# The Effects of Transport on Reactions in Homogeneous Tubular Flow

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## Abstract

Numerical solutions have been carried out for representative conditions in a tubular reactor in fully developed laminar and turbulent flow. The computations take into account the radial transport of both species and energy by molecular and turbulent fluctuations for energetic reactions and for heat exchange with the surroundings. The results reveal that finite radial rates of transport of species and energy by molecular diffusion, and in turbulent flow by eddy diffusion as well, do affect the mixed-mean conversion significantly for many practical conditions. Although the numerical solutions of the models are essentially exact, some idealizations such as invariant physical properties and a rate mechanism in terms of concentration have been made in the interests of generality. The numerical results are limited to a single first-order irreversible equimolar reaction, but the methodology can readily be extended to other reacting systems. The results differ from all previous ones in that an essentially exact model is utilized for turbulent flow and transport. Correlative equations based on asymptotic behavior are devised for the primary effects of the thermal parameters.

Key words: Tubular reactors, diffusion, energetic reactions

## Introduction

Process designers do not questions the utility of generalized predictive and correlative expressions for convection, for example of *Nu* as a function of *Re* and *Pr* or the justifiability of the postulate of invariant physical properties, nor do they question the need to impose idealized conditions, for example fully developed flow and convection and uniform heating or a uniform wall temperature, in order to obtain generalized solutions and correlations. The associated deviations from exactness and physical reality are not overlooked, but rather are recognized as the price of insight and generality.

Reaction engineering has followed a different path. Complex reaction mechanisms, stirred vessels, and packed-bed catalytic reactors have received great attention, but fluid-mechanical, radial diffusion, and thermal effects in tubular reactors have been rather neglected in an analytical and a correlative sense. Indeed, most of the canonical solutions in the literature for homogeneous chemical conversions in tubular flow are for a single reaction carried out isothermally and invoke the physically non-existent condition of “plug flow”. The obvious reasons for these extreme idealizations include the complexity associated with (a) the radial velocity distribution, (b) the exponential dependence of the rate constant on temperature, (c) the non-linearity arising from multiple, coupled reaction mechanisms, and (d) multiple empirical parameters such as the frequency factor, the energy of activation, and the heat of reaction for each reaction mechanism.

In previous related work, Churchill[1, 2] developed both general and asymptotic analytical solutions for the upper bounding conversion, corresponding to perfect radial mixing, and the lower bounding conversion, corresponding to negligible radial mixing, in both fully developed laminar flow and fully developed turbulent flow, and for both energetic and non-energetic reactions. Churchill et al.[3] subsequently carried out numerical solutions to test these expressions. The primary, unexpected finding of that work is of several invariances. These invariances not only suggest that generalizations are possible for both non-energetic and energetic reactions in tubular flow, but also give some guidance to their development. A second unrelated finding is that exact numerical solutions taking into account finite radial transport and energetic effects are not only upon feasible, but within the existing skills of undergraduate students and most practicing engineers.

In all of the analytical and numerical solutions described by Churchill and coworkers[1,2, 3], the behavior was one-dimensional and the models were in the form of ordinary differential equations. In the current work, exact numerical solutions have carried out for representative conditions in fully developed laminar and turbulent flow that take into account the radial transport of both species and energy by both molecular and turbulent fluctuations in both weakly and strongly energetic reactions and with heat exchange to the surroundings. The models thereby consist of coupled partial differential equations. The numerical results are limited to a single first-order irreversible equimolar reaction, but the methodology is readily extended to other reacting systems. The results differ from all previous ones in that an essentially exact model is utilized for turbulent flow and transport.

Because of the many dimensionless variables and parameters and the lack of a theoretical structure, the development of generalized algebraic, correlative, and predictive equations such as those that have been devised for pure convection, was considered in advance to be very difficult if not impossible. Accordingly, the objective of correlation, but not of computation, was reduced to the determination of sensitivity coefficients for the first-order effects on the mixed-mean conversion of the heat of reaction, the energy of activation, the frequency factor of the reaction, the Reynolds number, and an imposed heat flux density or fixed temperature of the wall.

## Prior Work

Cleland and Wilhelm[4], in a truly pioneering work, carried out numerical calculations for the effect of molecular diffusion on the conversion for a first-order, equimolar, irreversible reaction in the laminar regime of flow at constant density and temperature for a series of values of $D_f/ka^2$ ranging from 0 to $\infty$ and of $kx/2u_m$ ranging from 0 to 2.0, and concluded that diffusion was significant (which they defined as a decrease of greater than 1% in the conversion) for $(x/a)/ScRe < 5 \times 10^{-4}$. They further concluded from this result that radial diffusion is ordinarily negligible for liquids but may not be for gases in tubes of small diameter. Additionally, they carried out experimental work for a pseudo first-order liquid-phase reaction (the hydrolysis of acetic hydride in aqueous solution) and measured conversions corresponding to slightly higher rates of diffusion than those predicted. The discrepancies that they observed were attributed primarily to natural convection generated by temperature and concentration differences corresponding to a maximum Grashof number of 3700.

Finlayson and Rosendoll[5] recently devised a computer code called *CRDT* (Chemical Reactor Design Tool) for student use in carrying out numerical calculations for tubular reactors, and presented some illustrative results based on a crude model for the effects of turbulence. Ekambara and Joshi[6] recently reviewed previous work for the effects of axial mixing in a reactor in fully developed laminar flow and proposed a new model, but their illustrative calculations are for non-reacting conditions. The models of Fox[7] include molecular and turbulent diffusion but are for homogeneous turbulence.

These prior calculations, although pioneering in character, are fragmentary and the theoretically based ones for the turbulent regime are based on out-dated or overly simplified models. The current work is intended to correct the latter two deficiencies. It does share two formidable problems with the earlier work. The first is the very large number of parameters. The second is the lack of a theoretical structure for correlation such as that provided for convection by the analogy between momentum, heat, and mass transfer.

## Simplifications and Idealizations

In order to confine the calculations within reasonable limits as well as to assist in their generalization, several simplifications and idealizations were made.

The primary simplification is the limitation to a single, first-order, equimolar, irreversible reaction. Such simple, isolated reactions occur physically although most important chemical processes involve multiple and coupled reactions, including reversible ones of different orders. The results for the idealized reaction mechanism of the current analysis should be interpreted as a necessary first step in terms of modeling, numerical calculations, and correlation. In addition, they can be expected to provide a guideline for interpretation of the effects of other variables. Attention is also limited to flow though a round tube, a process that is, however, one of the most common in practice.

The principal idealizations in the modeling itself consist of the postulates of invariant physical properties other than the effect of temperature on the reaction-rate constant, fully developed flow, and negligible diffusion in the direction of flow. The postulate of invariant density eliminates buoyancy and thereby natural convection, which may be significant with gases in horizontal tubes. It also avoids changes in the local velocity field, which are apt to be significant with gases in non-isothermal and/or non-equimolar flow. The postulates of invariant viscosity, thermal conductivity, and diffusivity are of lesser significance, and may be compensated for to some extent by the use of mean values. The postulate of invariant physical properties and the associated use of mean values are almost universal practices in fluid mechanics and transport in the interests of generalization as well as of simplification; the consideration of variable properties restricts the results to a particular fluid and reaction and effectively precludes a generalized correlation for all fluids and reactants. The condition of fully developed flow is only approached some distance from the inlet to the reactor, and that distance depends on the inlet configuration and the rate of flow. This idealization is also an almost universal one in thermal convection but its applicability to a tubular reactor depends critically upon the rate of reaction relative to the rate of flow. The postulate of negligible longitudinal diffusion of energy and species has been shown in many prior investigations of both convection and reaction to be a valid one for most practical purposes. In turbulent flow, the transient fluctuations in the components of the velocity and hereby in temperature and composition, affect the reaction-rate constant. However Glassman [8] has, on the basis of a semi-theoretical model, concluded that this effect is negligible except possibly for gas-phase reactions at very high temperature.

## Mathematical Models

**Laminar Flow.** For laminar flow and subject to the idealizations mentioned above, the equation of conservation for species *A* can be written in dimensionless form as follows:

$$\left(1-R^2\right)\frac{\partial Z}{\partial X}=\frac{\left(u_m/k_0a\right)}{\mathrm{Re}\,Sc}\frac{1}{R\partial R}\left[R\frac{\partial Z}{\partial R}\right]+\left(\frac{1-Z}{2}\right)e^{(E/\hat{R}T_0)\left(1-\frac{1}{\Phi}\right)} \qquad (1)$$

The associated expression for the conservation of energy is

$$\left(1-R^2\right)\frac{\partial \Phi}{\partial X}=\frac{\left(u_m/k_0a\right)}{\mathrm{Re}\,\mathrm{Pr}}\frac{1}{R\partial R}\left[R\frac{\partial \Phi}{\partial R}\right]+\left(\frac{q_r}{c_M T_0}\right)\left(\frac{1-Z}{2}\right)e^{\left(E/\hat{R}T_0\right)\left(1-\frac{1}{\Phi}\right)} \qquad (2)$$

(See the **Notation** for the definitions of the symbols in eqs.1 and 2.)

This particular choice of dimensionless variables and parameters is arbitrary and was chosen primarily for comparisons with previous computations in which diffusion of species *A* and energy were neglected. The dependence of the rate of reaction on temperature according to the Arrhenius equation is implicit in eqs.1 and 2.

The boundary conditions for eq.1 are $Z = 0$ at $X = 0$ and $\partial Z/\partial R = 0$ at $R = 0$ and $R = 1$. Those for eq.2 are $\Phi = 1$ at $X = 0$, $\partial\Phi/\partial R = 0$ at $R = 0$, and $\Phi = T_w/T_0$ (for an isothermal wall) or $\partial\Phi/\partial R = j_w a/kT_0$ (for a uniformly heated wall) at $R = 1$. These latter two thermal boundary conditions, although arbitrary., are almost universal ones in theoretical analyses for convection because of their simplicity and in practice because of their physical attainability. The same reasons apply for combined reaction and convection.

**Turbulent Flow.** Formulations for turbulent flow analogous to eqs.1 and 2 are

$$\frac{u^+}{2u_m^+}\frac{\partial Z}{\partial X} = \frac{(u_m/k_0 a)}{\mathrm{Re}\,Sc}\frac{\partial}{R\partial R}\left[R\left(1+\frac{Sc}{Sc_t}\left[\frac{\left(\overline{u'v'}\right)^{++}}{1-\left(\overline{u'v'}\right)^{++}}\right]\right)\frac{\partial Z}{\partial R}\right]+\left(\frac{1-Z}{2}\right)e^{(E/\hat{R}T_0)\left(1-\frac{1}{\Phi}\right)} \tag{3}$$

and

$$\frac{u^+}{2u_m^+}\frac{\partial \Phi}{\partial X} = \frac{(u_m/k_0 a)}{\mathrm{Re}\,\mathrm{Pr}}\frac{1}{R\partial R}\left[R\left(1+\frac{\mathrm{Pr}}{\mathrm{Pr}_t}\left[\frac{\left(\overline{u'v'}\right)^{++}}{1-\left(\overline{u'v'}\right)^{++}}\right]\right)\frac{\partial \Phi}{\partial R}\right]+\left(\frac{q_r}{c_M T_0}\right)\left(\frac{1-Z}{2}\right)e^{(E/\hat{R}T_0)\left(1-\frac{1}{\Phi}\right)} \tag{4}$$

The boundary conditions are unchanged but supplementary expressions for $\left(\overline{u'v'}\right)^{++}$, $u^+$, and $u_m^+$ are necessary. The expressions used herein are those devised by Churchill [9], namely

$$\left(\overline{u'v'}\right)^{++} = \left(\left[0.7\left(\frac{y^+}{10}\right)^3\right]^{-8/7} + \left|\exp\left\{\frac{-1}{0.436\,y^+}\right\} - \frac{1}{0.436\,a^+}\left(1+\frac{6.95\,y^+}{a^+}\right)\right|^{-8/7}\right)^{-7/8} \tag{5}$$

$$\frac{du^+}{dR^2} = \frac{a^+}{2}\left[1-\left(\overline{u'v'}\right)^{++}\right] \tag{6}$$

and

$$\frac{du_m^+}{dR^4} = \frac{a^+}{4}\left[1-\left(\overline{u'v'}\right)^{++}\right] \tag{7}$$

The boundary condition for eq. 6 is $u^+ = 0$ at $R = 1$, and for Eq. 7 is $u_m^+ = 0$ at $R = 0$. Equations 6 and 7 are independent of eqs.3 and 4 and can be solved numerically in advance. Furthermore, the theoretically based correlative equation

$$u_m^+ = 3.2 - \frac{227}{a^+} + \left(\frac{50}{a^+}\right)^2 + \frac{1}{0.436}\ln\{a^+\} \tag{8}$$

can be used to predict the computed values of $u_m^+ \equiv u(\rho/\tau_w)^{1/2}$ almost exactly, thereby precluding the necessity for numerical solution of eq. 7. $Re$ can be evaluated from eq. 8 for a specified value of $a^+ \equiv a(\rho\tau_w)^{1/2}/\mu$) by virtue of $Re = 2\,u_m^+ a^+$.

**Functional Representations.** Considerable insight can be gained from the above model simply by identifying the corresponding functional relationships The mixed-mean conversion and dimensionless temperature at any dimensionless distance $X = k_0 x/u_m$ are obtained by integrating the local values, weighted by the velocity distribution, over the cross-section. Only mixed-mean values, as designated by $Z_m$ and $\Phi_m$, are considered hereafter. The mixed-mean dimensionless temperature, $\Phi_m$ is usually replaced by its exact equivalent, $Nu$, which for uniform heating is equal to $2aj_w/\lambda(T_w-T_m) = 2aj_w/\lambda T_0(\Phi_w-\Phi_m)$, and for a uniform wall-temperature to $2(\partial T/\partial R)_{R=1}/(T_m-T_w) = 2(\partial\Phi/\partial R)_{R=1}/(\Phi_m-\Phi_w)$.

It follows from eqs. 1 and 2, together with the thermal boundary conditions, that in terms of the individual variables,

$$\frac{C_{Am}}{C_{A0}},\frac{T_m}{T_0}=\varphi\left\{\frac{k_0x}{u_m},\frac{k_0a^2}{D_f},\frac{au_m\rho}{\mu},\frac{c\mu}{\lambda},\frac{E}{\hat{R}T_0},\frac{q_r}{c_MT_0},\frac{j_wa}{\lambda T_0}\text{ or }\frac{T_w}{T_0}\right\} \tag{9}$$

or, in terms of named or herein-defined dimensionless variables,

$$Z_m, Nu=\varphi\left\{X,\frac{a/x}{ScRe},Re.,Pr,\frac{E}{\hat{R}T_0},Q,J\text{ or }\frac{T_w}{T_0}\right\} \tag{10}$$

The groupings $au_m\rho/\mu$ in eq.9 and $Re$ in eq.10 drop out for laminar flow; $j_wa/\lambda T_0$, and $T_w/T_0$ in eq. 9 and $J$ and $T_w/T_0$ in eq. 10 drop out for adiabatic flow; and $q_r/C_MT_0$ and $E/\hat{R}\,T_0$ in eq. 9 and $Q$ and $E/\hat{R}\,T_0$ in eq. 10 drop out as well for isothermal flow.

**Supplemental expressions.** Expressions such as the following for the turbulent Prandtl and Schmidt numbers and the reaction rate constant are arbitrary but essential components of the model:

$$Pr_t=0.85+\frac{0.015}{Pr} \tag{11}$$

$$Sc_t=0.85+\frac{0.015}{Sc} \tag{12}$$

and

$$k=k_\infty\exp\{\frac{-E}{\hat{R}T}\}=k_0\exp\{\frac{E}{\hat{R}T_0}\left(1-\frac{T_0}{T}\right)\} \tag{13}$$

Equations 11 and 12 are purely empirical but have been shown to provide generally reliable approximations for forced convection (see Churchill and Zajic[10]). They no not alter eqs.9 and10. The Arrhenius equation (the first two terms of eq.13) has a semi-theoretical basis and provides an excellent representation for most reactions. Its expression in terms of $k_0$ is convenient herein because of the use of isothermal reaction at the inlet temperature as a reference state. Equation 13, in terms of $T_0$, was incorporated implicitly in eqs. 1 – 4, and thereby is also accounted for in eqs. 9 and 10.

**Parametric Values for the Numerical Solutions**. For the calculations, one constant and one condition were arbitrarily fixed, namely: $k_\infty = 5.605 \times 10^8\ s^{-1}$ (here $k$ is in $s^{-1}$ and $T$ in K) and $T_0 = 300$ K. In addition, fixed numerical values were specified for four dimensionless groups, namely: $Pr = 0.7$, for which $Pr_t = 0.871$; $Sc = 0.2$, for which $Sc_t = 0.925$; $k_0\,a/u_m = 0.096$, and $E/\hat{R}\,T_0 = 17.815$, for which $E/\hat{R} = 5344.5$ K and $k_0 = 10.28\ s^{-1}$.

These choices are intended to be representative for gaseous reactions at moderate temperatures. In addition $Re$ was chosen as 400 for laminar flow and 37,640 for turbulent flow. The latter value corresponds to $a^+=1000$. This value of 1000 was chosen because it is the lower limit of almost exact predictions by eq. 8, although a lower value of say $a^+=200$ would be more representative of tubular chemical reactors in the turbulent regime.

These specifications leave only two parameters for which numerical values need to be chosen, namely $Q \equiv q_r/c_M\,T_0$, which is a measure of the thermicity of the reaction, that is the change in temperature due to the heat of reaction, and $T_w/T_0$ or $J \equiv j_wa/\lambda T_0$, which characterize external heating or cooling with a uniform wall temperature or a uniform heat flux density, respectively. Calculations were carried out for the following numerical values:

| | |
|---|---|
| $Q$ | 0, ±0.005, ± 0.01, and ± 0.05 |
| $T_w/T_0$ | 0.8, 0.9, 1.0, 1.1, and 1.2 |
| $J$ | 0, ± 0.01, ± 0.05, ± 0.10, ± 0.15, and ±0.20 for laminar flow |

$J$ 0, ± 5, and ± 10 for turbulent flow

The higher values of $J$ for the turbulent regime were required to perturb the conversion by the same order of magnitude as those for laminar regime because of the nearly 100 times greater rate of flow. (This expediency could have been avoided by specifying the numerical values of the uniform heat flux density at the wall in terms of a grouping such as $j_w x/au_m \rho c T_0$ that incorporates the mean velocity.)

## Numerical Calculations

The two-dimensional numerical integrations were carried out using a second-order, central-divided-difference scheme. They converged satisfactorily and the numerical error due to discretization and round-off is concluded to be insignificant.

Although results for heat transfer itself are not presented here, the close agreement of the computed Nusselt numbers for asymptotically large values of $X$ with the theoretical values for pure convection in the laminar regime and with the previously computed values of Churchill et al.[3] for pure convection in the turbulent regime is a further assurance of the accuracy of the numerical calculations, at least in a thermal sense.

## Numerical Results and Correlating Equations for Non-energetic Reactions

Presentation of the numerical results in their entirety, which encompass the radial distribution of the velocity, composition and temperature, is neither feasible nor essential. The challenge is instead to find efficient formats that reveal both qualitatively and quantitatively the diffusive and thermal effects of on the conversion.

Table 1
Computed Mixed-Mean Conversions for a First-order, Equimolar Irreversible Reaction in Fully Developed Isothermal Tubular Flow at $k_0 a/u_m = 0.096$ and $Sc = 0.2$
Laminar Flow at $Re = 400$, Turbulent Flow at Re = 37650

| $k_0 x/u_m$ | Laminar Flow No Diffusion | Laminar Flow with Diffusion | Turbulent Flow No Diffusion | Turbulent Flow with Diffusion | Perfect Radial Mixing |
|---|---|---|---|---|---|
| 0.00 | 0.00000 | 0.00000 | 0.00000 | 0.00000 | 0.00000 |
| 0.20 | 0.16742 | 0.17522 | 0.17996 | 0.18054 | 0.18127 |
| 0.40 | 0.29611 | 0.31663 | 0.32631 | 0.32783 | 0.32968 |
| 0.60 | 0.39992 | 0.43273 | 0.44585 | 0.44826 | 0.45119 |
| 0.80 | 0.48453 | 0.52868 | 0.54370 | 0.54686 | 0.55067 |
| 1.00 | 0.55679 | 0.60820 | 0.62391 | 0.62764 | 0.63212 |
| 2.00 | 0.78062 | 0.84421 | 0.85535 | 0.85980 | 0.86466 |
| 3.00 | 0.88652 | 0.93803 | 0.94352 | 0.94692 | 0.95021 |
| 4.00 | 0.93973 | 0.97535 | 0.97768 | 0.97984 | 0.98168 |
| 5.00 | 0.96741 | 0.99019 | 0.99110 | 0.99234 | 0.99326 |

Representative results for the effect of transport under isothermal conditions are shown in Table 1 in which the fractional mixed-mean conversion, $Z_m$, is tabulated as a function of $k_0 x/u_m$ for laminar and turbulent flow, with and without radial transport, as well as for perfect radial transport of composition and energy. (This latter terminology, which implies the physical existence of a limiting state as the diffusivity of species $A$ increases indefinitely, is used herein rather than “plug flow”, a condition that does not occur with real fluids for any condition and is not approached in turbulent flow as $Re$

increases.) In the interests of brevity, the tabulated values are limited to a few widely spaced values of $k_0x/u_m$. In this form, which can be interpreted as corresponding either to the increase in mixed-mean conversion with length for a fixed volumetric rate of flow or to the effect of flow for a reactor of fixed length, the effects of both the velocity distribution and transport appear to be barely significant, although they clearly demonstrate the progressive increase in conversion from laminar flow without diffusion to laminar flow with diffusion to turbulent flow without diffusion to turbulent flow with diffusion to perfect radial mixing. It is worth noting that the perturbation due to the turbulent velocity distribution is greater than that due to the combination of molecular and eddy diffusion of species *A*. In Figure 1, in which curves corresponding to these cases are plotted as $x/x_{mixed}$ versus $Z_m$, the differences are exaggerated relative to Table 1 and thereby easier to identify.

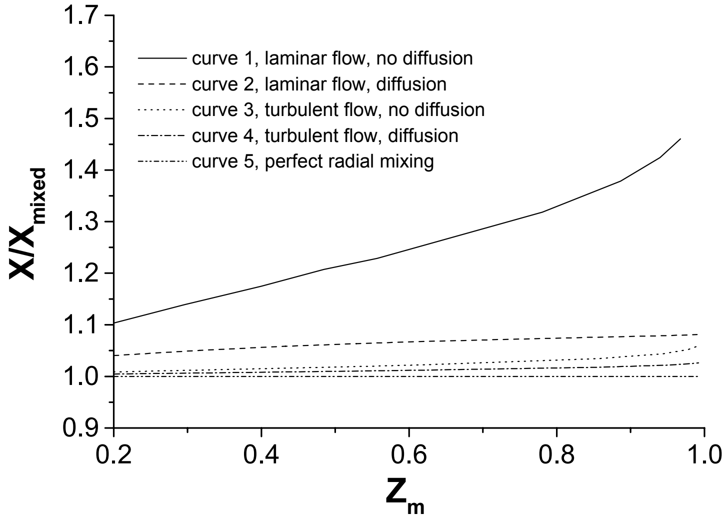

Figure 1. Effects of Velocity Distribution and Diffusion

The differences between the various curves in Figure 1 illustrate the effects of momentum and species transfer by molecular and eddy diffusion as follows:

a) The difference between Curves 1 and 2 represents the enhancement due to the radial molecular diffusion of species *A*.
b) The difference between Curves 1 and 3 represents the enhancement due to the turbulent velocity distribution relative to the laminar one, that is, due to momentum transfer by eddy diffusion.
c) The difference between Curves 2 and 4 represents the enhancement due to the eddy diffusion of both momentum and species *A*.
d) The difference between Curves 3 and 4 represents the enhancement due to the eddy diffusion of species *A*.
e) The difference between Curves 2 and 5 represents the false enhancement associated with the postulate of perfect radial mixing relative to laminar flow with molecular diffusion, but can also be interpreted as the possible enhancement with an asymptotically large molecular diffusivity.
f) The difference between Curves 4 and 5 represents the false enhancement associated with plug flow relative to turbulent flow at $a^+ = 1000$ but also the possible enhancement for an asymptotically large sum of the molecular and eddy diffusivities.

Curves for turbulent flow at lesser, and thereby more realistic values of $a^+$, would fall somewhat lower than Curves 2 and 4, that is, closer to the one for perfect radial mixing, but would never attain that limit. The results in Table 1 and Figure 1 are all in accordance with the assertion of Churchill[1] that solutions for laminar flow without molecular diffusion constitute a lower (conservative) bound for the conversion and those for perfect radial mixing an upper (non-conservative) bound. While the differences are modest, the ease of numerical solution of the relatively exact equations of conservation suggests that the direct use of either of the bounding solutions in design or analysis can no longer be justified.

**Representation of Dependence of $Z_m$ on $k_0x/u_m$ for Isothermal Conditions.** The values of $x/x_{mixed}$ in Table 2 reveal the relative invariance of this ratio over a moderate range of $k_0x/u_m$ and $Z_m$ for both laminar and turbulent flow. This observation suggests that the theoretical dependence of the mixed-mean conversion, $Z_m$, on $k_0x/u_m$ for complete radial mixing in isothermal flow, namely

$$Z_m = 1 - exp\{- k_0x/u_m\} \qquad (14)$$

might, with the incorporation of an arbitrary constant, serve as a structural form for an expression for isothermal laminar flow with a finite diffusivity. It should be noted that the subscript denoting the mixed-mean in eq.14 and all subsequent expressions for the limiting asymptotic condition of perfect radial mixing is redundant because the conversion does not then vary with radius. It is, however, included here and throughout for consistency with expressions for a finite degree of radial mixing. One such possible modification of eq.14 for a finite degree of radial mixing is

$$Z_m = 1 - exp\{- \alpha k_0x/u_m\} \qquad (15)$$

where $\alpha$ is an arbitrary coefficient. A value of $\alpha = 0.937$ produces the predictions for laminar flow in Table 2, which are very accurate for fractional conversions of 0.3 or greater, and sufficiently accurate for most practical purposes even for lower conversions. The corresponding value of $\alpha$ for turbulent flow at $a^+ = 1000$ is 0.988, and the corresponding predictions may be seen in Table 2 to be very accurate, even for low conversions. In view of the close correspondence of the computed and predicted values of the conversion for turbulent flow at $a^+ = 1000$ and for laminar flow, the value of 0.988 for the arbitrary coefficient $\alpha$ for $a^+ = 1000$ might be expected to be applicable for all values of $a^+$ in the turbulent regime. It may be noted in passing that for finite radial mixing the values of $x/x_{mixed}$ in Table 2 increase monotonically with $k_0x/u_m$ for both laminar and turbulent flow with finite radial mixing just as they did for they did for no radial mixing (see Churchill[1], Figures1and 2), but the increases and the differences between laminar and turbulent flow with diffusion are much less

Table 2
Predictions by Equation 15 of Mixed-Mean Conversion in Isothermal Flow with Diffusion
(Same general conditions as for Table 1)

| $k_\infty x/u_m$ | $Z_{m,laminar}$ Computed | $x_{\text{lam}}/ x_{\text{mixed}}$ Computed | $Z_{m,laminar}$ Predicted | $Z_{m,,\text{turbulent}}$ Computed | $x_{turb}/x_{mixed}$ Computed | $Z_{m,,\text{turbulent}}$ Predicted |
|---|---|---|---|---|---|---|
| 0.1 | 0.09266. | 1.02840 | 0.08944 | 0.09489 | 1.00302 | 0.09408 |
| 0.2 | 0.17522 | 1.03821 | 0.17089 | 0.18054 | 1.00447 | 0.17930 |
| 0.3 | 0.24950 | 1.04524 | 0.24505 | 0.25790 | 1.00580 | 0.25651 |
| 0.4 | 0.31663 | 1.05064 | 0.31257 | 0.32783 | 1.00694 | 0.32945 |
| 0.5 | 0.37748 | 1.05490 | 0.37406 | 0.39106 | 1.00799 | 0.38982 |
| 0.6 | 0.43273 | 1.05835 | 0.43004 | 0.44826 | 1.00895 | 0.44722 |
| 0.7 | 0.48297 | 1.06116 | 0.48103 | 0.50002 | 1.00983 | 0.49923 |
| 0.8 | 0.52868 | 1.06352 | 0.52744 | 0.54686 | 1.01067 | 0.54634 |
| 0.9 | 0.57030 | 1.06551 | 0.56971 | 0.58926 | 1.01147 | 0.58902 |
| 1.0 | 0.60820 | 1.06723 | 0.60820 | 0.62764 | 1.01225 | 0.62767 |
| 2.0 | 0.84421 | 1.07570 | 0.84649 | 0.85980 | 1.01797 | 0.86138 |
| 3.0 | 0.93803 | 1.07871 | 0.93986 | 0.94623 | 1.02633 | 0.94840 |
| 4.0 | 0.97535 | 1.08021 | 0.97644 | 0.97985 | 1.02445 | 0.98078 |
| 5.0 | 0.99019 | 1.08123 | 0.99077 | 0.99234 | 1.02633 | 0.99285 |

## Numerical and Predicted Results for Energetic Reactions in Adiabatic Flow

As a first-order approximation for the effect of the heat of reaction, the following, arbitrary linear perturbation of $Z_{m0}$, the mixed-mean conversion for a non-energetic reaction, was tested:

$$Z_m = Z_{m0} + \beta Z_m Q \tag{16}$$

For convenience, eq.16 can be rearranged as

$$Z_m = Z_{m0}/(1-\beta Q) \tag{16A}$$

Combining eq.15 with eq. 16A results in

$$Z_m = [1- exp\{- \alpha k_0x/u_m\}]/(1-\beta Q) \tag{17}$$

Based on the computed values for $Z_m$ at $k_0x/u_m$ =1, the arithmetic average of the values of $\beta$ *for* $Q$ = 0.05 and -.05 is 3.956 for laminar flow and 3.73 for turbulent flow at $a^+$ = 1000
Values predicted by eq. 17 with these values of $\beta$ are compared with the numerically computed values for $Q$ = 0.01, - 0.01, 0.05 and - 0.05 in Tables 3 – 6, respectively. The accuracy of the predictions is very good for $Q$ = ± 0.01 and perhaps acceptable for intermediate conversions for $Q$ = ± 0.05. This degree of agreement is somewhat surprising in that the nonlinearity of the dependence of the rate constant on temperature is not taken into account in eqs.16 and 17. A possible explanation for this relative success is the linearity of an exponential expression in the limit of a small argument. Although eq.17 would be expected to fail seriously for larger values of $Q$, most practical applications presumably involve small values such as those tested here. The presence of $k_0$ in an expression for an energetic reaction is an artifact of the incorporation of eq.15 in eq.17. (The computed and predicted values of $Z_m$ for $Q$ = ± 0.005 are not reproduced here because their accuracy, as might be expected, is even better than that for $Q$ = ± 0.01.)

An alternative expression for the prediction of the conversion for an energetic reaction carried out adiabatically can be derived by scaling the following solution derived by Churchill[1] for perfect radial mixing and an absolute value of $Z_m\psi$ much less than unity:

$$Z_m = \frac{1-\exp\{-(1+\psi)k_0x/u_m)\}}{1+\psi\exp\{-(1+\psi)k_0x/u_m\}} \tag{18}$$

Here $\psi \equiv ECq_r/c_M RT_0^2$ . Again, as discussed in connection with eq.14, the subscript designating the mixed-mean is redundant in eq.18. The ratio of the conversion, $Z_{mQ}$, for an energetic reaction to that for a non-energetic one, $Z_{m0}$, both with perfect radial mixing, is then

$$\frac{Z_{mQ}}{Z_{m0}} = \frac{1-\exp\{-(1+\psi)k_0x/u_m)\}}{[1+\psi\exp\{-(1+\psi)k_0x/u_m\}][1-\exp\{-k_0x/u_m\}]} \tag{19}$$

Applying the scaling of eq. 19 to a reaction with finite radial mixing, as represented by eq. 15, then results in

$$\frac{Z_{mQ}}{Z_{m0}} = \frac{[1-\exp\{-(1+\psi)k_0x/u_m\}][1-\exp\{-\alpha k_0x/u_m\}]}{[1+\psi\exp\{-(1+\psi)k_0x/u_m\}][1-\exp\{-k_0x/u_m\}]} \tag{20}$$

The appearance of the rate constant $k_0$ for isothermal conditions in eq. 20, which is proposed for adiabatic conditions, might be perceived as an anomaly, but it is merely a consequence of the asymptotic approximations by means of which eq.18 was derived. Equation 20 might be presumed to have an advantage over eq. 17 by virtue of the direct dependence on temperature inherent in eq.18, but this presumption might be countervailed by the limitation in the validity of eq.18 to absolute values of $Z_m\ \psi$ << 1.0, a restriction that is exceeded even for $Q$_= ± 0.01 as $Z_m \rightarrow 1.0$ for the chosen parametric condition of $E/\hat{R}\ T_0$ = 17..815.

These several presumptions are tested by the inclusion of the predictions of eq.20 in Tables 3 – 6. Inspection of the values in these tables reveals that eq. 20 provides more accurate predictions than eq.17 for some values of $Q$ and $k_0x/u_m$ and poorer ones for others. Unfortunately, their respective regimes of greatest inaccuracy are almost the same. Equation 17 has one clear advantage, namely of simplicity

Table 3. Comparison of Predictions by Equations 17 and 20 of Mixed-mean Conversion in Adiabatic Flow with Thermicity $Q = q_r/c_M T_0 = 0.01$
(Same general conditions as in Table 1)

.

| $k_0x/u_m$ | $Z_{\mathrm{m,laminar}}$ Computed | $Z_{\mathrm{m,laminar}}$ Eq (17) | $Z_{\mathrm{m,laminar}}$ Eq. (20) | $Z_{\mathrm{m,turbulent}}$ Computed | $Z_{\mathrm{m,turbulent}}$ Eq. (17) | $Z_{\mathrm{m,turbulent}}$ Eq. (20) |
|---|---|---|---|---|---|---|
| 0.00 | 0.00000 | 0.00000 | 0.00000 | 0.00000 | 0.00000 | 0.00000 |
| 0.10 | 0.09374 | 0.09314 | 0.09018 | 0.09571 | 0.09772 | 0.09485 |
| 0.20 | 0.17868 | 0.17794 | 0.17349 | 0.18337 | 0.18525 | 0.18203 |
| 0.30 | 0.25598 | 0.25516 | 0.25020 | 0.26349 | 0.26645 | 0.26190 |
| 0.40 | 0.32628 | 0.32548 | 0.32063 | 0.33652 | 0.33910 | 0.33487 |
| 0.50 | 0.39050 | 0.38950 | 0.38513 | 0.40296 | 0.40492 | 0.40135 |
| 0.60 | 0.44879 | 0.44780 | 0.44406 | 0.46328 | 0.46455 | 0.46180 |
| 0.70 | 0.50198 | 0.50088 | 0.49778 | 0.51792 | 0.51857 | 0.51662 |
| 0.80 | 0.55024 | 0.54922 | 0.54666 | 0.56736 | 0.56750 | 0.55625 |
| 0.90 | 0.59406 | 0.59323 | 0.59107 | 0.61201 | 0.61184 | 0.61109 |
| 1.00 | 0.63381 | 0.63309 | 0.63133 | 0.65227 | 0.65200 | 0.65155 |
| 2.00 | 0.87224 | 0.88144 | 0.87149 | 0.88650 | 0.89475 | 0.88682 |
| 3.00 | 0.95638 | 0.97866 | 0.95528 | 0.96369 | 0.98513 | 0.96395 |

Table 4
(Same conditions as in Table 3 except for $Q = q_r/c_M T_0 = -0.01$)

| $k_0x/u_m$ | $Z_{m\ laminar}$ Computed | $Z_{m,laminar}$ Eq. (17) | $Z_{m,laminar}$ Eq. (20) | $Z_{m,turbulent}$ Computed | $Z_{m,\ turbulent}$ Eq. (17) | $Z_{m,turbulent}$ Eq. (20) |
|---|---|---|---|---|---|---|
| 0.00 | 0.00000 | 0.00000 | 0.00000 | 0.00000 | 0.00000 | 0.00000 |
| 0.10 | 0.09162 | 0.08623 | 0.08871 | 0.09410 | 0.09069 | 0.09331 |
| 0.20 | 0.17195 | 0.16474 | 0.16833 | 0.17781 | 0.17285 | 0.17662 |
| 0.30 | 0.24346 | 0.23624 | 0.24001 | 0.25260 | 0.24729 | 0.25124 |
| 0.40 | 0.30763 | 0.30133 | 0.30471 | 0.31966 | 0.31472 | 0.31824 |
| 0.50 | 0.36555 | 0.36060 | 0.36324 | 0.37994 | 0.37580 | 0.37855 |
| 0.60 | 0.41791 | 0.41458 | 0.41633 | 0.43429 | 0.43114 | 0.43296 |
| 0.70 | 0.46551 | 0.46373 | 0.46456 | 0.48337 | 0.48127 | 0.48214 |
| 0.80 | 0.50884 | 0.50848 | 0.50846 | 0.52780 | 0.52669 | 0.52667 |
| 0.90 | 0.54836 | 0.54922 | 0.54847 | 0.56807 | 0.56784 | 0.56705 |
| 1.00 | 0.58445 | 0.58633 | 0.58499 | 0.60463 | 0.60510 | 0.60375 |
| 2.00 | 0.81559 | 0.81605 | 0.81794 | 0.83239 | 0.83040 | 0.83223 |
| 3.00 | 0.91654 | 0.90606 | 0.91897 | 0.92702 | 0.91429 | 0.92732 |

Table 5
(Same conditions as in Table 3 except for $Q = q_r/c_M T_0 = 0.05$)

| $k_0x/u_m$ | $Z_{m,laminar}$ Computed | $Z_{m,laminar}$ Eq. (17) | $Z_{m,laminar}$ Eq. (20) | $Z_{m,turbulent}$ Computed | $Z_{m,turbulent}$ Eq. (17) | $Z_{m,turbulent}$ Eq. (20) |
|---|---|---|---|---|---|---|
| 0.00 | 0.00000 | 0.00000 | 0.00000 | 0.00000 | 0.00000 | 0.00000 |
| 0.10 | 0.09857 | 0.11150 | 0.14273 | 0.09915 | 0.11564 | 0.15012 |
| 0.20 | 0.19507 | 0.21302 | 0.26166 | 0.19596 | 0.22041 | 0.27454 |
| 0.30 | 0.28782 | 0.30547 | 0.36078 | 0.28917 | 0.31532 | 0.37766 |
| 0.40 | 0.37533 | 0.38964 | 0.44344 | 0.37761 | 0.40129 | 0.46313 |
| 0.50 | 0.45648 | 0.46629 | 0.51240 | 0.46021 | 0.47919 | 0.53399 |
| 0.60 | 0.53051 | 0.56308 | 0.56997 | 0.53618 | 0.54975 | 0.59274 |
| 0.70 | 0.59708 | 0.59963 | 0.61806 | 0.60495 | 0.61368 | 0.64145 |
| 0.80 | 0.65619 | 0.65750 | 0.65826 | 0.66628 | 0.67159 | 0.68184 |
| 0.90 | 0.70812 | 0.71019 | 0.69191 | 0.72020 | 0.72405 | 0.71534 |
| 1.00 | 0.75330 | 0.75816 | 0.72008 | 0.77698 | 0.77158 | 0.74315 |
| 2.00 | 0.96058 | 1.05521 | 0.84328 | 0.97002 | 1.05899 | 0.85811 |
| 3.00 | 0.99439 | 1.17160 | 0.86886 | 0.99661 | 1.16581 | 0.87675 |

Table 6
(Same conditions as in Table 3 except for $Q = q_r/c_M T_0 = -0.05$)

| $k_\infty x/u_m$ | $Z_{m,laminar}$ Computed | $Z_{\mathrm{m,laminar}}$ Eq.(17) | $Z_{\mathrm{m,laminar}}$ Eq. (20) | $Z_m$ turbulent Computed | $Z_m$ turbulent Eq. (17) | $Z_m$ turbulent Eq. (20) |
|---|---|---|---|---|---|---|
| 0.00 | 0.00000 | 0.00000 | 0.00000 | 0.00000 | 0.00000 | 0.00000 |
| 0.10 | 0.08783 | 0.07467 | 0.08587 | 0.09108 | 0.07929 | 0.09032 |
| 0.20 | 0.16051 | 0.14266 | 0.15856 | 0.16784 | 0.15112 | 0.16637 |
| 0.30 | 0.22287 | 0.20458 | 0.22095 | 0.23379 | 0.21619 | 0.23129 |
| 0.40 | 0.27741 | 0.26096 | 0.27515 | 0.29124 | 0.27514 | 0.28737 |
| 0.50 | 0.32576 | 0.31228 | 0.32271 | 0.34187 | 0.32855 | 0.33631 |
| 0.60 | 0.36904 | 0.35903 | 0.36482 | 0.38690 | 0.37693 | 0.37939 |
| 0.70 | 0.40808 | 0.40159 | 0.40239 | 0.42726 | 0.42076 | 0.41761 |
| 0.80 | 0.44353 | 0.44034 | 0.43613 | 0.46366 | 0.46046 | 0.45175 |
| 0.90 | 0.47590 | 0.47563 | 0.46663 | 0.49670 | 0.49643 | 0.48244 |
| 1.00 | 0.50557 | 0.50776 | 0.49433 | 0.52681 | 0.52902 | 0.51017 |
| 2.00 | 0.70673 | 0.70671 | 0.67639 | 0.72636 | 0.72598 | 0.68829 |
| 3.00 | 0.81475 | 0.78465 | 0.77172 | 0.83004 | 0.79932 | 0.77872 |
| 4.00 | 0.87921 | 0.81519 | 0.82933 | 0.89062 | 0.82662 | 0.83302 |
| 5.00 | 0.91979 | 0.82715 | 0.86714 | 0.92817 | 0.83678 | 0.86896 |

A third alternative is the following inverse relationship derived by Churchill et al.[3] for energetic reactions with compete radial mixing, again for absolute values of $\psi Z_m << 1.0$:

$$\frac{x}{x_0} = (1-\psi Z)_{im} \cong 1-\psi Z_{im} \cong 1-\gamma\psi Z_m \qquad (21)$$

Here, $x_0$ is the length of a reactor required for the same conversion at the initial temperature, and the subscript *im* designates the use of an integrated-mean of an integral form of the differential balance of the mixed-mean conversion with respect to the axial distance through the reactor. The term $\gamma Z_m$ in the rightmost term of eq. 21 constitutes an approximation for $Z_{im}$. For example, an arithmetic mean of the conversion at the inlet and at length $x$ would yield a value of 0.5 for the coefficient $\gamma$. Test calculations by Churchill et al.[3] for $Z_m = 0.7$ for perfect radial mixing revealed that for these idealized condition the coefficient $\gamma$ was a function only of $\psi$, and furthermore the same function for all conditions, including second-order as well as first-order reactions and for both laminar and turbulent flow with no radial mixing This suggests determining a value of $\gamma$ from the computed values of $x/x_0$ for a series of values of $Z_m$ and $Q$ and thereby of $\psi$ for laminar and turbulent flow with finite radial transport. Such a set of values of $x/x_0$ is listed in Table 7 and the corresponding values of $\gamma$ in Table 8.

Table 7
Computed Values of $x/x_0$ for Adiabatic Reaction with $E/RT_0 = 17.815$
and Fixed Values of $Z_m$ and $Q$
(Same general conditions as in Table 1)

Laminar

| $Z_m/Q$ | A<br>0 | B<br>0.005 | C<br>-0.005 | D<br>0.01 | E<br>-0.01 | F<br>0.05 | G<br>-0.05 |
|---|---|---|---|---|---|---|---|
| 0.30 | 0.37439 | 0.36777 | 0.38102 | 0.36143 | 0.38764 | 0.31363 | 0.44525 |
| 0.40 | 0.53971 | 0.52761 | 0.55209 | 0.51580 | 0.56476 | 0.42950 | 0.67853 |
| 0.50 | 0.73612 | 0.71567 | 0.75715 | 0.69609 | 0.77903 | 0.55756 | 0.98093 |
| 0.60 | 0.97775 | 0.94550 | 1.01116 | 0.91439 | 1.04630 | 0.70473 | 1.38499 |
| 0.70 | 1.28937 | 1.23983 | 1.34179 | 1.19231 | 1.39679 | 0.88358 | 1.95379 |
| 0.80 | 1.72886 | 1.65110 | 1.81151 | 1.57823 | 1.89907 | 1.12175 | 2.82787 |
| 0.90 | 2.48111 | 2.35094 | 2.62051 | 2.22883 | 2.77113 | 1.50652 | 4.45766 |

Turbulent

| $Z_m/Q$ | A<br>0 | B<br>0.005 | C<br>-0.005 | D<br>0.01 | E<br>-0.01 | F<br>-0.01 | G<br>-0.05 |
|---|---|---|---|---|---|---|---|
| 0.30 | 0.35914 | 0.35395 | 0.36432 | 0.34877 | 0.36950 | 0.31190 | 0.41645 |
| 0.40 | 0.51494 | 0.50515 | 0.52531 | 0.49536 | 0.53568 | 0.53568 | 0.63129 |
| 0.50 | 0.70013 | 0.68285 | 0.71798 | 0.66614 | 0.73613 | 0.73613 | 0.91029 |
| 0.60 | 0.92707 | 0.89914 | 0.95645 | 0.87206 | 0.98697 | 0.98697 | 1.28649 |
| 0.70 | 1.22026 | 1.17590 | 1.26720 | 1.13414 | 1.31673 | 1.31673 | 1.81958 |
| 0.80 | 1.63526 | 1.56470 | 1.71043 | 1.49817 | 1.79021 | 1.79021 | 2.64758 |
| 0.90 | 2.34749 | 2.22566 | 12.4788 | 2.11161 | 2.61907 | 2.61907 | 4.21113 |

| Code: | A | B | C | D | E | F | G |
|---|---|---|---|---|---|---|---|
| $Q$ | 0 | 0.01 | -0.01 | 0.05 | -0.05 | 0.005 | - 0.005 |
| $\Psi$ | 0 | 0.17815 | 0.17815 | 0.89075 | -.089075 | 0.089075 | -0.089075 |

Although invariance of $\gamma$ is not observed with respect to $\psi$, $Z_m$, or the rate of flow, the variations are limited and have some regularity. For example, the values of $\gamma$ increase monotonically as cooling decreases and heating increases for each particular mixed-mean conversion. In both laminar and turbulent flow, the value of $\gamma$ increases monotonically with the mixed-mean conversion for $Q$ = -0.005, -0.01, and -0.05 in the turbulent regime, increases monotonically for $Q$ = - 0.05, and decreases monotonically. This less constrained behavior than that for no mixing and for perfect mixing may be attributed to the relatively large values of $\psi Z_m$.. Only the values for $Q = \pm 0.\ 005$ conform to $|\psi Z_m| << 1.0$ for all values of $Z_m$. The small deviations between $\gamma$ for $Q = 0.005$ and $-0.005$ can be attributed to the approximation of $e^{-\psi Z_m}$ by $1 - \psi Z_m$ and/or by $1/(1 + \psi Z_m)$ in the derivation of eq. 21. The greater differences with respect to flow in Table 8 relative to Tables 6 – 8 of Churchill et al.[3] can probably be attributed to turbulent transport of energy and species *A*. On the basis of the prior calculations for negligible or perfect mixing, the values of $\gamma$ in Table 8 are presumed to be relatively invariant with respect to $E/\hat{R}\,T_0$, *Q,* the degree of radial mixing, and possibly to the order of the reaction for the same value of $\psi$,. It follows that eq. 21 can be used to predict values of $x/x_0$, not only for the values of $\psi$ and $Z_m$ of Table 8, but also by interpolation for other values and conditions as well. In that sense, eq 21 is superior to eqs.17 and 20 as a predictive expression for adiabatic flow. However, it should be noted to be less convenient in that it is explicit in $Z_m$ whereas Eqs. 17 and 20 are explicit in $k_0x/u_m$. Also, the tests of eq. 21 in Tables 10 and 11 are limited arbitrarily to $k_0x/u_m = 1.0$.

Table 8
Computed Values of Coefficient $\gamma$ for Equation 21
$E/RT_0 = 17.815$
(Same general conditions as for Table 1)

| | Q | 0.005 | 0.01 | 0.05 | -0.005 | -0.01 | -0.05 |
|---|---|---|---|---|---|---|---|
| Flow | $Z_m/\Psi$ | 0.089075 | 0.17815 | 0.89075 | - 0.089075 | - 0.17815 | - 0.89075 |
| | | | | | | | |
| Laminar | 0.3 | 0.6621 | 0.6477 | 0.6074 | 0.6621 | 0.6621 | 0.7081 |
| | 0.4 | 0.6290 | 0.6216 | 0.5731 | 0.6440 | 0.6615 | 0.7218 |
| | 0.5 | 0.6237 | 0.6105 | 0.5446 | 0.6413 | 0.6544 | 0.7467 |
| | 0.6 | 0.6176 | 0.6064 | 0.5225 | 0.6390 | 0.6557 | 0.7777 |
| | 0.7 | 0.6165 | 0.6036 | 0.5047 | 0.6520 | 0.6679 | 0.8264 |
| | 0.8 | 0.6312 | 0.6113 | 0.4928 | 0.6709 | 0.6908 | 0.8921 |
| | 0.9 | 0.6545 | 0.6342 | 0.4900 | 0.7007 | 0.7290 | 0.9937 |
| | | | | | | | |
| Turbulent | 0.3 | 0.5402 | 0.5402 | 0.4921 | 0.5402 | 0.5402 | 0.5402 |
| ( $a^+$=1000) | 0.4 | 0.5337 | 0.5337 | 0.4824 | 0.5651 | 0.5651 | 0.6342 |
| | 0.5 | 0.5539 | 0.5448 | 0.4775 | 0.5730 | 0.5774 | 0.6752 |
| | 0.6 | 0.5638 | 0.5551 | 0.4737 | 0.5929 | 0.6045 | 0.7254 |
| | 0.7 | 0.5829 | 0.5659 | 0.4724 | 0.6170 | 0.6340 | 0.7877 |
| | 0.8 | 0.6055 | 0.5882 | 0.4758 | 0.6451 | 0.6646 | 0.8687 |
| | 0.9 | 0.6473 | 0.6267 | 0.4877 | 0.6978 | 0.7216 | 0.9903 |

## Numerical and Predicted Results for Uniform Heating

Heating or cooling of the wall of a reactor influences the local rate of reaction and thereby the conversion by virtue of the resulting perturbation of the radial and longitudinal temperature distributions and in turn the local values of the rate constant. Such effects obviously depend on the thermicity, *Q*, of the reaction. In the absence of an overall theoretical solutions for this behavior, an additive perturbation of the conversion for an adiabatic reaction was postulated. Based on eq. 17 for an adiabatic reaction, this expression becomes:

$$Z_m = [1 - exp\{-\alpha k_0 x/u_m\}]/(1-\beta Q) + \sigma J \qquad (22)$$

For moderate values of *J*, as defined by the resulting perturbation of the conversion, values of 0.710 and 0.00585 were determined for the coefficient $\sigma$ for laminar flow at $Re = 400$ and turbulent flow at $a^+ =$

1000 ($Re = 37640$), respectively. The predictions of eq. 22 are compared with numerically computed values for $k_0x/u_m = 1.0$ in Tables 9 and 10. The agreement is almost perfect for $Q = 0$ for all of the values of $J$ and for $J = 0$ for all of the values of $Q$. The agreement is also very good for non-zero values of $Q$ and $J$. The trends in the conversion with $Q$ and $J$ conform to expectations. Similar agreement to that shown in Tables 9 and 10 was found for other values of $k_0x/u$ in the range of 0.4 to 3.0. On the basis of qualitative reasoning it is suggested that eq. 22 be generalized for other rates of flow by replacing $\sigma$ in eq. 22 by $\eta/Re$, thereby obtaining

$$Z_m = [1- exp\{- \alpha k_0x/u_m\}]/(1-\beta Q) + \eta J/Re \qquad (23)$$

The corresponding value of $\eta$ for laminar flow at $Re = 400$ is 0.710(400) = 284, and that for turbulent flow at $a^+ = 1000$ is 0.00585(37640) = 220. The near equality of $\eta$ for rates of flow differing by an order of magnitude is supportive of this concept of generalization

Table 9
Computed Values and Predictions by Equation 22 of the Mixed-mean Conversion for Representative Values of the Uniform Heat Flux Density, $J = j_wa/\lambda T_0$, and the Thermicity, $Q = q_r/c_MT_0$, at $k_0x/u_m = 1.0$ in Laminar Flow
(Same general conditions as for Table 1)

| | *J/Q* | -0.05 | -0.01 | 0 | 0.01 | 0.05 |
|---|---|---|---|---|---|---|
| Calculated | -0.10 | | | 0.53993 | 0.56188 | 0.67100 |
| Predicted | -0.10 | | | 0.53720 | 0.56225 | 0.68716 |
| Calculated | -0.05 | | | 0.57304 | 0.59693 | 0.71317 |
| Predicted | -0.05 | | | 0.57270 | 0.59775 | 0.72266 |
| Calculated | 0.0 | 0.50557 | 0.58445 | 0.60820 | 0.63381 | 0.75330 |
| Predicted | 0.0 | 0.50776 | 0.58505 | 0.60820 | 0.63325 | 0.75816 |
| Calculated | 0.05 | 0.53453 | 0.61921 | 0.64434 | | |
| Predicted | 0.05 | 0.54325 | 0.62055 | 0.64370 | | |
| Calculated | 0.10 | 0.56474 | 0.65419 | 0.68007 | | |
| Predicted | 0.10 | 0.57876 | 0.65605 | 0.67920 | | |

Table 10
(Same general conditions as for Table 9 except flow is turbulent)

| | *J/Q* | -0.05 | -0.01 | 0 | 0.01 | 0.05 |
|---|---|---|---|---|---|---|
| Calculated | -10.0 | | | 0.57610 | 0.59860 | 0.70718 |
| Predicted | -10.0 | | | 0.56918 | 0.59349 | 0.71307 |
| Calculated | - 5.0 | | | 0.59936 | 0.62296 | 0.73561 |
| Predicted | -5.0 | | | 0.59843 | 0.62275 | 0.74232 |
| Calculated | 0.0 | 0.52685 | 0.60463 | 0.62764 | 0.65227 | 0.76698 |
| Predicted | 0.0 | 0.52902 | 0.60510 | 0.62768 | 0.65200 | 0.77157 |
| Calculated | 5.0 | 0.55339 | 0.63560 | 0.65916 | | |
| Predicted | 5.0 | 0.55827 | 0.63436 | 0.65693 | | |
| Calculated | 10.0 | 0.58333 | 0.66459 | 0.68747 | | |
| Predicted | 10.0 | 0.58752 | 0.66361 | 0.68618 | | |

## Numerical and Predicted Results for Uniform Wall-Temperature

A uniform wall-temperature perturbs the radial and longitudinal temperature distributions within the fluid and thereby the conversion just as does uniform heating but the reference condition is that for isothermal flow with $T_w = T_0$ rather than that for adiabatic flow. The following expression was postulated for this behavior:

$$Z_m = Z_{T_0} + \xi Q Z_m \qquad (24)$$

which may be rearranged for convenience as

$$Z_m = Z_{T_0} / (1 - \xi Q) \qquad (24A)$$

From the numerically computed conversions for $k_0x/u_m = 1$, mean values of 2.189 and 3.538 for $\xi$ were determined for laminar and turbulent flow, respectively. A high degree of success for the predictions of eq. 24A is demonstrated in Tables 11 and 12 in the column for $T_w/T_0 = 1$.

Table 11
Computed Values and Predictions by Equation 25 of the Mixed-mean Conversion for Representative Values of the Temperature Ratio $T_w / T_0$ and the Thermicity, $Q = q_r/c_MT_0$, at $k_0x/u_m = 1.0$ in Laminar Flow

(Same general conditions as for Table 1)

| | $Q/(T_w/T_0)$ | 0.8 | 0.9 | 1.0 | 1.1 | 1.2 |
|---|---|---|---|---|---|---|
| Calculated | 0.05 | 0.38004 | 0.49266 | 0.68471 | | |
| Predicted | 0.05 | 0.40344 | 0.48530 | 0.68295 | | |
| Calculated | 0.01 | 0.33830 | 0.43913 | 0.62189 | | |
| Predicted | 0.01 | 0.33744 | 0.41930 | 0.62181 | | |
| Calculated | 0.00 | 0.32955 | 0.42789 | 0.60820 | | |
| Predicted | 0.00 | 0.32869 | 0.41506 | 0.60820 | 0.80584 | 0.88771 |
| Calculated | -0.01 | | | 0.59522 | 0.77970 | 0.86883 |
| Predicted | -0.01 | | | 0.59517 | 0.79281 | 0.87468 |
| Calculated | -0.05 | | | 0.54942 | 0.74144 | 0.84524 |
| Predicted | -0.05 | | | 0.54831 | 0.74595 | 0.82782 |

Table 12
(Same conditions as for Table 11 except for turbulent flow)

| | $Q/(T_w/T_0)$ | 0.8 | 0.9 | 1.0 | 1.1 | 1.2 |
|---|---|---|---|---|---|---|
| Calculated | 0.05 | 0.69370 | 0.72495 | 0.75887 | | |
| Predicted | 0.05 | 0.69493 | 0.72873 | 0.76253 | | |
| Calculated | 0.01 | 0.58969 | 0.61752 | 0.65706 | | |
| Predicted | 0.01 | 0.58306 | 0.61686 | 0.65066 | | |
| Calculated | 0.00 | 0.56813 | 0.59501 | 0.62764 | 0.66343 | 0.69466 |
| Predicted | 0.00 | 0.56008 | 0.59388 | 0.62768 | 0.66148 | 0.70528 |
| Calculated | -0.01 | | | 0.60601 | 0.64195 | 0.67421 |
| Predicted | -0.01 | | | 0.60619 | 0.63999 | 0.67379 |
| Calculated | -0.05 | | | 0.53249 | 0.56788 | 0.60270 |
| Predicted | -0.05 | | | 0.53330 | 0.56710 | 0.60090 |

In the absence of any theoretical solutions, the perturbation in laminar flow at $Re = 400$ was found by trial and error to be proportional to $\left|\frac{T_w - T_0}{T_0}\right|^{1/2}$, leading to

$$Z_m = \frac{Z_{mT0}}{(1-\xi Q)} + \frac{\chi(T_w - T_0)}{|T_0(T_w - T_0)|^{1/2}} \tag{25}$$

The rightmost term of eq. (25) was devised to yield the correct sign. A mean value of 0.625 for the arbitrary coefficient, $\chi$, was determined from the numerically computed conversions for $k_0x/u_m = 1$. The resulting predictions in Table 11 are in fair agreement with the computed values. On the other hand for turbulent flow at $a^+ = 1000$ ($Re = 37640$), the perturbation in the conversion for $T_w \neq T_0$ was found to be proportional to $(T_w - T_0)/T_0$ rather than its square-root, leading to

$$Z_m = \frac{Z_{mT}}{(1-\xi Q)} + \varepsilon\left(\frac{T_w - T_0}{T_0}\right) \tag{26}$$

A mean value of 0.338 was determined for $\varepsilon$ from the numerically computed conversions, again for $k_0x/u_m = 1$. The predictions of eq. 26 with the indicated coefficient are observed in Table 12 to be in very good agreement with the numerically computed values, the one exception is the value for $T_w/T_0 = 0.8$ and $Q = 0.05$, which is 6.2% too high.

Similar agreement to that shown in Tables 11 and 12 was found for other values of $k_0x/u$ in the range of 0.4 to 3.0. However, the accuracy of the predictions of eqs. 25 and 26 was not tested for other rates of flow, greater perturbations in $(T_w - T_0)/T_0$, and values $k_0x/u_m$ other than 1.0, and is therefore open to greater uncertainty than the predictions of the other expressions.

## Overall Evaluation of Predictions

Since the predictions of the several different expressions derived herein were each compared in tabular form with the most relevant computed values, only an overall comparison is presented graphically in Figure 2 in which the predicted values of the mixed-mean conversion are plotted versus the computed values. Because the predictions and computations Tables 2-6 and 9-11 are for 108 conditions, the plotted values are coded only in terms of the predictive equation, the regime of flow, and the regime of heating or cooling - not separately for each value of $Q$, $J$, and $T_w/T_0$. The agreement is reasonably good for all but a few conditions. The outliers are almost all for adiabatic conditions with $Q = \pm 0.05$ and for fractional mixed-mean conversions approaching unity. These particular predictions could be brought in better agreement by adjusting the value of the coefficient $\beta$ in eq. 16, but at the expense of poorer agreement for the lesser values of $Q$ for which eq. 16 might be expected to apply and for the range of conversions of greatest practical interest.

At the outset of this work difficulty was anticipated in correlating and generalizing the numerical solutions for two reasons: first, the multiplicity of parameters even for a single simple reaction, and second, the lack of analytical solutions because of the inherent non-linearities of reacting systems, particularly energetic ones. Figure 2 appears to belie the anticipated difficulty. This success is primarily a consequence of the identification, derivation, and utilization of asymptotic expressions. For example, eq. 14, the solution for a tubular reactor with perfect radial mixing provided the basis for eq. 15 for finite molecular and eddy reaction diffusion, in both instances for a non-energetic reaction. In turn, an arbitrary linear perturbation converted eq.15 to eq. 17, which represents an adiabatic reaction. Scaling eq.15 with an asymptotic expression for perfect radial mixing and $|\psi Z_m| << 1.0$, namely eq.19, results in eq. 20 as an alternative to eq.17. An inverse relationship, namely eq. 21, is based on another asymptote for $|\psi Z_m| << 1.0$. Equation 22 for uniform heating was constructed by adding a linear perturbation to Eq. 17. Equations 25 and 26 for uniform wall-temperature were devised by first deriving eq. 24 for $T_w = T_0$ and then adding a perturbation to represent the contribution of $T_w \neq T_0$. In some respects, this pieced-together asymptotic structure is equivalent to the analogy between momentum, energy, and mass transfer as an aid to correlation and prediction, but overall it is inferior because of the limited range of applicability of each of the asymptotes. Indeed, it should be noted that out of respect for these limitations, the computed values were restricted to only moderate thermal perturbations.

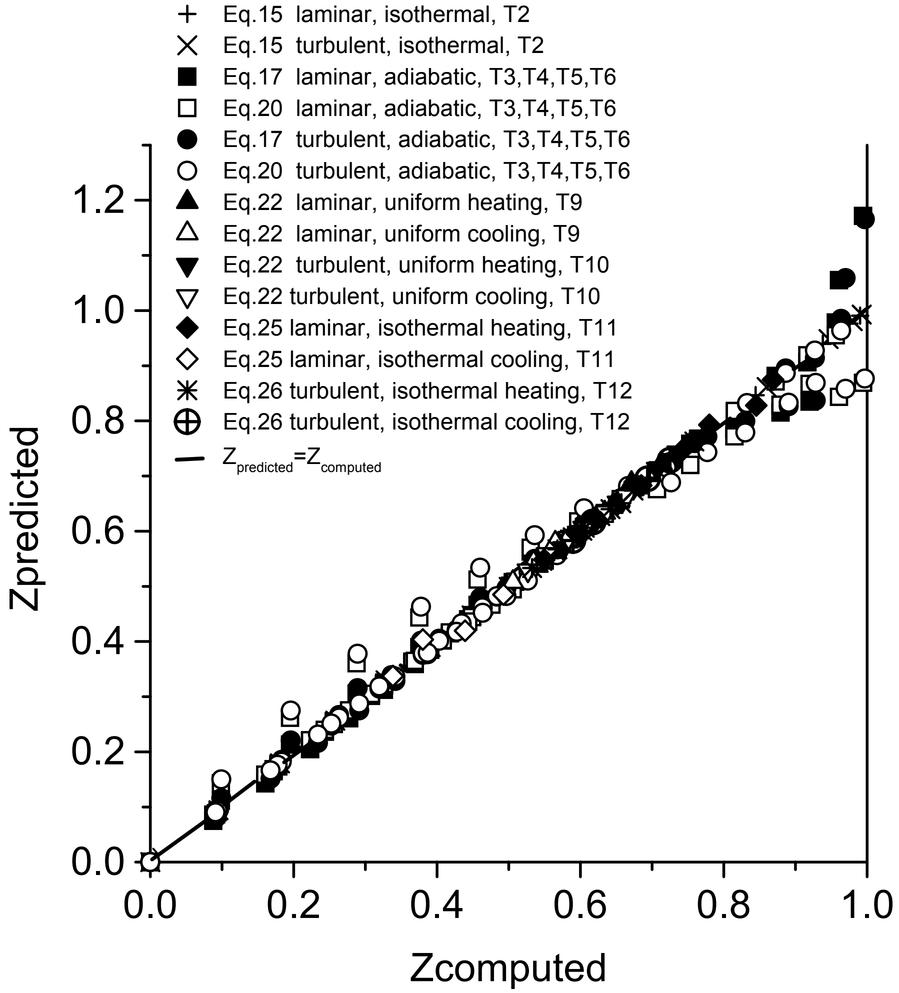

Figure 2. Comparison of Predicted and Computed Mixed-Mean Conversion

## Potential for Numerical Solutions

Although, as discussed in the previous paragraph, the predictive and correlative equations developed in this investigation are limited to small thermal perturbations, no such restriction was encountered in carrying out the numerical solutions. Indeed, numerical solution of the general partial differential model, namely eqs. 1 – 4, is within the capability of undergraduate students as well as of most practicing engineers. The execution of such numerical calculations is a valid and feasible alternative to the use of the correlative expressions solutions devised herein

Accounting for variations in physical properties results in a loss of generality and effectively requires a repeated solution for each set of reactants and thermal conditions. In particular, variations in the density and viscosity with temperature, as well as those due to a non-equimolar gas-phase reaction, affect both the radial and longitudinal velocity field and thereby require solution of the two-dimensional equations of conservation for momentum or the postulate of some gross approximation thereof.

Multiple reactions and more complex reactions may pose even greater difficulty. The most serious effect is not the obvious increase in magnitude of the computations but the possible introduction of "stiffness" and other forms of instability.

In retrospect and on the basis of the computed values of the conversion as a function of $k_0x/u_m$, a value of $k_0a/u_m$ smaller, perhaps by an order of magnitude should have been chosen in order to yield reasonable values of $x/a$ for moderate conversions. However, since the primary purpose of the computations was to illustrate affects and to provide a set of values to guide and test the construction of correlative and predictive expressions, a complete repetition of the calculations for a smaller value did not appear to be justified.

## Summary and Conclusions

Numerical integrations were carried out for a first-order irreversible equimolar reaction in fully developed laminar flow in a tubular reactor taking into account the molecular diffusion of species and energy in the radial direction, the heat of reaction, and two modes of heat exchange with the surroundings. The computations encompassed a set of representative thermal values. Invariant physical properties including density were postulated in the interests of generality. The same calculations were repeated for fully developed turbulent flow.

Predictive equations, based on the perturbation of asymptotic solutions for perfect radial mixing, were demonstrated to reproduce the numerically computed values with sufficient accuracy for all practical purposes.

Numerical integrations such as those carried out in this investigation were concluded to be within the capability of undergraduate students and practicing engineers both conceptually and computationally, and therefore to constitute a serious alternative to the predictive expressions derived herein as well to the super-idealized analytical solutions in the current literature. Knowing how to solve a problem in general is usually preferable to knowing one or more analytical solutions or algebraic predictive equations for special cases.

The numerical integrations were limited to particular values of $Re$, $Sc$, $Pr$, $E/RT_0$ and $k_0a/u_m$ and a limited range of values of $q_r/c_MT_0$, $j_wa/\lambda T_0$, and $T_w/T_0$ because they were intended to be illustrative and to provide a data base for the construction of correlative equations of first-order. However, the numerical methodology appears to be feasible without modification for other values of the parameters within reason. On the other hand, to account for the variation of physical properties with temperature, and for multiple reactions and/or other rate mechanisms calls for more sophisticated numerical algorithms and greatly increased computation.

## Notation

$A$ = reactant
$a$ = radius
$a^+ = a(\tau_w\rho)^{1/2}/\mu$
$C_A$ = concentration of species $A$
$c$ = specific heat capacity
$c_M$ = heat capacity per mole
$D_f$ = diffusivity
$E$ = energy of activation
$j_w$ = heat flux density at wall
$k$ = reaction rate constant

$k_\infty$ = frequency factor
$Nu$ = Nusselt number = $2j_w a/\lambda(T_w - T_m)$
$Pr$ = Prandtl number = $c\mu/\lambda$
$Pr_t$ = turbulent Prandtl number
$Q$ = thermicity = $q_r/c_M T_0 = C_{A0} q_r/\rho c T_0$
$q_r$ = heat of reaction per mole
$R = r/a$
$\hat{R}$ = universal gas constant
$Sc$ = Schmidt number = $\mu/\rho D_f$
$Sc_t$ = turbulent Schmidt number
$T$ = absolute temperature
$u$ = time-averaged velocity
$u^+ = u(\rho/\tau_w)^{1/2}$
$u_m^+ = u_m(\rho/\tau_w)^{1/2}$
$u'$ = fluctuation in $u$
$\overline{u'v'}$ = time-average of product of fluctuations
$(\overline{u'v'})^{++} = -\rho\left(\overline{u'v'}\right)/\tau$
$v'$ = fluctuation in velocity component normal to wall
$X = xk_0/u_m$
$x$ = distance from inlet
$x_{mixed}$ = distance for perfect radial mixing
$x_0$ = distance from inlet for isothermal reaction
$y$ = distance from wall = $a-r$
$y^+ = y(\tau_w\rho)^{1/2}/\mu$
$Z$ = fractional conversion = $(C_{A0} - C_A)/C_{A0}$

*Greek symbols*

$\alpha$ = arbitrary coefficient in eq.15 representing effect of diffusion
$\beta$ = arbitrary coefficient in eq.16 representing effect of thermicity
$\gamma$ = arbitrary coefficient in eq. 21 approximating integrated mean value
$\varepsilon$ = arbitrary coefficient in eq. 26 representing effect of wall temperature in turbulent flow
$\eta$ = arbitrary coefficient in eq. 23 representing effect of heat flux density at the wall
$\lambda$ = thermal conductivity
$\mu$ = dynamic viscosity
$\xi$ = arbitrary coefficient in eq. 24 representing effect of thermicity with $Tw = T_0$
$\rho$ = specific density
$\sigma$ = arbitrary coefficient in eq. 22 representing effects of heat flux density at the wall and the rate of flow
$\chi$ = arbitrary coefficient in eq. 25 representing effect of wall temperature in laminar flow
$\tau$ = shear stress
$\Phi = (T - T_0)/T_0$
$\psi = QE/c_M \hat{R}\, T_0^2$

*Subscripts*

$im$ = integrated mean
$m$ = mixed-mean
$Q$ = for energetic reaction
$w$ = at wall
$0$ = at inlet or for $T_0$ or $Q = 0$

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