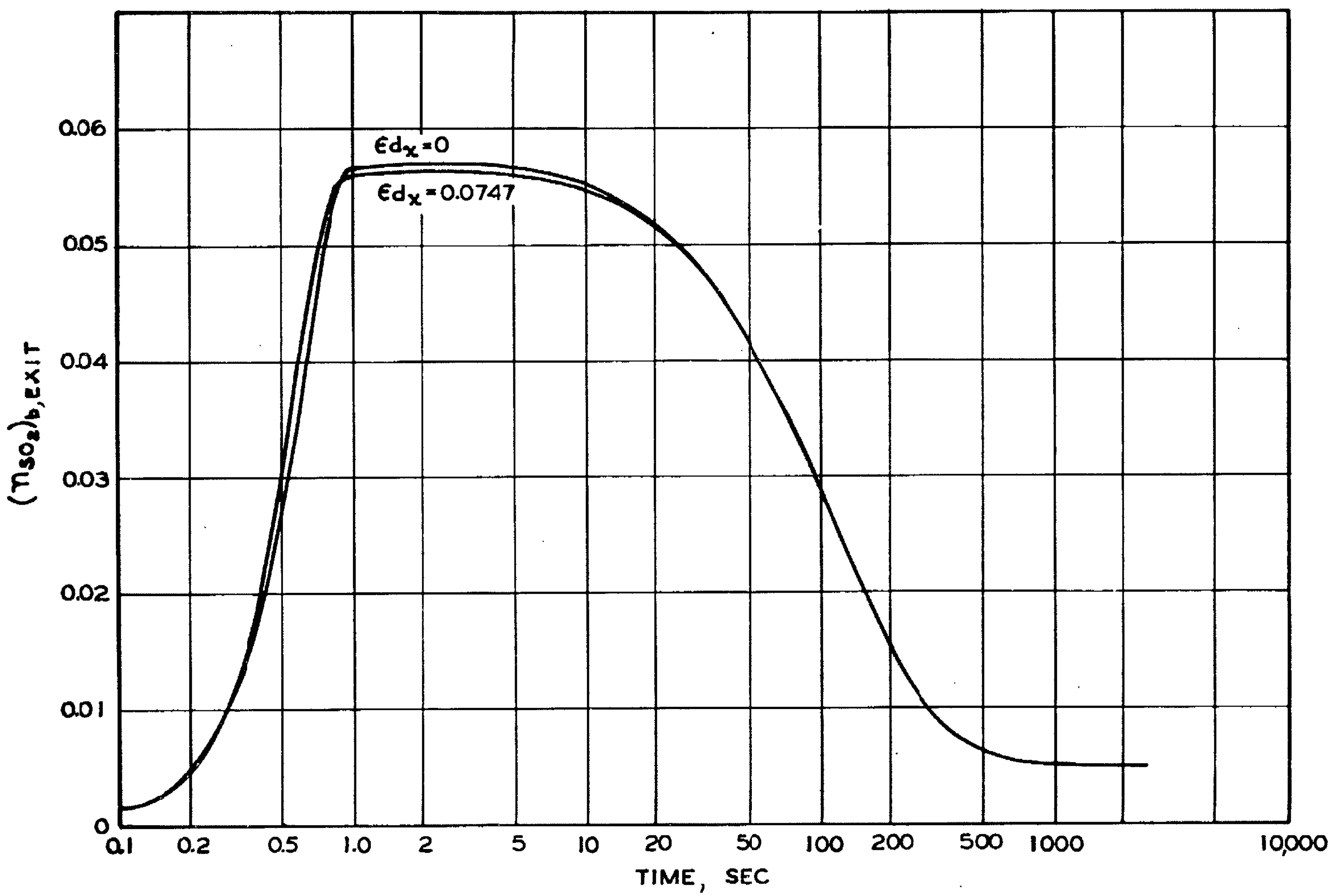


Figure 27. Effect of Neglecting Axial Diffusion; Problem (b); Method P.

Problem (c)

In an actual operation of a reactor, one might encounter an occasion where the cooling system suddenly breaks down for some reason. Therefore, it would be interesting to see how the reactor would respond in such a situation. In the following, the case in which the cooling at the wall is suddenly lost after a steady-state has been reached for problem (b) is studied. Also, a modified case in which after a temporary loss, the cooling will be restored is investigated.

In Figure 28, the response of the exit temperature is shown for both cases just mentioned. The results given by methods G', H and P are seen to be quite close.

The response of n_{SO_2} at the exit is plotted in Figure 29. Again the solutions by all three methods, namely, methods G', H and P, are not significantly different. The importance of the reverse reaction is clearly manifested in this solution. Because of the loss of cooling, the reactor warms up, with the result that reaction rate is increased and less SO_2 is left at the exit. But as the reactor temperature keeps going up, the reverse reaction also becomes more and more significant, and finally around 1000 seconds from the time cooling was lost, the trend reverses and the amount of SO_2 left at the exit increases as the reactor is further heated up. The case in which the cooling is restored at 1600 seconds from the time of the loss of cooling also points to the importance of the reverse reaction. After the restoration of the cooling, the reactor temperature drops, resulting in an increased yield due to a decrease in the reverse reaction. But when the reactor temperature has

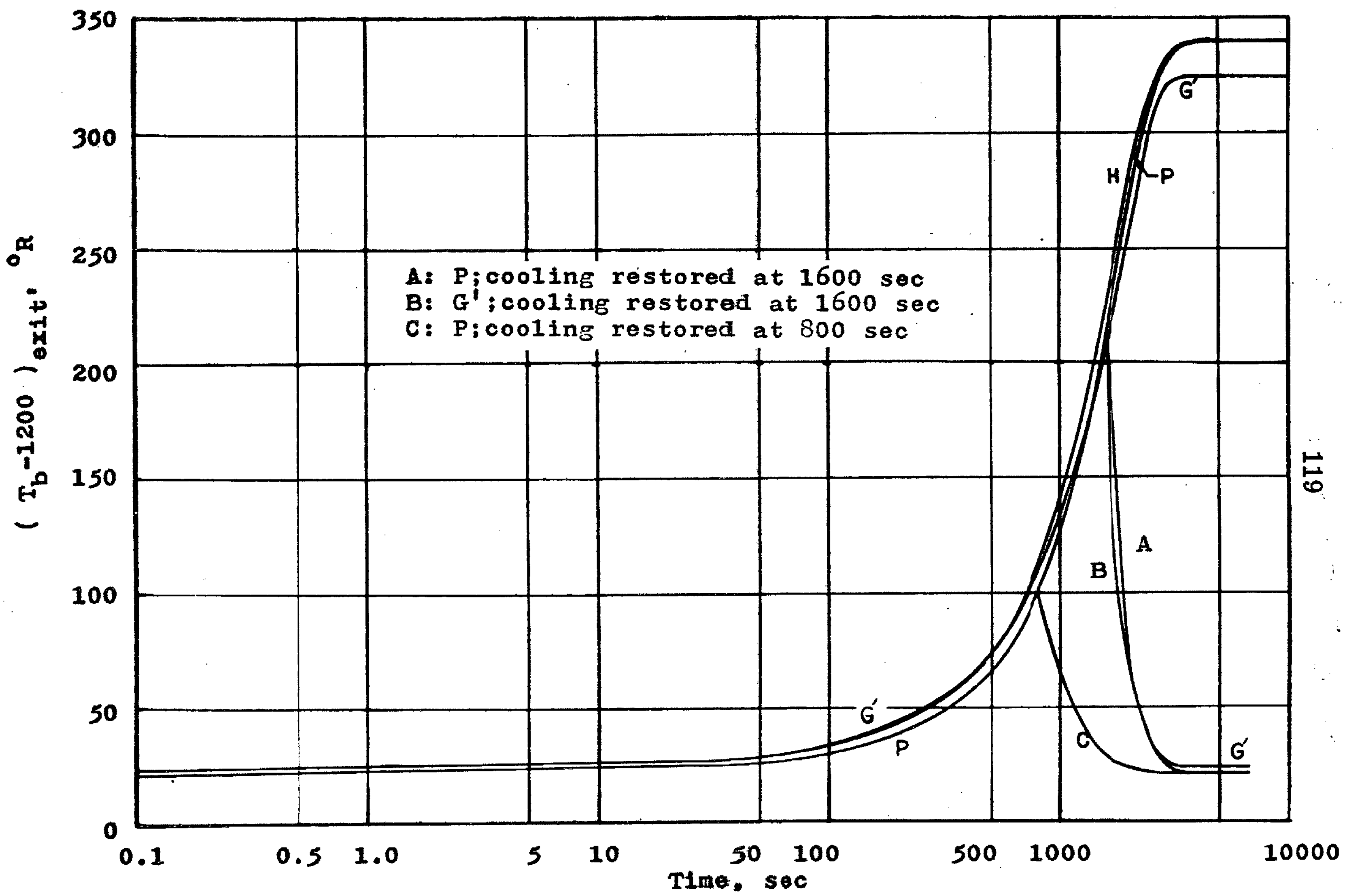


Figure 28. Response of Exit Temperature to Loss of Cooling at Time Zero; Problem (c).

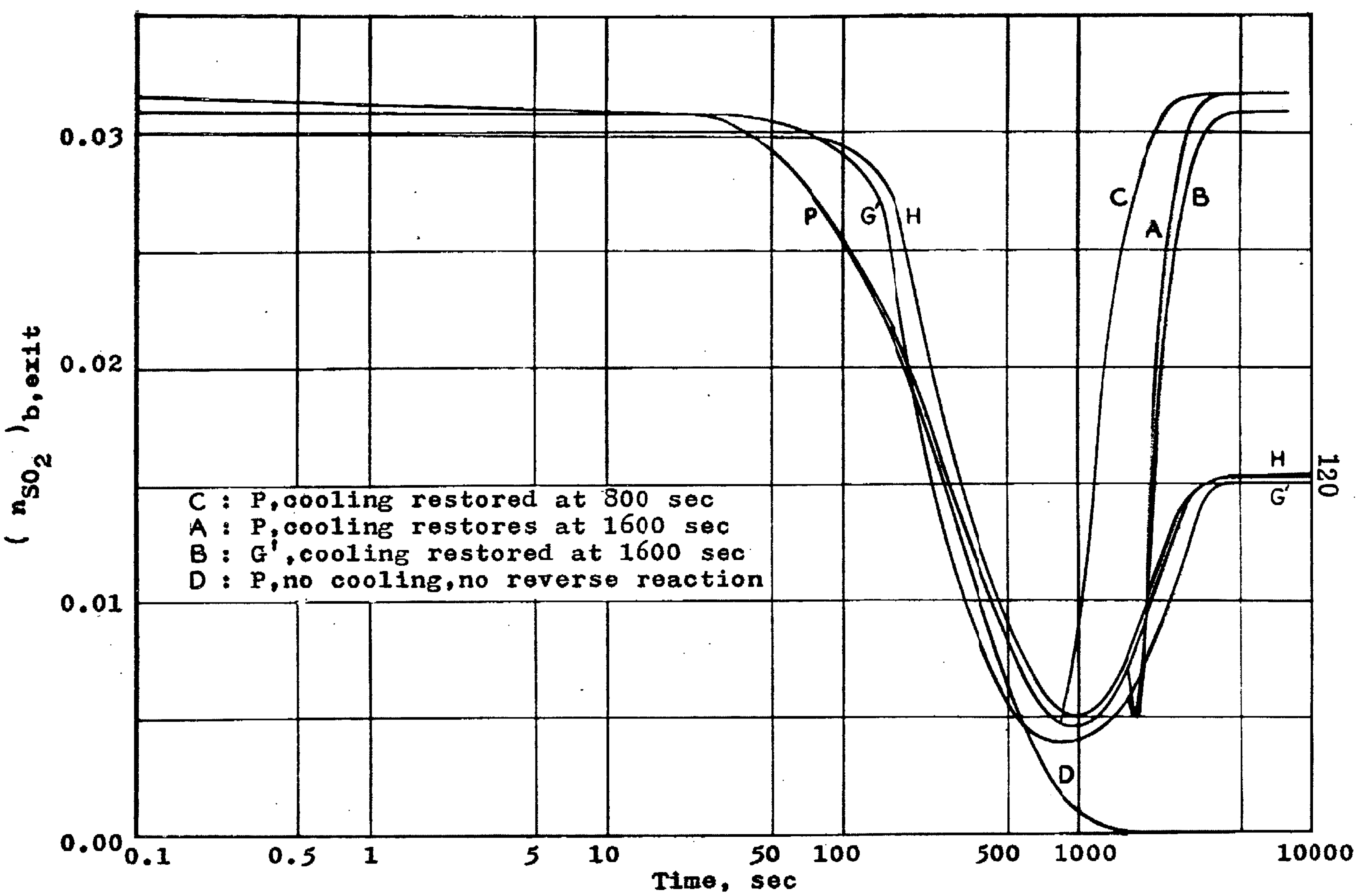


Figure 29. Response of Exit Composition to Loss of Cooling at Time Zero; Problem (c).

reached the optimum value -- the value which gives a maximum yield -- the yield starts to decline. The case where the cooling is restored at 800 seconds does not show a maximum yield point. This is so because the reactor temperature at 800 seconds is below the optimum reactor temperature. In the same figure, we also plot the result computed by method P with the reverse reaction neglected. After the loss of cooling, the yield keeps increasing until a steady-state temperature is reached and the amount of SO_2 at the exit is almost nil.

Problem (d)

A sinusoidal variation of SO_2-concentration is forced on the entrance stream after a steady-state has been reached for problem (b). The response of SO_2-concentration at the exit will be studied.

Figure 30 shows the response of the exit $n_{SO_2\ b}$ to the sinusoidal entrance condition $n_{SO_2\ b,o} = 0.146097 + 0.03 \sin(\theta)$. All the methods G', H and P are used, but the results are not much different. The amplitude of the sinusoidal wave is reduced to about one fifth of the entrance wave. The phase lag is about 1.26 seconds, which is larger than what would be expected from the time it takes for the fluid to travel the length of the reactor -- about 0.43 seconds. The larger lag can be caused by the axial diffusion, the material contained inside the catalyst, and the chemical reaction. For the case without chemical reactions taking place, Deisler and Wilhelm(12) derived an expression relating the phase lag to various parameters. However, for the present problem, no analytic expression can be

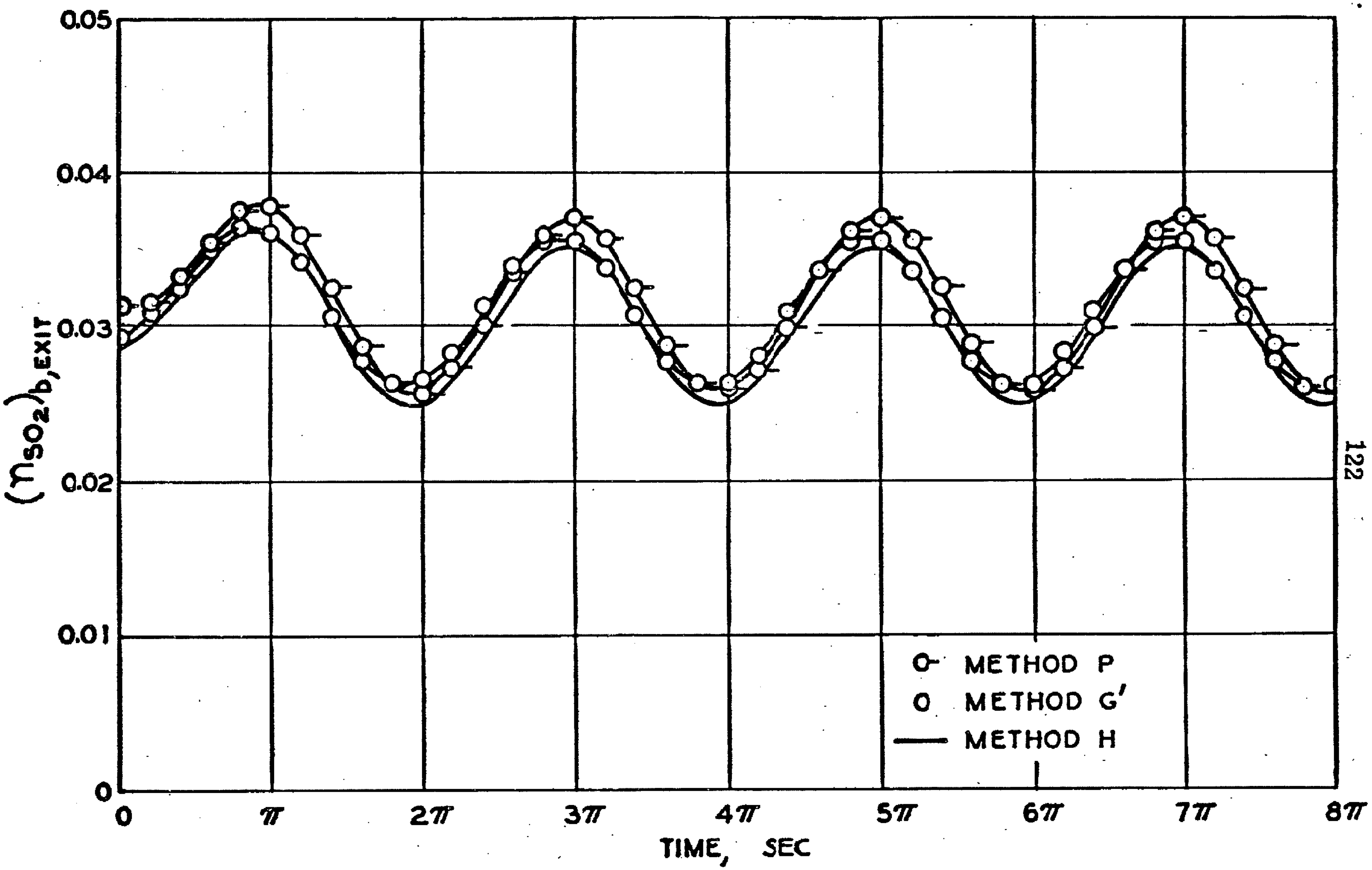


Figure 30. Response of Exit SO_2-Concentration to a Sinusoidal Entrance SO_2-Concentration Forcing.

found. Such an expression can be found by a frequency response study which will be made for problem (f).

Problem (e)

This is an optimization of the wall temperature to obtain the highest conversion of SO_2 to SO_3, with all the other parameters kept constant. In this study, it is assumed that there is no temperature limit for the fixed-bed below which the catalyst temperature should be kept. Method P is used and the result is plotted in Figure 31. The optimum wall temperature with the same entrance temperature of $1200^{o}R$ is found to be $(T_w - 1200) = 160^{o}R$. The steady-state solution with this new wall temperature is shown in Figure 32. With this wall temperature, the yield is 96.5%, while in problem (b) where the wall temperature was kept at $1200^{o}R$, the yield was only about 80.1%. We note that if the reverse reaction were neglected, the highest yield would be obtained without wall cooling.

Problem (f)

The frequency-response of the exit temperature to sinusoidal wall temperature forcing will be studied. This information should be useful for designing a control loop for the control of the exit temperature by wall-cooling. The maintenance of a correct temperature for the exit stream is of utmost importance in attaining the highest yield from a given reactor.

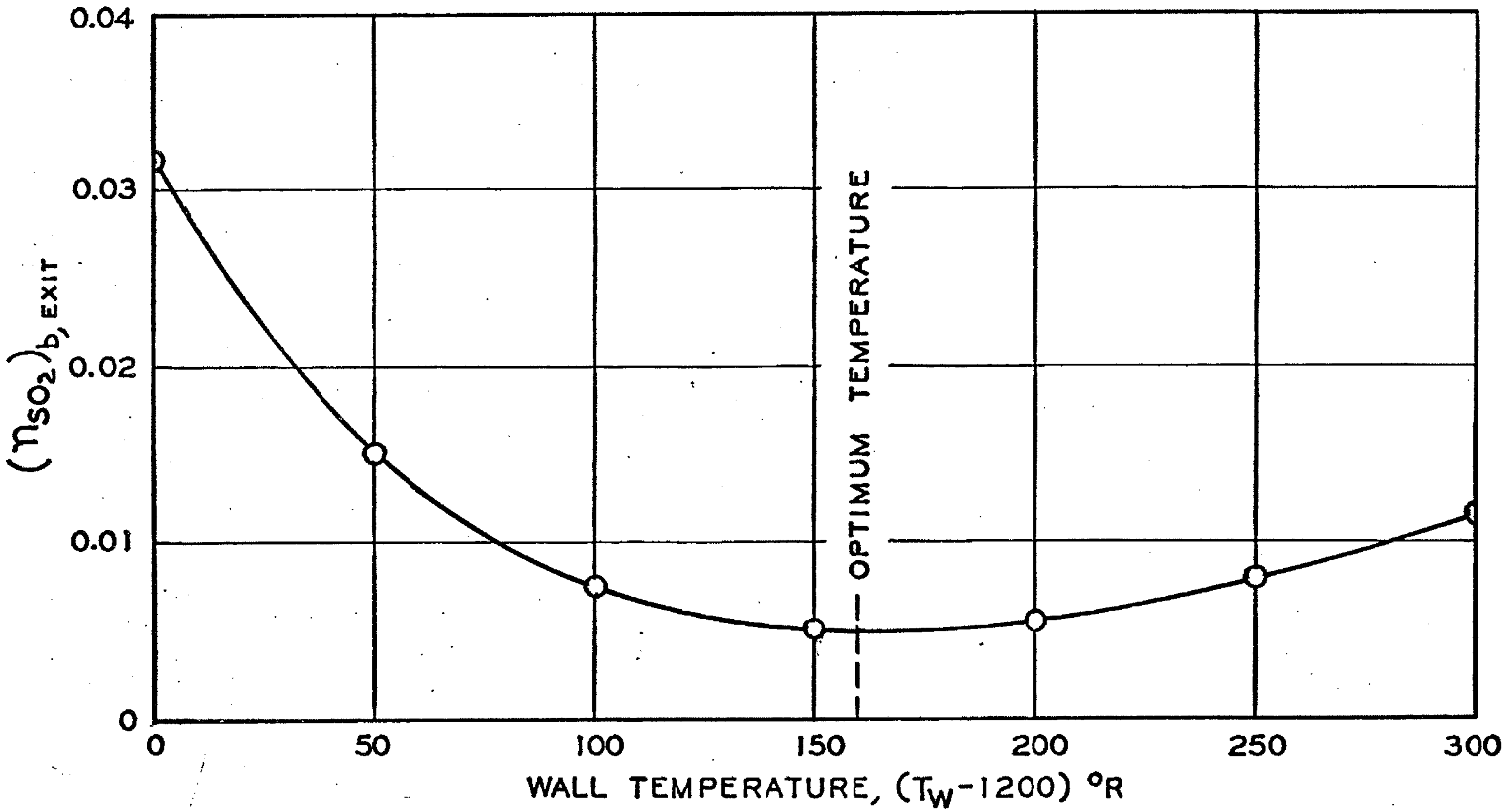


Figure 31. Optimization of Wall Temperature to Obtain the Highest Conversion; Method P.

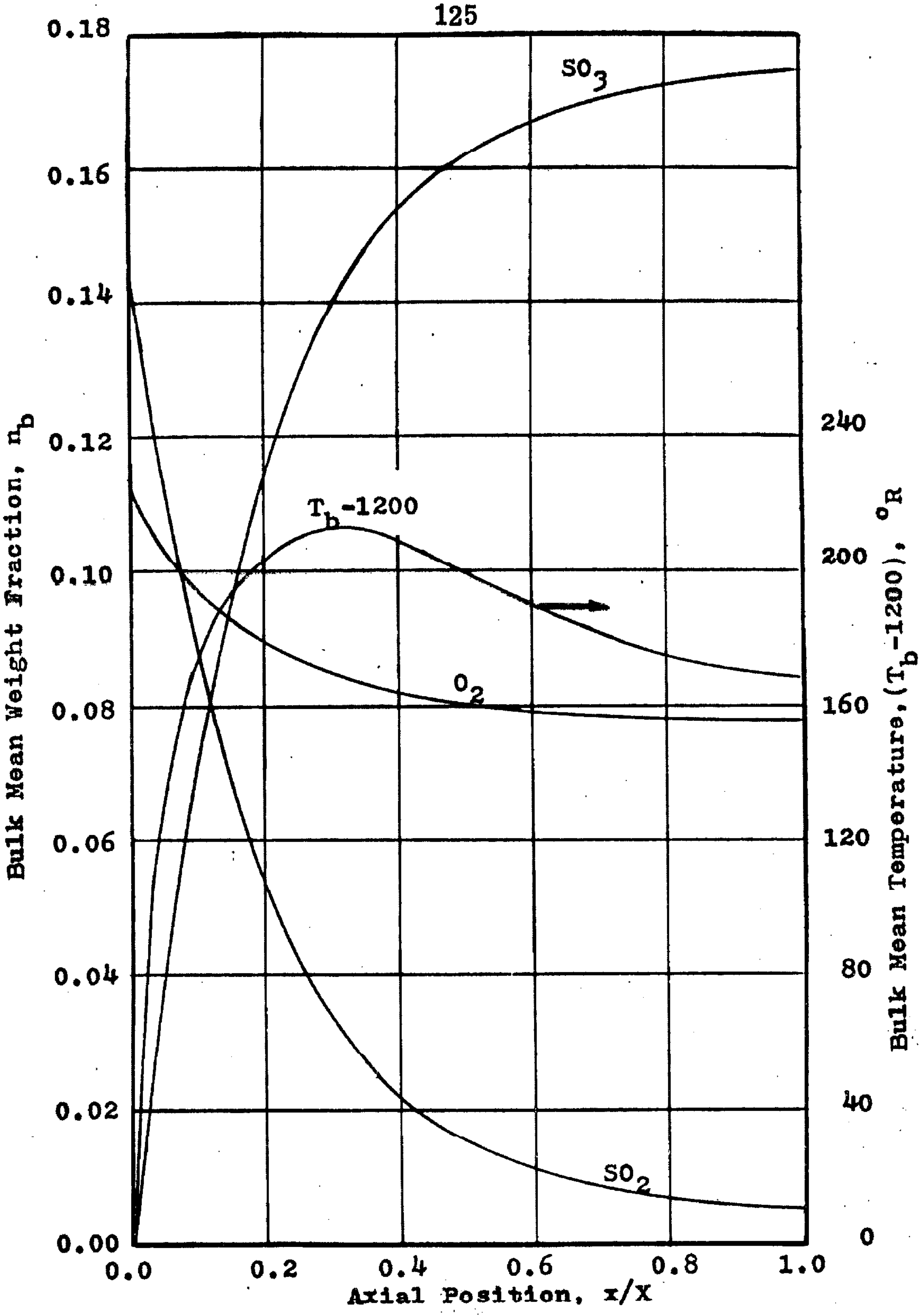


Figure 32. Steady-State Solution Using Optimum Wall Temperature; Problem (e); Method P.

Since method P has been shown to be reasonably accurate for solving the present problem, we use method P in studying problem (f).

After a steady-state has been attained with $(T_w - 1200) = 160^oR$, a sinusoidal wall temperature expressed by

$$(T_w - 1200) = 160 + 5 \sin (w\theta)$$

is used where w is a frequency in rad/sec.

For w = 0.001 rad/sec., the results are shown in Figure 33. Both the exit temperature and the SO_2-concentration are shown. From the temperature plot, gain = 0.902, and phase lag = 21.6^o.

Similar plots are obtained with other frequencies, and gain and phase lag are read from each plot. The combined relationship between gain and frequency is shown in Figure 34, and that between phase lag and frequency is shown in Figure 35. These two plots would be of use in the design of a control loop for the control of the exit temperature of the reactor.

Using the method described by Ceagiske(31), the transfer function represented by Figure 34 is found to be

$$G(s) = \frac{3.6 \times 10^{-3}}{2.15 \times 10^{-1}} \times \frac{s + 2.15 \times 10^{-1}}{s + 3.6 \times 10^{-3}}$$

$$= \frac{4.66s + 1}{278s + 1} \qquad (176)$$

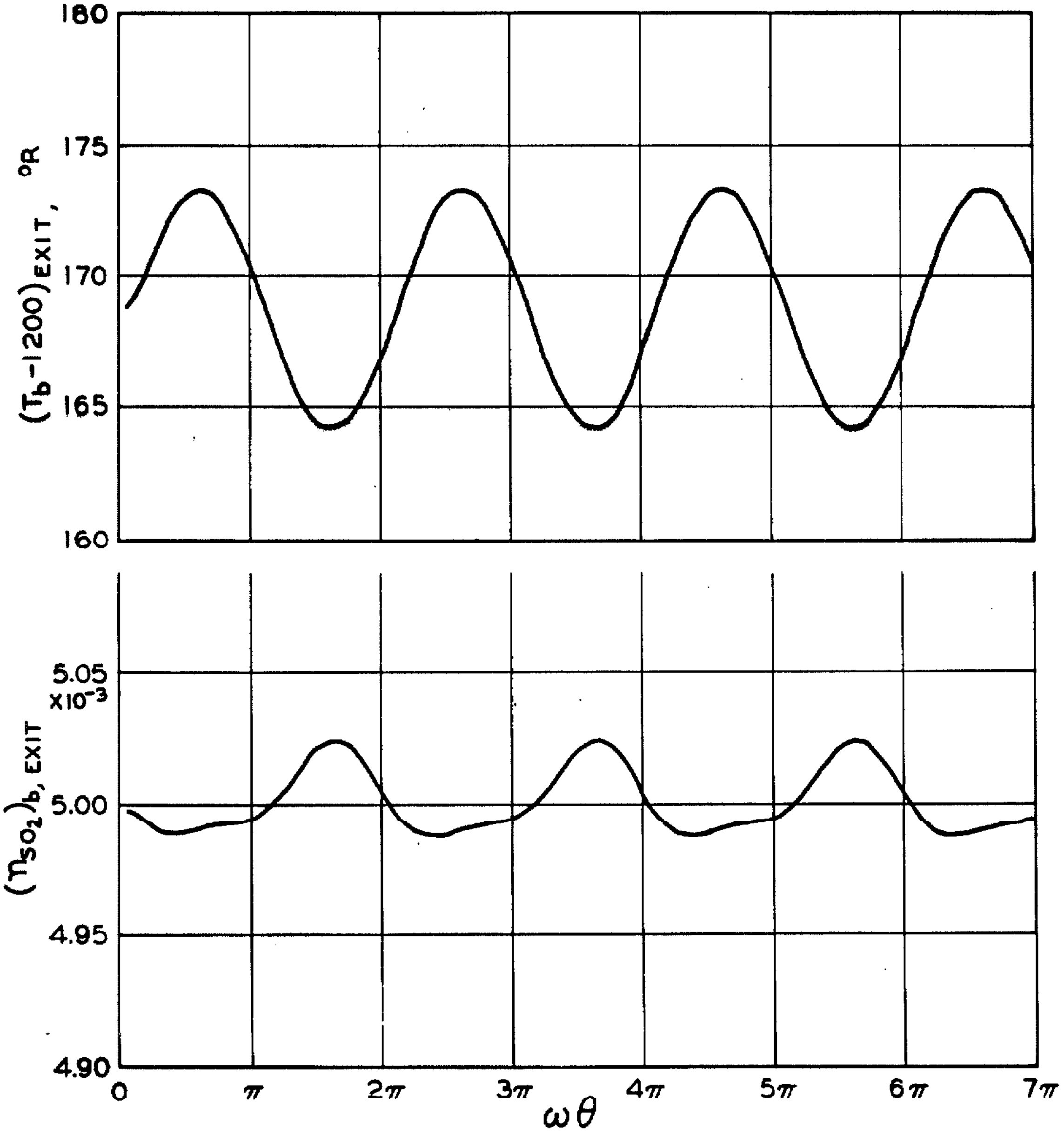


Figure 33. Response of Exit Temperature to Sinusoidal Wall Temperature Forcing; Problem (f); $\omega = 0.001$ rad/sec.

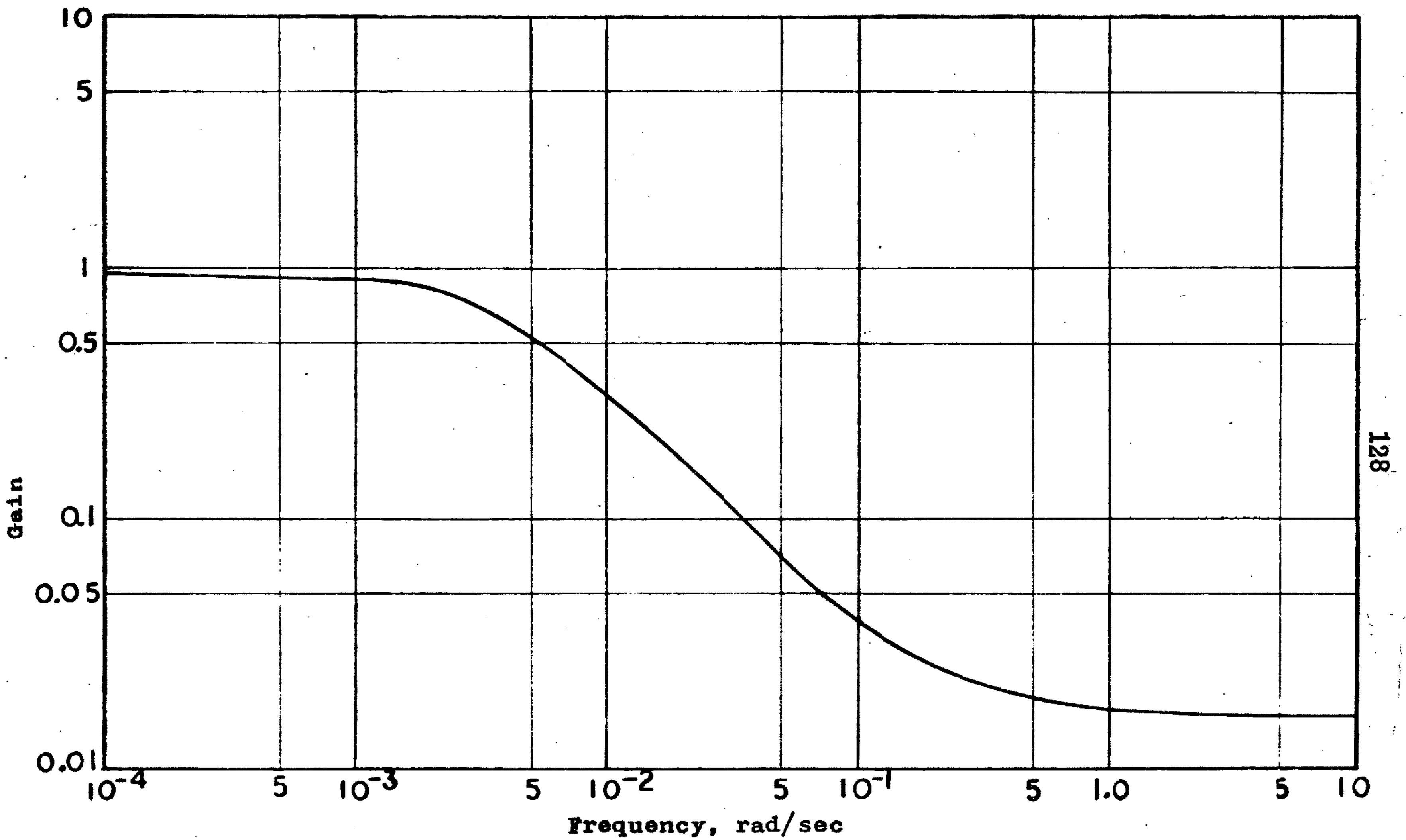


Figure 34. Frequency Response of Exit Temperature to Sinusoidal Wall Temperature; Gain vs. Frequency.

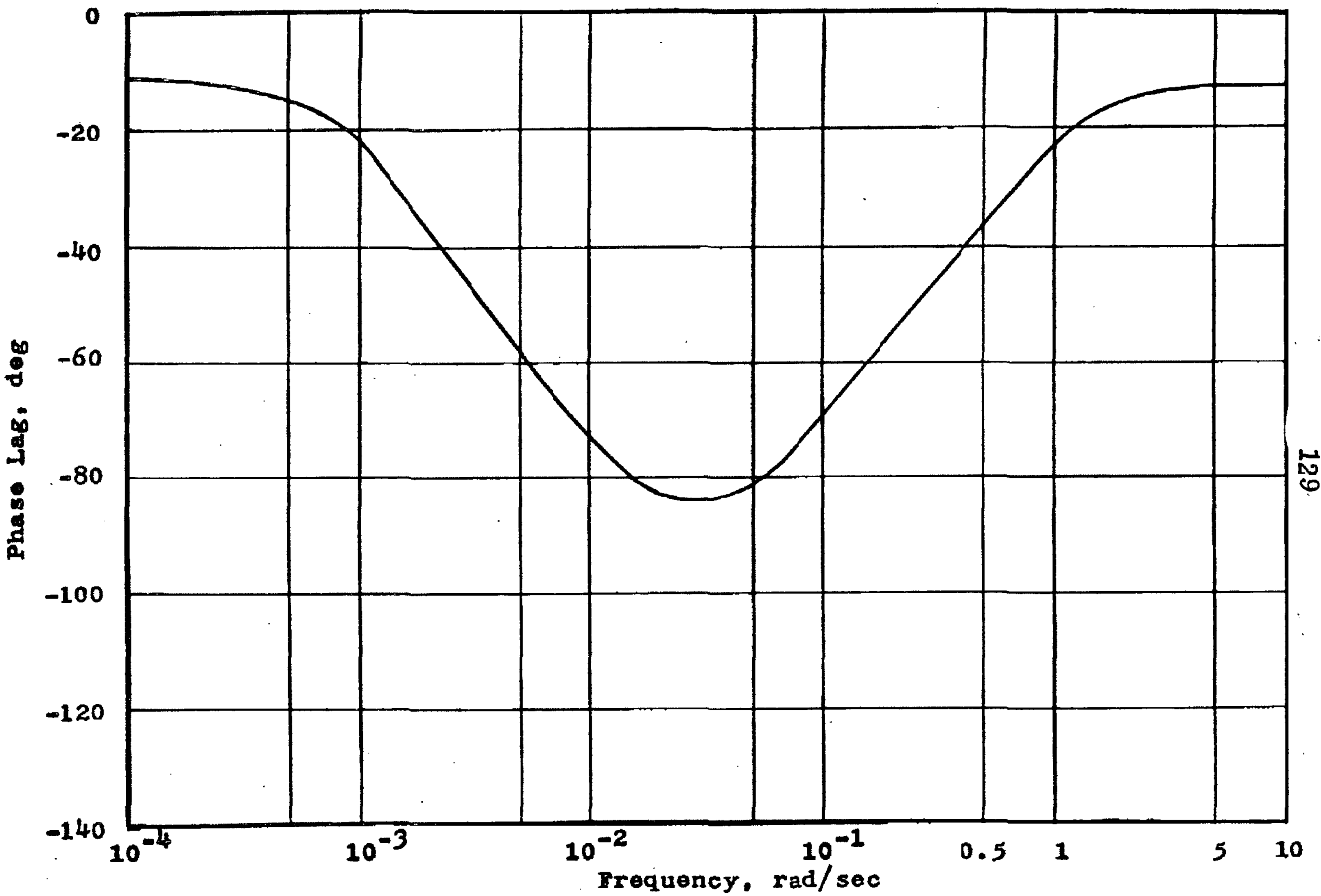


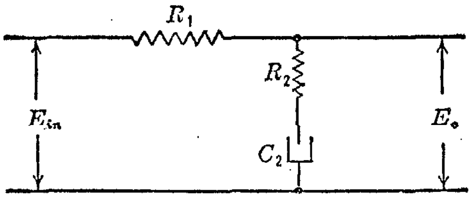
Figure 35. Frequency Response of Exit Temperature to Sinusoidal Wall Temperature Forcing; Phase Lag vs. Frequency.

This transfer function is equivalent to that of a phase lag network(32, 33) shown below, if

$$\frac{R_1}{R_2} = 58.74 \quad , \tag{177}$$

and

$$C_2 R_2 = 4.66 \quad . \tag{178}$$



A Phase Lag Network

It is not surprising that the exit temperature response to the wall temperature change should correspond to the phase lag network: Figure 31 shows that the yield is almost invariant to a slight change in wall temperature if the latter is close to the optimum one. Therefore, the reaction rate does not play a role in the present frequency response study, and the system is almost linear. The equivalence between the two systems simply means that we can assign a resistance to the transfer of heat between the wall and the exit stream, a resistance to the heat transfer between the exit stream and the catalysts, and a capacitance to the heat capacity of the catalysts.

VI. SUMMARY

In the present work, the differential equations describing the transient behavior of a fixed-bed reactor are derived with as few assumptions as possible. The stream equations are derived with the assumption that the same diffusivity can be used for turbulent material and energy diffusion.

Although the subject of stability analysis of numerical solutions of partial differential equations has been widely studied, the methods of analysis published so far are still inadequate for analyzing the complicated system of equations involved in the fixed-bed reactor. Hence, a large amount of effort has been put into stability investigations.

To carry out the stability analysis of the numerical solution of the system of partial differential equations, the source terms are first linearized. Then, it is assumed that the solution can be expanded into a complex Fourier series and, therefore, corresponding to each harmonic of the expansion, the system of partial differential equations becomes, at a particular location, a system of ordinary differential equations, such as equation (113). The stability region of a numerical solution of such a system of equations is obtained by finding the locus of the values of (λh) which give $|q| = 1$, where λ is an eigenvalue of (A_f) and q is the frequency factor of the numerical solution corresponding to the (λh). This method of stability analysis is found to be convenient and easy to understand. Also, the method of analysis is more practical for general problems with source and convection terms than the one given by Richtmyer(27). According to the latter's method, the presence of source terms does not affect the stability of a numerical method, nor does the presence of lower order derivatives, which, in our problem, are the predominating convective transport terms. Actual numerical solutions have revealed that Richtmyer's analysis is impractical. A numerical method which is stable in Richtmyer's sense has been found to be unstable in the sense defined in this work.

The present analysis has shown that the presence of source terms and convection terms presents stability problems as does the presence of the diffusion terms.

The partial differential equations in which convection terms dominate over diffusion terms are found to be unsuitable for solution by a forward-difference method because of instability. For the Crank-Nicolson method, the convection terms cause oscillations and a modified method, such as method W or method E with $w > 0.5$, is needed to make the oscillations decay.

The effects of various methods of handling the source terms are also investigated. It is found that positive source terms can be evaluated at the beginning of each time increment without causing any stability problems. For negative source terms, such a method will result in instability unless a severe criterion is met. The scheme suggested by Brian, or similarly that employed in a Runge-Kutta method for ordinary differential equations are found to be unstable unless similar stability criteria are satisfied. If the source terms are treated as the space derivatives are handled, as by the use of method W with $w > 0.5$, there would not be any stability problems. However, for the cases where the source terms are coupled, that is, if the source terms in the equation for one variable are functions also of some other variables, such a scheme would require iterative methods. For the fixed-bed reactor problem studied, the source terms, which are coupled, can be handled by using a special technique shown by equations (79) and (75) to avoid the necessity of iteration. The physical implications of using such a scheme are shown, and the results of such a solution have been shown to be reasonably accurate by comparing the solutions obtained using different time increment sizes. For the case of coupled source terms where no special techniques are applicable, it is proposed that only the source terms be iterated, with the space derivatives treated as in method W or method F, depending on the dimensionality of the problem.

Based on the stability analysis, a method which is unconditionally stable is devised to obtain a fairly rigorous solution of the system of equations including the equations for the interior of the catalyst. The method is called method G'. Using 5 space increments in each direction, it is demonstrated that such a rigorous solution can be obtained with a few minutes of computation time with an IBM-7094 computer. Such a solution is of primary importance not only for checking the legitimacy of various simplifying assumptions usually made in reactor calculations, but also because in some reaction systems, the solution could be the only one that would be reasonably accurate.

Using the rigorous solution as a standard, the effects of various simplifying assumptions have been established for the reaction system investigated:

1. Neglecting of the axial diffusion causes negligible effects -- less than 5% difference.

2. The assumptions that radial velocity can be neglected and axial velocity is constant and uniform are good. The maximum variation in axial velocity is only 10%, and the maximum radial velocity is 3×10^{-5} ft/sec.

3. The use of a constant effectiveness factor throughout gives a poor solution, with a maximum error of 70% in temperature.

4. Reverse reactions are not always negligible.

5. The use of an "effectiveness factor" model causes some error in transient concentration changes. This is to be expected because by making that assumption, one does not account for the accumulation of material in the catalyst. At the steady-state, the effect of the assumption is found to be negligible, even though an apparent first order rate expression has been substituted for the rigorous expression in order that the model can be used.

6. Neglecting radial changes in properties and using a heat transfer coefficient to approximate the transfer of heat from the stream to the wall causes some errors in transient temperature changes, but does not have much effect on steady-state solution.

Generally speaking, the effects of using an "effectiveness factor" model and neglecting radial changes are not large, and the use of the simplified method, namely, method P, is reasonably accurate for the problems studied.

A simplified method is valuable particularly in practical applications. A method should be faster than real time responses in order to be usable in an on-line computer for a reactor control.

In a preliminary design of a reactor, only a fairly good solution is needed, and a simplified method like method P should serve the purpose.

However, method P must be used with caution, as there are three obvious limitations on its use:

a. Method P just gives the bulk mean temperature in the stream and the surface temperature of the catalyst. The maximum value of the temperature in the catalyst located at the center of stream is needed if the catalyst cannot be overheated, and it is not given by the method.

b. The system of the oxidation of SO_2 is carried out under atmospheric pressure, and the main resistance to the response of the system is contributed by the heat capacity of the solid catalysts. In other words, the temperature equation is the one that controls the response of the system. Hence, the accumulation of material within the catalyst can be neglected without causing appreciable error. Under a high pressure reaction system, the "effectiveness factor" model might cause significant error.

c. The effect of neglecting radial changes was found to be not too large, but for a case in which the diffusivities in the catalyst are very large, the non-linearity of the reaction rate expression might become more pronounced, and the assumption of negligible radial changes could give an inaccurate over-all reaction rate.

Since for the system investigated, method P has been found to be fairly accurate, the method is used in finding the optimum wall temperature for obtaining a maximum yield. It should be emphasized that only by including the reverse reaction can such an optimization study be made.

The control of the exit temperature is essential to attaining the highest conversion. The exit temperature can be controlled by varying the wall temperature, according to the measured exit temperature. To obtain the information needed in the design of such a control loop, method P is used to find the frequency response of the exit stream temperature with a sinusoidal forcing upon the optimum wall temperature. The results show that the system is equivalent to a phase lag network commonly used in regulating systems.

These are merely two of the many applications for which method P can be employed. Needless to say, for some cases, the use of a more rigorous method, such as method G' may be required to give an accurate solution.

Although method G' was developed for the solution of reactor problems, the techniques used in the development of the method should be helpful in the solution of other problems. In the method, an implicit scheme is used, with non-linear source terms linearized to avoid the necessity of iterations. A special technique is employed to handle the coupling between the stream properties and the catalyst properties. Time increments are chosen each time to make the changes in properties within one time increment almost constant. The result is that method G' is more than one thousand times faster than the trial methods which employ the techniques available from the literature.

VII. NOMENCLATURE

a_i : outside surface area of catalyst per unit bed volume; (sq ft)/(cu ft).

(A), (B), (D), etc. : square matrices of order 5 for stream equations and 4 for catalyst equations.

$\vec{b}_j$: eigenvector corresponding to q_j.

C : heat capacity defined by equation (45); Btu/(cu ft)(^{o}F).

$\vec{C}$: column vector of 5 or 4 elements.

C_p : isobaric heat capacity per unit weight of fluid; Btu/lb^{o}F.

C_2 : electrical capacitance.

D_k : molecular diffusivity of component k; (sq ft)/sec.

D_k' : diffusivity of component k in catalyst; (sq ft)/sec.

$$D_k = \frac{-a_i \sigma_{fi}' K_k}{f \sigma_f} \quad .$$

$$DM1_k = \frac{a_i K_k M_k}{f \sigma_f RT} \quad .$$

$\Delta \underline{\underline{E}} ad_k$: heat of adsorption as defined by equation (43); Btu/lb-mole.

E_{in} : input voltage.

E_o : output voltage.

$\vec{e}_r$: unit vector in radial direction (of the bed).

$\vec{e}_x$: unit vector in axial direction.

F : factor defined in equation (30).

$\vec{F}_d$: drag force per unit bed volume; lb/(cu ft).

f : exterior void fraction.

f' : void fraction in catalyst.

$G(s)$: transfer function.

h : time increment, i. e., $\Delta\theta$.

h_i : heat transfer coefficient between catalyst and stream; Btu/(sq ft)(^{o}F)(sec).

$\vec{H}_d$: turbulent enthalpy flux; Btu/(sq ft)(sec).

i : $\sqrt{-1}$.

(I) : identity matrix.

$\vec{k}$: vector with components k_r and k_x.

k_s : thermal conductivity of catalyst; Btu/(sq ft)(^{o}F/ft)(sec).

K_k : D_k/(film thickness).

$\underline{K}_k$: adsorption coefficient of component k.

L_r, L_x, $L_{r'}$: periods in r, x and r' directions respectively.

$\vec{m}_k$: diffusional mass flux of component k; lb/(sq ft)(sec).

M_k : molecular weight of the k-th component.

n_k : weight fraction of k-th component in stream.

p_k' : partial pressure of component k in catalyst; atm.

$\vec{q}$: heat flux plus enthalpy flux due to molecular mass diffusion; Btu/(sq ft)(sec).

q : frequency factor shown in equations (116) and (120).

r : radial distance from center of reactor; ft.

r' : radial distance from center of catalyst particle; ft.

R_1, R_2 : electrical resistance.

R_k : rate of generation of component k per unit volume of catalyst; lb-moles/(cu ft)(sec).

R_T : $-\frac{1}{C}\sum_k \underline{\overline{E}}_k{}' R_k$.

$\vec{u}$: interstitial mass average velocity in stream; ft/sec.

u' : velocity in the catalyst interior, which is assumed to be in the radial direction of spherical pellet; ft/sec.

u_x'' : axial velocity outside the exit of reactor; ft/sec.

$\vec{y}$: vector with components r and x.

Greek Letters:

α : real part of an eigenvalue.

β : imaginary part of an eigenvalue.

ϵ_{dr} : turbulent diffusivity in radial direction; (sq ft)/sec.

ϵ_{dx} : turbulent diffusivity in axial direction; (sq ft)/sec.

$\underline{\epsilon}_{dr}$: $\epsilon_{dr} + D$.

$\underline{\epsilon}_{dx}$: $\epsilon_{dx} + D$.

$\vec{\beta}_j$: eigenvector of matrix (A), corresponding to λ_j.

γ_k : an exponent depending on mechanism of adsorption of component k on catalyst.

η : viscosity; (lb)(sec)/(sq ft).

θ : time; sec.

λ : eigenvalue of matrix (A).

ξ_j's : coefficients in equation (114).

σ_f : specific weight of stream; lb/(cu ft).

$\vec{\Phi}$: column vector of order 5 or 4.

Φ : viscous dissipation = $-(f\tau : \nabla u)$.

τ : shear stress tensor; lb/(sq ft).

ω_j's : coefficients in equation (116).

Superscripts:

$\rightarrow$: vector.

$'$: interior of catalyst.

— : partial quantity.

o : initial.

Subscripts:

c : catalyst.

d : diffusion.

e : entrance.

f : stream.

i : interface between catalyst and stream.

k : k-th component.

s : solid.

t : tangential.

$\sim$: molal quantity.

o : at reference time.

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APPENDIX I

COMPARISON OF COMPUTER TIME REQUIRED BY VARIOUS METHODS

A. Various Methods Employed:

Method G':

This is a rigorous method employing a minimum of simplifying assumptions.

Method H:

An "effectiveness factor" model is used in this method in addition to making the assumptions used in method G'.

Method P:

In addition to making all the assumptions employed by method H, assumptions of negligible radial changes and axial velocity variations are used in this method.

B. Problems Studied:

Problem (b):

The start-up of the reactor is studied.

Problem (c):

The behavior of the reactor upon loss of cooling with subsequent restoration is studied.

Problem (d):

The response of the exit concentration to a sinusoidal variation of SO_2-concentration at the entrance is studied.

C. Comparison of Computer Time Requirement by the Various Methods:

The amount of computer time required on an IBM-7094 by the various methods for solving the various problems are tabulated, the time being shown in minutes:

	Problem (b)	Problem (c)	Problem (d)
Method G'	6	7.5	2.5
Method H	2	2.5	1
Method P	0.5	0.7	0.2

APPENDIX II

A FORTRAN PROGRAM FOR METHOD G' - A RIGOROUS SOLUTION METHOD TO FIND THE TRANSIENT BEHAVIOR OF A FIXED-BED REACTOR FOR THE OXIDATION OF SO_2

Notations

Stream equations are written in the form:

$$\frac{\partial G}{\partial \theta} = B \frac{\partial G}{\partial r} + C \frac{\partial G}{\partial x} + ER \frac{\partial^2 G}{\partial r^2} + EX \frac{\partial^2 G}{\partial x^2}$$

$$+ DM1 \times G_{cat} + D \times G \quad . \qquad \text{(A-1)}$$

Catalyst equations are written in the form:

$$\frac{\partial G}{\partial \theta} = B \frac{\partial G}{\partial r'} + ER \frac{\partial^2 G}{\partial r'^2} + SOURCE \quad . \qquad \text{(A-2)}$$

ADT : time increment; $\Delta\theta$.

ADT1 : $w\,(\Delta\theta)$.

B, C, D, ER, EX, DM1 : coefficients in equations (A-1) and (A-2).

BTEMP : temporary variable used in carrying out integration.

CM1, CM2, CM3 : coefficients in finite difference equations.

DM : right-hand-side of finite difference equations.

DR : Δr

DX : Δx

DR1 : $\Delta r'$

D1 : coefficients in boundary conditions for catalyst equations.

D2 : same as above.

DT : $\Delta\theta$ to be used for the first increment.

E : allowable increase in G per one time increment.

FU : F factor in the momentum equation.

G(K, M, N): K = 1: weight fraction of SO_2 in stream.

K = 2: weight fraction of SO_3 in stream.

K = 3: weight fraction of O_2 in stream.

K = 4: temperature in stream.

K = 5: pressure.

K = 6 to 11: partial pressure of SO_2 in catalyst; 11 for surface.

K = 12 to 17: partial pressure of SO_3 in catalyst. 17 for surface.

K = 24 to 29: temperature in catalyst; 29 for surface of catalyst.

GENT : entrance concentrations, temperature and pressure.

M : radial index.

MR1 : number of radial increments.

MR : MR1 + 1.

N : axial index.

NX1 : number of axial increments.

NX : NX1 + 1.

QTEMP : temporary variable used in carrying out integration.

RP : radius of catalyst.

RW : radius of reactor tube.

RATE1 : factor in reaction rate expression.

SPWT : specific weight of fluid in stream.

TIME : total time from beginning, θ.

TW : wall temperature.

UX : u_x

UR : u_r

W : weighting factor.

<u>Input</u>

Card No. 1 : NOGO, NOT, (2I3)

If NOGO = 1, start from time 0.

If NOGO = 2, read in previous solution and continue from that.

NOT: number of increments before stop.

Card No. 2 : RATE1, DT, (2F10. 0).

Card No. 3 : E(1 to 7), (7F10. 0).

Card No. 4 : E(8 to 9), (2F10. 0).

Card No. 5 : RW, XEXIT, RP, (3F10. 0).

Card No. 6 : GENT(1 to 5), TW, (6F10. 0).

Print-out

E(1 to 9)

RW, XEXIT, RP

GENT, TW

TIME, Stream properties. Properties at catalyst interior for the location M = 1, N = 2. For other locations, results are printed out every 10 time increments only.

Flow Diagram

The flow diagram of the program for method G' is shown in Figure A-1.

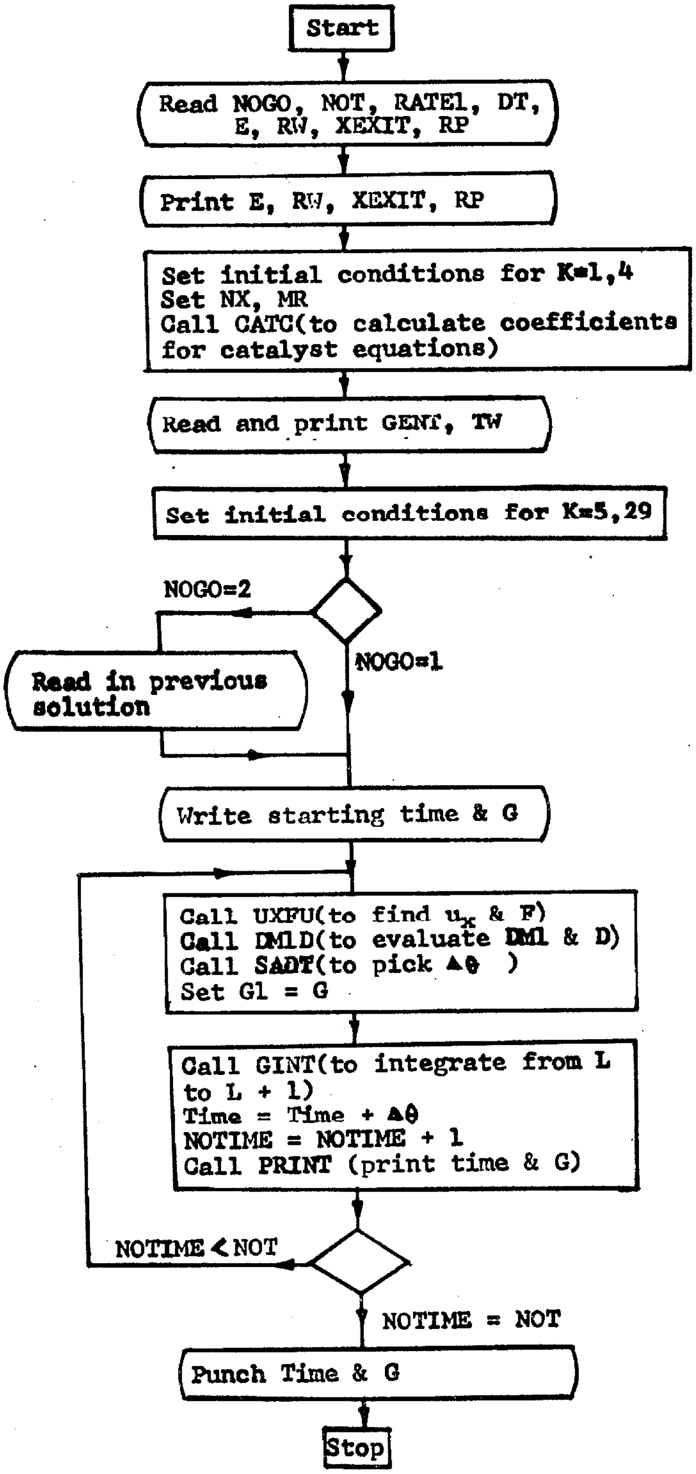

Figure A-1. Flow Diagram for Method G'.

COMPLETE FORTRAN PROGRAM FOR METHOD G'

```
$IBFTC MAI
C       THIS IS MAIN PROGRAM
C
C
      COMMON /RP/ RP
      COMMON /DT/ DT
      COMMON /NOTM/ NOTIME
      COMMON /CON/ X2, XEXIT
      COMMON /DP/ DP
      COMMON    G1(29,6,6),G(29,6,6),GL(29,6,6),B(29,6,6),C(5,6,6),ER(29
     1,6,6),EX(5 ,6,6),D(29,6,6),CM1(29,6,6),CM2(29,6,6),CM3(29,6,6),
     2DM(29,6,6),W1,W2,W3,W4,W5,W6,ADT1,NX,NX1,MR,MR1,DR,DX,DR1,TW,
     3GENT(5),GI(5),    E(9),UX(6,6),UR(6,6),A(29,6,6),DM1( 5,6,6),D1(4,6
     4,6),D2(4,6,6),BTEMP(6),QTEMP(6),I,K,SPWT(6,6),TIME,ADT,RATE1
      READ (5,100) NOGO,NOT
  100 FORMAT(2I3)
      READ  (5,9)RATE1,DT
    9 FORMAT(2F10.2)
      READ  (5,5)E
    5 FORMAT ( 7F10.0/2F10.0)
      READ  (5,6)RW, XEXIT,RP
    6 FORMAT ( 3F10.0)
      WRITE (6,8)(E(I), I = 1, 9)
    8 FORMAT (1H1/////35H0  INCREMENTS IN G      =                / 9F12.6)
      WRITE (6,2)RW, XEXIT, RP
    2 FORMAT ( 40H0               RADIUS OF REACTOR   =            , F30.6/
     140H0            LENGTH OF REACTOR   =               , F30.6/
     2 40H0    RADIUS OF CATALYST PELLET     =           , F30.6)
```

```
C
C     SET INITIAL CONDITIONS
C
      JACK = 0
       DO 500 K = 1, 5
  500 GI(K) = 0.
      NOTIME = 0
      X2 = 0.0104/4./XEXIT**2
       NP = 1
      NX = 6
      NX1 = 5
      MR = 6
      MR1 = 5
      DR = RW/5.0
      DX = XEXIT/5.
      DR1 = 1./5.5
      DO 50 N = 1, 6
      DO 50 M = 1, 6
      G(1,M,N) = 0.
       G(2,M,N) = 0.
      G(3,M,N) = 0.233
   50 G(4,M,N) = 0.
      CALL CATC
C
C     BIG LOOP, I = 1, 2
C
   17 TIME = 0.0
      ADT = 0.
      READ  (5,7)GENT, TW
    7 FORMAT ( 6F10.0)
      WRITE (6,3)GENT, TW
    3 FORMAT(1H1/////35H0   ENTRANCE CONDITIONS =                 ,5F16.6/
```

```
      140HO    WALL TEMPERATURE =                              , F14.6)
      DP = GENT(5)/XEXIT
      DO 10 N = 1, 6
      AN = N
      AN = (AN*DX)**2
      DO 10 M = 1, 6
   10 G(5,M,N) = GENT(5)*( 1. - AN)
      DO 54 M = 1, 6
      DO 54 N = 1, 6
      DO 51 K = 6, 11
   51 G(K,M,N) = 0.
      DO 52 K = 12, 17
   52 G(K,M,N) = 0.
      DO 53 K = 18, 23
   53 G(K,M,N) = 0.21*(G(5,M,N)+14.7)/14.7
      DO 54 K = 24,29
   54 G(K,M,N) = 0.
      DO 13 N = 1, 6
   13 G(4,6,N) = TW
      GO TO(40,41),NOGO
   41 READ(5,19) TIME, G
   40 WRITE (6,4) TIME, ADT,(((G(K,M,N),N=1,NX),M=1,MR),K=1,5)
      WRITE (6,204)(((G(K,M,N),K=6,29),N=1,6),M=1,6)
  355   CALL UXFU
        DO 29 K = 1, 5
        CALL CO15
   29 CALL DMID
      CALL SADT
      DO 21 K = 1, 29
      DO 21 M = 1, 6
```

```
      DO 21 N = 1, 6
   21 G1(K,M,N) = G(K,M,N)
   25 CALL GINT
C
C     PRINT OUT RESULTS
C
   27 TIME = TIME + ADT
      NOTIME = NOTIME + 1
      CALL PRINT
    4 FORMAT(1H1, 2F40.6///(6F19.6/6F19.6/6F19.6/6F19.6/6F19.6/6F19.6//)
     1)
  204 FORMAT(6F19.6/6F19.6/6F19.6/6F19.6//)
C
      NPRT = NOTIME/10
      IF(NPRT - NP) 101, 102, 101
  102 WRITE(6,204)((G(K,M,N), K = 6, 29),N=1, 6), M= 1, 6)
      NP = NP + 1
  101 IF (NOTIME - NOT)355,18,18
   18 PUNCH 19, TIME, G
   19 FORMAT (4E17.8)
      STOP
      END


$IBFTC CAT      DECK
      SUBROUTINE CATC
C
C     THIS IS A SUBROUTINE TO EVALUATE COEFFICIENTS FOR CATALYST EQUQTIONS
C
```

```
      DIMENSION E1(4)
      COMMON /RP/ RP
      COMMON    G1(29,6,6),G(29,6,6),GL(29,6,6),B(29,6,6),C(5,6,6),ER(29
     1,6,6),EX(5 ,6,6),D(29,6,6),CM1(29,6,6),CM2(29,6,6),CM3(29,6,6),
     2DM(29,6,6),W1,W2,W3,W4,W5,W6,ADT1,NX,NX1,MR,MR1,DR,DX,DR1,TW,
     3GENT(5),GI(5),    E(9),UX(6,6),UR(6,6),A(29,6,6),DM1( 5,6,6),D1(4,6
     4,6),D2(4,6,6),BTEMP(6),QTEMP(6),I,K,SPWT(6,6),TIME,ADT,RATE1
      RP1 = RP*RP
       E1(1) = 0.000015
       E1(2) = 0.000014
       E1(3) = 0.000022
        E1(4) = 0.00000781
      DO 15 M = 1, MR
      DO 15 N = 1, NX
       DO 15 L = 1, 6
       R1 = L - 1
       R1 = R1 + 0.5
      R1 = R1*DR1
      R2 = SQRT(R1)
      R3 = R1**1.5
       DO 15 I = 1, 4
      K = 6*I - 1 + L
       ER(K,M,N) = E1(I)*16.*R3/RP1
   15  B(K,M,N) = 20.*E1(I)*R2/RP1
      RETURN


$IBFTC UXF     DECK
      SUBROUTINE UXFU
```

```
C
C     THIS IS A SUBROUTINE TO CALCULATE UX AND F
C
      COMMON /DP/ DP
      COMMON    G1(29,6,6),G(29,6,6),GL(29,6,6),B(29,6,6),C(5,6,6),ER(29
     1,6,6),EX(5  ,6,6),D(29,6,6),CM1(29,6,6),CM2(29,6,6),CM3(29,6,6),
     2DM(29,6,6),W1,W2,W3,W4,W5,W6,ADT1,NX,NX1,MR,MR1,DR,DX,DR1,TW,
     3GENT(5),GI(5),    E(9),UX(6,6),UR(6,6),A(29,6,6),DM1( 5,6,6),D1(4,6
     4,6),D2(4,6,6),BTEMP(6),QTEMP(6),I,K,SPWT(6,6),TIME,ADT,RATE1
     5,FU(6,6)
   11 DO 30 M = 1, 6
      DO 30 N = 1, 6
      SUM = (1.-G(1,M,N)-G(2,M,N)-G(3,M,N))/28.02+G(1,M,N)/64.06+G(2,M,N
     1)/80.06+G(3,M,N)/32.
   30 SPWT(M,N) = (G(5,M,N)+14.7)/14.7/SUM/0.73/(G(4,M,N) + 1200.)
      DO 124 M = 1, 6
      DP(M,1) = (1.5*G(5,M,1)-2.*G(5,M,2)+0.5*G(5,M,3))/(DX)
      DP(M,6)=(-1.5*G(5,M,6)+2.*G(5,M,5)-0.5*G(5,M,4))/DX
      DO 120 N = 2, 5
  120 DP(M,N)=0.5*(G(5,M,N-1)-G(5,M,N+1))/DX
      DO 124 N = 1, 6
      UX(M,N) =(-0.00556+SQRT(0.0000286+0.1348*SPWT(M,N)*DP(M,N)))/0.067
     14/SPWT(M,N)
  124 FU(M,N) =0.055*(0.404+1.224*SPWT(M,N)*UX(M,N))
       RETURN
       END

$IBFTC C05
```

```
      SUBROUTINE C015
C
C     THIS IS A SUBROUTINE TO CALCULATE COEFFICIENTS FOR STREAM EQUATIONS
C
      COMMON    G1(29,6,6),G(29,6,6),GL(29,6,6),B(29,6,6),C(5,6,6),ER(29
     1,6,6),EX(5 ,6,6),D(29,6,6),CM1(29,6,6),CM2(29,6,6),CM3(29,6,6),
     2DM(29,6,6),W1,W2,W3,W4,W5,W6,ADT1,NX,NX1,MR,MR1,DR,DX,DR1,TW,
     3GENT(5),GI(5),    E(9),UX(6,6),UR(6,6),A(29,6,6),DM1( 5,6,6),D1(4,6
     4,6),D2(4,6,6),BTEMP(6),QTEMP(6),I,K,SPWT(6,6),TIME,ADT,RATE1
      IF(K-5)6,7,7
    6 DO 125 N = 1, 6
      DO 125 M = 1, 6
  125 C(K,M,N) = -UX(M,N)
      DO 127 N = 1, 6
      UR(1,N) = 0.
      UR(6,N) = 0.
      DO 126 M = 2, 5
  126 UR(M,N) = 0.5*(G(5,M-1,N)-G(5,M+1,N))/(FU(M,N)*DR)
       DO 141 M = 1, 6
      EX(K,M,N)=0.0104*UX(M,N)
  141 ER(K,M,N) = 0.00189*UX(M,N)
      DO 127 M = 2, 6
      BM=M-1
  127 B(K,M,N) = ER(K,M,N)/(BM*DR)-UR(M,N)
      GO TO 801
    7 DO 9 N = 1, 6
      DO 8 M = 1, 6
      EX(5,N,N) = (G(5,M,N)+14.7)/FU(M,N)
    8 ER(5,M,N) = EX(5,M,N)
      DO 9 M = 2, 6
```

```
      BM = M - 1
    9 B(5,M,N) = EX(5,M,N)/(BM*DR)
      DO 14 N = 2, 5
       DO 13 M = 2, 5
   13 B(5,M,N)=B(5,M,N)+(G(5,M,N)+14.7)/SPWT(M,N)*(SPWT(M+1,N)/FU(M
     1+1,N)-SPWT(M-1,N)/FU(M-1,N))/(DR*2.)
      DO 14 M = 1, 6
   14 C(5,M,N) = (G(5,M,N)+14.7)/SPWT(M,N)*(SPWT(M,N+1)/FU(M,N+1)- S
     1PWT(M,N-1)/FU(M,N-1))/(DX*2.)
  801 RETURN
      END


$IBFTC ADT      DECK
C
C     THIS IS A SUBROUTINE TO PICK UP TIME INCREMENT
C
      SUBROUTINE SADT
      COMMON /DT/ DT
      COMMON    G1(29,6,6),G(29,6,6),GL(29,6,6),B(29,6,6),C(5,6,6),ER(29
     1,6,6),EX(5 ,6,6),D(29,6,6),CM1(29,6,6),CM2(29,6,6),CM3(29,6,6),
     2DM(29,6,6),W1,W2,W3,W4,W5,W6,ADT1,NX,NX1,MR,MR1,DR,DX,DR1,TW,
     3GENT(5),GI(5),    E(9),UX(6,6),UR(6,6),A(29,6,6),DM1( 5,6,6),D1(4,6
     4,6),D2(4,6,6),BTEMP(6),QTEMP(6),I,K,SPWT(6,6),TIME,ADT,RATE1
      COMMON /NOTM/ NOTIME
      IF (NOTIME) 1, 1, 2
    1 ADT = DT
      GO TO 3
    2 ADT = 100.
```

```
      M = 1
      DO 4 N = 1, 5, 2
      DO 33 K = 1, 4
      ADT2 = ADT1*E(K)/ABS(G1(K,M,N) - G(K,M,N) + 0.0001)
      IF (ADT - ADT2) 33,33,34
   34 ADT = ADT2
   33 CONTINUE
      DO 4 I = 1, 4
      DO 4 J = 1, 6, 2
      K = 6*I - 1 + J
      L = I+5
      ADT2 = ADT1*E(L)/ABS(G1(K,M,N) - G(K,M,N) + 0.0001)
       IF (ADT - ADT2) 4,4,36
   36 ADT = ADT2
    4 CONTINUE
    3 ADT1 = ADT
      W1 = ADT1/(2.0*DR)
      W3 = ADT1/(2.0*DX)
      W4 = ADT1/(DX*DX)
      W2 = ADT1/(DR*DR)
      W5 = ADT1/(2.*DR1)
      W6 = ADT1/DR1**2
      RETURN
       END


$IBFTC INT     DECK
C
C     THIS IS A SUBROUTINE TO CARRY OUT INTEGRATION FROM TIME L TO L + W
```

```
C
      SUBROUTINE GINT
      COMMON    G1(29,6,6),G(29,6,6),GL(29,6,6),B(29,6,6),C(5,6,6),ER(29
     1,6,6),EX(5 ,6,6),D(29,6,6),CM1(29,6,6),CM2(29,6,6),CM3(29,6,6),
     2DM(29,6,6),W1,W2,W3,W4,W5,W6,ADT1,NX,NX1,MR,MR1,DR,DX,DR1,TW,
     3GENT(5),GI(5),   E(9),UX(6,6),UR(6,6),A(29,6,6),DM1( 5,6,6),D1(4,6
     4,6),D2(4,6,6),BTEMP(6),QTEMP(6),I,K,SPWT(6,6),TIME,ADT,RATE1
   50 CALL D1D2D
      DO 15 K = 1, 4
      DO 15 M = 1, 6
   15 D(K,M,1) = D(K,M,1) - 2.*DX*UX(M,1)/EX(K,M,1)*(-W3*
     1C(K,M,1)+W4*EX(K,M,1))/ADT1
      K = 12
   60 CALL DCDM
      DO 242 I = 1, 4
      DO 242 M = 1, 6
      DO 242 N = 1, 6
      A(6*I,M,N) = CM3(6*I,M,N)/CM2(6*I,M,N)
      DO 241 J = 2, 5
      K = 6*I - 1 + J
  241 A(K,M,N) = CM3(K,M,N)/(CM2(K,M,N) - CM1(K,M,N)*A(K-1,M,N))
      GL(6*I,M,N) = DM(6*I,M,N)/CM2(6*I,M,N)
      DO 242 J = 2, 5
      K = 6*I - 1 + J
  242 GL(K,M,N) = (DM(K,M,N) - CM1(K,M,N)*GL(K-1,M,N))/(CM2(K,M,N) - CM
     1 1(K,M,N)*A(K-1,M,N))
   31 DO 24 K = 1, 4
      DO 53 M = 1, 6
      DO 53 N = 1, 6
      A(K,M,N) = CM2(6*K+5,M,N) - CM1(6*K+5,M,N)*A(6*K+4,M,N)
```

```
      GL(K,M,N) = DM1(K,M,N)*ADT1*(DM(6*K+5,M,N) - CM1(6*K+5,M,N)*GL(6*
     1 K+4,M,N))/A(K,M,N)
   53 D(K,M,N) =-CM3(6*K+5,M,N)*D2(K,M,N)*DM1(K,M,N)        /A(K,M,N)+D(K,M
     1,N)
   45 CALL CND
   24 CALL DCDM
     DO 75 M = 1, 6
     DO 75 N = 1, 6
     SUM1 = (1.-G(1,M,N)-G(2,M,N)-G(3,M,N))/28.02+G(1,M,N)/64.06+G(2,M,
    1N)/80.06+G(3,M,N)/32.
     SUM2=(1.-G1(1,M,N)-G1(2,M,N)-G1(3,M,N))/28.02+G1(1,M,N)/64.06
    1+G1(2,M,N)/80.06+G1(3,M,N)/32.
   75 D(5,M,N) = ((G(4,M,N)-G1(4,M,N))/(1200.+G(4,M,N))-(1./SUM1-
    11./SUM2)*SUM1)/ADT1
     CALL GPE
      CALL GPS
      DO 180 I = 1, 4
       DO 180 M = 1, 6
      DO 180 N = 1, 6
      K = 6*I+5
      GL(K,M,N) = (DM(K,M,N) - CM3(K,M,N)*D2(I,M,N)*G(I,M,N) - CM1(K,M,
     1 N)*GL(K-1,M,N))/A(I,M,N)
      G(K,M,N) = GL(K,M,N)
      DO 180 J = 2,6
      K = 6*I + 6 -J
  180 G(K,M,N) = GL(K,M,N) - A(K,M,N)*G(K+1,M,N)
      RETURN
      END
```

```
$IBFTC D1D      DECK
       SUBROUTINE D1D2D
C
C     THIS IS TO CALCULATE D1, D2 AND D FOR CATALYST INTERIOR
C
      COMMON /RP/ RP
      COMMON /SOCE/ SOURCE(6,6,6)
      COMMON    GI(29,6,6),G(29,6,6),GL(29,6,6),B(29,6,6),C(5,6,6),ER(29
     1,6,6),EX(5 ,6,6),D(29,6,6),CM1(29,6,6),CM2(29,6,6),CM3(29,6,6),
     2DM(29,6,6),W1,W2,W3,W4,W5,W6,ADT1,NX,NX1,MR,MR1,DR,DX,DR1,TW,
     3GENT(5),GI(5),   E(9),UX(6,6),UR(6,6),A(29,6,6),DM1( 5,6,6),D1(4,6
     4,6),D2(4,6,6),BTEMP(6),QTEMP(6),I,K,SPWT(6,6),TIME,ADT,RATE1
      DIMENSION D1C(4)
      DATA (D1C(L),L=1,4)/-0.5632E 4, -0.4942E 4, -0.7824E 4, -0.2274/
      FD1 = RP/4.
  100 DO 165 M = 1, 6
      DO 165 N = 1, 6
      DO 165 J = 1, 6
   13  SOURCE (J,M,N) =
     1      ADT1*RATE1*      EXP(14.154-14400./(1200.+G(J+23,M,N)))*(G(
     1J+5,M,N)*SQRT(G(J+17,M,N))-G(J+11,M,N)/EXP(-10.1+2.08E4/(1200.+G(J
     1+
     223,M,N))))/(1.+SQRT(G(J+17,M,N))*EXP(-5.79+9224./(1200.+G(J+23,M,N
     3)))+G(J+11,M,N)*EXP(-8.82+15220./(1200.+G(J+23,M,N))))**2
      SQ = SQRT(G(J+17,M,N))
      ESO3 = EXP(10.1 - 2.08E4/(G(J+23,M,N)+1200.))
      SOCE = SOURCE(J,M,N)/ADT1/(G(J+5,M,N)*SQ - G(J+11,M,N)*ESO3)
      DO 66 I = 1, 3
      K = 6*I - 1 + J
```

```
   66 D(K,M,N) = -1.216*(G(J+23,M,N) + 1200.)*SOCE*(SQ+ESO3+G(J+5,M,N)/
     1SQ/4.)
  165 D(J+23,M,N) = -2237.8*20800.*G(J+11,M,N)*ESO3/(G(J+23,M,N)+1200.)*
     1*2*SOCE
  101 DO 63 I = 1, 4
      IF (I-4) 61,62,62
   61 DO 60 M = 1, 6
      DO 60 N = 1, 6
      D1(I,M,N)=D1C(I)*DR1*SPWT(M,N)*DM1(I,M,N)*FD1
   60 D2(I,M,N)=D(I,M,N)/DM1(I,M,N)*D1(I,M,N)
      GO TO 63
   62 DO 64 M = 1, 6
      DO 64 N = 1, 6
      D1(4,M,N) = -88.96*(SPWT(M,N)*UX(M,N)/0.476)**0.49*((G(4,M,N)+1200
     1.)/1247.)**0.26*DR1*FD1
   64 D2(4,M,N) = -D1(4,M,N)
   63 CONTINUE
      RETURN
      END


$IBFTC DM1     DECK
       SUBROUTINE DM1D
C
C     THIS IS TO CALCULATE DM1 AND D FOR STREAM EQUATIONS
C
      COMMON G1( 9,1,21),G( 9,1,21),GL( 9,1,21),C(5,1,21),EX( 9,1,21),
     1D( 9,1,21),CM1( 9,1,21),CM2( 9,1,21),CM3( 9,1,21),DM( 9,1,21),W3,
     2W4,ADT1,NX,NX1,DR,DX,DR1,TW,GENT(5),GI(5),E(9),UX(1,21),A(9,1,21)
```

```
     3,DM1(5,1,21),D1(4,1,21),D2(4,1,21),BTEMP(21),QTEMP(21),I,K,SPWT(1,
     421), TIME, ADT, RATE1, M,H
       DIMENSION DM1C(5), DC(5)
      DATA (DM1C(L),L=1,5)/1.367E 3,1.726E 3,0.945E 3, 1.104E 3,0./
      DATA (DC(L),L=1,5)/-0.0114,-0.00912,-0.0228, 0.,0./
   50 DO 52 N = 1, NX
      DO 13 K = 1, 3
      DM1(K,M,N)=DM1C(K)*((G(4,M,N)+1200.)/1247.)**1.5*(UX(M,N)/13.45)*
     1*0.49
   13 D(K,M,N)=DC(K)*DM1(K,M,N)*SPWT(M,N)*(G(4,M,N)+1200.)
   51 DO 52 N = 1, NX
      DM1(4,M,N)=DM1C(4)*((G(4,M,N)+1200.)/1247.
     1                                           )**0.26*(UX(M,N)/13.45)**
     10.49*(0.0354/SPWT(M,N))**0.51
   52 D(4,M,N) = -DM1(4,M,N)
   56  RETURN
       END


$IBFTC DCM     DECK
      SUBROUTINE DCDM
C
C     THIS IS A SUBROUTINE TO INTEGRATE STREAM EQUATIONS IN RADIAL DIRECTION
C     AND EVALUATE COEFFICIENTS FOR FINITE DIFFERENCE EQUATIONS FOR THE
C     INTERIOR OF CATALYST
C
      COMMON /SOCE/ SOURCE(6,6,6)
      COMMON    GI(29,6,6),G(29,6,6),GL(29,6,6),B(29,6,6),C(5,6,6),ER(29
     1,6,6),EX(5 ,6,6),D(29,6,6),CM1(29,6,6),CM2(29,6,6),CM3(29,6,6),
```

```
     2DM(29,6,6),W1,W2,W3,W4,W5,W6,ADT1,NX,NX1,MR,MR1,DR,DX,DR1,TW,
     3GENT(5),GI(5),    E(9),UX(6,6),UR(6,6),A(29,6,6),DM1( 5,6,6),D1(4,6
     4,6),D2(4,6,6),BTEMP(6),QTEMP(6),I,K,SPWT(6,6),TIME,ADT,RATE1
      I = K/6
      IF(I) 10,10,24
   10 DO 80 N = 1, 6
      DO 80 N = 1, 6
      DO 80 M = 1, 6
      CM1 (K, M, N) = W1*B(K,M,N) - W2*ER(K,M,N)
      CM2(K,M,N) = 1.0+ 2.0*W2*ER(K,M,N) -D(K,M,N)*ADT1
   80 CM3(K,M,N) = -W1*B(K,M,N) - W2*ER(K,M,N)
      DO 160 N = 1, 6
      CM1(K,1,N) = 0.0
      CM2(K,1,N) = CM2(K,1,N) +2.*W2*ER(K,1,N)
   32 CM3(K,1,N) = -4.0*W2*ER(K,1,N)
      CM1(K,MR,N) = -2.0*W2*ER(K,MR,N)
  160 CM3(K,MR,N) = 0.0
      DO 35 M = 1, 6
      DO 170 N = 2, 5
  170 DM(K,M,N) = G(K,M,N-1)*(-W3*C(K,M,N) + W4*EX(K,M,N)) - G(K,M,N)*
     1              2.0*W4*EX(K,M,N)   + G(K,M,N+1)*(W3*C(K,M,N) + W4*
     2 EX(K,M,N)) +G1(K,M,N)+GL(K,M,N)
      DM(K,M,1) = -G(K,M,1)*2.*W4*EX(K,M,1)+G(K,M,2)*2.*W4*EX(
     1K,M,1)+ 2.*DX*UX(M,1)/EX(K,M,1)*(-W3*C(K,M,1)
     2+W4*EX(K,M,1))*GENT(K)  +G1(K,M,1)+GL(K,M,1)
      DM(K,M,NX) = G(K,M,NX1)*(-W3*C(K,M,NX)
     1*2.
     2                                     + W4*EX(K,M,NX))   +G(K,M,6
     1)*(-W4*EX(K,M,6)+W3*C(K,M,6)*2.)          + GL(K,M,NX)+      G1(K,M,
     2NX)
```

```
   35 CONTINUE
      GO TO (13,13,13,14,15),K
   14 DO 34 N = 1, 6
      CM1(4,MR,N) = 0.
      CM2(4,MR,N) = 1.
      CM3(4,MR,N) = 0.
   34 DM(4,MR,N) = TW
   15 CONTINUE
   13 DO 43 N = 1, NX
      BTEMP(1) = CM3(K,1,N)/CM2(K,1,N)
      DO 41 J = 2, MR1
   41 BTEMP(J) = CM3(K,J,N)/(CM2(K,J,N)- CM1(K,J,N)*BTEMP(J - 1))
      QTEMP(1) = DM(K,1,N)/CM2(K,1,N)
      DO 42 J = 2, MR
   42 QTEMP(J) = (DM(K,J,N) - CM1(K,J,N)*QTEMP(J-1))/(CM2(K,J,N) -
     1CM1(K,J,N)*BTEMP(J-1))
      G     (K,MR,N) = QTEMP(MR)
       DO 43 J = 2, MR
      L = MR + 1 - J
   43 G     (K,L,N) = QTEMP(L) - BTEMP(L)*G     (K,L+1,N)
   44 CONTINUE
       GO TO 83
   24 DO 18 M = 1, 6
      DO 18 N = 1, 6
       DO 18 I = 1, 4
      DO 17 J = 1, 6
       K = 6*I - 1 + J
      GO TO (181,182,183,184),I
  181 DM(K,M,N) =        -D(K,M,N)*ADT1*G(K,M,N)+G
     1 1
```

```
     2                                                    (K,M,N)-1.216*(1200.+G(
     1J+23,M,N))*SOURCE(J,M,N)
      GO TO 185
  182 DM(K,M,N) =     -D(K,M,N)*ADT1*G(K,M,N)+G
     1 1
     2                                                 (K,M,N)+1.216*(1200.+G(
     1J+23,M,N))*SOURCE(J,M,N)
      GO TO 185
  183 DM(K,M,N) =          -D(K,M,N)*ADT1*G(K,M,N)+G1(K,M,N)
     1-0.608*(1200.+G(J+23,M,N))*SOURCE(J,M,N)
      GO TO 185
  184 DM(K,M,N) = 2237.8*SOURCE(J,M,N)
     1                         -D(K,M,N)*ADT1*G(K,M,N)+G1(K,M,N)
  185 CONTINUE
      CM1(K,M,N)=W5*B(K,M,N)-W6*ER(K,M,N)
      CM2(K,M,N) = 1. + 2.*W6*ER(K,M,N) - D(K,M,N)*ADT1
   17 CM3(K,M,N)=-W5*B(K,M,N)-W6*ER(K,M,N)
      K = 6*I
       CM2(K,M,N) = CM1(K,M,N) + CM2(K,M,N)
      K = 6*I + 5
      CM1(K,M,N) = -2.*W6*ER(K,M,N)
      CM2(K,M,N) = CM2(K,M,N)+CM3(K,M,N)*D1(I,M,N)
   18 CONTINUE
   83 RETURN
      END


 $IBFTC CND     DECK
      SUBROUTINE CND
```

```
C
C     THIS IS A SUBROUTINE TO CARRY OUT INTEGRATION OF STREAM EQUATIONS
C     IN AXIAL DIRECTION
C
      COMMON    G1(29,6,6),G(29,6,6),GL(29,6,6),B(29,6,6),C(5,6,6),ER(29
     1,6,6),EX(5  ,6,6),D(29,6,6),CM1(29,6,6),CM2(29,6,6),CM3(29,6,6),
     2DM(29,6,6),W1,W2,W3,W4,W5,W6,ADT1,NX,NX1,MR,MR1,DR,DX,DR1,TW,
     3GENT(5),GI(5),    E(9),UX(6,6),UR(6,6),A(29,6,6),DM1( 5,6,6),D1(4,6
     4,6),D2(4,6,6),BTEMP(6),QTEMP(6),I,K,SPWT(6,6),TIME,ADT,RATE1
       DIMENSION CN1(29,6,6), CN2(29,6,6), CN3(29,6,6), DN(29,6,6)
       EQUIVALENCE (CN1,CM1), (CN2,CM2), (CN3,CM3),( DM,DN)
      IF (K-5) 10,11,11
   11 CALL GPE
      GO TO 12
   10 CONTINUE
      DO 44 M = 1, 6
      DO 44 N=1, 6
      CN1(K,M,N) =W3*C(K,M,N) - W4*EX(K,M,N)
      CN2(K,M,N) = 1.0+ 2.0*W4*EX(K,M,N) -D(K,M,N)*ADT1
   44 CN3(K,M,N) = - W3*C(K,M,N) - W4*EX(K,M,N)
      DO 203 N = 1, 6
      DO 202 M = 2, 5
  202 DN(K,M,N)=G(K,M-1,N)*(-W1*B(K,M,N)+W2*ER(K,M,N))+G(K,M+1,N)*(W1*B(
     1K,M,N)+W2*ER(K,M,N))+G(K,M,N)*(-2.*W2*ER(K,M,N)                  )+
     2 GL(K,M,N) + G1(K,M,N)
      DN(K,1,N)=G(K,1,N)*(-4.*W2*ER(K,1,N)                  )+G(K,2,N)*4.*W2
     1*ER(K,1,N)+ GL(K,1,N) + G1(K,1,N)
  203 DN(K,6,N)=G(K,5,N)*2.*W2*ER(K,6,N)+G(K,6,N)*(-2.*W2*ER(K,6,N)
     1          )+  GL(K,6,N) + G1(K,6,N)
```

```
      DO 13 M = 1, 6
      CN3(K,M,1) = CN1(K,M,1) + CN3(K,M,1)
      CN1(K,M,6) = 2.*W3*C(K,M,6) - W4*EX(K,M,6)
   13 CN2(K,M,6) = 1. - 2.*W3*C(K,M,6) + W4*EX(K,M,6) -D(K,M,6)*ADT1
       DO 47 M = 1, 6
   47 DN(K,M,1) = 2.*DX*UX(M,1)/EX(K,M,1)*(-W3*C(K,M,1)+W4*EX(K,M,1))*GE
     1NT(K)+DN(K,M,1)
      IF (K-4) 4,5,5
    5 DO 6 N = 1, 6
      CN1(4,6,N) = 0.
      CN2(4,6,N) = 1.
      CN3(4,6,N) = 0.
    6 DN(4,6,N) = TW
    4 DO 56 M = 1, MR
      BTEMP(1) = CN3(K,M,1)/CN2(K,M,1)
       DO 52 J = 2, NX1
   52 BTEMP(J) = CN3(K,M, J)/(CN2(K,M,J) - CN1(K,M,J)*BTEMP(J-1))
      QTEMP(1) = DN(K,M,1)/CN2(K,M,1)
      DO 53 J = 2, NX
   53 QTEMP(J) = (DN(K,M,J) - CN1(K,M,J)*QTEMP(J-1))/(CN2(K,M,J) -
     1CN1(K,M,J)*BTEMP(J - 1))
        G (K,M,6) = QTEMP(6)
      DO 56 J = 2, NX
      L = NX + 1 - J
   56  G (K,M,L) = QTEMP(L) - BTEMP(L)*G (K,M,L+1)
   12 RETURN
      END
```

```
$IBFTC PRT      DECK
      SUBROUTINE PRINT
C
C     THIS IS  A PRINT-OUT ROUTINE
C
      COMMON    G1(29,6,6),G(29,6,6),GL(29,6,6),B(29,6,6),C(5,6,6),ER(29
     1,6,6),EX(5  ,6,6),D(29,6,6),CM1(29,6,6),CM2(29,6,6),CM3(29,6,6),
     2DM(29,6,6),W1,W2,W3,W4,W5,W6,ADT1,NX,NX1,MR,MR1,DR,DX,DR1,TW,
     3GENT(5),GI(5),    E(9),UX(6,6),UR(6,6),A(29,6,6),DM1( 5,6,6),D1(4,6
     4,6),D2(4,6,6),BTEMP(6),QTEMP(6),I,K,SPWT(6,6),TIME,ADT,RATE1
      WRITE (6,4)TIME, ADT,(((G (K,M,N),N=1,NX),M=1,MR),    K = 1, 5)
     1,((UX(M,N),N=1,6), M=1, 6),((UR(M,N),N=1,6),M=1,6)
      WRITE(6,205) (G(K,1,2), K=6,29)
  205 FORMAT(6F19.6/6F19.6/6F19.6/6F19.6//)
    4 FORMAT(1H1, 2F40.6///(6F19.6/6F19.6/6F19.6/6F19.6/6F19.6/6F19.6//)
     1)
      RETURN
      END


$IBFTC GPE      DECK
      SUBROUTINE GPE
C
C     THIS IS TO CARRY OUT INTEGRATION OF PRESSURE EQUATION IN AXIAL DIRECTI
C     A DOUBLE PRECISION IS USED
C
      COMMON    G1(29,6,6),G(29,6,6),GL(29,6,6),B(29,6,6),C(5,6,6),ER(29
     1,6,6),EX(5  ,6,6),D(29,6,6),CM1(29,6,6),CM2(29,6,6),CM3(29,6,6),
     2DM(29,6,6),W1,W2,W3,W4,W5,W6,ADT1,NX,NX1,MR,MR1,DR,DX,DR1,TW,
```

```
     3GENT(5),GI(5),    E(9),UX(6,6),UR(6,6),A(29,6,6),DM1( 5,6,6),D1(4,6
     4,6),D2(4,6,6),BTEMP(6),QTEMP(6),I,K,SPWT(6,6),TIME,ADT,RATE1
      COMMON /P/ CM1P(6,6),CM2P(6,6),CM3P(6,6),DMP(6,6),GP(6,6),BTP(6)
     1,QTP(6),W1P,W2P,W3P,W4P,ADT1P
      DOUBLE PRECISION CM1P,CM2P,CM3P,DMP,GP,BTP,QTP,W1P,W2P,W3P,W4P,ADT
     11P
      DO 11 M = 1, 6
      DO 11 N = 1, 6
   11 GP(M,N) = G(5,M,N)
      W1P = W1
      W2P = W2
      W3P = W3
      W4P = W4
      ADT1P = ADT1
      DO 44 M = 1, 6
      DO 44 N = 1, 6
      CM1P(M,N) = W3P*C(5,M,N)-W4P*EX(5,M,N)
      CM2P(M,N) = 1.+ 2.*W4P*EX(5,M,N)-D(5,M,N)*ADT1P
   44 CM3P(M,N)=-W3P*C(5,M,N)-W4P*EX(5,M,N)
      DO 203 N = 1, 6
      DO 202 M = 2, 5
  202 DMP(M,N)=GP(M-1,N)*(-W1P*B(5,M,N)+W2P*ER(5,M,N))+GP(M+1,N)*(W1P*
     1B(5,M,N)+W2P*ER(5,M,N))+GP(   M,N)*(-2.*W2P*ER(5,M,N))+G1(5,M,N)
      DMP(1,N)=GP(1,N)*(-4.*W2P*
     1ER(5,1,N))
     2                                          +GP(2,N)*4.*W2P*ER(5,1,N)+
     2 G1(5,1,N)
  203 DMP(6,N)=GP(5,N)*2.*W2P*ER(5,6,N)+GP(6,N)*(-2.*W2P*ER(5,6,N))+
     1 G1(5,6,N)
      DO 191 M = 1,6
```

```
      DMP(M,1)=GENT(5)
      DMP(M,6) = GI(5)
      CM1P(M,1) = 0.
       CM2P(M,1) = 1.
      CM3P(M,1) = 0.
       CM1P(M,6) = 0.
      CM2P(M,6) = 1.
  191  CM3P(M,6) = 0.
      DO 56 M = 1, 6
      BTP(1) = CM3P(M,1)/CM2P(M,1)
       DO 52 J = 2, 6
   52 BTP(J) =CM3P(M,J)/(CM2P(M,J)-CM1P(M,J)*BTP(J-1))
       QTP(1) = DMP(M,1)/CM2P(M,1)
       DO 53 J = 2, 6
   53 QTP(J) =(DMP(M,J)-CM1P(M,J)*QTP(J-1))/(CM2P(M,J)-CM1P(M,J)*BTP(J-1
     1 ))
      GP(M,6) = QTP(6)
       DO 56 J = 2, 6
       L = 7-J
   56 GP(M,L)  =       QTP(L)-BTP(L)*GP(M,L+1)
       RETURN
      END


$IBFTC GPS     DECK
      SUBROUTINE GPS
C
C     THIS IS TO CARRY OUT INTEGRATION OF PRESSURE EQUATION IN THE AXIAL
C     DIRECTION -- A DOUBLE PRECISION IS USED
```

```
C
      COMMON    G1(29,6,6),G(29,6,6),GL(29,6,6),B(29,6,6),C(5,6,6),ER(29
     1,6,6),EX(5  ,6,6),D(29,6,6),CM1(29,6,6),CM2(29,6,6),CM3(29,6,6),
     2DM(29,6,6),W1,W2,W3,W4,W5,W6,ADT1,NX,NX1,MR,MR1,DR,DX,DR1,TW,
     3GENT(5),GI(5),    E(9),UX(6,6),UR(6,6),A(29,6,6),DM1( 5,6,6),D1(4,6
     4,6),D2(4,6,6),BTEMP(6),QTEMP(6),I,K,SPWT(6,6),TIME,ADT,RATE1
      COMMON /P/ CM1P(6,6),CM2P(6,6),CM3P(6,6),DMP(6,6),GP(6,6),BTP(6)
     1,QTP(6),W1P,W2P,W3P,W4P,ADT1P
      DOUBLE PRECISION CM1P,CM2P,CM3P,DMP,GP,BTP,QTP,W1P,W2P,W3P,W4P,ADT
     11P
      DO 80 M = 1, 6
      DO 80 N = 1, 6
      CM1P (M,N) = W1P*B(5,M,N)-W2P*ER(5,M,N)
      CM2P(M,N) = 1.+2.*W2P*ER(5,M,N) -D(5,M,N)*ADT1P
   80 CM3P(M,N) = -W1P*B(5,M,N)-W2P*ER(5,M,N)
      DO 160 N = 1, 6
      CM1P(1,N) = 0.
       CM2P(1,N)=CM2P(1,N)+2.*W2P*ER(5,1,N)
      CM3P(1,N)=-4.*W2P*ER(5,1,N)
      CM1P(6,N) = -2.*W2P*ER(5,6,N)
  160 CM3P(6,N) = 0.
       DO 35 M = 1, 6
      DO 170 N = 2, 5
  170 DMP(M,N) = GP(M,N-1)*(-W3P*C(5,M,N)+W4P*EX(5,M,N))-GP(M,N)*2.*W4P
     1*EX(5,M,N)+GP(M,N+1)*(W3P*C(5,M,N)+W4P*EX(5,M,N))+ G1(5,M,N)
      CM1P(M,1) = 0.
       CM2P(M,1) = 1.
      CM3P(M,1) = 0.
      CM1P(M,6)=0.
      CM2P(M,6) = 1.
```

```
      CM3P(M,6) = 0.
       DMP(M,1) = GENT(5)
   35 DMP(M,6) = GI(5)
      DO 43 N = 1, 6
       BTP(1) = CM3P(1,N)/CM2P(1,N)
      DO 41 J = 2, 6
   41 BTP(J) = CM3P(J,N)/(CM2P(J,N)-CM1P(J,N)*BTP(J-1))
      QTP(1) = DMP(1,N)/CM2P(1,N)
      DO 42 J = 2, 6
   42 QTP(J) = (DMP(J,N)-CM1P(J,N)*QTP(J-1))/(CM2P(J,N)-CM1P(J,N)*BTP(J-
     11))
      GP(6,N)=QTP(6)
      DO 43 J = 2, 6
      L = 7-J
   43 GP(L,N)=QTP(L)-BTP(L)*GP(L+1,N)
      DO 11 M = 1, 6
      DO 11 N = 1, 6
   11 G(5,M,N) = GP(M,N)
      RETURN
       END
```

APPENDIX III

TRIAL METHODS WHICH FAILED TO SOLVE THE REACTOR PROBLEM

In the following, the various trial methods which failed to solve the reactor problem are listed. The notations used in Part IV of the thesis will be employed.

Method 1.

This method can be represented by:

$$\vec{\Phi}_{\ell+1} - \vec{\Phi}_{\ell-1} = h_{avg}(D)(\vec{\Phi}_{\ell+1} + \vec{\Phi}_{\ell-1}) + 2h_{avg}(S)\vec{\Phi}_{\ell} \qquad \text{(A-3)}$$

$$\text{where } h_{avg} = \frac{\theta_{\ell+1} - \theta_{\ell-1}}{2} \qquad \text{(A-4)}$$

For the case where all the eigenvalues of (S) are positive, this method was found to be more efficient than any of the methods proposed in the literature. For such a case, the method is as accurate as Crank-Nicolson method. The former is faster than the latter as the former does not require an iterative scheme, while the latter does.

If the matrix (S) has a negative eigenvalue, the method is always unstable. This can be seen from the relationship between an eigenvalue of (S) and its corresponding q for the case (S)>> (D):

$$\lambda_s h = \frac{q^2 - 1}{2q} \quad . \tag{A-5}$$

For the reactor problem, the eigenvalues of (S) can be negative, and the method is unstable.

Method 2.

This method is expressed by:

$$\vec{\Phi}_{\ell+1} - \vec{\Phi}_{\ell} = h\,(D)\,(0.5\,\vec{\Phi}_{\ell+1} + 0.5\,\vec{\Phi}_{\ell}) + h\,(S)\,(1.5\,\vec{\Phi}_{\ell} - 0.5\,\vec{\Phi}_{\ell-1}) \quad . \tag{A-6}$$

For the case (S) >> (D), the relationship between an eigenvalue of (S) and its corresponding q is:

$$\lambda_s h = \frac{q^2 - q}{1.5q - 0.5} \quad . \tag{A-7}$$

It is easy to see that $\lambda_s h > -1$ is required for the method to be stable. This criterion is twice as severe as that for the method in which the source terms are evaluated at the beginning of each time increment.

Method 3.

In this method the stream equations are integrated from time ℓ to time $\ell+1/2$, with the source terms evaluated at time ℓ. Then the catalyst equations are first integrated from time ℓ to time $\ell+1/2$, with the source terms evaluated at time $\ell+1/2$, and further integrated to time $\ell+1$, using the same source terms evaluated at time $\ell+1/2$. Stream equations are then integrated from time $\ell+1/2$ to time $\ell+1$, using the source terms at time $\ell+1$. In this way, no iterations are needed. This scheme looks logical but was found to give wave-like oscillations, unless extremely fine time increments were used.

Method 4.

The method is shown by:

$$\vec{\Phi}_{\ell+\overset{*}{w}} - \vec{\Phi}_{\ell} = wh(A_1)\,\vec{\Phi}_{\ell+\overset{*}{w}} + wh(A_2)\,\vec{\Phi}_{\ell} + wh(A_3)\,\vec{\Phi}_{\ell} \quad . \qquad \text{(A-8)}$$

$$\vec{\Phi}_{\ell+w^{**}} - \vec{\Phi}_{\ell} = wh(A_1)\,\vec{\Phi}_{\ell+w^{*}} + wh(A_2)\,\vec{\Phi}_{\ell+w^{**}} + wh(A_3)\,\vec{\Phi}_{\ell} \,. \qquad \text{(A-9)}$$

$$\vec{\Phi}_{\ell+w^{***}} - \vec{\Phi}_{\ell} = wh(A_1)\,\vec{\Phi}_{\ell+w^{*}} + wh(A_2)\,\vec{\Phi}_{\ell+w^{**}} + wh(A_3)\,\vec{\Phi}_{\ell+w^{***}}. \qquad \text{(A-10)}$$

$$\vec{\Phi}_{\ell+1} - \vec{\Phi}_{\ell} = h(A_1)\,\vec{\Phi}_{\ell+w^{*}} + h(A_2)\,\vec{\Phi}_{\ell+w^{**}} + h(A_3)\,\vec{\Phi}_{\ell+w^{***}} \,. \qquad \text{(A-11)}$$

Where $(A_1)\vec{\Phi}$ corresponds to the transfer between stream and catalyst surface, $(A_2)\vec{\Phi}$ to axial transfer, and $(A_3)\vec{\Phi}$ to radial transfer.

This four-step method can be reduced to an equivalent one-step method shown below:

$$\vec{\Phi}_{\ell+1} - \vec{\Phi}_{\ell} = [\,(I) + w^2h^2\,(A_1)\,(A_2) + w^2h^2\,(A_1)\,(A_3) + w^2h^2\,(A_2)\,(A_3) - w^3h^3\,(A_1)\,(A_2)\,(A_3)\,]^{-1}\,h\,(A)\,[\,w\vec{\Phi}_{\ell+1} + (1-w)\vec{\Phi}_{\ell}\,]\,. \qquad \text{(A-12)}$$

An exact stability region for this method is hard to find, but some qualitative observations can be made: This method should be stable for the case where the eigenvalues of (A_1) are negative. For the case where the eigenvalues of (A_1) are positive, the method would be unstable unless time increments are very small.

In the above, only major methods have been listed. Those methods which are just slight modifications of the above methods are not listed. If methods 2, 3 or 4 had been used, a transient solution of a typical problem investigated in this work would have taken at least a couple of hundred hours of computation time with an IBM-7094 computer. In contrast to this, method G' took only a few minutes of computer time.

PROPOSITIONS

PROPOSITION I

This proposition is concerned with a graphical solution of transient heat transfer in cylindrical coordinates.

Schmidt developed a method in which temperature is plotted against the logarithm of the radius, and the method has been in common use for a long time. The proposition is that more accurate results can be obtained by the use of another function w (n) in place of ℓn (n) used in Schmidt method.

The equation describing transient transfer of heat in the radial direction is

$$\frac{\partial T}{\partial \theta} = K \quad \frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \qquad \text{(P-1)}$$

where T = temperature
K = thermal diffusivity
r = radial distance
θ = time

The following finite difference approximations are commonly used:

$$\frac{\partial T}{\partial \theta} = \frac{T_{m+1,\, n} - T_{m,\, n}}{\Delta \theta} \qquad \text{(P-2)}$$

$$\frac{\partial^2 T}{\partial r^2} = \frac{T_{m,\, n+1} - 2T_{m,\, n} + T_{m,\, n-1}}{\Delta r^2} \qquad \text{(P-3)}$$

$$\frac{\partial T}{\partial r} = \frac{T_{m,\, n+1} - T_{m,\, n-1}}{2\Delta r} \quad , \qquad \text{(P-4)}$$

where m refers to time and n to space.

Substituting equations (P-2), (P-3) and (P-4) into equation (P-1) and taking $\frac{K\Delta\theta}{\Delta r^2} = \frac{1}{2}$, there is obtained, after rearranging

$$T_{m+1,\, n} = \frac{1}{\frac{1}{n+\frac{1}{2}} + \frac{1}{n-\frac{1}{2}}} \left(\frac{1}{n-\frac{1}{2}} T_{m,\, n+1} + \frac{1}{n+\frac{1}{2}} T_{m,\, n-1} \right) . \qquad \text{(P-5)}$$

Equation (P-5) can be exactly satisfied by plotting T against w (n). w (n) is such a function of n that $\Delta w_{n-\frac{1}{2}} = \frac{1}{n-\frac{1}{2}}$, $\Delta w_{n+\frac{1}{2}} = \frac{1}{n+\frac{1}{2}}$, as is shown in Figure P-1. This function can also be approximated by

$$w\,(n) = \ell n\,(n) + 0.035\, n^{-1.834} \tag{P-6}$$

Equation (P-6) indicates that Schmidt method is inadequate for small values of n, i.e., toward the center of the cylinder. The new method has been shown to give better results than Schmidt method.*

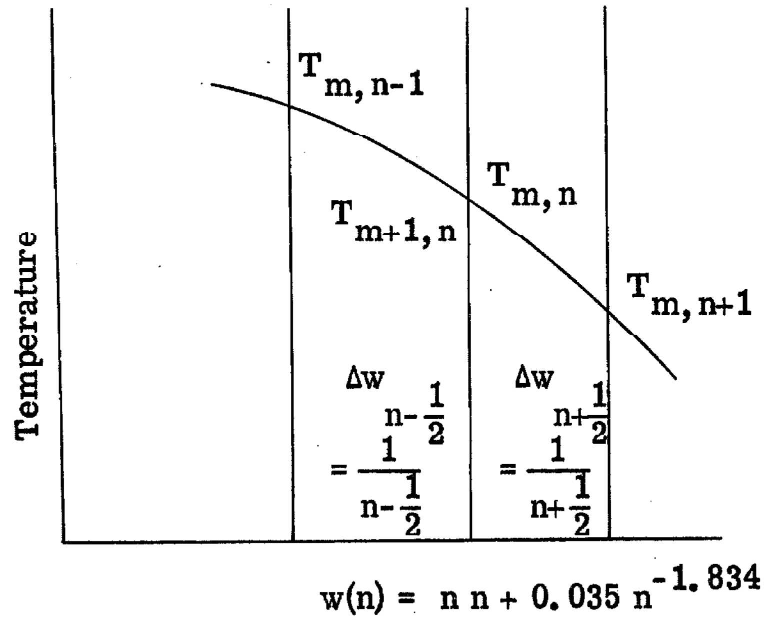

Figure P-1

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[*] See Student Report No. 954.

PROPOSITION II

It is proposed that a horizontal distillator as shown in Figure A be employed in high vacuum distillations, and that a conventional bubble-cap distillation column be modified as shown in Figure B so that a much shorter column can be used without causing flooding.

In Figure A, q's are perforated plates dividing the horizontal distillator into a number of compartments in series. The purpose of the dividing plates is to reduce the mixing of the vapor. The liquid in each compartment is sprayed at the top in order that the vapor-liquid contact will be sufficient. The liquid level is maintained by leaving the separating plates unperforated at the lower part as shown in the figure. Since the vapor is not bubbled through the liquid as in a bubble-cap column, the pressure drop of the vapor upon travelling through the distillator is much less than the corresponding drop through a bubble-cap column. Therefore, the horizontal distillator should be more suitable for high vacuum distillations than a bubble-cap distillator.

Figure B shows a vertical bubble-cap column, in which the conventional down-spouts have been replaced by the simple level controllers utilizing the fact that a centrifugal pump is far more effective in pumping the liquid than the vapor. Other kinds of liquid-level controlling devices can be used. The centrifugal pumps should keep the liquid-level in each tray fairly constant. In a conventional bubble-cap column, a large liquid head in a down-spout is required to overcome the large pressure drop in the vapor. The result is that the height of the column is undesirably large. If the liquid-level is controlled as is shown in Figure B, the spacing between two consecutive trays can be smaller, and the total column height would be smaller, with a possible net saving in the total construction cost, as the cost of the liquid-level controlling device should not be expensive.

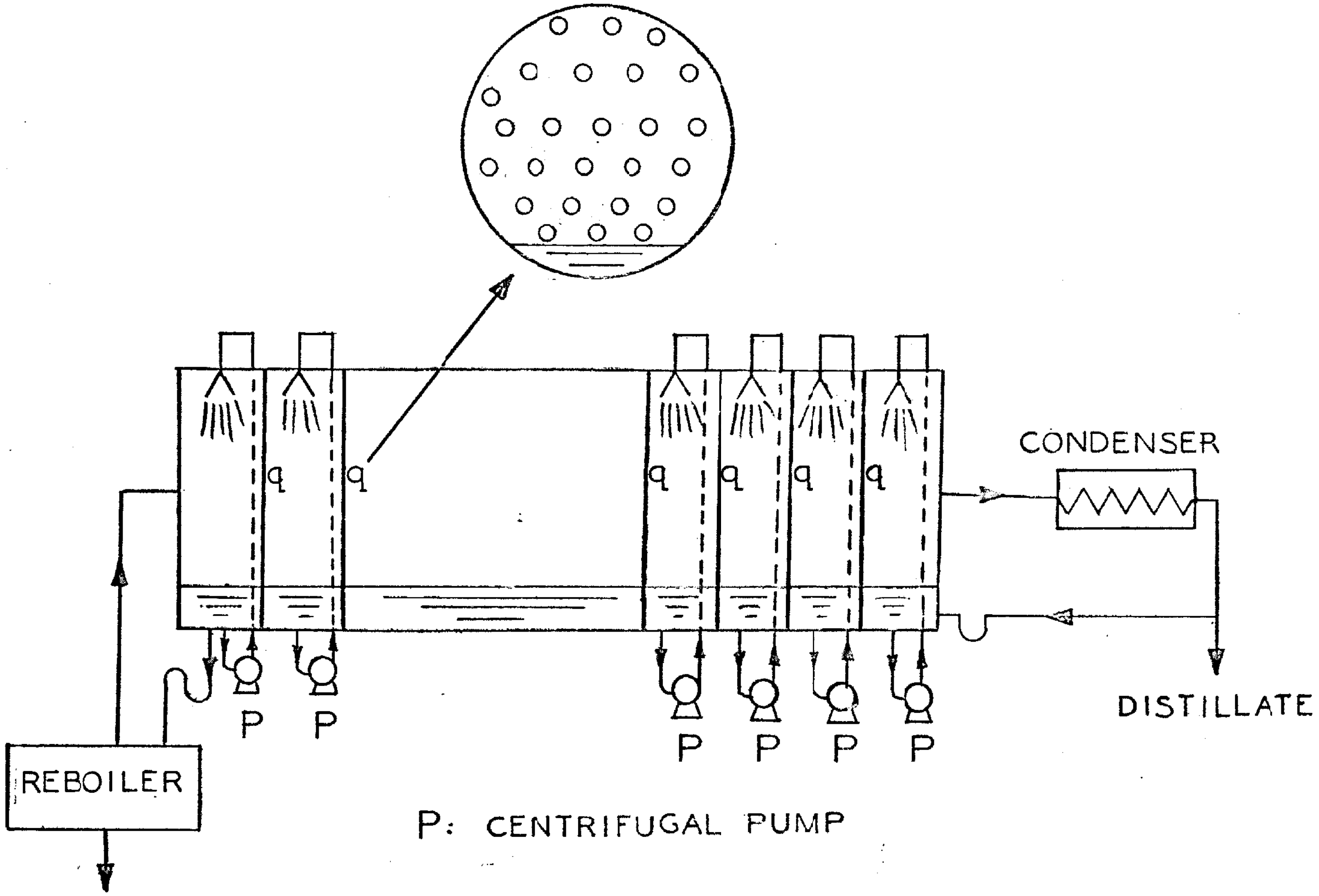

Figure A. A Horizontal Distillator.

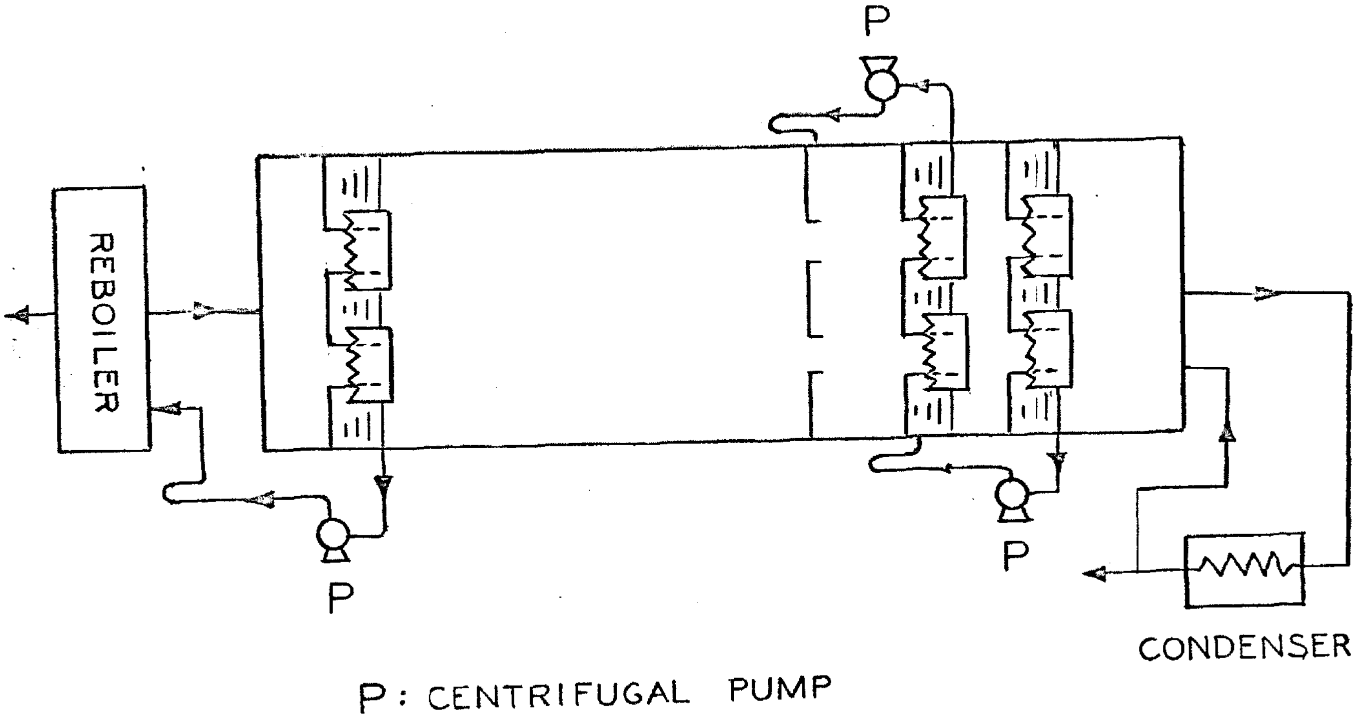

Figure B. A Bubble-Cap Distillator Using Different Liquid Level Controlling Device.

PROPOSITION III

This proposition was originally made in May 1962, and was concerned with the article by Reamer, Opfell and Sage, which appeared in I. E. C. 48, 475(1956). The article deals with measurements of liquid diffusivities with a diffusion cell shown in Figure P-2.

It was proposed at that time that equation (2) in that article be modified to take into account the transfer across the interface of the less volatile component. It was also proposed that the diffusion equation describing the problem be solved by transforming the space coordinate into a new one with the origin at the liquid-vapor interface. The diffusion equation based on the new coordinate system was derived but was not solved by the writer.

Since that time, things have changed in the Chemical Engineering Laboratory. Graue* has given a complete solution of the problem. In the following, the solution to the problem will be obtained in a different way.

The partial differential equation describing the problem can be written in a fixed coordinate system as

$$\left(\frac{\partial \sigma_k}{\partial \theta}\right)_x = D_{ckj} \left(\frac{\partial^2 \sigma_k}{\partial x^2}\right)_\theta \quad . \qquad \text{(P-7)}$$

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*Student Report 993

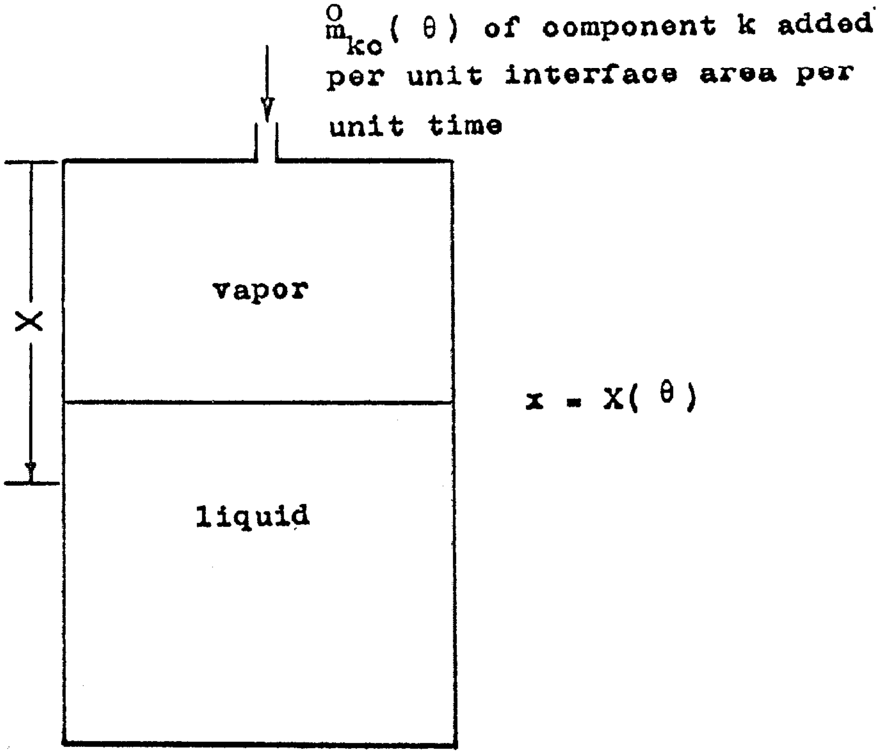

Figure P-2. Diffusion Chamber

Boundary conditions are:

$$\theta = 0, \quad \sigma_k = \sigma_{k_o} \quad . \tag{P-8}$$

$$x = X(\theta), \quad \sigma_k = \sigma_{k_b} \quad . \tag{P-9}$$

$$x = \infty, \quad \sigma_k = \sigma_{k_o} \quad . \qquad \text{(P-10)**}$$

$$\frac{dX(\theta)}{d\theta} = - \overset{o}{m}_{kc} \quad \frac{\bar{V}_{k\ell}^*}{1 - \bar{V}_{k\ell}^* \sigma_{kd} - \bar{V}_{j\ell}^* \sigma_{jd}} \tag{P-11}$$

$$x = X(\theta),$$

$$- D_{ckj} \left(\frac{\partial \sigma_k}{\partial x}\right) - \frac{dX}{d\theta} \sigma_{k_b} = \overset{o}{m}_{kc} \left(1 + \frac{\sigma_{kd} \bar{V}_{k\ell}^*}{1 - \bar{V}_{k\ell}^* \sigma_{kd} - \bar{V}_{j\ell}^* \sigma_{jd}} \right) \quad . \tag{P-12}$$

Let the solution of equation (P-7) subject to the boundary conditions be

$$\sigma_k = \sigma_{k_o} - B \operatorname{erf} c \left(\frac{x}{2 (D_{ckj} \theta)^{1/2}} \right) \quad . \tag{P-13}$$

[**] This condition is used for simplicity.

It is obvious that equation (P-13) satisfies the differential equation, so, if it also satisfies all the boundary conditions, it would be the solution of the problem.

The boundary condition (P-10) is automatically satisfied. Using boundary condition (P-9), there is obtained:

$$\sigma_{k_b} = \sigma_{k_o} - B \operatorname{erf} c \left(\frac{X(\theta)}{2 \, (D_{ckj} \, \theta)^{1/2}} \right) \quad . \tag{P-14}$$

Since equation (P-14) has to be satisfied for all θ, there follows:

$$\frac{X(\theta)}{2 \, (D_{ckj} \, \theta)^{1/2}} = \lambda = \text{constant} \quad . \tag{P-15}$$

Substituting equation (P-15) into equation (P-14), there is obtained:

$$B = - \frac{(\sigma_{kb} - \sigma_{ko})}{\operatorname{erf} c \, \lambda} \quad . \tag{P-16}$$

Differentiating equation (P-13) with respect to x and combining with equations (P-15) and (P-16), the gradient at the interface is obtained

$$\left(\frac{\partial \sigma_k}{\partial x}\right)_{\text{at } X(\theta)} = - \frac{(\sigma_{k_b} - \sigma_{k_o})}{\sqrt{\pi}\,(D_{ckj}\ \theta)^{1/2}} \left(\frac{e^{-\lambda^2}}{\text{erf c } \lambda}\right) \quad . \tag{P-17}$$

Substituting equations (P-11) and (P-17) into equation (P-12), there results

$$(\sigma_{k_b} - \sigma_{k_d}) \sqrt{\frac{D_{ckj}}{\theta}} \left(\frac{e^{-\lambda^2}}{\text{erf c } \lambda}\right) = \overset{o}{m}_{kc} \left[1 - \frac{\overline{V}_{k\ell}{}^* (\sigma_{k_b} - \sigma_{k_d})}{1 - \overline{V}_{k\ell}{}^* \sigma_{k_d} - \overline{V}_{j\ell}{}^* \sigma_{jd}} \right] \quad . \tag{P-18}$$

Now, from equation (P-15)

$$X(\theta) = 2\,\lambda\,(D_{ckj}\ \theta)^{1/2} \quad . \tag{P-19}$$

Therefore

$$\frac{dX(\theta)}{d\theta} = \lambda \sqrt{\frac{D_{ckj}}{\theta}} \quad . \tag{P-20}$$

Combination of equations (P-20) and (P-11) gives

$$\sqrt{\frac{D_{ckj}}{\theta}} = \frac{-\overset{o}{m}_{kc}}{\lambda} \frac{\bar{V}_{k\ell}^{*}}{1 - \bar{V}_{k\ell}^{*} \sigma_{kd} - \bar{V}_{j\ell}^{*} \sigma_{jd}} \quad . \tag{P-21}$$

Substituting equation (P-21) into equation (P-18), there results

$$\lambda e^{\lambda^2} \operatorname{erf} c \, \lambda = \frac{-(\sigma_{k_b} - \sigma_{k_o}) \dfrac{\bar{V}_{k\ell}^{*}}{1 - \bar{V}_{k\ell}^{*} \sigma_{kd} - \bar{V}_{j\ell}^{*} \sigma_{jd}}}{\sqrt{\pi} \left(1 - \dfrac{\bar{V}_{k\ell}^{*} (\sigma_{k_b} - \sigma_{k_d})}{1 - \bar{V}_{k\ell}^{*} \sigma_{kd} - \bar{V}_{j\ell}^{*} \sigma_{jd}} \right)} \quad . \tag{P-22}$$

The right-hand side is known. λ can then be found from a plot of $[\lambda e^{\lambda^2} \operatorname{erf} c(\lambda)]$ vs. λ. Such a plot can be easily made.

The value of λ so found is then substituted into equation (P-21), and there is obtained

$$\overset{o}{m}_{kc} = \frac{-\lambda\sqrt{D_{ckj}}\ \theta^{-1/2}}{\dfrac{V_{k\ell}*}{1 - V_{k\ell}*\ \sigma_{kd} - V_{j\ell}*\ \sigma_{jd}}} \quad . \qquad \text{(P-23)}$$

Integrating equation (P-23) with respect to time and squaring the result, the expression for the diffusivity is obtained

$$D_{ckj} = \frac{m^2}{4\lambda^2\theta}\left(\frac{\bar{V}_k*}{1 - V_k*\ \sigma_{kd} - V_j*\ \sigma_{jd}}\right]^2 \quad . \qquad \text{(P-24)}$$

To compare with the approximate solution given by Graue, equation (P-24) is combined with equation (P-22) to become

$$D_{ckj} = \frac{m^2\pi\left(e^{\lambda^2}\ \mathrm{erf}\ c\,(\lambda)\right)^2}{4\theta\,(\sigma_{k_b} - \sigma_{k_o})^2}\left(1 - \frac{\bar{V}_k*\ (\sigma_{k_b} - \sigma_{k_d})}{1 - V_k*\ \sigma_{kd} - V_j*\ \sigma_{jd}}\right]^2 \quad . \qquad \text{(P-25)}$$

This is the expression for evaluating the diffusivity from measured quantities m and θ.

NOTATIONS

D_{ckj} : Chapman-Cowling diffusivity of component k with respect to component j.

$\overset{o}{m}_{kc}$: rate of addition of component k per unit area per unit time.

m : total amount of component k added.

x : coordinate shown in Figure P-2.

$X(\theta)$: coordinate of the interface.

σ_k : weight of component k per unit volume.

θ : time.

Subscripts:

o : initial.

b : bubble point.

d : dew point.

Superscripts:

* : average quantity.

$-$: partial quantity.

PROPOSITION IV

This proposition deals with the finite stage model of Deans and Lapidus for solving transient problems in fixed-bed reactors.

For the case of no chemical reactions and non-porous packings, a differential balance for a trace component can be written as follows, if the axial Peclet number is 2:

$$\frac{\partial C}{\partial t} = -\frac{\partial C}{\partial x} + \frac{1}{2}\frac{\partial^2 C}{\partial x^2} + \frac{1}{N_{pe_r}}\left(\frac{\partial^2 C}{\partial r^2} + \frac{1}{r}\frac{\partial C}{\partial r}\right) \qquad \text{(P-26)}$$

where C : concentration.

N_{pe_r} : radial Peclet number.

r : dimensionless radial distance based on particle diameter.

x : dimensionless axial distance defined as above.

t : dimensionless time based on d_p/u.

d_p : particle diameter.

u : axial velocity.

To solve equation (P-26), they proposed a finite stage model consisted of a two-dimensional array of perfectly stirred tanks. They showed the equivalence between the differential balance and the finite stage model only for the one-dimensional case. For the two-dimensional case, they performed a numerical experiment to choose the required radial increment size which would bring the model into exact agreement with an experimental value of N_{pe_r}*.

In the following, it will be shown that the choice of the radial increment size can be determined mathematically without resorting to experimental calculations. In this way, the analogy between the two models would be more clearly seen. The merits and demerits of the finite stage model will also be discussed.

Let the size of a mixing stage be (Δx) (Δr), and let m represent the radial stage number, and n the axial stage number. As an approximation to equation (P-26), the finite stage model employs

$$\left(\frac{dC}{dt}\right)_{m,n} = \Phi_{m,\, n-1} - C_{m,\, n} \quad , \qquad \text{(P-27)}$$

where $\Phi_{m,\, n-1} = \left(\frac{1}{2} - \frac{\Delta r}{8r}\right) C_{m-\frac{1}{2},\, n-1}$

$$+ \left(\frac{1}{2} + \frac{\Delta r}{8r}\right) C_{m+\frac{1}{2},\, n-1} \quad . \qquad \text{(P-28)}$$

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*Deans and Lapidus chose $\Delta r = \sqrt{\frac{8.2}{N_{pe_r}}}$.

From equations (P-27) and (P-28), it is seen that in the finite stage model, the right-hand side of equation (P-26) is approximated by the concentrations at three mesh points only. In connection to this, it is noted that by using a central difference method, the approximation requires the concentrations at five mesh points.

Using Taylor series expansions for two independent variables, there result:

$$C_{m-\frac{1}{2},\, n-1} = C_{m,\, n} - \frac{\Delta x}{1!}\left(\frac{\partial C}{\partial x}\right)_{m,\, n} - \frac{\Delta r}{2 \times 1}\left(\frac{\partial C}{\partial r}\right)_{m,\, n} + \frac{(\Delta x)^2}{2!}\left(\frac{\partial^2 C}{\partial x^2}\right)_{m,\, n} + \frac{(\Delta r)^2}{2!\,4}\left(\frac{\partial^2 C}{\partial r^2}\right)_{m,\, n} + \frac{(\Delta x)\,(\Delta r)}{2}\,\frac{\partial^2 C}{\partial x \partial r} + 0\,(\Delta x^3,\ \Delta r^3)\ , \tag{P-29}$$

$$C_{m+\frac{1}{2},\, n-1} = C_{m,\, n} - \frac{\Delta x}{1!}\left(\frac{\partial C}{\partial x}\right)_{m,\, n} + \frac{\Delta r}{2 \times 1}\left(\frac{\partial C}{\partial r}\right)_{m,\, n} + \frac{(\Delta x)^2}{2!}\left(\frac{\partial^2 C}{\partial x^2}\right)_{m,\, n} + \frac{\Delta r^2}{2!\,4}\left(\frac{\partial^2 C}{\partial r^2}\right)_{m,\, n} - \frac{(\Delta x)\,(\Delta r)}{2}\,\frac{\partial^2 C}{\partial x \partial r} + 0\,(\Delta x^3,\ \Delta r^3)\ . \tag{P-30}$$

Adding equations (P-29) and (P-30), neglecting terms of order (Δx^3, Δr^3) and dividing through by $2\Delta x$:

$$-\left(\frac{\partial C}{\partial x}\right)_{m,\,n} + \frac{\Delta x}{2}\left(\frac{\partial^2 C}{\partial x^2}\right) + \frac{(\Delta r)^2}{8\Delta x}\left(\frac{\partial^2 C}{\partial r^2}\right)_{m,\,n}$$

$$= \frac{C_{m+\frac{1}{2},\,n-1} + C_{m-\frac{1}{2},\,n-1} - 2C_{m,\,n}}{2\Delta x} \quad . \qquad \text{(P-31)}$$

Subtracting equation (P-29) from equation (P-30), and dividing through by $r(\Delta r)N_{pe_r}$:

$$\frac{1}{N_{pe_r} r}\left(\frac{\partial C}{\partial r}\right)_{m,n} = \frac{C_{m+\frac{1}{2},\,n-1} - C_{m-\frac{1}{2},\,n-1}}{r(\Delta r)\,N_{pe_r}} + \frac{(\Delta x)}{rN_{pe_r}}\,\frac{\partial^2 C}{\partial x\,\partial r} \quad . \qquad \text{(P-32)}$$

If we take $\Delta x = 1$, $\Delta r = \sqrt{\frac{8}{N_{pe_r}}}$, equations (P-31) and (P-32) can be combined to give:

$$-\left(\frac{\partial C}{\partial x}\right)_{m,\,n} + \frac{1}{2}\left(\frac{\partial^2 C}{\partial x^2}\right) + \frac{1}{N_{pe_r}}\Bigg(\left(\frac{\partial^2 C}{\partial r^2}\right)_{m,\,n}$$

$$+ \frac{1}{r}\left(\frac{\partial C}{\partial r}\right)_{m,\,n}\Bigg] = C_{m+\frac{1}{2},\,n-1}\left(\frac{1}{2} + \frac{\Delta r}{8r}\right)$$

$$+ C_{m-\frac{1}{2},\,n-1}\left(\frac{1}{2} - \frac{\Delta r}{8r}\right) - C_{m,\,n} + \frac{1}{rN_{pe_r}}\ \frac{\partial^2 C}{\partial x \partial r}$$

$$= \Phi_{m,\,n-1} - C_{m,\,n} + \frac{1}{rN_{pe_r}}\ \frac{\partial^2 C}{\partial x \partial r}\quad . \qquad \text{(P-33)}$$

Combining this equation with equation (P-26), there is obtained:

$$\left(\frac{dC}{dt}\right)_{m,n} = \Phi_{m,\,n-1} - C_{m,\,n} + \frac{1}{rN_{pe_r}}\ \frac{\partial^2 C}{\partial x \partial r}\quad . \qquad \text{(P-34)}$$

This is identical to equation (P-27) excluding the term $\frac{1}{rN_{pe_r}}\ \frac{\partial^2 C}{\partial x \partial r}$, which is therefore, the error of the finite stage model. If central difference approximations were used for all the space derivatives in equation (P-26), errors of such a method would be $\left[(\Delta x)^2\ \frac{\partial^3 C}{\partial x^3} + (\Delta r)^2\ \frac{\partial^3 C}{\partial r^3}\right]$, which is smaller than the one for the model.

There is one definite advantage in the finite stage model: No boundary conditions are needed at the reactor exit so that a steady state solution can be obtained by integrating from the entrance toward the exit without using any iterations. If the model were not used, the same thing would be possible only by neglecting the axial diffusion. However, the model has a serious disadvantage that as many axial increments are required as there are catalyst pellets in the axial direction. The total number of axial increments required is in the order of hundreds for actual reactors. This is much more than what is required by accuracy considerations. Besides, for the same size of space increments, the finite stage model is less accurate than an usual numerical method employing central difference approximations.

In conclusion, the model is of doubtful value in reactor calculations.

Reference: Deans, H. A. and L. Lapidus, A. I. Ch. E. Journal, 6, 656 (1960).

PROPOSITION V

In a non-isothermal non-isobaric multicomponent system, it is proposed that the transports of material and energy by turbulent mixing be described in the following analogous ways:

$$(\overset{o}{m}_{dk})_y = -\sigma \epsilon_{dy} \frac{dn_k}{dy} \quad . \tag{P-35}$$

$$(\overset{o}{H}_d)_y = -\sigma \epsilon_{dy} \frac{dH}{dy} \quad . \tag{P-36}$$

where $(\overset{o}{m}_{dk})_y$: mass flux of the k-th component in the y-direction due to turbulent mixing.

$(\overset{o}{H}_d)_y$: enthalpy flux in the y-direction due to turbulent mixing.

σ : specific weight of the mixture.

ϵ_{dy} : eddy diffusivity in the y-direction.

n_k : weight fraction of the k-th component.

H : enthalpy of the mixture.

By using the concept of enthalpy diffusion expressed by equation (P-36), an interesting relationship can be obtained.

Since

$$dH = C_p dT + \sum_k \overline{H}_k dn_k + \left(\frac{\partial H}{\partial P}\right)_{T,n} dP \quad , \tag{P-37}$$

by combining equation (P-36) with equation (P-37), there is obtained

$$(\overset{o}{H}_d)_y = - \sigma C_p \, \epsilon_{dy} \frac{dT}{dy} - \sigma \, \epsilon_{dy} \sum_k \bar{H}_k \frac{dn_k}{dy}$$

$$+ \left(\frac{\partial H}{\partial P}\right)_{T,n} \frac{dP}{dy} \quad . \qquad \text{(P-38)}$$

Substituting equation (P-35) into equation (P-38), there results

$$(\overset{o}{H}_d)_y = \sigma C_p \, \epsilon_{dy} \frac{dT}{dy} + \sum_k (\overset{o}{m}_{dk})_y \, \bar{H}_k$$

$$+ \left(\frac{\partial H}{\partial P}\right)_{T,n} \frac{dP}{dy} \quad . \qquad \text{(P-39)}$$

Equation (P-39) is identical to the one frequently used in the literature, except that the last term is not present in the latter.