Convective Diffusion in a Rectangular Duct with One Catalytic Wall—Laminar Flow—Arbitrary Reaction Order

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In a recent experimental study of reaction rates measured in a rectangular duct with a reaction of arbitrary order occurring on one wall, the results were analyzed in terms of an infinite parallel plate duct. The subject of this paper is the determination of the requirements necessary to treat a rectangular duct as a flat duct in the fully developed laminar flow regime. To this end, the rectangular duct problem is solved numerically. The results obtained show that mixing-cup concentrations, average wall concentrations, and Nusselt numbers for any aspect ratio γ (between a square duct and parallel plates) may be estimated from the parallel plate results when a reduced distance is used. These parameters vary only slightly with aspect ratio. If the actual distance instead of this reduced coordinate is used, an aspect ratio of one to ten would be required to obtain results which are accurate to 6%. These conclusions are not valid for a catalytic reactor with four catalytic walls.

The rectangular duct geometry is quite common industrially in heat exchangers, catalytic reactors, and fuel cells. The geometry is advantageous in experimental determinations of catalytic reaction rates. For example, a catalyst may be applied uniformly to the catalytic wall and can be examined in detail before the duct is assembled. Deterioration of the catalyst can be checked periodically by disassembly, whereas in a tubular reactor this is generally impossible. In a rectangular duct reactor with one catalytic wall, concentration, velocity, and temperature probes can be inserted in the opposite noncatalytic wall so that catalytic plates of different materials may be used interchangeably in the same reactor.

In our recent studies of convective diffusion (*10, 11*) with a reaction occurring on one wall the results were reported for a parallel plate duct. The subject of this paper is the determination of the necessary requirements which will allow a rectangular duct to be treated as a parallel plate duct in the laminar flow regime. Such information is necessary for proper analysis of reaction rate and diffusion data obtained in a real rectangular duct which approximates a parallel plate reactor. Experimental mass transfer coefficient and reaction rate data obtained in a rectangular duct with one catalytic wall were analyzed by Kulacki and Gidaspow (*6*) using Solbrig and Gidaspow's (*11*) parallel plate analysis. One of the consequences of the results reported in this paper is that the data analysis with a parallel plate Reynolds number was justified for the duct with only one catalytic wall. It appears that even a square duct would have been a satisfactory approximation to a parallel plate reactor for analysis of mixing-cup concentrations.

The articles reviewed by the authors which pertain to the present discussion may be grouped as follows:

1. Completely analytical solutions which treat only the region in which the concentration profile is fully developed and the boundary conditions are constant flux conditions.

2. Variational solutions which can be used to describe the thermal entrance as well as the fully developed region with constant concentration or flux boundary conditions.

3. Numerical techniques which pertain to the fully developed concentration profiles with constant concentration or flux conditions on the boundary.

Completely analytical solutions have not been reported in the literature for the general three-dimensional problem because the differential equation is not completely separable. In the constant flux case, however, a fully developed solution exists which allows an analytical solution to be obtained. Marco and Han (*7*) showed that the problem of constant flux boundary conditions with identical concentrations on all walls at any cross section could be reduced to the well-known Lagrange equation in small deflection theory. This method may be used for many shapes other than rectangular. Savino and Siegel (*8*) solved the constant flux problem analytically. The boundary conditions considered were symmetric with opposite walls emitting the same flux. In a later paper (*9*) they included the effect of peripheral wall conduction.

Sparrow and Siegel (*12*) presented a variational method which consists of formulating integrals which must be minimized to produce the solution in the fully developed region. This method can be used when the flux is taken to be uniform in the axial direction, although variation of conditions around the periphery is permitted. This method allows any function with arbitrary constants to be selected as the solution, and the minimization allows the selection of optimum constants which minimize the integrals. In a later paper (*13*), they extend this method to solving eigenvalue problems so that this method can be used in the entrance region of a rectangular duct. Dennis (*3*) presented a method which utilized the Galerkin technique and allowed the solution of any problem with homogeneous boundary conditions.

Clark and Kays (*2*) utilized a numerical technique to determine profiles in the fully developed temperature region. Their technique allowed the consideration of boundary conditions of constant function or constant flux at the wall.

It is unfortunate that the references reviewed by the authors considered boundary conditions which were different enough from the authors' that no comparisons could be made even in degenerate cases.

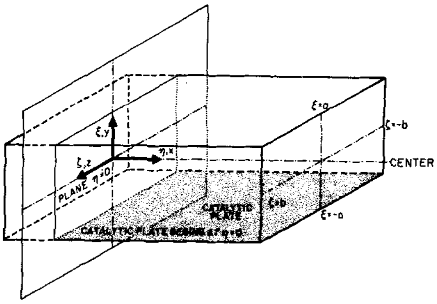

Fig. 1. Rectangular duct geometry.

FORMULATION OF EQUATIONS

The problem under consideration involves the transfer of mass from a mixture of reactants flowing in a rectangular duct with one catalytic wall. The duct is long enough to allow the laminar velocity profile to become fully developed before reaching the catalytic wall. The geometry is illustrated in Figure 1. The reactants diffuse to the catalytic surface where reaction takes place forming products. The reaction rate is assumed to be a power function of the concentration of one of the reactants such as methane. The products diffuse back into the mixture causing the density to be constant and the total system mass to be conserved. Any heat liberated or absorbed by the reaction is transferred through the catalytic wall. The temperature of the inside surface of the catalytic wall is maintained at a constant value equal to the inlet temperature of the entering fluid. In this way it is possible to maintain the system under consideration at a constant temperature. Furthermore, changes in total number of moles of the fluid are assumed to be sufficiently small to preserve the fully developed laminar velocity profile. This will be true even if there are mole changes during reaction as long as there is also a large fraction of inert, such as the nitrogen in air.

The velocity profile (5, *14*) may be expressed in terms of the average velocity U and aspect ratio as

$$v_\eta = \frac{3}{2} U \frac{(1-y^2) + \dfrac{32}{\pi^3} \displaystyle\sum_{o}^{\infty} \frac{(-1)^{n+1}}{(2n+1)^3} \dfrac{e^{\frac{\alpha_n}{\gamma}(z-1)} + e^{\frac{-\alpha_n}{\gamma}(z+1)}}{1+e^{-2\frac{\alpha_n}{\gamma}}} \cos \alpha_n y}{1 - \dfrac{192 \cdot \gamma}{\pi^5} \displaystyle\sum_{o}^{\infty} \frac{1}{(2n+1)^5} \dfrac{1-e^{-2\frac{\alpha_n}{\gamma}}}{1+e^{-2\frac{\alpha_n}{\gamma}}}} \tag{1}$$

where $\alpha_n = (2n+1)\pi/2$. Equation (1) appears to be the best form for computer evaluation in the range of $1 \geqq \gamma \geqq 0$ which is all that is necessary because of the symmetry of the velocity profile. That is, the profile for γ is the same as $1/\gamma$ with the roles of a and b interchanged. The normalized velocity profile f may be introduced at this point and is defined by

$$f(y, z) = \frac{v_\eta}{\frac{3}{2} U} \tag{2}$$

Conservation of mass for the reactant a with Fick's law of diffusion (*1*), written in terms of an effective constant binary diffusivity D_{ae} used, yields the following steady state mass balance (*1, 10*):

$$v_\eta \frac{\partial \rho_a}{\partial \eta} = D_{ae} \left(\frac{\partial^2 \rho_a}{\partial \eta^2} + \frac{\partial^2 \rho_a}{\partial \xi^2} + \frac{\partial^2 \rho_a}{\partial \zeta^2} \right) \tag{3}$$

This equation can be expressed in dimensionless terms in several ways. The results desired are to be applicable to large Peclet numbers. It is therefore helpful to use the usual Graetz type of combination to define a dimensionless distance in the direction of bulk flow. If the Reynolds number is defined as it is normally used in engineering practice, in terms of a hydraulic diameter D where

$$D = 4 \frac{2a \cdot 2b}{4(a+b)} = \frac{4a}{1+\gamma} \tag{4}$$

the dimensionless distance x becomes

$$x = \frac{1}{\frac{3}{8}(1+\gamma) N_{Re} \cdot N_{Sc}} \left(\frac{\eta}{a} \right) \tag{5}$$

Thus the Reynolds number in Equation (5) is defined by $N_{Re} = U\, D\, \rho/\mu$. The use of such a distance shows in the usual way that diffusion in the direction of bulk flow can be neglected for sufficiently large Peclet numbers.

The boundary condition at the catalytic wall is obtained by equating the mass flux of species a to the wall to its rate of mass production at the wall. This results in the boundary condition

$$D_{ae} \frac{\partial \rho_a}{\partial \xi} = \frac{k_w}{M_a^{(n-1)}} \rho_a^n \tag{6}$$

At the noncatalytic walls the gradients of mass concentration are zero. The inlet composition is taken as a constant and equal to ρ_{ao}. It is used as a scale factor to obtain a dimensionless concentration $C = \rho_a/\rho_{ao}$. The dimensionless concentration can be interpreted as the weight fraction of species a unreacted.

Therefore, the mathematical statement of this problem may be reduced to solving the boundary value problem

$$f(y, z) \frac{\partial C}{\partial x} = \frac{\partial^2 C}{\partial y^2} + \gamma^2 \frac{\partial^2 C}{\partial z^2} \tag{7}$$

$$\begin{aligned} & C(o, y, z) = 1 \\ & \frac{\partial C}{\partial y}(x, +1, z) = 0 \\ & \frac{\partial C}{\partial y}(x, -1, z) = K_{wn}\ C^n \\ & \frac{\partial C}{\partial z}(x, y, \pm 1) = 0 \end{aligned} \tag{8}$$

where

$$K_{wn} = \frac{k_w a}{D_{ae}} \left(\frac{\rho_{ao}}{M_a} \right)^{n-1}$$

The heat transfer analogies to this problem include the case of heat transfer with a finite wall resistance or a radiation boundary condition and are discussed in reference *10*. Further interpretations are possible. For example, the case of a second-order reaction is equivalent to the case of heat or mass transfer in an adiabatic channel with a rate constant proportional to the first power of temperature, when the Lewis number for the fluid is unity. This results from the fact that for equal Schmidt and Prandtl numbers the differential equations and the boundary conditions become identical when properly expressed in dimensionless terms.

SOLUTION BY FINITE DIFFERENCES

The method of Dufort and Frankel (*4*) has been extended to solve this three-dimensional problem. The finite-difference equation used may be written in the form

$$\begin{aligned} C(I+1,J,K) &= C(I-1,J,K) \\ &+ \frac{2R}{[f(y,z)+2R+2\gamma^2 S]}\,[C(I,J+1,K) \\ &\quad -2C(I-1,J,K)+C(I,J-1,K)] \\ &+ \frac{2\gamma^2 S}{[f(y,z)+2R+2\gamma^2 S]}\,[C(I,J,K+1) \\ &\quad -2C(I-1,J,K)+C(I,J,K-1)] \end{aligned}$$

where

$$R = \frac{\Delta x}{(\Delta y)^2} \text{ and } S = \frac{\Delta x}{(\Delta z)^2}. \qquad (9)$$

The function $C(I, J, K)$ denotes an approximation to $C(x, y, z)$ where $x = (I-1)\cdot\Delta x$ and the relation of y and z to J and K is indicated in Figure 2. This figure illustrates a typical grid perpendicular to the flow direction at some value of x. Unlike the usual explicit finite-difference scheme, the two-dimensional Dufort and Frankel scheme is stable for all values of the increment sizes. If a Taylor series is substituted into Equation (9), one observes that if the requirements $\Delta x = R\cdot(\Delta y)^2$ and $(\Delta z)^2 = (R/S)\cdot(\Delta y)^2$ are made, the finite-difference molecule becomes a closer approximation to the differential equation as Δy approaches zero. Values of $R = \gamma^2 S = 0.5$ were found satisfactory in all the computations which were limited to $\gamma \leqq 1$. This implies that $(\Delta z)^2 = \gamma^2 (\Delta y)^2$. If Δz were taken equal to Δy, the computational scheme became unstable as the aspect ratio was decreased. This is caused by the large change in the velocity profile near $z = \pm 1$ for small γ.

Because of stability requirements, Equation (9) cannot be used to calculate the concentrations on the catalytic wall. The fact that the velocity is zero on the wall combined with the boundary condition at the catalytic surface yields the following set of equations to be solved:

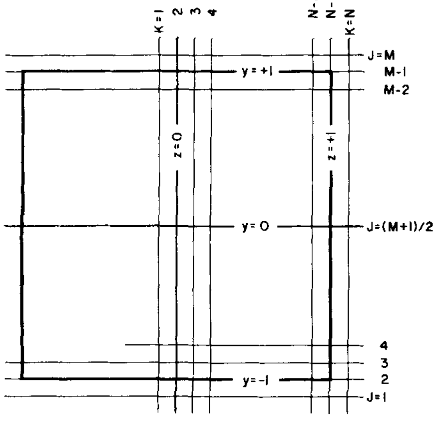

Fig. 2. Rectangular duct cross section with superimposed finite-difference grid.

$$\begin{aligned} &2R\,[C(I,3,K) - C(I,2,K) - \Delta y\cdot K_{wn}\,C(I,2,K)^n] \\ &\quad + \gamma^2 S\,[C(I,2,K+1) - 2C(I,2,K) \\ &\qquad + C(I,2,K-1)] = 0 \qquad (10) \end{aligned}$$

where the $C(I, 3, K)$ are all calculated from Equation (9).

Equations (9) and (10) in addition to the zero flux boundary conditions at the other walls allow all of the concentrations on any grid to be determined if the concentrations on the first two grids are known. The concentrations on grid 1 are determined by the initial condition and the use of Equation (10) to determine the concentrations at the catalytic boundary. The concentrations on grid 2 were determined by an equation similar to Equation (9) (with, however, a two-point expansion instead of a three-point expansion in the direction of flow) and with Equation (10) on the catalytic walls.

Most of the computations were performed with $\Delta y = 0.1$ (that is, twenty subdivisions). The accuracy was checked with $\Delta y = 0.05$, and it was observed that the results between the two different computations agreed to the third significant figure.

OVERALL PARAMETERS

The mixing-cup concentration, defined as

$$C_b = \frac{3}{8}\int_{-1}^{+1}\int_{-1}^{+1} C(x,y,z)\cdot f(y,z)\,dy\,dz \qquad (11)$$

was evaluated by a two-dimensional analog of Simpson's rule.

The Nusselt number was defined in such a manner as to allow an equivalent first-order reaction rate coefficient to be evaluated in the first-order case. Integration of the differential equation over the y, z cross section yields the overall balance

$$\frac{\partial}{\partial x} C_b + \frac{3}{8} K_{wn}\int_{-1}^{+1} C(x,-1,z)^n\,dz = 0 \qquad (12)$$

The Nusselt number was defined as

$$N_{Nu_m} = \frac{\displaystyle\int_{-1}^{+1} \frac{\partial C}{\partial y}(x,-1,z)\,dz}{2\,C_b - \displaystyle\int_{-1}^{+1} C(x,-1,z)\,dz} \qquad (13)$$

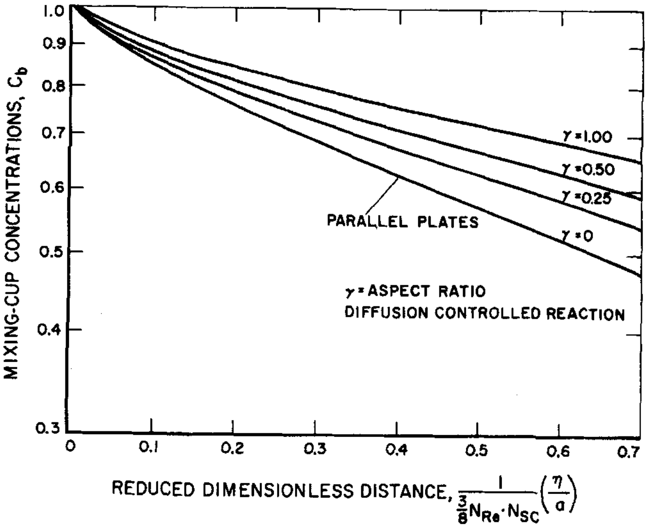

Fig. 3. Longitudinal concentration distribution—laminar flow in a rectangular duct—diffusion controlled reaction on one wall.

In the first-order case, Equations (12) and (13) may be combined to yield

$$\frac{\partial}{\partial x} C_b + \frac{3}{4} K_E \; C_b = 0 \qquad (14)$$

where the first-order reaction rate coefficient K_E is

$$K_E = \frac{1}{\dfrac{1}{N_{Num}} + \dfrac{1}{K_{w1}}} \qquad (15)$$

It was shown in reference *10* that in the first-order case the Nusselt number must approach a constant value for large x and that the average concentration is given as

$$C_b = A \; e^{-3/4 \, K_E x} \qquad (16)$$

RESULTS AND COMPUTATIONS

Sufficient results have been calculated to estimate the effect of aspect ratio. Although a facility was developed which allows the solution of the rectangular duct problem for the general case, the amount of information which could be obtained from this program is immense. Results are reported for only a few representative cases.

Average Concentrations

An important feature of the solution was discovered as a result of the method used to define the dimensionless parameters. This important result is illustrated in Figures 3 and 4. Mixing-cup concentrations have been plotted in Figure 3 for several aspect ratios for the diffusion controlled problem. It is noted that an aspect ratio of one to four (0.25) is significantly different from the parallel plate case. However, when the mixing-cup concentrations are plotted as a function of the dimensionless group

$$x = \frac{1}{\dfrac{3}{8}(1+\gamma)\, N_{Re} \cdot N_{Sc}} \left(\frac{\eta}{a}\right)$$

as in Figure 4, the mixing-cup concentrations are almost coincident for practical purposes. It may be concluded when considering Figure 3 that it is necessary to have a rather small aspect ratio if one were to consider the rectangular duct as a parallel plate channel when plotting results in terms of the actual distance η. For example, an aspect ratio of one to ten is required if one wishes agreement of conversions within 6%. However, if one were to plot average concentrations against x, any $0 \leq \gamma \leq 1$ will yield approximately the same conversions. This behavior is not restricted to diffusion controlled reactions. Figure 5 illustrates that this principle also applies to a second-order reaction rate of $K_{w2}\, C(x, -1, z)^2$. The average wall concentrations as well as the mixing-cup concentrations are approximately the same for aspect ratios of zero and one.

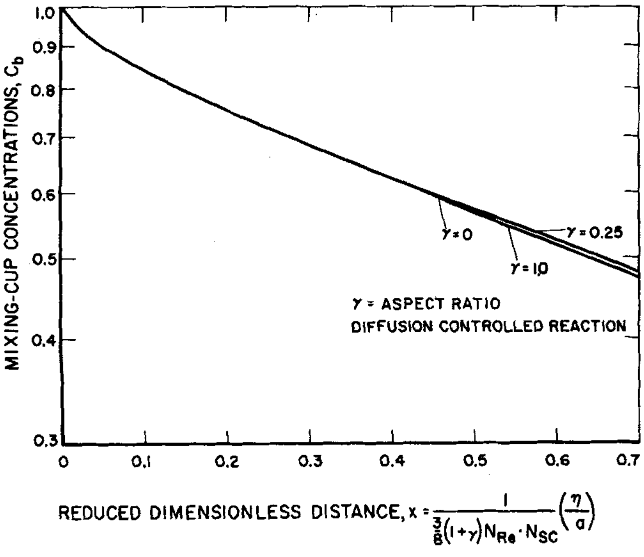

Fig. 4. Coincidence of mixing-cup concentrations for a given reduced axial distance.

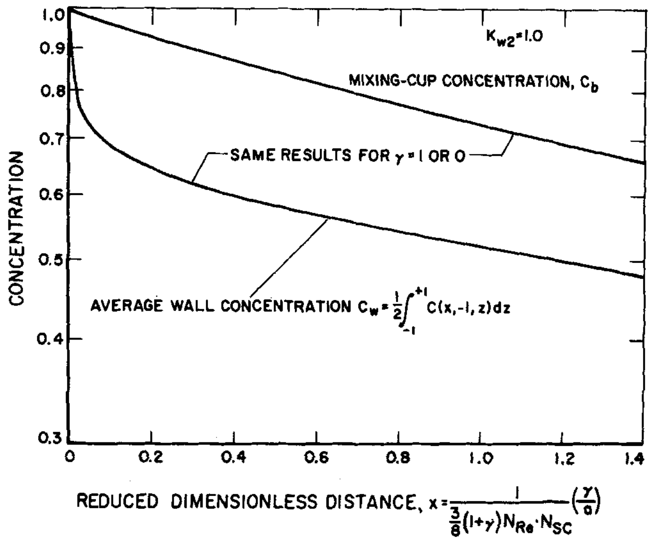

Fig. 5. Coincidence of mixing cup and wall concentrations for given reduced axial distance for a second-order reaction.

It should be noted that this important result would not be valid if all four walls were catalytic (2).

An Example of Point Concentrations

An example of point concentrations is presented in Figure 6 for the second-order reaction (K_{w2} = 1.0). These

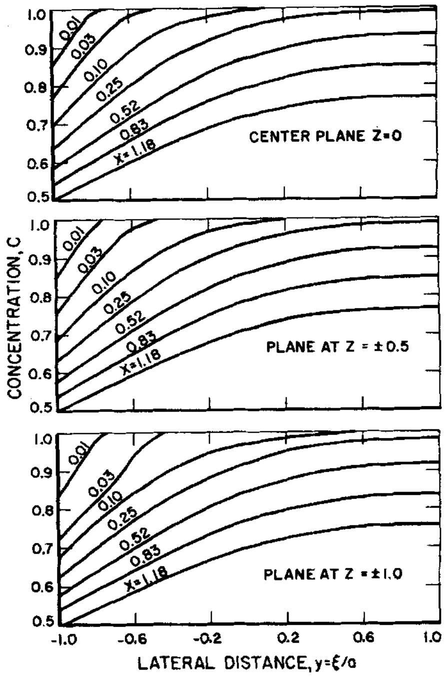

Fig. 6. Concentration profiles—laminar flow in a rectangular duct with one catalytic wall—reaction order of two—reaction coefficient of one—aspect ratio of one.

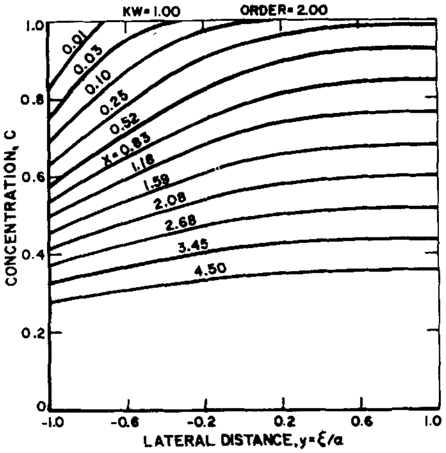

Fig. 7. Lateral concentration profiles—laminar flow in a parallel plate duct with one catalytic wall.

concentrations are plotted as a function of the dimensionless distance x for comparison with the parallel plate case. It is observed that for small x the curves differ, but as the distance x becomes larger, all curves for the various z are almost the same and approximate the parallel plate solution. The parallel plate solution is presented in Figure 7 for comparison purposes.

The variation of concentration on the catalytic wall with the z variable is illustrated in Figure 8. The values decrease near the corners because the fluid moves slower in this region, and thus more time is available for diffusion to the catalyst. However, the overall effect of these concentration profiles makes the total conversion less efficient than for parallel plates. For example, the actual distance η required for the same conversion in a square duct is twice that of parallel plates for equal Reynolds numbers. The same trend in the point concentrations is observed for values of y other than those at the catalytic wall, but these curves are much flatter.

The conclusion which may be drawn from these comparisons is that the term $\gamma^2(\partial^2C/\partial z^2)$ in the differential equation is very small for the boundary conditions being considered. The fact that $f(y, z)$ differs from the parabolic velocity profile drastically for a square duct apparently produces only a small effect in the calculation of the overall mass transfer parameters.

Nusselt Numbers

The important results obtained in the calculation of the Nusselt number according to the definition, Equation (13), are that the values are almost the same for any aspect ratio when plotted as a function of x. This was true for arbitrary reaction order as well as first order. This implies that the actual distance required for a fully developed solution in the diffusion controlled and first-order case is larger for larger aspect ratios and is proportional to $(1 + \gamma)$ for a constant Reynolds number. As mentioned previously, the Nusselt number in the first-order case must approach a constant value, and the numerical work was verified by agreement in this point.

The Nusselt number does vary slightly with aspect ratio and exhibits a minimum value for $\gamma = 0.5$. For example, at $x = 0.46$ and a diffusion controlled reaction, the Nusselt numbers for aspect ratios of 1.0, 0.5, 0.25, 0.1, and 0 are 1.224, 1.206, 1.208, 1.220, and 1.234, respectively.

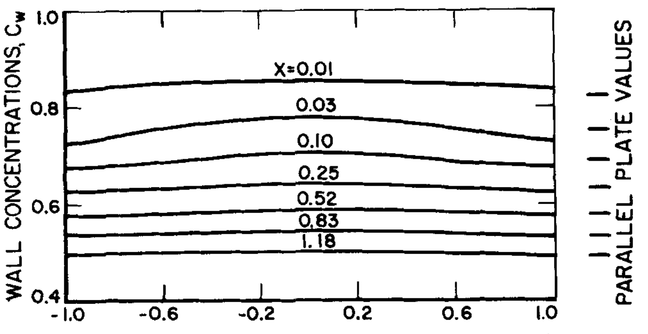

Fig. 8. Lateral wall concentration profiles—laminar flow in a rectangular duct with one catalytic wall—reaction order of two—reaction coefficient of one—aspect ratio of one.

CONCLUSIONS

An important conclusion reached in this paper is that approximate results for a rectangular duct catalytic reactor with one catalytic wall of any aspect ratio between one and zero can be obtained from only the knowledge of the parallel plate solution. Information concerning mixing-cup concentrations, average wall concentrations, and Nusselt numbers may be obtained from parallel plate results by utilizing the dimensionless distance x. These results are not valid for catalytic reactors with all walls catalytic.

The point concentrations show a greater difference than the overall parameters. In the second-order case considered, the concentration profiles approached the parallel plate results for large x but differed at small x. The point concentration profiles agreed within 3% by use of the parallel plate profiles and the reduced distance x.

If the actual distance instead of this reduced distance is used, an aspect ratio of one to ten would be required to obtain results which are accurate to 6%. The Nusselt number is almost independent of the aspect ratio when plotted as a function of x.

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NOTATION

a = one-half the distance between the catalytic and noncatalytic plate
b = half distance between the noncatalytic plates
C = dimensionless concentration = ρ_a/ρ_{ao}
C_b = mixing-cup concentration
D = hydraulic diameter
D_{ae} = effective diffusivity of species a in a mixture
f = velocity function = $v_\eta/1.5\,U$
K_{wn} = dimensionless wall reaction rate constant for an n^{th} order reaction
K_E = effective dimensionless reaction rate constant
k_c = mass transfer coefficient
k_w = wall reaction rate constant
M_a = molecular weight of species a
N_{Nu} = Nusselt number for mass transfer = $k_c\, a/D_{ae}$
N_{Pe} = Peclet number = $4aU/D_{ae}$
R = ratio $\Delta x/\Delta z^2$
N_{Re} = Reynolds number = $U\, D\, \rho/\mu$
S = ratio $\Delta x/\Delta y^2$
N_{Sc} = Schmidt number = $\mu/\rho D_{ae}$
U = mass average velocity
v_i = mass velocity component in the i direction

x = dimensionless coordinate parallel to flow = $\eta / \frac{3}{2} \frac{Ua^2}{D_{ae}}$
y = dimensionless coordinate = ξ / a
z = dimensionless coordinate = ζ / b

Greek Letters

γ = aspect ratio = a/b
ζ = spatial coordinate perpendicular to the flow direction and parallel to the catalytic plate
η = spatial coordinate parallel to the flow direction
μ = viscosity
ξ = spatial coordinate perpendicular to the flow direction and the catalytic plate
ρ_a = mass concentration of species a
ρ_{ao} = mass concentration of species a at $x = 0$
Σ = summation symbol

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A Fourth Parameter for the Vapor Pressure and Entropy of Vaporization of Polar Fluids

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Pitzer's acentric factor approach has been extended to the vapor pressure and entropy of vaporization of polar fluids. Normal fluid vapor pressure functions have been determined for 0.44 $\leqq T_R <$ 0.56. A polarity factor has been defined and polar correction terms established for the vapor pressure for 0.44 $\leqq T_R <$ 0.70 and for the entropy of vaporization for 0.56 $\leqq T_R \leqq$ 0.72. The polar correction terms enable the accurate calculation of the vapor pressure and entropy of vaporization of a polar fluid from its normal boiling point and normal latent heat of vaporization. The results of this study also form the basis for the extension of this approach to other thermodynamic properties of polar fluids.

Accurate values of the volumetric and thermodynamic properties of pure substances and mixtures are required in many important applications. Reliable methods have been presented for the calculation of these properties for nonpolar fluids and certain nonpolar gas mixtures. Similar procedures are presently not available for polar fluids and for mixtures containing at least one polar constituent.

Pitzer (*17*) has shown that the original theorem of corresponding states which has formed the basis of many reduced state correlations for thermodynamic properties is only applicable for simple fluids such as argon, krypton, and xenon. This is because the potential energy curves of simple fluids can be adequately described by functions containing two characteristic parameters, such as the Lennard-Jones potential. Pitzer proposed an extended theorem of corresponding states for *normal fluids in which* a third parameter ω accounts for the effects of the size and shape of the molecules. The extended theory is equivalent to the use of an intermolecular potential which contains an additional shape parameter (such as the Kihara potential). The acentric factor ω is empirically defined as

$$\omega = -\log P_R\big|_{T_R=0.700} - 1.000 \qquad (1)$$