NOTATION

A_p/A_f = amplitude of surface center-line oscillation/amplitude of floor oscillation
B = model parameter related to the amount of deformation at which the surface loses its memory (see Gardner, 1975)
D = ratio of depth to annular spacing
G' = dynamic surface rigidity
i = $\sqrt{-1}$
$Im\{\ \}$ = imaginary part of $\{\ \}$
$m(s)$ = memory function
s = time into the past
t = time
T_f/T_p, $(T_f/T_p)_0$, $(T_f/T_p)_\infty$ = period of floor rotation/period of surface center-line rotation; period ratios for $\dot\gamma \to 0$ and $\dot\gamma \to \infty$, respectively
V^* = complex velocity function
y = radial distance from inside wall of canal
y_0 = annular spacing in canal

Greek Letters

α = model parameter
β = model parameter
$\delta(s)$ = dirac delta function
$\dot\gamma$ = surface shear rate magnitude
$\eta(\dot\gamma)$ = steady shear surface shear viscosity
η^* = complex surface viscosity
η' = dynamic surface viscosity (real part of η^*)
η'' = imaginary part of η^*
η_0 = zero shear rate surface viscosity
η_∞ = infinite shear rate surface viscosity
λ = relaxation time
π = surface pressure
Ω, Ω_{max} = floor rotation rate, maximum allowable rotation rate
ω = frequency

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Applications of a Stretch Model to Mixing, Diffusion, and Reaction in Laminar and Turbulent Flows

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In a Lagrangian frame of reference based on lamina (fluid filament) thickness and in a warped time scale based on a single, flow dependent quantity, mixing, diffusion, and reaction can be described in a relatively simple way. Applications are presented for stretch and fold in taffy pull, egg beater and static mixer, shear stretch, stretch of laminae in a vortex, mixing with diffusion, reaction rate controlled by diffusion of reactant through a product layer, and very fast reactions in a turbulent flow.

SCOPE

Mixing, diffusion, and reaction of soluble fluids have been analyzed primarily in a fixed frame of reference and in terms of the statistical descriptions and theories of fluid mechanics or in terms of variables of distributed value such as residence time. The objective here is to introduce in terse form a type of description and analysis which results in deterministic and predictive models capable of extensive application and development, and to demonstrate use with brief examples.

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The ultimate aim is quantitative understanding of the essential features of such complex processes and phenomena as coloring of polymers, mixing of doughs, compounding of viscous liquids and fine particles, reaction injection molding, specificity of homogeneous reaction sequences in pipeline and stirred-tank reactors, unburned fuel, and carbon monoxide-aldehyde-smoke-NO_x formation in turbulent combustion, aging reactions in materials which were not homogeneous on a molecular scale at the time their fine grain structure was established. Previous studies of these subjects have been qualitative and empirical with limited success in scaling and in prediction. In the present paper, a modeling technique, which greatly simplifies analysis of these types of systems, is presented. Here is another way of scrutinizing a difficult class of problems in chemical engineering.

CONCLUSIONS AND SIGNIFICANCE

If space is scaled to a thinning lamina thickness and time is warped in a special way in a frame of reference that moves with the fluid and is based on the instantaneous thickness of a material filament, diffusion, convection, and even first-order homogeneous reaction are described by an ordinary diffusion equation. The mixing effect of fluid distortion and flow is represented by one of three quantities which individually contain all of the time independency for the diffusion-convection-reaction problem. The three quantities are material striation thickness s, intermaterial area per unit volume a_v, and velocity gradient α in the contraction direction of the moving frame. In general, they are simply related, and dimensionless warped time is defined as an integration of diffusivity divided by s^2 over real time. Any one of these time dependent quantities provides a means for decoupling mechanical mixing from diffusional mixing.

s, a_v, and α are obtained in real time for characteristic mixing systems: stretch and fold in taffy pull, egg beater and static mixer, shear stretch, and stretch of laminae in a vortex. Example applications involving simultaneous diffusion and reaction are also presented: mixing with diffusion, reaction rate controlled by diffusion through a product layer, and very fast reactions in a turbulent flow. If one allows reasonable physical approximations and invests in modest numerical procedures, this method of fluid system description should open up the mixing arts to useful engineering analysis.

Mixing, as described by scale of segregation and concentration intensity, and chemical reactions in turbulently mixed flows have been analyzed primarily in a fixed frame of reference and in terms of the statistical theories of fluid mechanics. The status of such descriptions, as well as research associated with the field, was well represented in 1974 by the proceedings of a Project Squid Workshop (Murthy, 1975) entitled "Turbulent Mixing in Nonreactive and Reactive Flows." Analysis of mixing, interdiffusion, and reaction in a frame of reference which follows the flow are less developed but are represented by such concepts as residence time and residence time distribution, by detailed studies of special cases such as mass transfer at a wavy phase interface, and by striation thickness measures of purely mechanical mixing in polymer processing (Middleman, 1977). The purpose here is to present the second point of view as a coherent method of analysis, which includes diffusion and reaction, and to demonstrate use in a number of applications.

Consider, first, the self-evident fact that initially designated volumes of a one-phase fluid being mechanically mixed remain connected in time. Cross sectioning of the flow at a particular time will reveal a laminar marbleized structure. If the initial volumes were also characterized by differences in solute concentration, then parallel structures of concentration variation would be seen, except that these could be modified by diffusion and chemical reaction.

Flow in a small region near the origin of a frame of reference which moves with a fluid particle can be viewed as a pure straining motion, characterized by the rate-of-strain tensor, and a rigid body rotation (Batchelor, 1967). Within this frame, fluid laminae expand or contract depending on the orientation of their normals with respect to the principal axes of the rate of strain. From a fluid mechanical standpoint, rate of mixing and state of mixedness cannot be defined until this orientation is followed timewise as a continuum variable. Whatever the orientation, however, an alternative Lagrangian frame of reference based on a particle in a lamina surface and the direction normal to that surface will appear to have also a local straining motion made up of appropriate components of the fluid straining motion.

LOCAL FLOW

If a Lagrangian frame of reference in an incompressible fluid translates and rotates with the fluid, the local flow at small space scales in that frame is necessarily an elliptically symmetrical stagnation flow. If this frame is an inertial frame at small scales, the local flow is constrained by mechanical laws as well as by continuity to a two-dimensional stagnation flow. Such a two-dimensional flow exists in simple shear, in laminar flow, and in a vortex. A two-dimensional tendency is observed in the microscales of turbulence (Batchelor, 1956).

There is much dynamic uniformity and symmetry in a stagnation or stretching flow. The instantaneous flow field appears to be the same to every particle in the flow. Viscous dissipation of energy within any volume is equal to viscous work on the volume.[*] A straight material line remains straight and a material plane remains planar while increasing dimension in the direction of stretch. A material volume soon becomes a thinning slab (Fisher, 1968).

Flow in this special frame of reference can be characterized by a single, time dependent quantity $\alpha'(t)$, where

$$v_{x}' = \alpha' x', \quad v_{y}' = -\alpha' y', \quad v_{z}' = 0 \tag{1}$$

---

[*] $-\underline{v} \cdot [\nabla \cdot \underline{\underline{T}}] = -\nabla \cdot [\underline{\underline{T}} \cdot \underline{v}] + \underline{\underline{T}}:\nabla \underline{v} = 0$ for viscous stress $\underline{\underline{T}}$ in an incompressible Newtonian fluid.

DESCRIPTION OF MATERIAL LAMINAE

If particular and mutually soluble volumes of incompressible fluid are brought together at some initial time and mix thereafter in a flow, the nature of the flow will be such that these volumes become laminae. At time t, the laminae will be characterized by a particular striation thickness s, perhaps an average thickness if initial volumes were of various sizes, and by a particular order of contact if more than two kinds of volumes were involved in the initial mix. Laminae thickness can be represented equivalently by intermaterial area per unit volume a_v. Both quantities s and a_v are quantities describing a structured continuum. In special frames of reference chosen for the flow, they become functions only of time.

A single lamina $-ap$ of material, designated $-a$ at initial time in contact only with another material $-b$ in a fluid of constant density and with striation thickness s_{ap}, contributes intermaterial area $a_{bap} = 2/s_{ap}$ per unit volume of mix. If the initial contact were among three materials in order b-a-c-b rather than b-a-b, then $a_{bap} = a_{cap} = 1/s_{ap}$. Since the distribution of laminae thicknesses in terms of some average thickness s will be time independent, $f(s_{ap}/s)$ can represent an invariant distribution function for s_{ap}. The intermaterial area between a and b can then be represented by

$$a_{ba} = \frac{2}{\overline{s_{ap}(0,-1)}} = \frac{2}{\overline{s_{bp}(0,-1)}} = \frac{1}{\overline{s_{ap}(0,-1)}} + \frac{1}{\overline{s_{bp}(0,-1)}} \equiv \frac{2}{s} \tag{2}$$

where the overbars indicate statistical means, and where the final identity defines a convenient s. Because of laminae geometry, volume fractions ϵ_a and ϵ_b of materials $-a$ and $-b$, easily measured invariants, are related to different means; that is

$$\epsilon_a = \frac{\overline{s_{ap}(1,0)}}{\overline{s_{ap}(1,0)} + \overline{s_{bp}(1,0)}} = 1 - \epsilon_b \tag{3}$$

and the average of these means is not simply related to a_{ba}.

If the Lagrangian frame of reference is now fixed on the laminae, with s measuring y distances, the local y flow in this new frame (Figure 1) is specified by

$$v_y = \alpha y \tag{4}$$

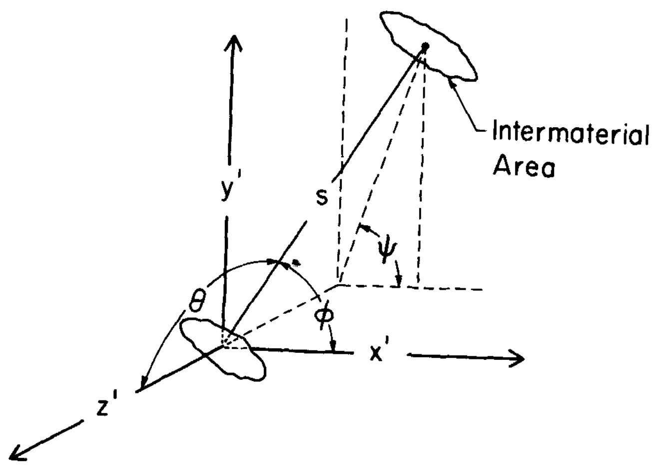

Fig. 1. Orientation of lamina in a stretching flow. s = thickness of lamina, x' = axis of flow stretch, y' = axis of flow contraction, z' = neutral axis.

The relationship between α and α' of the two-dimensional stretching flow is

$$\alpha = \sin^2\theta(\cos^2\psi - \sin^2\psi)\alpha' \tag{5}$$

When $\psi = 0$, it is noted that lamina thickness s is expanding rather than contracting ($0 < \alpha \leqq \alpha'$). When $\psi = \pi/4$, $\alpha = 0$, and s is neither expanding nor contracting. When $\psi = \pi/2$, s is contracting, and intermaterial area is increasing ($-\alpha' \leqq \alpha < 0$). α is at its largest value for contraction when $\theta = \pi/2$ and $\psi = \pi/2$; that is, s is oriented in the direction y:

Since there are orientations for expansion of s as well as for contraction, it is worthwhile to establish an average value of α' if every orientation were equally probable, say a time average in turbulence that is isotropic in this sense. The weighting factor above averaged over all θ and ψ is zero. This means that turbulence does not help mixing if the stretch axis becomes uncorrelated with the laminae normal.

Finally, it should be noted that for a two-material fluid, time dependency can be assigned to any one of three quantities, α, a_v, or s, which are related as follows (Fisher, 1968; Kwon, 1976):

$$\alpha = -\frac{d(\ln a_v)}{dt} = \frac{d(\ln s)}{dt} \tag{6}$$

Striation thickness s was used by Mohr et al. (1957, 1959) to describe the laminar mixing of nondiffusive fluids.

LAMINAE THINNING AND INTERMATERIAL AREA GENERATION IN SIMPLE FLOWS

Stagnation Flow

Consider an initial s_o oriented in the y' direction in a two-dimensional stagnation flow with constant α'. s will remain oriented in the y' direction, $\alpha = -\alpha'$, and

$$s = s_o \exp(-\alpha' t) \tag{7}$$

Thus, if the orientation and the flow could be maintained for a long distance, individual lamina would thin exponentially with time, and intermaterial area would increase exponentially with time. An axially symmetrical case of stagnation flow, as with impinging jets, gives a similar rapid thinning. Coalescence of colliding bubbles and droplets is possible only because of such a rapid thinning of continuous phase fluid layered between mobile interfaces.

As an example of rapid reduction of striation thickness in a stagnation flow, consider the case where two submerged jets of 1 cm diameter containing striations of 1 mm thickness collide at 10 cm/s. $\alpha' \approx 40\ s^{-1}$, and any striation which passes through the stagnation region in 10^{-1} s will emerge with $s = s_o \exp(-4)$, that is, decreased in size by a factor of more than ten. Two more such flow experiences will decrease the size to less than 10 μm. However, there is great variation in time spent and extent of striation thinning in a stagnation region, depending on how far the streamline for a particular portion of the flow is from the stagnation streamline and how far the expansion continues in the outflow before slowing in folds. A complex averaging problem then arises if one wants to assess mixing in the whole flow.

Stretch and Fold; Taffy Pull

If a fluid mass is stretched in such a way that a material point at one end of a material line maintains a particular velocity $v_x'(t)$ with respect to another point on that line, s of laminae oriented transverse to this flow will shorten with time as

$$\frac{ds}{dt} = \frac{s\, v_x'(t)}{\int_o^t v_x'(t)\,dt} \tag{8}$$

If $v_x'(t)$ is a constant in time, then

$$\alpha = \frac{d \ln s}{dt} = -t^{-1} \tag{9}$$

The rate of mixing, measured quantitatively by $-\alpha$, starts out nearly infinite in value for this method of mixing but quickly becomes inversely proportional to time t. To increase the rate of this kind of mixing, the mass is stretched only for time t_s. It is then folded and restretched in like fashion. Then, for long times $t >> t_s$

$$s/s_o = t_s/t \tag{10}$$

where s_o is an original striation thickness at $t = t_s \rightarrow 0$. Thus, the striation thickness becomes equal to s_o divided by the number of folds, a common rule of thumb for mixing.

A taffy pulling machine can stretch and fold every second. To change a 5 cm thread of white taffy and a 5 cm thread of red taffy into pink taffy with striations less than the eye can easily see, say 50 μm, 10^3 folds and 10^3 s would be needed. However, a striation thickness of molecular scale, say 500 pm, is not achieved until 10^8 s or after more than 3 yr on this taffy machine.

Egg Beater and Static Mixer

A stretch and periodic fold is also achieved by an egg beater which can be modeled as two sets of submerged cylinders whose forward stagnation regions rotate on circles that intersect. Behind each cylinder the separated wake flow, which is not being stretched, is periodically stretched and folded by a cylinder moving across it on the intersecting circle.

Flow through the forward stagnation regions ahead of the submerged cylinders can be simplified as entering through the plane at $y' = R$ for $-R < x' < R$ and as leaving at $x' = \pm R$. $\alpha' = 2V_o/R$. Any s_o oriented in the y' direction entering the stretching region at x' will leave with $s = s_o(x'/R)$. A boundary layer will prevent s from becoming zero, but on the average $s = s_o/2$ in the flow leaving the stretch region. The common rule of thumb again applies but for a different reason.

It should be noted that the effect of viscosity must be included to find how much fluid is stretched and exactly how it is stretched and to model pumping of bulk fluid through the beater.

A so-called static mixer achieves the same kind of stretch and fold by subjecting a flow periodically to immersed objects over which the laminae, which are anchored to the walls of the flow channel, are stretched and folded.

Shear Stretch

In simple two-dimensional shear $v_x' = Gy'$, with $v_y' = v_z' = 0$, an s_o, initially oriented in the y' direction, becomes at time t in a flow of constant G:

$$s/s_o = [1 + (Gt)^2]^{-1/2} = \sin\left(\phi - \frac{\pi}{2}\right) \tag{11}$$

For constant G, therefore

$$\alpha = \frac{d \ln s}{dt} = -\frac{G(Gt)}{1 + (Gt)^2} \tag{12}$$

Such a stretching process can be achieved in a Couette flow between concentric cylinders. The striations originally are oriented in a radial direction, and subsequently one cylinder rotates. Initially, α is zero, but it rapidly decreases to a minimum value of $-G/2$ at $Gt = 1$, after which and at long times α becomes equal to $-t^{-1}$.

It should be noted that the Couette process can be reversed. The striations will increase in thickness, reach their original orientation and thickness, then stretch in the opposite direction. It should also be noted that the time average of α is minimized at a value of $-0.36G$ if the striations can be returned to their original orientation periodically in the time interval $Gt = 3.9$.

Since a periodic reorientation is difficult to achieve in a real continuous flow, $\alpha = -t^{-1}$ is a fair measure of mechanical mixing by shear. For example, if one were to force striations with axial normals through length L of parabolic laminar flow in a tube of diameter D, the outgoing striations would appear as circular bands in a cross section of the flow. These striations would all be anchored to the entrance edge, and the width of the band in the outflow cross section would depend on time in the tube L/v_z. Thus, as a practical approximation at the outflow cross section

$$\frac{s(r)}{s_o} = \frac{1}{Gt} = \frac{v_z}{(dv_z/dr)L} = \frac{(D/2)^2}{2rL}\left[1 - \frac{r^2}{(D/2)^2}\right]$$

which demonstrates the fact that $s(r = 0)$ tends to large values $(s > s_o)$ at the center and $s(r = D/2)$ tends to zero at the wall. A flow averaged s at the outlet cross section would be $8D/15L$; that is, the flow averaged striation is one tenth that of the entering striation if the tube is of the order of $6D$ long, but the resulting striations would be widely distributed in size.

Stretch of Laminae in a Vortex

A variety of vortices can be considered as flows for mixing. Two striations formed initially in a vortex of radius s_o can thin subsequently if the vortex lines are attached to a boundary and stretch, if d^2v_θ/dr^2 is initially nonzero in the vortex system, or if the vortex continues to roll up like a rug with d^2v_θ/dr^2 outside a viscous core having a positive value subsequently. An initial situation of a vortex forming new striations is pictured in Figure 2. Old striations of smaller scale embedded in the new striations will thin under the action of the same $\alpha'(t)$.

If striations are fed sideways at radius r_o into a steady ideal vortex with a sink flow of value Q per unit axial length, $v_r = -Q/2\pi r$ in the vortex system. At time t, the striation will be at $r/r_o = [1 - (Qt/\pi r_o^2)]^{1/2}$, and

$$\alpha = \frac{-Q/2\pi r_o^2}{1 - (Q/\pi r_o^2)t} \quad \text{for} \quad 0 < t < \pi r_o^2/Q \tag{13}$$

If for the case of Figure 2 one interprets Q to be $2v_\theta(r = s_o/2)s_o$ and $r_o = s_o/2$, the initial order of magnitude of α' is $(4/\pi)[v_\theta(r = s_o/2)/s_o]$. For an ideal vortex, the absolute value of α' increases for only a limited time, until some smaller axial outflow radius is reached by a striation fed at r_o.

For a vortex newly formed, geometry will decree an initial α' of magnitude v_o/s_o, where v_o is measured by kinetic energy devoted to the vortex of initial scale s_o. A wrapping process, caused by radial gradients in angular momentum, will tend to maintain and even increase this

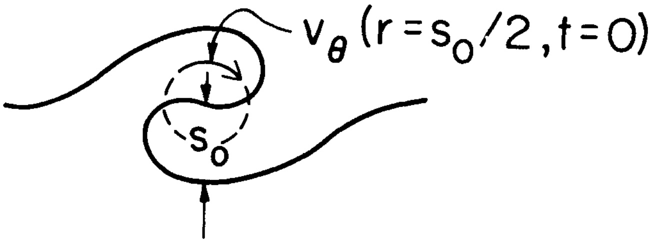

Fig. 2. Vortex forming.

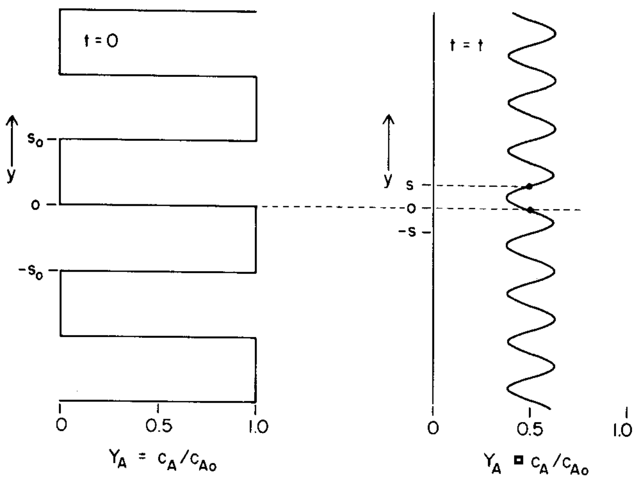

Fig. 3. Effect of stretch on diffusion between lamina.

initial value of α' for a short time, of order s_o/v_o, after which geometry and viscous action will cause a decrease in value. However, if this vortex soon becomes part of a new vortex of the same energy and size, the value of α' is restored. Such a process probably occurs in turbulent pipe flow. The most energetic vortices, large scale structures forming periodically, are anchored to the pipe wall, and new laminae form croissant rolls stretched downstream. These are soon folded into a new vortex. Pipe flow would experience a periodic α' having a mean value of nearly the order of α' in the most energetic eddies.

The above examples show how mechanical mixing can be described in terms of initial conditions and a single time dependent quantity. The rate of laminae thinning is bounded by the magnitude of velocity gradients, that is, by mechanical energy dissipation rate, but it is apparent that some flows mix better than others for the same expenditure of effort. A periodic reorientation of striations, or folding, is seen also to be a feature of good mixing. It is noted, furthermore, that many of the flows described will produce smaller laminae of distributed sizes from a feed of uniform large size. The need for appropriate averaging and statistical treatments of striations in real flows is recognized, but only the main structure of analysis is the subject here.

DIFFUSION AND REACTION IN STRETCHING LAMINAE

Since a fluid material $-a$ containing chemical species $-A$ in concentration c_A assumes the form of a stretching or contracting lamina with nearly uniform conditions in planes parallel to the laminae, the differential equation of change of c_A in the Lagrangian frame fixed on the lamina takes the form

$$\frac{\partial c_A}{\partial t} + \alpha y \frac{\partial c_A}{\partial y} = D_A \frac{\partial^2 c_A}{\partial y^2} + R_A \qquad (14)$$

for an incompressible fluid in which there are relatively small concentrations of c_A with constant diffusivity D_A. If there is homogeneous chemical reaction, R_A is the volumetric generation rate of A. In a not uncommon case, $R_A = -k_i''' c_A$ for an apparent first order reaction of A with some other reactant in large excess. A comparable equation can be written for temperature change in case hot and cold laminae are in contact or the chemical reaction produces significant enthalpy changes.

The convection term involving α and the reaction rate term R_A, when it is represented by a first-order reaction or when there is no reaction and $k_i''' = 0$, can be made to disappear with changes of variable that feature a warped time τ (Fisher, 1968; Kwon, 1976):

$$Y_A \equiv (c_A/c_{Ao}) \exp[k_i''' t(\tau)]$$
$$\xi \equiv y/s$$
$$\tau \equiv D_A \int_o^t \frac{1}{s^2} dt'$$

The differential equation of change for Y_A thereby reduces to

$$\frac{\partial Y_A}{\partial \tau} = \frac{\partial^2 Y_A}{\partial \xi^2} \qquad (15)$$

a familiar differential equation having solutions for a variety of initial and boundary conditions (Carslaw and Jaegar, 1959; Crank, 1975).

Thus, an elaborately complex system has been reduced to a level of rational analysis by describing convection, diffusion, and reaction in a Lagrangian frame of reference with one spatial and one time dimension, and by assigning all time independency to a single quantity whose value comes only from fluid mechanics. The general applicability of this model is now demonstrated by a few examples.

WARPED TIME

By definition

$$\tau \equiv D_A \int_o^t \frac{dt'}{[s(t')]^2} = \frac{D_A}{s_o^2} \int_o^t \frac{dt'}{\exp\left[2\int_o^{t'} \alpha(t'')dt''\right]}$$

The nature of τ is found by examining various cases of $\alpha(t)$:

1. τ can be made dimensionless only in terms of some characteristic time from the flow experienced after $t = 0$ and/or from a diffusional time s_o^2/D_A. τ is always positive, even though α can have positive as well as negative values.
2. If there is no fluid mechanical mixing, $\alpha = 0$ and $\tau \equiv D_A t/s_o^2$. This is mixing by pure diffusion. The characteristic time for this case is s_o^2/D_A.
3. If there is no diffusional mixing, $D_A = 0$; $Y_A(\xi)$ is invariant in real time and $Y_A(y/s, t) = Y_A(y/s_o, 0)$. The characteristic time for this case is from the flow, say the reciprocal of the absolute value of a characteristic α.
4. If α is constant in time

$$\tau \equiv \frac{D_A}{2s_o^2(-\alpha)} \{\exp[2(-\alpha)t] - 1\} \qquad (16)$$

If α is positive in value, warped time increases in value from $\tau = 0$ at $t = 0$ to $\tau = D_A/2s_o\alpha$ at infinite time. If α is negative in value, the usual mixing case, warped time increases in value from $\tau = 0$ at $t = 0$ to a τ which is soon increasing exponentially with time by a factor — e for each time interval $|2\alpha|^{-1}$. However, the preexponential factor is a ratio of characteristic diffusional and stretch times, respectively, s_o^2/D_A and $|2\alpha|^{-1}$. This τ can also be used in cases where α is periodic with an amplitude which is small compared to an average value and with a frequency which is much larger than t^{-1}, the reciprocal of real time in which significant changes occur.

If $\alpha = -G(Gt)/[1 + (Gt)^2]$, then

$$s = s_o[1 + (Gt)^2]^{-1/2}$$

and

$$\tau = \frac{D_A}{s_o^2} t + \frac{D_A G^2}{3s_o^2} t^3 \qquad (17)$$

While this is a direct case of shear stretch, it is also approximately a case of stretch and shear, say one element of a static mixer, where α of the stagnation flow is directly related to G of the shear flow. For a periodic stretch and shear and for large t, of course, the case reduces to an average α and to an asymmetric wave form.

MIXING WITH DIFFUSION

Consider a case of mixing and diffusion without reaction ($k_1''' = 0$) when initially $c_A = 0$, where $-s_o/2 \leqq y \leqq 0$ and $c_A = c_{Ao}$, where $0 \leqq y \leqq s_o/2$. At $t = 0$, alternating layers of thickness s_o have concentration c_{Ao} of species $-A$. Subsequently the laminae are stretched, and $\partial c_A/\partial y = 0$ at $y = \pm s(t)/2$. In dimensionless variables and warped time, initial conditions at $\tau = 0$ are $Y_A = 0$, where $-0.5 \leqq \xi \leqq 0$ and $Y_A = 1$, where $0 \leqq \xi \leqq 0.5$ and boundary conditions are $\partial Y_A/\partial \xi = 0$ at $\xi = \pm 0.5$ for $\tau > 0$. Solution of the differential equation in warped time is (Crank, 1975, page 63; Kwon, 1976):

$$Y_A(\xi, \tau) = 0.5 + \sum_{n=\infty}^{n=\infty} \frac{2\sin(0.5n\pi)\cos[n\pi(\xi + 0.5)]}{n\pi} \exp(-n^2\pi^2\tau) \tag{18}$$

The concentration field $Y_A = c_A/c_{Ao}$ is now given in terms of $\xi = y/s(t)$ and $\tau(t)$ for both molecular diffusion and the convection of laminae thinning if $\alpha(t)$ or $s(t)$ is known for the flow situation. An initial flat toothed concentration function $c_A(y)$ becomes at some later time a smoothed ripple function of small amplitude and short wavelength with an ultimate uniform $c_A = 0.5c_{Ao}$ at infinite time. Figure 3 shows what happens. This result is a prediction of "scale and intensity of segregation" (Danckwerts, 1952), quantities previously defined to describe the state of mixing.

When τ is sufficiently large, the series of Equation (18) is dominated by its first term, and the maximum deviation from final value $Y_A = 0.5$ will be approximately $(2/\pi)\exp(-\pi^2\tau)$. To diminish the maximum deviation to 0.05, that is, a deviation of less than 10% of the final mean, $\tau > \frac{1}{4}$. To reconcile this result with representative numbers, consider turbulent mixing and diffusion in pipe flow at velocity V and diameter D. An average $\alpha = -c_1V/D$ and a $s_o = c_2D$, where c_1 and c_2 are constants of order $\frac{1}{4}$ and $\frac{1}{2}$, respectively, are probably appropriate for this case. Equation (16) for $\tau = \frac{1}{4}$ becomes $(c_1c_2^2/2)(VD/D_A) \approx \exp(2c_1L/D)$, where pipe length $L = Vt$ has been substituted for t. If we use the suggested values of c_1 and c_2, the L/D at which 10% deviation remains becomes $L/D \approx 5\log_{10}(N_{Re}N_{Sc}/30)$. For a Reynolds number $N_{Re} = 3 \times 10^5$ and Schmidt number $N_{Sc} = 1$ (gas flow), $L/D \approx 20$. For $N_{Re} = 3 \times 10^5$ and $N_{Sc} = 10^3$ (liquid flow), $L/D \approx 35$. These are approximate values for something which is, unfortunately, difficult to measure. As expected, L/D at a particular concentration intensity is a function of VD/D_A, a Peclet number for mass transfer.

REACTION RATE CONTROLLED BY DIFFUSION OF REACTANT THROUGH A PRODUCT LAYER

In a fast polymerization, say one which occurs on contact between a liquid monomer and monomer catalyst as they flow through a mixing head and into a mold, reaction product may form as a viscous lamina between liquid layers. Diffusion of one of the monomers through the polymer could be postulated as controlling the rate of reaction.*

If s_o is the original thickness of the monomer $-A$ which subsequently diffuses with diffusivity D_A through a polymer layer of uniform thickness, if the solubility of A in the polymer is c_A, and if the density of the polymer is essentially the same as the monomers, the reaction rate is controlled by the extent of reaction and the rate of growth of intermaterial area, that is, by the instantaneous width of the polymer layer which thickens by reaction and thins by stretching.

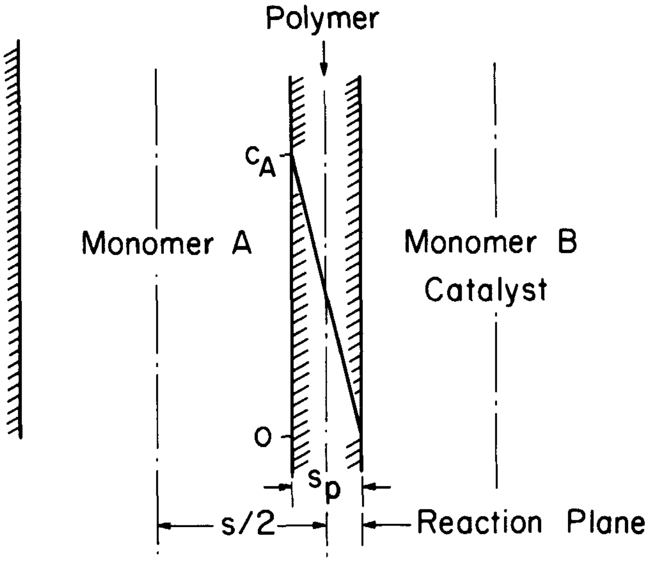

Fig. 4. Situation at time *t*; simplified polymerization reaction.

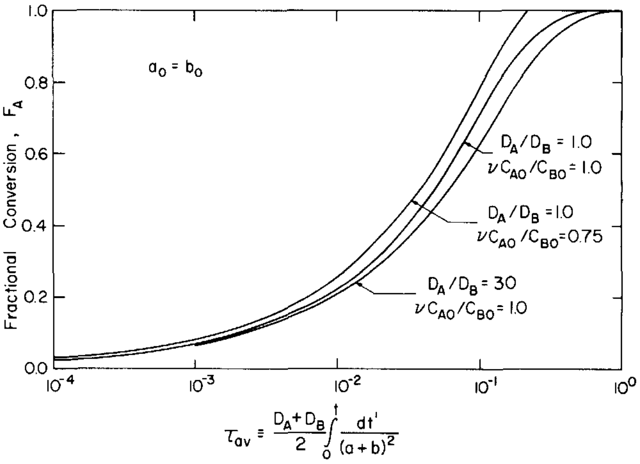

Fig. 5. Extent of reaction at τ_{av} for equal lamina thicknesses, showing also effects of unequal diffusivities and stoichiometry (from Fisher, 1968). $a = b$ striation thickness of regions containing A and B for instantaneous reaction $A + {}^{\nu}B =$ products.

In a highly simplified model, assuming a pseudo steady diffusion of A, the thickness s_p of the polymer lamina at time t is given by

$$\frac{d(a_v s_p)}{dt} = \frac{a_v D_A c_A}{\rho s_p} \tag{19}$$

Figure 4 shows the situation at some time after contact. This equation becomes, in terms of α

$$\frac{d(s_p^2)}{dt} - 2\alpha\, s_p^2 = 2\, D_A c_A/\rho \tag{20}$$

where $s_p = 0$ at $t = 0$. If $\alpha = 0$ (diffusion without mixing), $s_p = (2D_A c_A t/\rho)^{1/2} \leqq s_o$. If $\alpha = -C$, where C is effectively constant in time scale t

$$s_p^2 = (D_A c_A/C\rho)[1 - \exp(-2Ct)] \tag{21}$$

At the end of the reaction, when $s_p(t) = s(t) = s_o\exp(-Ct)$ and $t = t_f$

$$t_f = \frac{1}{2C}\ln\left(1 + \frac{s_o^2C\rho}{D_A c_A}\right) \approx \frac{1}{2C}\ln\left(\frac{s_o^2C\rho}{D_A c_A}\right) \tag{22}$$

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* Another mechanistic view would be broken patches of polymer sheet in an expanding surface of newly formed intermaterial area.

showing a rather complex effect for C which represents the role of mechanical mixing in such a reaction.

In reaction injection molding, monomer and monomer catalyst are mixed in a prechamber and in mold flow for times of the order of a few seconds. While some reaction occurs during mixing, the striation thickness of monomers at the end of injection should be predictable eventually from a detailed analysis of the flow. However, a back calculation from measurable results illustrates use of the above relationships. If reaction occurs in the mold in times of order 10^2 s, $s_o = s_p = (2D_AC_At/\rho)^{1/2}$. For $t = 10^2$ s, $\rho/C_A = 2$, and $D_A = 4 \times 10^{-10}$ m²/s, the striation thickness in the filled mold is indicated to be 20 μm. Going back further in time to the mixing process, an initial striation s_o of jet size, say 2 mm, must have been reduced to an s of order 20 μm; that is, s_o/s had to be of order 10^2 for mechanical mixing. If the mixing all occurred in the prechamber, with holdup time of 10^{-2} s, Equation (7) would require a time averaged α of 500 s^{-1} for the expanding, folding, and slowing sheet flow from the impact of monomer jets.

VERY FAST REACTIONS IN A TURBULENT FLOW

A more elaborate example is very fast reactions, say of an acid and base, at a plane of reaction parallel to the intermaterial area (Fisher, 1968). Here the concentrations of reactant A and B are zero, and the instantaneous rate of reaction is given by the rate of diffusion of reactants to this reaction plane.

Initial and boundary conditions take the form of uniformity of concentration in phase $-A$ and phase $-B$ followed by symmetry of concentration in striation $-A$ and striation $-B$ with diffusion to a stoichiometric reaction at the reaction plane, which may move relative to the frame of reference. Coupling between the transformed differential equations for regime $-A$ and regime $-B$ in general, requires numerical analysis for solution. Analytic solutions (Fisher, 1968) can be obtained for three special cases: equal diffusivities, $D_B = D_A$; nonmoving reaction zone where a stoichiometric condition $\nu c_{Ao}s_{Ao}/c_{Bo}s_{Bo}$ and a diffusion condition $\nu c_{Ao}\sqrt{D_A}/c_{Bo}\sqrt{D_B}$ must be satisfied; and semiinfinite reactant domains, which will be a good approximation of the general case at early times.

Figure 5 (Fisher, 1968, 1974) shows extent of reaction vs. τ for the first two cases. The nature of $\alpha(t)$ is still not a question in this figure; only the nature of the reaction has been decided. Experimental data of extent of reaction vs. real time and predicted extent of reaction vs. τ can be matched for $\tau(t)$ to obtain values of $\alpha(t) = -(1/2)\, d\ln(d\tau/dt)/dt$. In the case of an acid base reaction in a turbulent water flow downstream of a mixing head (Fisher, 1974), the indicated $\alpha(t)$ becomes positive in value toward the end of the reaction. Since unmixing is an impossibility in such a case, it is probable that the reaction rate is not fast enough to maintain a reaction plane and that this premise of the analysis is not valid for such reactions. A more complex model, involving a reaction zone of finite thickness, is apparently required to predict the course of this reaction in turbulent mixing.

NOTATION

a_{ba}, a_v = intermaterial area per unit volume, subscript ba indicates contact of fluid $-b$ with $-a$
c_A, c_B = concentration of chemical species A and B, c_{Ao} and c_{Bo} are initial values. In Equation (19) to (22) C_a is the solubility of the monomer in units of mass of A per unit volume
D_A, D_B = diffusivity of chemical species A and B
G = velocity gradient in uniform shear field
k_1''' = first-order, homogeneous reaction rate constant
R = effective half width of cylinder, egg beater
s = striation or material lamina thickness; s_a for fluid a; s_b for fluid b; s_p for polymer lamina; s_o for initial value
t = time
V_o = cylinder speed
$\underline{v}$ = fluid velocity in Lagrangian frame of reference
v_x' = velocity in direction of stretch
v_y' = velocity in direction of contraction
v_z' = velocity in neutral direction
v_y = velocity in direction of s
v_z = axial velocity at r in tube flow
x' = principal direction of stretch
y = space coordinate in the direction of s
y' = principal direction of contraction
$Y_A \equiv c_A/c_{Ao}$ = dimensionless concentration

Greek Letters

α, α' = velocity gradient in the s direction $v_y = \alpha y$, velocity gradient in stretch direction $v_x' = \alpha' x'$, α' has only positive values, α can have both negative and positive values
θ = momentary angle between s and z', the null flow direction
$\xi \equiv y/s$ = dimensionless space coordinate in the direction of s
ρ = common density for polymer and monomers
$\tau = D_A \int_0^t \frac{dt'}{s^2}$ = warped time
ϕ = orientation of s with respect to x' at time t
ψ = momentary angle between plane z'-s and plane z'-x', the principal plane of stretch

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