An analysis of convective dispersion and reaction in the fixed-bed reactor

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Abstract

The physics of dispersion in fixed beds of randomly-placed particles are considered against the background of experimental and theoretical work published during the past several years. The general equations for the reactor are shown as developments of the Central Limit Theorem, that may be presented as a second order equation defined by two-point boundary conditions. When dispersion is convective it is shown that the boundary conditions may be transformed into initial conditions and a numerical solution, if required, may be obtained without iteration. Illustrations of the method are given for non-linear processes including single and non-isothermal reactions. The application of the method to multiple reactions is described.
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1. Introduction

When fluid flows through a conduit packed with particles, the constituent molecules are spread about the mean flow by molecular diffusion, and by velocity profiling due to the stagnancy of fluid in contact with the solid surfaces of particles and the walls of the conduit. The separate actions of axial spreading are well understood in the simple configuration of an empty tube. For a round tube, axial spreading due to the velocity profile is such that a planar injection of tracer across the tube extends linearly with time in parabolic form in the direction of flow, while for molecular diffusion spreading about the initial position follows the second order diffusion equation.

The phenomenon of axial spreading of an injection of tracer across a cross section of a round tube was studied by Taylor [31], who distinguished axial spreading under velocity-dominated conditions when the effect of molecular diffusion was insignificant because of the short contact time, and for longer contact times when molecular diffusion was significant. He showed that for sufficiently long contact times molecular diffusion smoothed out radial variations in concentration, and a planar injection of tracer material could be observed as a band travelling down the tube at the mean fluid velocity but spreading axially about the mean according to the second order diffusion equation. The axial spreading was characterised by an effective 'diffusion' coefficient that was dependent upon both the molecular diffusivity and the mean fluid velocity; the coefficient is usually referred to as the coefficient of dispersion.

Taylor's work was extended by Aris [1], who added the effect of molecular diffusion in the axial direction, and obtained expressions for the dispersion coefficient in other shapes of conduit. In both studies it was found that axial spreading could be described by the second order diffusion equation only when the contact times were long, while for short contact times axial spreading was determined by velocity profile.

Although these studies are helpful in visualising the mechanisms of dispersion, the geometry of a bed randomly-packed with particles is much more complex, and it is possible that there may be mechanisms of dispersion in addition to those identified for empty conduits. Dispersion of a tracer component in flow through a randomly-packed fixed bed may in theory be studied from the equations of motion and conservation for fluid flowing through the arrangement of particles in the bed. Because the boundary conditions are specified on the surfaces of randomly-placed particles, the solution of the

Nomenclature

A_i	transformed molar flux of component, kmoles/s
c	total molar concentration, kmoles/m^3
d_p	particle equivalent diameter, m
D_x	dispersion coefficient, m^2/s
f	rate function
g	defined by Eq. (19)
G	gas constant, bar m^3/kmol K
k	reaction velocity constant, kmol/m^3 s
k_0	reaction velocity constant, kmol/m^3 s
k_1	reaction velocity constant, kmol/m^3 s
k_2	reaction velocity constant, kmol/m^3 s
n	exponent
p	pressure, bar
t	time, s
T	temperature, K
U	velocity, m/s

w	$y - y_{eq}$
x	distance, m
x_e	reactor exit
y	concentration of key component
y_i	concentration of ith component
y_i^t	defined by Eq. (12)
y_e	concentration in reactor exit section
y_{eq}	concentration at equilibrium
y_0	concentration in reactor entry section
z	derivative of y with respect to x
λ	defined by Eq. (30)
v_i, v_{ij}	stoichiometric coefficient
ρ	mass density of fluid kg/m^3

Subscripts

eq	equilibrium
i	component

equations is required for a randomised distribution of geometries to be formulated, a task that is complicated by the occurrence of flow instabilities and consequent perturbations. This computational task is so complex that it has not been attempted in this form, and even the most ambitious simulations are restricted to simple regular geometries and steady laminar flow. Moreover simulations based upon regular geometries lack an important stochastic element contributed by the random arrangement of particles and therefore may not be a reliable basis for predictions of reactor behaviour.

The basis for many analyses of random processes of Markovian type i.e. without a memory effect, is the Central Limit Theorem that describes an asymptotic condition attained by a wide range of stochastic processes [26]; a proof of the theorem together with applications to statistical mechanics has been given by Khinchin [20]. The theorem is concerned with the asymptotic form of the sum of terms of independent random quantities.

Let the random quantities be fluid particle displacements generated by molecular diffusion and by convection in flow fields dominated by the random placement of solid-phase catalyst particles or other solids. If η_{ix} and σ_{ix}^2 are the first and second moments of the probability densities of fluid particle displacements in the ith time interval, the sum F_{xn} of n displacements has the form,

$$y = F_{xn} = \frac{1}{2(\pi D_x t)^{1/2}} \exp\left[-\frac{(x - U_x t)^2}{4 D_x t} \right] + O\left(\frac{1}{n}\right),$$

$$D_x t = \frac{1}{2} \sum_{i=1}^{n} \sigma_{ix}^2, \; U_x t = \sum_{i=1}^{n} \eta_{ix}$$

$$(1)$$

where U_x is the mean velocity and D_x is the dispersion coefficient. The sum F_{xn} for large n may be identified as a concentration y of a molecular component with a multitude of molecular displacements mapping out the same space.

The constituent stochastic process may be complex and not amenable to an analytical or even a numerical description, but the asymptotic form is independent of the detailed process. The asymptote of the expression for y above satisfies the partial differential equation,

$$\frac{\partial y}{\partial t} = D_x \frac{\partial^2 y}{\partial x^2} - U_x \frac{\partial y}{\partial x} \qquad (2)$$

The rate of approach to the asymptote depends upon the process. Thus Taylor estimated that Eq. (2) is applicable for dispersion in round tubes providing that $L/U_x >> a^2/(3.8^2 D)$. In experiment Gunn and Pryce [13] found that the asymptotic condition was not attained during gas flow through a 300 mm length of 6 mm diameter spheres in a regular cubic array, evidently not long enough to approach the asymptote. However the limiting condition was sensibly attained during gas flow through a length of 15 mm of 6 mm diameter spheres in random placement, a length that is often small compared to a processing unit.

Fig. 1 illustrates some experimental measurements for axial dispersion in fixed beds of impermeable spheres; both gas-phase and liquid-phase measurements are shown, selected representatives of a large number of experimental studies Gunn [10,11]. The experimental measurements of Gunn and Pryce [13] and Edwards and Richardson [9] for the mixing of argon and air in fixed beds of spheres for which the Schmidt group is 0.77 are shown as the dependence of the Peclet group upon the product of the Schmidt group and the particle Reynolds
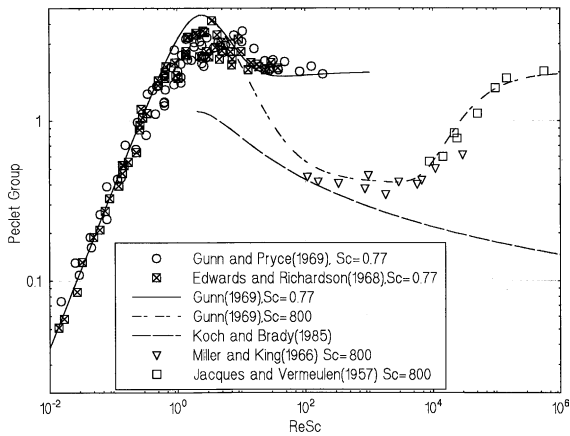
Fig. 1. Experimental data on axial dispersion in fixed beds and comparison with some theories.

number for flow in the bed. At small values of *ReSc* the gas-phase measurements are closely distributed about a line of gradient + 1, corresponding to a dispersion coefficient directly proportional to the molecular diffusivity, while above this value the variation of the Peclet group is small, rising to a gradual maximum and falling to approach a value of 2 as the Reynolds number increases to 1000. In this region the dispersion coefficient is broadly proportional to the fluid velocity.

The selected experimental measurements for axial dispersion in the liquid phase are those of Vermeulen and Jacques [34] and Miller and King [24]. A maximum in the Peclet group would be expected for liquid-phase measurements but because of experimental difficulties there are no reliable measurements at low velocities and only the region of convective dispersion for which *ReSc* > 1, is well-defined [12].

Mixing in fixed beds of randomised arrays of particles has been defined in terms of mixing in stages [22], by transverse exchange between stages [7], in terms of Taylor dispersion in tubes [27,32], in terms of a stochastic view of fluid-mechanical dispersion Gunn [11], in terms of Taylor dispersion in regular particle arrays [28]; and in terms of particle interactions and Brinkman's theory of flow through arrays of particles [21]. Models of the dispersion process may be compared with experiment and if the comparison between experiment and theory is close then it is plausible to assume that the physics of the model are likely to portray aspects of the real dispersion process.

Koch and Brady considered the permeability of a dilute concentration of spheres following Maxwell and Jeffrey while using Brinkman's equation's to introduce the effect of convection. The figure shows the predictions of the theory when the spheres are impermeable and *ReSc* > 1; the equation has been taken from Table 1 of their 1985 paper. From their analysis they found that the

ratio of the dispersion coefficient to the molecular diffusivity was a function of the product *ReSc* only, corresponding to the Peclet group as a function of *ReSc* only. Although the line showing their equation touches the liquid-phase measurements over a small range it is clear that the experimental measurements show that the Peclet group is a function of both Reynolds and Schmidt groups as $Pe = f(Re, Sc)$ and not $Pe = f(ReSc)$. The same functional limitation applies to applications of the Taylor–Aris analysis including that of Shapiro and Brenner [28] where the difference between experiment and theory can be very large [29].

Saffman's model of a random network of capillary tubes showed variations from the experimental tensor attributed by him to inaccuracies in the choice of the angular density distribution of the randomised capillary network that he analysed. However some of the qualitative features shown in Fig. 1 were portrayed in his analysis [19].

The predictions of the theory of dispersion in fixed beds due to Gunn [11] are illustrated in the graph for values of the Schmidt group of 0.77 and 800. The theory is founded upon a representation of the mechanics of fluid flow through beds of particles as a probability of axial displacement due to regions of differing velocity with the dependence of the probability density upon the Reynolds number of flow determined from experiments in which there is no effect of molecular diffusion. Axial dispersion was analysed as transport between regions of dynamic and slowly moving fluid in which transverse transport occurred by molecular diffusion with axial displacement a result of velocity transport and molecular diffusion. There is good agreement between the theory and experiment for both gas and liquid-phase dispersion although the absence of reliable measurements at low liquid velocities precludes testing the theory in that region.

Eq. (2) applies when, for example, a tracer component under consideration is conserved. If the component is consumed by chemical reaction at a rate $f(y)$, then

$$\frac{\partial y}{\partial t} = D_x \frac{\partial^2 y}{\partial x^2} - U_x \frac{\partial y}{\partial x} - f(y) \qquad (3)$$

Eq. (3) is the basic equation for the longitudinal fixed-bed reactor with axial dispersion.

The increased difficulty of estimating transport coefficients in fixed beds promoting chemical reaction, is the main reason for the practice of estimating dispersion and other transport coefficients in non-reactive experiments where the number of unknown parameters is smaller and parameter interactions in the estimation process are less important. As a consequence the question of whether dispersion or other transport parameters are changed by chemical reaction in randomly packed beds has been raised on a number of occasions.

It has been shown by Shapiro and Brenner [28], that when chemical reaction is promoted at the walls of a straight tube or at the surfaces of a regular array of particles under conditions of laminar flow, dispersion coefficients measured under reactive conditions differ from those estimated in the absence of chemical reaction. Thus when a first order reaction is promoted at the surfaces of a straight tube and fluid is in laminar flow, fluid contiguous to the solid surface is denuded of reactant in the region that is also characterised by low fluid velocity. If convection is significant, the analysis shows that the dispersion coefficient is smaller under conditions of heterogeneous reaction because axial spreading has been reduced in the low velocity region. On the other hand if chemical reaction is homogeneous, dispersion coefficients estimated under reactive and non-reactive conditions are the same because chemical reaction takes place in the same distributed space as the dispersion of reactant.

Gunn and Vortmeyer [18] considered dispersion in reactive and non-reactive beds on the basis of the experimentally established validity of the second order dispersion equation for the measurement of axial dispersion in radially uniform beds. By means of a transformation they showed that a study of Aris and Amundson [3] on the equivalence between the cell and dispersion models under unreactive conditions would also hold under reactive conditions. Their paper was subsequently criticised by Shapiro and Brenner, and Stewart on the grounds that it had been shown by Brenner and coworkers that the reactive and unreactive dispersion coefficients were different under some conditions, and that the proof offered by Gunn and Vortmeyer was based upon an intrinsic assumption that the coefficients were the same. In the fairly lengthy discussion [29] it emerged that the mixing of fluids in flow through regular arrays of particles and flow through random arrangements exhibited fundamental differences and therefore findings from numerical simulations based on regular arrays were unlikely to apply to randomly packed beds. The treatment of reactive and unreactive coefficients offered by Gunn and Vortmeyer was based upon the established experimental validity of the second order equation for dispersion without chemical reaction but not just upon experiments on inactive particles.

Intraparticle phenomena are linked to the equations for the fixed bed. Under conditions of heterogeneous reaction catalysed by porous particles, the surfaces of the particles act as a sink for the reactant; under conditions of transient mass transfer during flow through a bed of porous particles without reaction the surfaces of the particles act as a sink when the concentration of diffusant outside the particle is greater than that inside. In both circumstances the flux between the bed and the particles is driven by concentration gradients at the surfaces of the particles. An analogous condition is found for transient heat transfer during flow through beds of particles. Because the pattern of diffusive interaction between particles and fluid is the same in reactive and active beds it is expected that the dispersion coefficients would be the same because of similarity in the constituent diffusive and dispersive processes. Experiments with active particles including validation studies have been carried out by Gunn and England [14], Gunn and de Souza [17], Bashi and Gunn [4], Gunn and Misbah [15] and Gunn and Misbah [16].

In 1962 Hiby published an influential study in which he described a dye tracer experiment in a randomly packed bed that showed there was no diffusion of dye against the flow when convection was dominant. Although his observation was for a randomly packed bed there has been a general interest in mixing processes that did not permit transport against the direction of flow. Eqs. (2) and (3) have been used as descriptive tools for a variety of chemical and physical processes but it has been shown by Sundaresan et al. [30], Westerterp et al. [35,36] and Kronberg et al. [23] that if the process precludes back-mixing and the development of the asymptotic form of the Central Limit Theorem is slow, a system of first order hyperbolic equations defined by initial conditions can give a better simulation once the process has been accurately characterised by establishing the parameters in the differential equations. The spreading of tracer in laminar flow through a round tube has been taken as a common example in these studies.

The rapid development of the asymptotic form has been experimentally-established for the randomly-packed fixed-bed reactor so that when back-mixing is excluded the reactor may be accurately and properly described by Eq. (3) and its variants when dispersion is convective. The two-point boundary conditions are not a difficulty in describing transient processes as the initial conditions are defined, but for the steady state there is a major difficulty when the processes are non-linear.

2. The differential equations for the fixed-bed reactor

The subject of boundary conditions for fixed-bed reactors has been discussed at length elsewhere, but two proposed sets contain the essential elements.

The boundary conditions proposed by Danckwerts [6] are

$$N = U_x y - D_x \frac{\mathrm{d}y}{\mathrm{d}x} \quad \text{at the reactor inlet} \tag{4}$$

$$\frac{\mathrm{d}y}{\mathrm{d}x} = 0 \quad \text{at the reactor outlet} \tag{5}$$

N is the rate of feed to the reactor. With these conditions a change in reactor length, for example, will change the

concentration profile upstream as back diffusion is possible.

The second set is that of Gunn [10,11] who suggested that the Danckwerts' conditions applied only if molecular diffusion is dominant, and when convection is dominant he proposed that the inlet condition should be retained but the downstream condition should be that of asymptotic equilibrium,

$$\text{Lt}(y_i \to y_{i\,\text{eq}})[f(y_i)] = 0, \quad \text{as } x \to \infty \tag{6}$$

Condition (6) ensures that downstream conditions are not propagated upstream so preventing back-mixing, and Eq. (3) is now defined by two-point boundary conditions of input flux and downstream equilibrium. This downstream condition was tested statistically by Dixon et al. [8] in describing two-dimensional packed-tube heat transfer experiments, and was shown to give a significantly better fit than that obtained with zero gradient at the outlet.

In practice the form of Eq. (3) is often overlysimple. There are important variations in velocity and dispersion coefficient due to changes in pressure, temperature and to volume generation on chemical reaction. In the case of a single reaction with concentration and temperature changes restricted to one-dimension, an appropiate generalisation of the equation might be,

$$\frac{d}{dx}\left(cD_x\left(\frac{dy_i}{dx}\right)\right) - \frac{d}{dx}(U_x c y_i) - f(y_i) = c\frac{\partial y_i}{\partial t},$$
$$i = 1, 2, \ldots, n \tag{7}$$

where $f(y_i)$ is the rate of consumption of component i in the reaction and the molar volume c is related to the properties of state of the system by $c = p/GTz_c$. The implied dependences of molar velocity and dispersion coefficient in Eq. (7) reflect the common circumstances in fixed-bed reactors when molar quantities are not usually conserved in the chemical reaction, and the reactors are often not isothermal. The form of the transport terms in Eq. (7) follows that suggested for molecular diffusion [37], with $f(y_i)$ the rate of reaction in unit volume of reactor for component i. Although the mass flux may be affected in addition by pressure diffusion, surface diffusion, and by the temperature gradient through the Soret effect coupled with the Dufour effect, these effects are generally taken to be of second order in comparison with molecular diffusion. It would be therefore expected that the relative importance would be even smaller in a practical reactor where mixing by molecular diffusion is increased by convection.

The units of composition are often the molar content in unit volume in theoretical studies, but in practice the units are usually partial pressures or mole fractions for gas-phase reactions and mole fractions for liquid-phase reactions. Representation of compositions in terms of molar content in unit volume is theoretically unsatis-

factory in non-isothermal reactors and for rates of transport in diffusive or dispersive processes partial pressures or mole fractions are preferred.

In the convection-dominated regime, dispersion is principally due to the cumulative effect of small-scale velocity distributions, and as indicated in Fig. 1, the sensitivity of the Peclet group in a given phase to the Reynolds group and to the product $ReSc$ is small. Thus changes in the velocity and dispersion parameters cancel out in the Peclet group, $U_x d_p/D_x$.

On substitution of the Peclet group into Eq. (7),

$$\frac{\partial}{\partial x}\left((U_x c)\left(\frac{d}{Pe}\frac{\partial y_i}{\partial x} - y_i\right)\right) - v_i r = c\frac{\partial y_i}{\partial t},$$
$$i = 1, 2, \ldots, n \tag{8}$$

Eq. (8) applies to non-linear, non-isothermal, and non-isobaric reaction. When the kinetic rate is non-linear Eq. (8) is also non-linear and a numerical solution is required to take the concentration profiles forward in time from the initial conditions.

On summing Eq. (8) over the n components,

$$\frac{d}{dx}(U_x c) + \sum_i v_i r = 0 \tag{9}$$

The boundary conditions for convective dispersion when $ReSc > 1$ are,

$$y_{i0} = y_i - \frac{d}{Pe}\frac{\partial y_i}{\partial x} \quad \text{at the reactor inlet,}$$
$$i = 1, 2, 3, \ldots, n \tag{10}$$

and,

$$y_{ie} = y_i - \frac{d}{Pe}\frac{\partial y_i}{\partial x} \quad \text{at the reactor outlet,}$$
$$i = 1, 2, 3, \ldots, n \tag{11}$$

The boundary conditions at the reactor inlet have been chosen for consistency with the material balance since as evident from the discussion on Eq. (7) the mixing process does not lead to a unique set of initial conditions at the reactor inlet. Boundary condition (10) imposes a component mass flow from a non-reactive environment into a reactive one where y_{i0} is the concentration of component i in the reactor entry, while (11) is the statement of mass conservation for flow into the unreactive exit where the concentration is y_{ie}. Eq. (11) specifies the product of the reactor.

Some simplification of the set of Eq. (8) is possible. Let $i = 1$ be designated as the key component. From Eq. (8) defined for components $i = 2, 3, \ldots$ subtract a multiple v_i/v_1 of Eq. (8) for the key component to give,

$$\frac{\partial}{\partial x}\left((U_x c)\left(\frac{d}{Pe}\frac{\partial(y_i - v_i y_1/v_1)}{\partial x} - (y_i - v_i y_1/v_1)\right)\right)$$
$$= c\frac{\partial(y_i - v_i y_1/v_1)}{\partial t}, \quad i = 2, 3, \ldots, n$$

or

$$\frac{\partial}{\partial x}\left((U_x c)\left(\frac{d}{Pe}\frac{\partial y_i^t}{\partial x}-y_i^t\right)\right)=c\frac{\partial y_i^t}{\partial t},$$
$$y_i^t = y_i - v_i y_1/v_1, \quad i = 2, 3, \ldots, n \tag{12}$$

with

$$y_{i0}^t = y_i^t - \frac{d}{Pe}\frac{\partial y_i^t}{\partial x} \quad \text{at the reactor inlet,}$$
$$i = 2, 3, \ldots, n, \text{and} \tag{13}$$

$$y_{ie}^t = y_i^t - \frac{d}{Pe}\frac{\partial y_i^t}{\partial x} \quad \text{at the reactor outlet,}$$
$$i = 2, 3, \ldots, n \tag{14}$$

The system specification is completed by the initial conditions of concentration for each component, and the bed temperature and pressure distribution. That Eqs. (10) and (11) satisfy the requirement of no back-mixing may be seen when an extension of the reactor is introduced at the exit. When introduced, the boundary conditions will be (10) and (11) at the unchanged inlet and the outlet of the extension. At the interface between original bed and extension the boundary condition will be,

$$\left[y_i - \frac{d}{Pe}\frac{\partial y_i}{\partial x}\right]_{\text{upstream}} = \left[y_i - \frac{d}{Pe}\frac{\partial y_i}{\partial x}\right]_{\text{downstream}} \tag{15}$$

In other words the boundary conditions for the upstream section are unchanged and the concentration distribution may be obtained independently of the downstream section. This is the requirement for no back-mixing. Further since the upstream and downstream sections are homogeneous within the reactor, the concentration and gradient are continuous over the interface.

For transient systems the initial concentrations are specified, and when the temperature distribution is determined, the solution to Eq. (8) subject to (9) and constrained by boundary conditions, is well-posed and can be carried forward in time. If the temperature distribution has to satisfy a thermal balance, the differential equations including the thermal balance carry forward the solution in time subject to (10) and (11) and boundary conditions arising from the thermal system. Although the differential equations are well-posed for transient systems, boundary conditions (10) and (11) create difficulties at the steady state because neither condition is fully known at the outset. Of course the steady state may be obtained from the transient equations by integrating forward in time from a specified initial condition but a less time-consuming procedure is desirable.

3. Fixed-bed reactors at the steady state when dispersion is dominated by convection

It may be observed that the usual manner of formulating kinetic rate equations is to represent kinetic data from a microscale or pilot scale reactor by means of an empirical expression that will hold over the range of conditions of the experimental investigation. For a homogeneous reaction the form of the kinetic rate equation represents the intrinsic kinetics unless considerations of micro-mixing are introduced. For a heterogeneous reaction catalysed by solid catalyst particles, the rate expression $f(y_i)$ is an effective rate of consumption in unit reactor volume; the mass conservation and any associated energy equation constitute the equations of a one-phase dispersion model. Alternatively $f(y_i)$ may be obtained from the solution to the partial differential equation or equations that describe reaction and heat and mass transport within the catalyst particle when the equations constitute a two-phase dispersion model. There are possibilities of complex transitions in temperature and concentration within the particles since it is known that the equations for intraparticle concentration and temperature can admit multiple solutions at the steady state some of which may be unstable (see for example [2], for a discussion of this aspect).

It will often be considered essential that the rate expression will extrapolate in a thermodynamically-consistent manner to give zero rate at equilibrium. Even though kinetic expressions derived from small-scale experiments may be pseudo-first order, (see for example [5]), it is desirable that rate expressions should be thermodynamically consistent when used in chemical reactor analysis. This consideration applies both to effective rate expressions and to the rate expressions employed in the intraparticle equations.

The boundary conditions transformed for convective dispersion at the steady state, Eq. (8), includes the effect of a change in the number of moles on reaction. For the moment this effect is excluded and Eq. (8) at the steady state is reduced to (16),

$$\frac{d_p}{Pe}\frac{d^2 y}{dx^2} - \frac{dy}{dx} - \frac{f(y)}{U_x c} = 0 \tag{16}$$

where $f(y)$ is a non-linear kinetic rate expression.

To satisfy the requirement of thermodynamic consistency we require that,

$$\text{Lt}(y \to y_{\text{eq}})[f(y)] = 0 \tag{17}$$

where y_{eq} is the value of y attained at equilibrium. Thus for a reaction of order n $f(y)$ may be,

$$f(y) = ky^n - ky_{\text{eq}}^n \tag{18}$$

When dispersion is convection-dominated, the dispersion coefficients are effectively the same for all species in

single-phase flow [12]. Upstream conditions in the reactor may be perturbed from a downstream change only if transport against the flow, i.e.back-mixing, is significant. In the regime of convection-dominated dispersion back-mixing is insignificant and the reactor may be extended from the exit without affecting distributions of composition and temperature within the reactor. The condition of equilibrium may be approached provided that within the reactor and extension the general conditions for existence and uniqueness of the solution are satisfied.

Eq. (16) may be put in the form,

$$\frac{dy}{dx} = z \tag{19}$$

$$\frac{dz}{dx} = az + bf(y), \quad a = \frac{Pe}{d_p}, \quad b = \frac{Pe}{d_p U_x c} \tag{20}$$

The existence and uniqueness theorem for the system of differential equations (19) and (20) states that within the bounded domain of integration, provided that the right hand sides are continuous and satisfy Lipschitz conditions in $f(y)$, y and z, that are also bounded within the domain, then the system possesses one and only one solution that satisfies the initial conditions for y and z. A Lipschitz condition with respect to a function $F(x)$ within an interval requires that the increments of the function remain bounded within the interval [33]. Thus there exists a positive constant A such that for any two points x_1, x_2 within the interval of integration,

$$|F(x_1) - F(x_2)| \leqslant A|x_1 - x_2| \tag{21}$$

For the purposes of analysis the reactor is extended from the exit to approach the condition of equilibrium; the extension is taken to be isothermal at least in the neighbourhood of equilibrium even though the reactor may not be. We consider the case when $f(y)$ is non-linear in y and suppose that $f(y)$ may be expressed as a Taylor series expansion in $(y - y_{eq})$ in the neighbourhood,

$$f(y) = f(y_{eq}) + (y - y_{eq})\left(\frac{df}{dy}\right)_{y=y_{eq}} + O(y - y_{eq})^2 \tag{22}$$

Since $f(y_{eq})$ is zero $f(y)$ will show a linear dependence upon $(y - y_{eq})$ in the neighbourhood according to Eq. (22) with,

$$\left(\frac{df}{dy}\right)_{y=y_{eq}} = g = \frac{f(y)}{(y - y_{eq})} + O(y - y_{eq}) \tag{23}$$

and therefore on substituting Eq. (23) into (16) after neglecting the residual,

$$\frac{d_p}{Pe}\frac{d^2 y}{dx^2} - \frac{dy}{dx} - \frac{g}{U_x c}(y - y_{eq}) = 0 \tag{24}$$

On setting $y - y_{eq}$ to a new dependent variable w, the differential equation in the neighbourhood region is,

$$\frac{d_p}{Pe}\frac{d^2 w}{dx^2} - \frac{dw}{dx} - \frac{g}{U_x c}w = 0 \tag{25}$$

The general solution to Eq. (25) is,

$$w = A \exp(\lambda_1(x - x_0)) + B \exp(\lambda_2(x - x_0)) \tag{26}$$

where A and B are constants to be determined and the λs are defined,

$$\lambda_{1,2} = \frac{Pe}{2d_p}\left(1 \pm \sqrt{1 + \frac{4gd_p}{U_x cPe}}\right) \tag{27}$$

In view of the approach to the equilibrium condition downstream, the term containing a positive exponent in Eq. (26) is discarded giving the solution,

$$w = w_0 \exp(\lambda(x - x_0)) \tag{28}$$

and therefore,

$$\frac{dw}{dx} = z = \lambda w \tag{29}$$

where $\lambda = \frac{Pe}{2d_p}\left(1 - \sqrt{\left(1 + \frac{4gd_p}{U_x cPe}\right)}\right) \tag{30}$

Eq. (29) is a single-valued relationship between w and z in the downstream extreme of the virtual extension of the reactor. Within the same region the value of λ is also given by substituting for g from Eq. (23),

$$\lambda = \frac{Pe}{2d_p}\left(1 - \sqrt{\left(1 + \frac{4f(y)d_p}{(y - y_{eq})U_x cPe}\right)}\right) \tag{31}$$

and the values of y and its derivative satisfy both the linear equation (25) and the non-linear equation (16).

For a chosen value of y that is sufficiently close to the equilibrium condition, the value of the spatial derivative is given by Eq. (29). Boundary condition (6) is embedded within this expression.

With initial values of w and z that are equivalent to the boundary conditions (10) and (11) for the extended reactor, numerical integration of Eq. (16) may be started towards the reactor inlet with the initial value of y given by,

$$y = w + y_{eq} \quad \text{at } x = x_e \tag{32}$$

and the initial value of the gradient given by,

$$\frac{dy}{dx} = \lambda(y - y_{eq}) \quad \text{at } x = x_e \tag{33}$$

where x_e lies within the region of constant λ corresponding to the linear region given by Eq. (28). The solution to (16) is continued away from the equilibrium condition until y attains the value given by the set mass flow at the reactor entrance shown in Eq. (34),

$$y = \frac{U_x y_0 + D_x \frac{\mathrm{d}y}{\mathrm{d}x}}{U_x} \qquad (34)$$

that is boundary condition (10) at the beginning of the reactor, when the integration is complete.

As both y and its gradient satisfy Lipschitz conditions within the reactor, the mass flows of each component within the reactor are continuous, increasing from the reactor exit to the entrance for reactants, and decreasing for products of the reactions. The integration paths from the initial conditions (32) and (33) pass through the composition and gradient values associated with Eq. (34). The solution is valid from the neighbourhood of equilibrium to the reactor entrance and constitutes the locus on which all exit compositions lie.

Since Eq. (16) is valid within the reactor and extension and the setting of initial conditions equivalent to the boundary conditions in the downstream extension is valid in the absence of back-mixing, the solution mapped out by this procedure satisfies the conditions of the existence and uniqueness theorem. The unique solution has been obtained without iteration resulting from the transformation of the two-point boundary problem to one of the initial value type, corresponding to a considerable reduction in the difficulty of computation. The qualifying condition is that the value of x_e, the virtual reactor exit, lies within the region of convergence of the non-linear function $f(y)$ and the linear terms of the Taylor series expansion of $f(y)$ about the point $y = y_{eq}$. The value of λ given by Eq. (31) is constant within the region of convergence so that the condition is easily checked. There is no restriction on the position of any practical reactor exit that may lie anywhere on the composition-x curve as required by the desired reactor performance; the position of the virtual exit within the linear region of the rate equation is chosen solely to obtain the initial conditions for the numerical integration of Eq. (16).

In this development there is no change in the number of moles on reaction. A change in the number of moles on reaction does not affect the form or the method of obtaining the initial conditions, although the numerical solution continued from the initial conditions is applied to Eq. (8) rather than (16).

In practice some consideration of the form chosen for $f(y)$ will be necessary, although the requirement that $f(y)$ be expressible as a Taylor series expansion about the equilibrium condition is not normally restrictive.

4. A simple steady-state example

It is not intended to carry out an exhaustive study here but rather to give an example of the application to a non-linear form of industrial importance, a reversible reaction of fractional order. Eq. (18) with $n = 1/2$ is the chosen example set in a study intended to demonstrate

only the validity of the analysis, and not the effect of system variables on concentration distributions. Thus the Peclet group has been taken as 1, the velocity as 0.1 m/s and the particle diameter as 10 mm. In the kinetic expression $k_0 = 2$ moles/m³s with y rendered dimensionless by dividing by the inlet concentration of the key component with the inlet concentration incorporated into k_0. The choice of Peclet group, velocity and particle diameter will correspond to Reynolds numbers of the order of 500 for liquid-phase systems and 50 for gas-phase systems so that the product $ReSc$ is greater than 1. Dispersion is dominated by convection for these conditions.

The set of Eqs. (19) and (20), has been integrated using an explicit fourth order Runge–Kutta method [25] from the initial conditions (32) and (33).

In many cases of practical interest the concentration of the key component at the equilibrium condition is not small; this circumstance is examined in Fig. 2 for square root kinetics where $y_{eq} = 0.3$ and the kinetic expression is,

$$f(y) = k_0 y^{1/2} - k_0 y_{eq}^{1/2}, \quad \left(\frac{\mathrm{d}f}{\mathrm{d}y}\right)_{eq} = g = \frac{1}{2} k_0 \frac{1}{y_{eq}^{1/2}} \qquad (35)$$

Eq. (16) is integrated from a condition close to equilibrium at $y = 0.3002$ that is chosen as the initial value of y with the associated gradient given by Eqs. (30) and (31). The value of y is chosen to lie within the neighbourhood of equilibrium so that the kinetic expression is accurately represented by the linear term of the Taylor series. The integration is carried out from this initial point until the values of y and its spatial derivative satisfy the condition set by Eq. (34) when the integration has been completed. The completed concentration profile is the locus from which possible reactor outlet concentrations may be chosen.

The profile is the full solution to the second order Eq. (16) shown by the solid line. There is a significant disparity between the exponential form of the solution to the linearised equation and the full solution in the vicinity of the reactor entrance, but as may be observed in Fig. 2a, a magnification of Fig. 2, the linearised and the full solution converge in the vicinity of equilibrium.

To ensure that integration is started within the downstream region in which the linear representation of Eq. (25) is an accurate approximation to the non-linear second order equation, the constancy of λ was examined from Eq. (31). The corresponding values of λ are shown in Fig. 2b illustrating the constancy of λ near the equilibrium condition and showing that the starting point of the numerical integration lies well within the linear region.

The axial length scale is set with reference to the reactor inlet by a procedure that may be implemented after the integration. An arbitrary value of x at the virtual reactor outlet in the neighbourhood of equilibrium
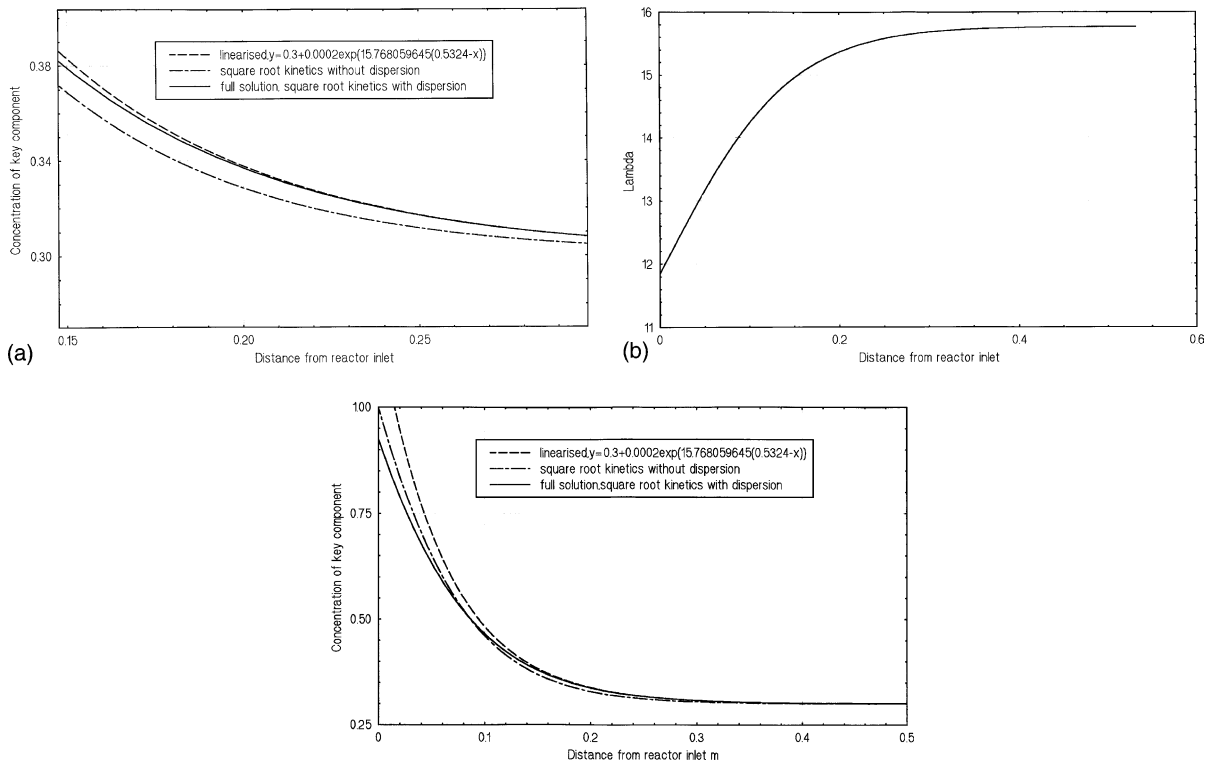
Fig. 2. Concentration profiles obtained for convection-dominated dispersion and square root chemical reaction, $k_0 = 2$, $y_{eq} = 0.3$, $Pe = 1$. (a) Concentration profiles obtained for convection-dominated dispersion and square root chemical reaction showing convergence near equilibrium, $k_0 = 2$, $y_e = 0.3$, $Pe = 1$. (b) Dependence of lambda upon x for square root kinetics, $Pe = 1$.

is chosen as the point x_e. The integration is started from this point using the initial conditions (32) and (33) and the length scale is set by accumulating the length increments in the numerical integration. At the conclusion of the numerical integration the value of x at the reactor inlet is subtracted from the length scale to set the axis with reference to the reactor inlet.

The additional path shown for reference in Fig. 2 is the integral for the reactor without mixing corresponding to the solution to the first order differential equation,

$$\frac{dy}{dx} + \frac{f(y)}{U_x c} = 0 \tag{36}$$

Fig. 2 show the distributions of the concentration of the key component within the reactor from the entrance to the virtual exit. Since the virtual exit is in the neighbourhood of equilibrium there is no apparent jump in concentration at the exit. In all cases the dimensionless concentration of the key component in the entrance section is $y = 1$ since the conditions under which dispersion is observable are created by chemical reaction and chemical reaction is taken not to occur in the entrance section. Thus there is a discontinuity in concentration at the entrance described by the entrance

boundary condition Eq. (11), and in the computational algorithm by incorporating Eq. (34).

For any practical choice of reactor exit a similar discontinuity in concentration is manifest where condition (37) is reached:

$$y_e = y - \frac{D_x}{U_x} \left(\frac{dy}{dx} \right) \tag{37}$$

Here y is the composition on the curve at the position chosen as the real reactor exit, while y_e is the concentration in the exit section where the rate of reaction is zero and therefore the concentration is constant. In conditions of negative composition gradient the second term on the right is positive so that there is a jump in concentration from y to y_e.

On the computational experience shown in the figures the transformation of the solution to Eq. (16) from the boundary value definition of Eqs. (10) and (11) to the equivalent initial conditions of Eqs. (32) and (33) while selecting only the reactor region of interest, is simple and straightforward giving a considerable reduction in the complexity of computation compared to the two-point boundary formulation.
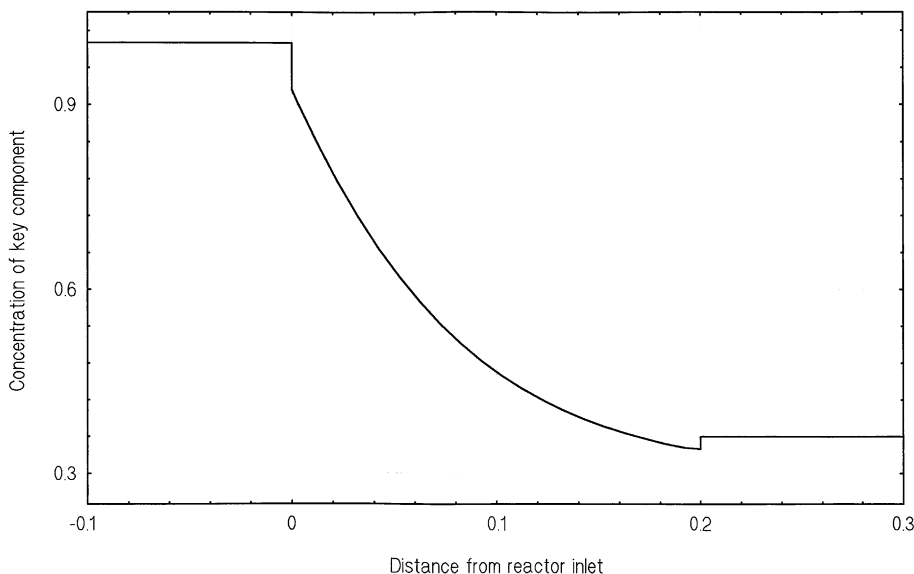
Fig. 3. Concentration distribution of key component for square root reaction in reactor and entrance and exit sections.

The discontinuities in concentration at the reactor inlet and outlet mark the transition between idealised reactor and flanking sections; in practice the inlet and outlet of the reactor will not be idealised planes of zero thickness and the changes in concentration will not be abrupt.

The concentration distribution for square root kinetics illustrated in Fig. 2 where the concentration at the end of the reactor has been set at 0.34, has been plotted to include the concentrations of the key component in entrance and exit sections. This graph is shown as Fig. 3. Changes in concentration occur at the reactor entrance and exit with the exit change a rise from $y = 0.34$.

5. An approximate first order form

In the preceding development the full form of Eq. (16), an equation of the second order has been solved subject to the restriction of convection-dominated dispersion and in this mode Eq. (29) is the relationship between y and its derivative at the reactor exit. It is a condition for the solution that the reactor exit should be within the radius of the linear representation of the rate equation. If the exit does not meet this requirement the reactor should be extended virtually to bring the virtual exit into the linear region.

In the full solution to the second order Eq. (16), Eqs. (29) and (30) define only the initial conditions; once the initial conditions are established the integration of (16) is continued by a numerical method. However Eq. (29) is specified for the entire reactor length both real and vir-

tual raising the possibility of a non-linear first order form as an approximation to Eq. (16).

The first order form and λ are defined by Eq. (38) in which the Taylor series coefficient g has been replaced by $f(y)/(y - y_{eq})$.

$$
\begin{aligned}
\frac{dy}{dx} &= z = \lambda(y - y_{eq}), \\
\lambda &= \frac{Pe}{2d}\left(1 - \sqrt{\left(1 + \frac{4f(y)d}{(y - y_{eq})U_x cPe}\right)}\right)
\end{aligned}
\tag{38}
$$

There are formal difficulties in starting the integration since the value of y at the reactor entrance is not known. However if y is set to y_0 at the start integration may be continued, and the reactor entrance is found in the course of computation when Eq. (34) is satisfied by the calculated values of y and the gradient. It would be expected that equation should give an acceptably accurate solution provided that the dependence of λ upon x is sufficiently small.

We note that in these methods y_{eq} is a local value that will differ from the downstream value when the reactor is not isothermal for example.

To give some idea of the maximum errors that might be developed by this procedure the non-linear first order form has been solved for the entire reactor starting from the entrance and the solution will be compared with the solution to the second order equation as described for the single reaction of half order kinetics. The approximate solution obtained by integration of Eq. (38) for square root kinetics is compared with the solution to Eq. (16) for square root kinetics with $y_{eq} = 0.30$ in Fig. 4. In this example it is evident that agreement between the full
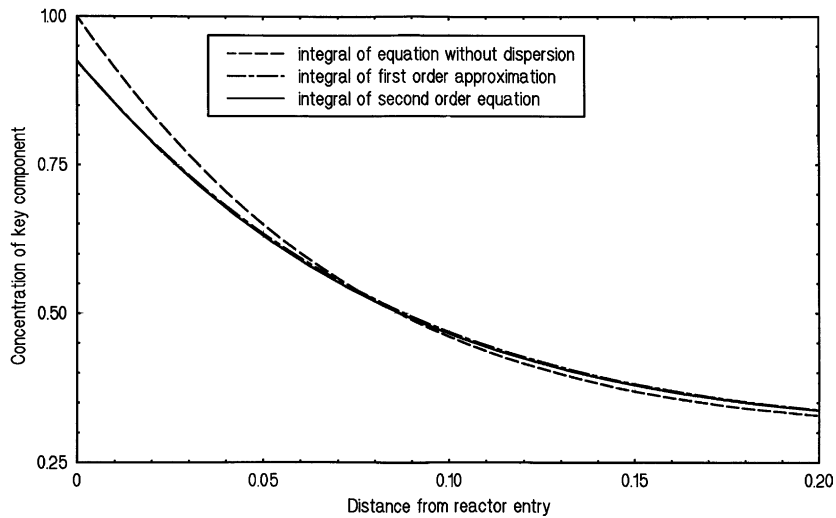
Fig. 4. Comparison of concentration profiles obtained from the first order approximation and the solution to the second order equation.

solution to Eq. (16) obtained by backward integration and the solution to the approximate first order form Eq. (38) obtained by forward integration, is close and in practice may be of acceptable accuracy. The corresponding integration without dispersion is shown for reference, where it is apparent that the approximate first order form is much closer to the solution of the second order equation.

Another view of the relative agreement between the second order and the approximate first order equation may be obtained by examining the dependence of the gradient dy/dx upon the concentration of the key component y including reference to the dependence in the absence of dispersion. The dependence of the spatial gradient upon y for square root kinetics is shown in Fig. 5 for a Peclet group of 1. The solution to the second order equation and the approximate first order form converge in the vicinity of equilibrium, but it is apparent that agreement is fairly close throughout the range of concentration with agreement much better than that between the second order equation and the equation without dispersion.
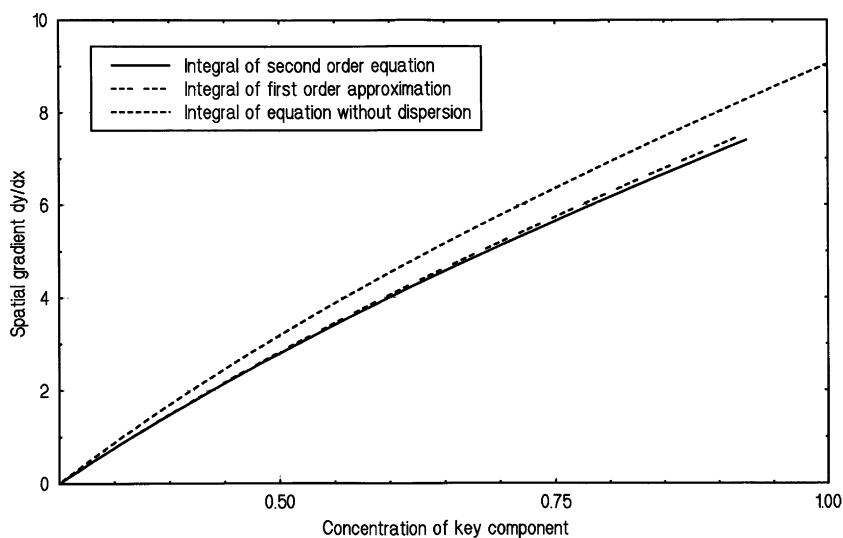

Fig. 5. Comparison of concentration spatial gradients obtained from the first order approximation and the solution to the second order equation.

At the expense of some loss in accuracy, the first order form may be used to give initial conditions at the actual reactor exit for the second order equation even if the linear requirement is not satisfied. Errors generated when initial conditions at the actual reactor exit are set in the non-linear region with the numerical solution continued by the second order Eq. (16), will be smaller than errors obtained when a first order equation only is used. One reason for using a first order form alone is that possible difficulties of stability given by the second order equation will not usually be experienced, although some assessment of the first order approximation should be made in particular circumstances, since the accuracy suggested by Figs. 4 and 5 may not be general.

6. An example of a steady-state non-isothermal reaction

For reactors other than isothermal the associated thermal balance will normally be formulated. Thus if the reaction is endothermic without change in the number of moles the mass balance is given by Eq. (16) with the boundary conditions given by Eqs. (10) and (11). The reactor may be heated when the temperature condition at the reactor outlet will depend upon heat transfer into the reactor from a heat source, and therefore equations for the heat transfer source as well as the thermal balance for the reactor are required to complete the system of equations. However to avoid additional complexities that are peripheral to the central purpose of the paper we have chosen simply to specify the temperature along the reactor with an isothermal virtual reactor extension at the reactor exit temperature T_e. The temperature T_e is suitable for the required conversion.

In this example we consider the reaction of half order kinetics with Arrhenius temperature dependence as follows,

$$f(y) = k \exp(-E/GT)(y^{1/2} - y_{eq}^{1/2}) \tag{39}$$

with y_{eq} a function of the local temperature. The temperature distribution has been chosen to be 500 K at the reactor entrance rising to 700 K at the reactor exit with the virtual extension isothermal at the reactor exit temperature as shown in Fig. 6. Such a temperature distribution might arise from the application of external heat transfer combined with an endothermic heat of reaction.

The concentration distribution arising from this temperature distribution is shown in Fig. 7 for the following parameter values: the pre-exponential factor $k = 5000$ moles/m^3 s, the activation energy $E = 60$ kJ, the Peclet group $= 1$, the particle diameter $= 10$ mm, the velocity $= 0.1$ m/s, and the equilibrium composition $y_{eq} = 0.0000079 \exp(5000/T)$. As in the earlier examples
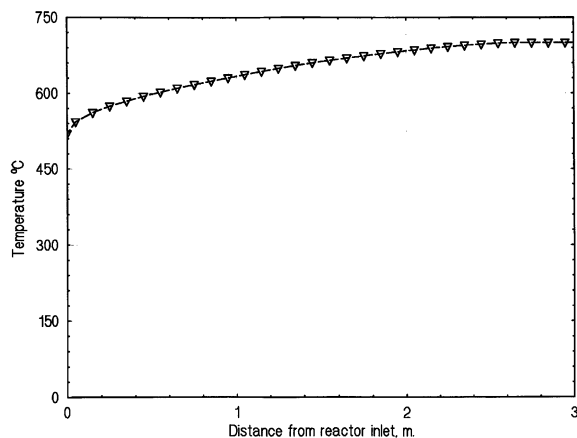

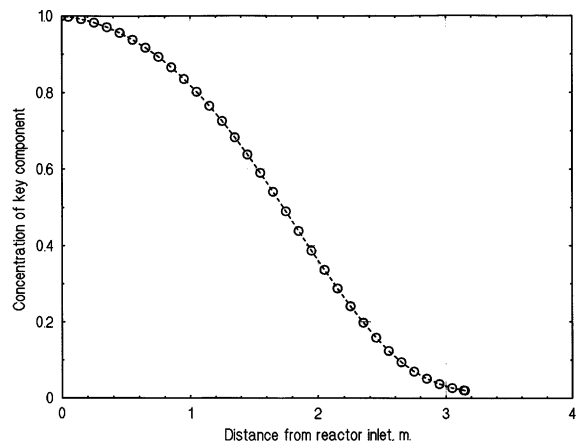Fig. 6. Temperature distribution for non-isothermal reactor and square root kinetics.

Fig. 7. Concentration distribution for non-isothermal reactor and square root kinetics.

the concentration distribution is shown for a long reactor; the concentration distribution in shorter reactors will show a jump in concentration similar to that demonstrated in Fig. 3. The fall in concentration at the reactor entrance demonstrated in Figs. 2 and 3 is not evident in Fig. 7 because of the low rate of reaction at the entrance temperature.

There are significant differences between the concentration distribution shown in Fig. 7 and the isothermal distributions illustrated in Figs. 2 and 3. The rate of fall in concentration at the reactor entrance is low because of the effect of the low temperature upon the rate of reaction. As the temperature rises the rate of reaction increases causing a sharp fall in concentration, with the rate of fall of concentration declining with concentration as the distance from the reactor entrance increases.

7. Multiple reactions

In many processes of industrial significance two or more reactions take place simultaneously. The essential features of the analysis may be adapted for the occurrence of multiple reactions. The material balances for a system of m reactions are given by,

$$\frac{d}{dx}\left((U_x c)\left(\frac{d_p}{Pe}\frac{dy_i}{dx} - y_i\right)\right) - \sum_{j=1}^{m} v_{ij} r_j = 0,$$
$$i = 1, 2, \ldots, n \tag{40}$$

with the equation corresponding to (9) as

$$\frac{d}{dx}(U_x c) + \sum_{i=1}^{n}\sum_{j=1}^{m} v_{ij} r_j = 0 \tag{41}$$

The stoichiometric coefficient v_{ij} for component i in reaction j, is taken as positive for reactants and negative for products. Each of the m reactions is thermodynamically consistent. We may calculate the equilibrium composition at the chosen exit temperature, or calculate the equilibrium temperature and composition if the reactor is adiabatic, for example. The boundary conditions are Eqs. (10) and (11) written for each component.

The form of Eq. (40) depends upon the kinetic scheme with differences for systems of parallel reactions, reaction schemes with some consecutive reactions, and reaction schemes with elements of redundancy whereby the same products are produced by different reaction paths. If the first m components may be selected as the key components for the m reactions, Eq. (40) may be transformed into two equations by row operations,

$$\frac{d}{dx}\left((U_x c)\left(\frac{d_p}{Pe}\frac{dy_i}{dx} - y_i\right)\right) - \sum_{j=1}^{m} v_{ij} r_j = 0,$$
$$i = 1, 2, \ldots, m \tag{42}$$

$$\frac{d}{dx}\left((U_x c)\left(\frac{d_p}{Pe}\frac{dy_i^t}{dx} - y_i^t\right)\right) = 0, \quad i = m+1, \ldots, n \tag{43}$$

where y_i^t represents the variable y_i after row transformation. Eq. (42) may be rearranged in the neighbourhood of equilibrium to give,

$$\frac{d_p}{Pe}\frac{d^2 y_i}{dx^2} - \frac{dy_i}{dx} - \frac{\sum_{j=1}^{m} v_{ij} r_j}{U_x c} = 0, \quad i = 1, 2, \ldots, m \tag{44}$$

and on defining,

$$\sum_{j=1}^{m} v_{ij} r_j = f_i(y_i) = f_i(y_{ieq}) + (y_i - y_{ieq})\left(\frac{df_i}{dy_i}\right)_{y_i = y_{ieq}}$$
$$+ O(y_i - y_{ieq})^2 \tag{45}$$

then

$$\left(\frac{df_i}{dy_i}\right)_{y_i = y_{ieq}} = g_i = \frac{f(y_i)}{(y_i - y_{ieq})} + O(y_i - y_{ieq}),$$
$$i = 1, 2, \ldots, m \tag{46}$$

The set of non-linear equation (42) is transformed into the set (47) that holds within the linear neighbourhood of equilibrium,

$$\frac{d_p}{Pe}\frac{d^2 w_i}{dx^2} - \frac{dw_i}{dx} - \frac{\lambda_i w_i}{U_x c} = 0,$$
$$\lambda_i = \frac{Pe}{2d_p}\left(1 - \sqrt{\left(1 + \frac{4 g_i d_p}{U_x c Pe}\right)}\right)$$
$$i = 1, 2, \ldots, m \tag{47}$$

where $w_i = y_i - y_{ieq}$.

Within the linear neighbourhood of equilibrium the solution provides the relationship between the dependent variables and the associated spatial derivatives,

$$\frac{dy_i}{dx} = \lambda_i(y_i - y_{ieq}), \quad i = 1, 2, \ldots, m \tag{48}$$

This set of equations represents the initial conditions for the set of non-linear equation (42) that are applied within the neighbourhood. The initial value of the first key component is chosen within the linear region of equilibrium. The corresponding values of the second and subsequent components may be obtained from the kinetic rates within the linear region according to,

$$y_i - y_{ieq} = \frac{\lambda_i}{\lambda_1}(y_1 - y_{1eq}), \quad i = 2, 3, \ldots, m \tag{49}$$

By integration of Eq. (43), the material balances for the non-key components are,

$$\left(c D_x \frac{dy_i^t}{dx} - U_x c y_i^t\right) = A_i, \quad i = m+1, \ldots, n \tag{50}$$

The initial values of the non-key components are obtained from the initial values of the key components and the stoichiometry of the reactions.

The solution is obtained by numerical integration of the sets (42) and (43) from the initial conditions incorporating Eq. (6) within the numerical scheme. The integration is continued until the condition at the reactor inlet is attained.

That the choice of initial conditions lies within the linear region of equilibrium may be ascertained by examining the constancy of the exponents according to the following expression with $f_i(y_i)$ given by Eq. (45),

$$\lambda_i = \frac{Pe}{2d_p}\left(1 - \sqrt{\left(1 + \frac{4 f_i(y_i) d_p}{(y_i - y_{ieq}) U_x c Pe}\right)}\right) \tag{51}$$

The initial condition for temperature is simply to set the temperature at the exit temperature of the bed so that the virtual extension of the reactor is isothermal. The material balance conditions set at the reactor entrance are used to calculate the equilibrium conditions at the reactor exit temperature, a problem that requires the solution of simultaneous non-linear equations to give the equilibrium concentrations of the key components.

From the examples and the discussion it is apparent that the equations are appropriately formulated to include the ramifications of non-isothermality, and for either adiabatic conditions or single-dimensional heat transfer conditions, the method of transforming boundary conditions to initial conditions is equally effective. When the equations for mass and energy conservation are expressed in more than one-dimension, the steady-state transformation of boundary to initial conditions is equally valid, and because the initial conditions are set in the approach to equilibrium where the dimensionality is reduced to one, the method of application is straightforward.

The peculiar difficulty of the theory of the fixed-bed reactor given the differential equations, has been the formulation of boundary conditions in a manner that is consistent with the experimentally-observed absence of mixing against the direction of flow when dispersion is convection-dominated. The circumstances suggest either that the dispersion process is first order, or that the dispersion process is defined by initial conditions rather than boundary conditions. By invoking thermodynamic as well as kinetic considerations, we have shown that the latter alternative when formulated as shown in this paper, has achieved the desired consistency of experiment and theory in the description of chemically reacting systems in fixed-bed reactors.

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