When do Chemical Reactions Promote Mixing ?

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Abstract

This paper reviews various situations, in which a chemical reaction promotes the mixing (of reactants and products) in an unstirred reactor. One example is an exothermic chemical reaction, which of course increases the local temperature of an unstirred reacting fluid and hence decreases the density. This can produce natural convection. Thus if the walls of the reactor are cooled, there is often toroidal motion in the reacting mixture and consequently enhanced mixing. Of course, the flow field depends on the shape of vessel, but usually natural convection moves fluid up the middle of the vessel and downwards near the cooler walls. Such convective motion influences, in turn, the temperature field and consequently local rates of reaction and heat release. In a large vessel, the velocities associated with natural convection can be large enough for turbulence to arise and so considerably improve mixing. A second example is so-called “critical mixing”; this occurs when a substance is close to its critical point and large fluctuations of density, temperature, concentration, *etc.*, can occur. These fluctuations sometimes lead to intense mixing, likely to develop into turbulence. Similar features are manifested by a continuously stirred tank reactor (CSTR) approaching a bifurcation point (critical chaos), consideration of which requires a review of Russian work on the dynamics of a CSTR. Next, a chemical reaction with several steps might behave chaotically. Chaotic behaviour in time implies the generation of spatial inhomogeneities, which can promote mixing. In contrast to driven mixing or stirring, the scales for this “self-mixing” are, as a rule, much smaller than the reactor. This latter property is important for encouraging mixing. Finally, the important cases of a liquid or fluidised bed being mixed by bubbles produced, *e.g.* by chemical reaction, is briefly considered.

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Notation

A	pre-exponential factor of rate constant, k , for first-order reaction
a	coefficient in Eq. (15)
B	coefficient in Eq. (15)
b	coefficient in Eq. (16)
Bi	Biot number = ratio of internal and external resistances to heat transfer
C_b	concentration of a reactant in bulk fluid
C_p	specific heat at constant pressure of reacting fluid per unit volume
C_v	specific heat at constant volume of reacting fluid per unit volume
C_s	concentration of a reactant at a catalyst's surface
c_0	initial concentration of reactant (mol/m^3)
D	diffusion coefficient or diffusivity
d	a distance scale in Eq. (17)
Da	Damköhler number = τ_{res}/τ_{reac}
Da'	modified Damköhler number = τ_{conv}/τ_{reac}
E	activation energy for rate constant, k , of first-order chemical reaction
F	strength of applied field
f	frequency of chaotic variations of concentration or temperature
Gr	Grashof number = Ra/Pr
g	acceleration due to gravity
h	heat transfer coefficient from reactor to heat exchanger
k	rate constant of first-order chemical reaction = $A \exp(-E/RT)$
k_0	value of k at $T = T_0$
k_s	rate constant for a surface reaction
k_*	value of k at $T = T_*$
n	order of a chemical reaction

L	characteristic dimension (radius) of reactor
P	absolute pressure
P_c	pressure above critical point
Pr	Prandtl number = ν/κ
p	dimensionless pressure above critical point = $(P - P_c)/P_c$
Q	exothermicity of a chemical reaction
R	gas constant
r	rate of a chemical reaction per unit volume
Ra	Rayleigh number = $\beta g L^3 \Delta T / \kappa \nu$
S	surface area of heat exchanger in a reactor
Se	Semenov number = $Da/(1 + \tau_{res}/\tau_{cool})$
T	absolute temperature
T_0	absolute temperature of inlet to a CSTR or of coolant entering heat exchanger
T_s	critical temperature (absolute) for the onset of ignition in a CSTR
T_*	a reference temperature (absolute) for defining θ
T'	temperature in excess of the critical point
t, t'	time
$\underline{u}$	velocity
U	scale for velocity associated with natural convection
V	volume of reactor or system; potential defined by Eq. (22)
X	variable in Eq. (24)
x	deviation from a limit point, as in Eq. (8)
x_i	a dependent variable
Y	variable in Eq. (25)
y	source term defined by Eq. (8)
Z	variable in Eq. (26)

Ze Zel'dovich number = $c_0EQ/C_pRT_*^2$

Greek letters

α parameter in Eq. (24)

β coefficient of thermal expansion = $1/T$ for an ideal gas

γ dimensionless group = RT_*/E

ΔT scale for temperature increase

Δx distance scale for chaotic variations in T or concentration

δ Frank-Kamenetskii number = $QEL^2k_0c_0/\kappa C_pRT_0^2$

ζ parameter in Eq. (15)

η fractional conversion of reactant

θ dimensionless temperature rise = $E(T - T_*)/RT_*^2$

θ_0 value of θ at $T = T_0$

θ_{ad} dimensionless rise in temperature for adiabatic reaction = $c_0EQ/C_pRT_0^2$

κ thermal diffusivity

λ first order coefficient defined by Eq. (8)

μ chemical potential

ν kinematic viscosity

ξ “friction coefficient” defined by Eq. (21)

ρ_0 initial density of a gaseous mixture

σ susceptibility

τ dimensionless time = $t k_*$

τ_{cool} cooling time for CSTR = c_0C_pV/hS

τ_{conv} characteristic time for natural convection = L/U

τ'_{conv} induction period for natural convection

τ_{diff}	characteristic time for diffusion (of enthalpy or matter) in a reactor
τ_H	characteristic time for reaction to heat fluid to adiabatic temperature = $C_p RT_0^2 / k_0 c_0^n EQ$
τ_{mix}	characteristic time for mixing
τ_{reac}	time constant for first-order reaction = $1/k$
τ_{res}	mean residence time in CSTR = reactor's volume/volumetric flow rate out
φ	parameter in Eq. (26)
χ	mass or thermal diffusivity or kinematic viscosity
ω	frequency, so that in Eq. (8) $y \propto e^{i\omega t}$

1. Introduction

Mixing is sometimes a major problem in chemical engineering. Usually good mixing is desirable and is ensured by stirring or somehow generating shear or turbulence, but of course followed by diffusion at the molecular level. If mixing precedes a relatively fast chemical reaction, the extent of mixing will inevitably affect the course of the reaction. The reverse effect of a chemical reaction influencing or promoting mixing would seem to be unusual. This paper examines some cases of a chemical reaction improving mixing in a reacting fluid. If this can be engineered, there are very obvious rewards from *e.g.* saving energy by not using mechanical stirrers. The problem has widespread interest, so it is surprising there is no particular literature on the topic. Inevitably some aspects are relevant for novel reactors, such as microreactors, where stirring might be difficult. The topic is surprisingly important for the safe operation and risk assessment of those chemical reactors, in which heat is liberated.

Of course, in general, the start of a reaction can produce inhomogeneities (of *e.g.* temperature and concentration) in the particular medium, so that mixing might be needed for the process to proceed. In many systems, chemical reaction and mixing occur simultaneously and a full description becomes complicated. To model such a situation one uses approximations. In particular, the model of a CSTR (continuously stirred tank reactor) is common with its assumption of instantaneous mixing; thus the concentrations and temperature inside such a reactor are the same as in the outflow. This enables a real reactor with imperfect mixing and also its probably unusual residence time distribution to be modelled by CSTRs and plug flow reactors (with no mixing) arranged in series or parallel [1,2], possibly with recycle loops. We accordingly begin by considering the simple, first-order, irreversible, exothermic reaction $A \rightarrow B$ proceeding in the liquid phase in a CSTR, from which heat is removed *via* a heat exchanger

immersed in the reactor. The mass and thermal balances can be cast [3 – 7] in terms of η , the fractional conversion of the reactant, A, and θ ($= E(T - T_*)/RT_*^2$), the dimensionless rise in temperature above an arbitrary reference temperature, T_* , as:

$$\frac{d\eta}{d\tau} = (1 - \eta)e^{\{\theta/(1+\gamma\theta)\}} - \eta/\text{Da} \quad (1)$$

$$\frac{d\theta}{d\tau} = \text{Ze}(1 - \eta)e^{\{\theta/(1+\gamma\theta)\}} - (\theta - \theta_0)/\text{Se} \quad (2)$$

Here τ is a dimensionless time and is the ratio of the actual time to the time constant for the first-order chemical reaction at T_* , *i.e.* $\tau_{\text{reac}} = 1/k_* = 1/\{A\exp(-E/RT_*)\}$, where k_* is the rate constant at T_* , A is the pre-exponential factor in the Arrhenius expression for the rate constant, k , E is its activation energy and $\gamma = RT_*/E$. In the inlet stream of the CSTR and initially in the coolant of the heat exchanger, $T = T_0$ and $\theta = \theta_0$. Otherwise, $\text{Da} = \tau_{\text{res}}/\tau_{\text{reac}}$, is a Damköhler number, *i.e.* the dimensionless mean residence time (τ_{res}) of liquid in the CSTR. Finally, the Semenov number, Se , is related to this Damköhler number in:

$$\text{Se} = \text{Da}/(1 + \tau_{\text{res}}/\tau_{\text{cool}}) = \tau_{\text{reac}}^{-1}/(\tau_{\text{res}}^{-1} + \tau_{\text{cool}}^{-1}), \quad (3)$$

where τ_{cool} ($= c_o C_p V/hS$) is a cooling time for the CSTR and its contents; Ze is a Zel'dovich number, with $\text{Ze} = c_o E Q / C_p R T_*^2$, so that Ze is characterized by the reaction, as well as T_* and C_p for the reacting fluid, *i.e.* by the reaction and its environment. Other symbols are defined in the Notation. The Semenov number is analogous to the slightly different Se used in the theory of thermal explosions [8, 9]. Of course, if $\gamma\theta \ll 1$, which amounts to the rise in temperature being small enough for $(T - T_*) \ll T_*$, the exponentials in Eqs (1) and (2) simplify to e^θ ; this is Frank-Kamenetskii's [10] approximation. This often holds true, in which case the dimensionless group γ disappears from Eqs (1) and (2), leaving only three dimensionless numbers (Se , Da and Ze) to characterize the dependence of both η and θ on τ . In fact, in this situation, the above two equations have the important significance that the dynamics of the approach to a steady state for the reactor and also the stability of each steady state of a CSTR can be characterized on a plot of Se versus Da for the appropriate value of Ze [5, 11]. It is well known that there is a domain on the (Da, Se) plane, corresponding to the CSTR having two steady states: one is at a high temperature, the other at a lower temperature. In fact, the boundary of this domain also encompasses a cusp, where these two steady states degenerate. This cusp is referred to again

below. Some examples are now introduced of mixing caused by chemical reactions, *etc*; each example will be considered in greater detail below.

1a. Natural Convection

Natural convection driven by the heat released from an exothermic step must be considered as an example of how mixing might be promoted by chemical reactions occurring without mechanical stirring. For this it is possibly easiest to consider a batch reactor containing an unstirred fluid, in which heat is released by chemical reaction. If heat is also removed at the walls, it is likely that the fluid in the middle of the reactor is hottest and consequently least dense and also experiencing the most rapid reaction. The fluid adjacent to the relatively cold wall is likely to be cooler and denser and so is reacting slower than the fluid in the centre of the vessel. The result is that concentration differences and temperature gradients are created in the vessel. The associated differences in density result in natural convection, so that, depending on the geometry, fluid often flows toroidally, *i.e.* vertically up the middle of the reactor and downwards at the walls, leading to enhanced heat loss to the walls [12 – 14], as well as improved mixing, particularly when the flow becomes turbulent. Turbulence occurs in a fluid, when the Rayleigh number $Ra (= \beta g L^3 \Delta T / \kappa \nu)$ exceeds a value varying from $\sim 10^5$ [13] to $\sim 10^6$ [16], depending on the geometry of the system. Another consequence of natural convection in a reactor is that ignition and explosion can be suppressed [17, 18] by enhancing heat and mass transfer in a reactor. Natural convection, which is strongest in large vessels (because $Ra \propto L^3$, where L is the characteristic dimension of the reactor), is thus an important way whereby chemical reaction promotes mixing. Another common example, considered briefly below, is when a product of reaction appears as gaseous bubbles in a liquid. The upwards motion of these bubbles can be vigorous enough to enhance mixing.

1b. Self-mixing

To apply the above model of a CSTR leading to Eqs (1) and (2), one must be sure that the strong inequality: $\tau_{res} \gg \tau_{mix}$ holds, where τ_{mix} is the characteristic time for mixing. However, mixing is not determined solely by the one parameter, τ_{mix} . When an agitator or stirrer operates in such a reactor, energy is usually transmitted first to large scales, roughly as big as the reactor. Subsequently energy is redistributed to smaller scales, until dissipation starts at local Reynolds numbers of ~ 1 [19]. As will be seen below, mixing of another kind (called here “self-mixing”) is possible, when the preliminary stages of such a decrease in scales are absent. Self-mixing is a feature of a system with chemical reaction (possibly with several elementary steps) behaving chaotically and causing seemingly random changes in concentrations, temperature, and density. Such fluctuating changes in density result in compressions and expansions, similar, in some sense, to Brownian motion, but limited to macroscopic scales, *i.e.* confined to scales much larger

than atomic ones. The fact that there are changes of temperature, concentrations and density in both time and space [20, 21] results in diffusional fluxes of matter and enthalpy, *i.e.* “self-mixing”. Thus, the scales of self-mixing are normally smaller than the reactor and so are of interest for chemical technology. This paper discusses the properties and features of self-mixing, as compared to those of driven or forced mixing, emphasising ways of controlling processes by fitting the values of appropriate parameters.

At this stage it should be mentioned that self-mixing requires the timescale for diffusion to be less than the time-interval between these fluctuations of composition and temperature. This condition, together with the Einstein-Smoluchowski relation [22] for the timescale for diffusion, can be expressed as:

$$\frac{(\Delta x)^2}{2D} \ll \frac{1}{f}. \quad (4)$$

If this condition holds, the fluctuations will be damped (or possibly eliminated) by the relatively rapid dispersion of matter or heat, thereby leading to self-mixing. Here Δx is the distance scale for the variations in composition and temperature, D is the relevant diffusivity and f is the frequency of the fluctuations. If the inequality (4) does not hold for a particular frequency, those fluctuations will be too rapid to be affected by diffusion. In that case, there is no self-mixing and the high frequency oscillations should be clearly observable, because they are unaffected by diffusion. Of course, another condition for self-mixing is that $\Delta x \ll L$. By way of an example, suppose that $\Delta x = 10$ mm and $D = 4 \times 10^{-5}$ m²/s for a species in the gaseous phase, so that the inequality (4) requires that only oscillations with frequencies, $f \ll 8$ kHz, can promote self-mixing. This means that Eq. (4) is not likely to impose much of a constraint and self-mixing is expected to be a real phenomenon in this particular case.

Besides obvious practical applications, self-mixing phenomena are of significant theoretical interest. The problems in question can be formulated in terms of partial differential equations (*pdes*). For such *pdes*, the dimensionality of phase space equals infinity. At the same time, one can expand the solution of the *pdes* in terms of orthogonal functions of spatial coordinates. The expansion coefficients can be found by solving a system of ordinary differential equations (*odes*). The number of *odes* is formally also infinite. However, short-wavelength modes in the expansion appear negligible, because of dissipation, so that the number of *odes* becomes finite. The theory of systems of *odes* for dynamic systems shows that chaotic solutions are possible for three or more *odes*. In phase space, a strange attractor is formed. The effect of self-mixing corresponds in this language to the extinction of a pair of correlation functions $\langle x_i(t)x_k(t') \rangle$, where t and t' are instants of time and x_i and x_k are dependent variables of the system of *odes*.

1c. Critical Mixing

Another example of chemically promoted mixing is by so-called “critical mixing”. Near its critical point, a substance has a large susceptibility, defined as the ratio of (i) the change in temperature, caused by a periodic disturbance of some parameter, from its stationary value and (ii) the magnitude of this disturbance. Large fluctuations, especially in density, can appear near a substance’s critical point. Often the energy is concentrated in long-wavelength motion only, with scales much larger than atomic dimensions, but much smaller than the containing vessel. Thus, mixing is characterized by both a correlation radius and time. In the vicinity of critical points of layered solutions, concentration fluctuations can be generated, with mixing being caused by the fact that the density depends on concentration.

A large susceptibility is also an inherent property of a CSTR near a bifurcation point [23]. As mentioned above, several reactions may occur in a chaotic fashion and therefore lead to self-mixing. The possibility arises of controlling self-mixing by fitting the bifurcation parameters. The above considerations merit further investigation of processes involving reactions and self-mixing. The various situations mentioned above are now considered in more detail.

2. Natural convection in a reacting medium inside a batch reactor

Consider first an exothermic reaction proceeding in a fluid inside a batch reactor (*i.e.* no substance flows in or out of the closed reactor), from which heat is removed. The equation analogous to the mass balance (1) for the simple, irreversible, first-order reaction $A \rightarrow B$ occurring in a batch reactor, when its contents are well-stirred, but cooled by an immersed heat exchanger, is:

$$\frac{d\eta}{d\tau} = (1 - \eta)e^{\{\theta / (1 + \gamma\theta)\}} \quad (5)$$

However, the conservation of energy as expressed in Eq. (2) for a CSTR also holds for a batch reactor with perfect mixing. Of course, for a batch reactor Se has the value τ_{cool}/τ_{reac} , because $\tau_{res} = \infty$. If T_0 is the initial temperature of the contents of the vessel and also the inlet temperature of the coolant in the heat exchanger, T_0 can be taken to be the reference temperature, T^* . In that case, the dimensionless rise in temperature is $\theta = E(T - T_0)/RT_0^2$ and $\theta_0 = 0$. Also, the Zel’dovich number ($Ze = c_0EQ/C_vRT_0^2$) in the appropriate form of Eq. (2) can be seen to equal θ_{ad} , the dimensionless rise in temperature, when the reaction proceeds adiabatically. This brings out some of the importance of Ze . However, it will be seen that Eq. (2) has two terms on its right hand side, *viz.* those for the release and loss of heat, respectively. Quite often it turns out that there is a temperature T_s , called the ignition temperature, above which the rate of heat generation exceeds the rate of heat loss. Thus, at or above this temperature, there is likely to be

an explosion of some kind. In this language, Ze is also the ratio, $\tau_{\text{reac}}/\tau_H$, of the characteristic times for reaction (*i.e.* $\tau_{\text{reac}} = 1/k_0$ for the first-order reaction: $A \rightarrow B$) and for the heat released to warm up the reacting fluid ($\tau_H = C_p RT_0^2 / k_0 c_0 EQ$) to its ignition temperature [18]. That $Ze = \tau_{\text{reac}}/\tau_H$ is important and this conclusion will be used again below. It is now worth noting that, if Frank-Kamenetskii's approximation holds, the behaviour of this well-stirred batch reactor is characterized by only two dimensionless groups, Se ($= \tau_{\text{cool}}/\tau_{\text{reac}}$) and Ze ($= \tau_{\text{reac}}/\tau_H$). Importantly, both these dimensionless groups are fixed by the reaction under consideration and its environment. Of course, if the temperature rises sufficiently for Frank-Kamenetskii's approximation not to hold, the third group, $\gamma = RT_0^*/E = RT_0/E$, must be considered, in addition to Se and Ze .

The situation described above corresponds physically, not only to a well-mixed batch reactor, but also to a nominally unstirred reactor, in which the external resistance to heat transfer far exceeds the internal resistance. In such a case, the Biot number, Bi , which is defined as the ratio of the internal and external resistances to heat transfer, is much less than unity. Inside such a vessel, the temperature is likely to be spatially uniform, and so the fluid, in which the reaction occurs, is likely to be well-mixed. By contrast, at the other extreme when $Bi \gg 1$, there is likely to be significant spatial variation in the temperature inside the reactor. Such variations can lead to the development of natural convection, thereby introducing some mixing. Merzhanov and Shtessel' [24] were one of the first to study the effects of natural convection, particularly on whether it inhibits thermal explosion.

Significant natural convection in fact occurs inside an unstirred spherical vessel, when $Bi \gg 1$ and, more importantly, when $Ra > 400$ (see below), although there is some evidence [25] that the threshold is lower at more like $Ra = 200$. In the absence of natural convection, the spontaneous ignition temperature for the reaction $A \rightarrow B$ corresponds to a rise in temperature of $1.6 \times (RT_0^2 / E)$ [10]. However, when natural convection occurs, the resulting motion augments both heat and mass transfer inside the reactor, with the net result that ignition is suppressed, so that it occurs [25] after a temperature rise of almost $5 \times (RT_0^2 / E)$. Varma *et al.* [26] give a further discussion of the criteria for thermal explosion in the presence of natural convection. The general behaviour of such a batch reactor is summarised in Fig. 1, which is a plot against Ra of the computed value of $\delta/\delta(0)$; this is the ratio of the Frank-Kamenetskii number δ ($= QEL^2 k_0 c_0 / \kappa C_p RT_0^2$) to its value $\delta(0)$ for zero gravity, when $Ra = 0$. The critical value of δ for the onset of an explosion in the absence of convection (*i.e.* $\delta(0)$) depends on the shape of the reactor; thus it is 3.32 [10] for a spherical vessel. Figure 1 shows the results of computations by Shtessel'

et al. [27] for the zeroth-order reaction $A \rightarrow B$ proceeding in a fluid inside an infinitely long, horizontal batch reactor with a square cross-section; in this case $\delta(0) = 0.88$ [10]. There is no mechanical stirring and the vessel's top and bottom horizontal walls are held at a constant temperature, T_0 ; there is no flow of heat through the two vertical walls, which are well insulated. These boundary conditions imply that $Bi \gg 1$. As discussed above, this means that the main resistance to heat transfer is from the vessel's contents, which are not at all well-mixed, to the wall of the reactor. The curve between regions 2 and 3 in Fig. 1 demonstrates that increasing Ra increases δ , with turbulence beginning to appear very gradually and imperceptibly at $Ra \sim 10^{5.5}$ (e^{13}). Region 4 is where the mixture at low Ra explodes before natural convection has had time to develop. In region 3 there is an explosion, but this occurs in the presence of natural convection, which merely postpones the onset of ignition. At the highest Ra in area 2, convection is strong enough to completely inhibit an explosion. In region 1, Ra is low, so there is no convection; also because δ is lower than its critical value, there no explosion. Thus Fig. 1 emphasises the importance of the relative magnitudes of the characteristic time for natural convection to develop and of the ignition delay.

Fig. 1 hereabouts

It should be noted that the above theoretical considerations have, in effect, been checked experimentally by Cullis and Foster [28]. They measured temperatures in gaseous mixtures of decane and oxygen in a spherical vessel and found that for low Ra , the critical value of δ for an explosion to occur was $\delta(0) = 3.35$, in excellent agreement with the theoretical value for a spherical reactor of 3.32, deduced by Frank-Kamenetskii [10]. Furthermore Cullis and Foster [28] found that δ was constant up to $Ra = 4000$, above which δ increased linearly to become 6 at $Ra = 30,000$. The computations in Fig. 1 for a quite different geometry indicate that δ is constant up to roughly $Ra = e^{8.3} = 4024$, in excellent agreement with Cullis and Foster's [28] value of 4000. By way of further comparison, when $Ra = 30,000$ and $\ln Ra = 10.3$, Fig. 1 indicates that $\delta/\delta(0) \sim 1.8$. This compares with Cullis and Foster's [28] measured value of $\delta \sim 6$, which gives $\delta/\delta(0) \sim 6/3.32 \sim 1.8$. In fact, the measurements of Cullis and Foster [28] correspond to the linear relationship $\delta/\delta(0) = 1.0 + 2.7 \times 10^{-5} Ra$; this applies well up to $Ra = 30,000$, but when $Ra = 3.27 \times 10^6$ and $\ln Ra = 15$, the equation predicts $\delta/\delta(0) = 89$, *i.e.* much higher than the value of ~ 11 indicated by Fig. 1. The excellent agreement between Fig. 1 and Cullis and Foster's correlation [28] makes the curve separating areas 2 and 3 in Fig. 1, together with the above equation, useful for predicting explosions inside vessels with quite dissimilar geometries, but, of course, only for $Ra < 10^4$. It is not totally clear why the above linear relation for $\delta/\delta(0)$ does not

apply above $Ra \sim 10^4$ to the different geometry of Fig. 1, *i.e.* to a cylinder with a square cross section, instead of a hollow sphere. It could be that for the square cylinder, secondary flows are more important and that turbulence appears at a different Ra ; certainly the removal of heat will be different for the two geometries.

A unique experimental result [17] induced by convection has been obtained for the critical conditions for a thermal explosion during the thermal decomposition of the explosive ‘Dina’ (dinitroxydiethylamine) in cylindrical vessels, whose diameters ranged from the laboratory to pilot scale. Figure 2 shows the measured critical values, δ , for explosion, when plotted against the effective diameter of the vessel, or to be more exact, logarithmically against $Ra (\propto L^3)$. The plot has an unusual shape with a minimum separating the two branches a and b. The presence of the descending branch, a, was a totally unexpected result. Also it is striking that δ attains such large values. The explanation is that the substance ‘Dina’ melts at 52.5°C and then decomposes, releasing a large amount of gas as bubbles in a liquid melt. The bubbling action results in the liquid being well stirred. Thus, this is an important case of convection being caused by two mechanisms: natural and bubbling. From Fig. 2 these two mechanisms clearly have opposite effects. Thus, under laboratory conditions (relatively narrow cylinders and high temperatures required for an explosion), bubbling-induced convection dominates, whereas in pilot-scale tests (large vessels and low temperatures), natural convection takes over. Thus with narrow cylinders (*i.e.* Ra is tiny), the bubbling causes efficient removal of heat and hence a substantial rise in temperature before explosion occurs. Consequently, $\delta (= QEL^2 k_0 c_0 / \kappa C_p R T_0^2)$ is large on account of a big k_0 . With progressively wider cylinders, the removal of heat by bubbling is less rapid, so there is a smaller rise in temperature on explosion. This leads to a fall in δ , when Ra is increased, *i.e.* in part a of Fig. 2. The subsequent dominance of heat removal by natural convection, which gives part b of Fig. 2, explains the unusual minimum in Fig. 2.

Fig. 2 hereabouts

The general situation of exothermic reactions [29, 30] driving natural convection in a gas or liquid without mechanical stirring and contained in a batch reactor has been considered theoretically several times, particularly in the context of thermal explosions being suppressed by natural convection. Thus Merzhanov and co-workers [31, 32] have investigated how δ depends on the dimensionless temperature rise, θ_{ad} , *i.e.* Ze . Others [33] have measured temperature profiles during the self-heating, which accompanies spontaneous ignitions in a gaseous explosion. In addition, the development of natural convection in a spherical batch reactor, in which the first-order reactions $A \rightarrow B \rightarrow C$ proceed, involving mainly gases, has been studied in some detail by Cardoso *et al.* [34, 35] and by Campbell *et al.* [12, 13, 36, 37]. In this idealized

scheme, the reactant A is assumed to isomerise to the intermediate, B, thermoneutrally and without an activation energy. The second step, giving the final product C from B, is exothermic and has a significant activation energy. The walls of the spherical reactor are permanently held at the initial temperature; herein lies a problem, of course, when it comes to comparing the results of computations with those from experiments, because in practice it can be sometimes difficult to prevent the walls of a reactor from warming up. No chemical reaction is assumed to occur at the wall. Inside the vessel there is diffusion of species and thermal conduction. The release of heat by the second chemical reaction, $B \rightarrow C$, coupled with heat being removed rapidly at the wall, results in spatial temperature gradients and natural convection in the gaseous mixture. In fact, hot gas flows up the vertical axis of symmetry and then downwards near the vessel's wall, thereby creating a toroidal flow field [34]. Experiments in the gas phase [38, 39] using a spherical reactor indicated that natural convection becomes conspicuous when the Grashof number ($Gr = Ra/Pr$, with $Pr \sim 1$ for a gas) reaches ~ 600 , *i.e.* much below Frank-Kamenetskii's threshold [10] of $Gr \sim 10^4$. Such a conclusion has been supported by Merzhanov and Shtessel's [15] experimental work on natural convection in a liquid inside a horizontal cylinder. Subsequent theoretical work (analytical and numerical) by Shtessel' *et al.* [27] and Jones [40] indicated a threshold Ra of ~ 500 for a gas. Even so, some work, *e.g.* by Liu *et al.*, [25], does suggest that convection in a gas just begins to be noticeable inside a spherical reactor, when Ra reaches about 200.

Fig. 3 hereabouts

As for the flow of fluid in this situation, Fig 3 shows some results of numerical simulations of convective flows inside a spherical reactor, as reported by Cardoso *et al.* [35]. In fact, Fig. 3 gives velocity vectors for a fairly low $Ra = 605$. Near the centre of the vessel the flow is vertically upwards, but adjacent to the walls it is downwards. There is a ring (located on the equator of the system in Fig. 3), where the local velocity is zero. The system is cylindrically symmetric about the vertical axis and natural convection is not strong enough for the ring of zero velocity to lie above the equator. However, this is what actually happens in Fig. 4, which shows the approximate nature of the flow-field for the very much higher Ra of 7.5×10^5 . Here Ra is almost large enough for turbulence. The situation in Fig. 4(i) is for 2 s after chemical reaction ($\tau_{\text{reac}} = 3.85$ s) began. The “eye” of the vortex is now well above the equator. The picture in Fig. 4(ii) is for 6 s after the start. Here the “eye” has moved farther upwards. Also, at the very top of the vessel a new vortex has developed, because of the large upward velocities near the central vertical axis. Figure 4 (ii) gives a rough idea of the broad outlines of the turbulent circulation inside a spherical reactor.

Fig. 4 hereabouts

Some of these matters have been considered in more detail by Campbell *et al.* [37], who compared previously measured temperatures (particularly by Archer, [41]) inside a spherical batch reactor with those calculated numerically and analytically. The main reaction investigated was the thermal decomposition of the gas azomethane, or $A \rightarrow \text{products}$, with an order of 1.4 with respect to the reactant, A. That work brought out the importance of the characteristic timescales for diffusion, for chemical reaction and for natural convection. Thus the rise in temperature at the centre of the vessel is proportional to the ratio of the timescales for diffusion and reaction, when diffusion is the dominant mechanism for transport, *i.e.* $Ra < 500$ and the system retains spherical symmetry. Otherwise, when natural convection is more important than diffusion in effecting transport inside the reactor, *i.e.* when $Ra > 500$, the temperature rise at the centre is proportional to the ratio of the timescales for convection and reaction. Thus the proportionality is to the ratio of the time scale for the dominant transport process and that for chemical reaction. It thus appears that in general the behaviour of one of these unstirred reacting systems is characterized by ratios of the timescales for diffusion (of heat and matter), for chemical reaction, for natural convection and, of course, for heating up the vessel's contents. We consequently might expect three ratios of these four timescales to define how a particular reactor behaves. In that sense, these three ratios are analogous to the dimensionless groups Da, Se and Ze, which in section 1 were shown to characterise the behaviour of a cooled CSTR.

Returning to Campbell *et al.*'s analysis [37] of $A \rightarrow B$, it is clear that when Ra is increased gradually above 500, the spherical symmetry is progressively lost. Such a conclusion is similar to the results of a scaling analysis by Campbell *et al.* [12, 36] for Sal'nikov's reaction mechanism of $A \rightarrow B \rightarrow C$. Excellent agreement between theory and experimentally measured temperatures was found [37], with natural convection starting to actually dominate diffusion at $Ra \sim 500$ for a spherical reactor only. Interestingly some effects of natural convection were observed at Ra as low as ~ 100 . Particularly noteworthy are the computations by Campbell *et al.* [37] for a high Ra of 2.19×10^4 , when, for the particular conditions selected, it takes ~ 5 s for natural convection to develop, as manifested by a tiny hot zone at the very top of the reactor. Elsewhere, the reacting azomethane remains relatively cool and unreacted, but subsequently reaction spreads vertically downwards under the toroidal motion of the gas. Of course, natural convection in large vessels can be turbulent. The transition from laminar to turbulent natural convection usually occurs at $Ra \sim 10^6$ [16], when the contents of a vessel become well-mixed, apart from inside the fairly thin boundary layers adjacent to the wall.

The simpler chemistry of one exothermic reaction ($A \rightarrow B$) occurring in a fluid inside an unstirred spherical batch reactor has been considered by Campbell *et al.* [37] and Liu *et al.*

[18, 25]. Again the walls of the reactor are held at a constant temperature, which might require an unusually efficient system of external cooling and also $Bi \gg 1$. To ensure the fluid is incompressible, in all but the buoyancy term in the Navier-Stokes equations, they made the Boussinesq approximation, which requires that any increase in temperature is much smaller than the system's initial absolute temperature. This is quantitatively the same as Frank-Kamenetskii's approximation, mentioned above. In this case, seven dimensionless groups were required to describe the system's behaviour with an unstirred first-order reaction. This compares with only two groups (see above) for a cooled batch reactor, when stirred very rapidly. Even so, for a specified reaction in a particular unstirred batch reactor only three dimensionless groups (τ_H/τ_{diff} , τ_H/τ_{reac} and τ_H/τ_{conv}) are necessary to characterise the system's behaviour. These quantities are: $\tau_H = C_p RT_0^2 / k_0 c_0^n Q E$, the time-scale for the exothermic reaction to heat the fluid up by the scale for temperature, *i.e.* RT_0^2 / E ; $\tau_{diff} = L^2 / \kappa$, the time-scale for the diffusion of heat; $\tau_{reac} = 1/k_0$; $\tau_{conv} = L/U$, the time-scale for fluid to move by natural convection over the scale for distance, which was taken to be L , the radius of the reactor. Reaction has now been assumed to be of n -th order in the reactant A. Also, U is the scale for velocity and is given [37] by

$$U \sim \left(\frac{\beta g Q k_0 c_0^n L^2}{C_p} \right)^{1/3} \quad (6)$$

This is a regime diagram devised by plotting three dimensionless groups made up as ratios of τ_H to the other three time-scales. In Fig. 5 a surface has been plotted to divide the space into two regions. That nearest the origin is where the reactor explodes, whereas no explosions occur if the working point of the system lies far from the origin in Fig. 5.

Fig. 5 hereabouts

Interestingly, it can be shown that $\tau_H/\tau_{diff} = 1/\delta$, where δ is the Frank-Kamenetskii number discussed above. Also $\tau_H/\tau_{reac} = Ze$ and $\tau_H/\tau_{conv} = (RaPr)^{1/2}/\delta$. However, this last ratio can also be written as $\tau_H/\tau_{conv} = 1/(Ze.Da')$, where Da' ($= \tau_{conv}/\tau_{reac}$) is an alternative Damköhler number [42]. This highlights the conclusion that the behaviour of either a cooled CSTR or a cooled unstirred reactor with natural convection can be fully described by three dimensionless groups: Ze , an appropriate Da and either δ or Se .

That $\tau_H/\tau_{conv} = (RaPr)^{1/2}/\delta$ means that on a plane of fixed τ_H/τ_{reac} (*i.e.* we are considering a particular chemical reaction proceeding in a selected fluid with a chosen value of T_0) a straight line through the origin of Fig. 5 (*i.e.* when $\tau_H/\tau_{diff} = \tau_H/\tau_{conv} = 0$) has a slope $\sqrt{(RaPr)}$. This

means that Ra is represented on such a plot by the slope of this line. Thus the three regimes, where natural convection is, respectively, unimportant, laminar or turbulent are denoted in Fig. 6, which is for $\tau_H / \tau_{\text{reac}} = 0$ and for $Pr = 1$, *i.e.* for reaction in a gas inside a spherical vessel. When $Ra < 500$, natural convection is insignificant, so that in one such case [24] the maximum speed (inside a spherical vessel of i.d. 128 mm) was only 7.1 mm/s, in the central upwards flow. In that situation the hottest region is only slightly above the centre of the reactor. In fact, the temperature and concentration fields were close to being symmetric about the centre. However, calculations [24] for $Ra = 10^5$ show that the hottest region is actually near the top of the vessel; this is in marked contrast to the bottom third of the reactor, where the temperature hardly rises. In the top half, the temperature is stratified horizontally.

Fig. 6 hereabouts

The flowing fluid brings heat from the centre to the top of the vessel. The reacting fluid then cools, whilst moving downwards close to the colder wall. The maximum speed of 32.6 mm/s is reached in gas flowing downwards near the wall after a dimensionless time of $t/\tau_{\text{conv}} \sim 13.3$. Significant motion in the gas appears after $t/\tau_{\text{conv}} \sim 7.5$ (2.75 s) and the flow-field is fully developed at $t/\tau_{\text{conv}} \sim 15.8$ (5.7 s). The eye of the vortex is only slightly above the equator, but Fig. 4 for the higher $Ra = 7.5 \times 10^5$ shows the eye is much higher up the reactor. Other calculations [24] show that U , the scale for velocity, turns out to be lower for higher $\tau_H/\tau_{\text{conv}}$. Also, there can be oscillations on plots of velocity and temperature against time, so the flow field does take time to stabilize; this can take as long as $t/\tau_{\text{conv}} \sim 40$.

The indications are that the time taken to establish natural convection, τ'_{conv} , is lower at higher Ra ; this was found by Merzhanov and Shtessel' [43] for a system without any chemical reaction proceeding. They found that the dimensionless induction time for natural convection (*i.e.* the ratio of the induction period to the time-scale L^2/ν) is $70Ra^{-2/3}Pr^{5/6}$ for convection in an inert fluid [27]. This ratio is $\tau'_{\text{conv}}/\tau_{\text{diff}}$ and Shtessel' *et al.*, [27] have suggested that its dependence on Ra changes from $Ra^{-2/3}$ to $Ra^{-2/5}$, when natural convection is set up in a reacting gas. Thus $\tau'_{\text{conv}}/\tau_H$ ($= \tau'_{\text{conv}}/\tau_{\text{diff}} \times \tau_{\text{diff}}/\tau_H$) should then vary as $\delta Ra^{-2/5}$, but this omits any dependence on $\tau_H/\tau_{\text{reac}}$. The matter clearly needs further attention.

As mentioned above, Campbell [44] and Campbell *et al.* [14] have numerically solved the equation:

$$\frac{C_v}{C_p} \frac{\partial T}{\partial t} + \underline{u} \cdot \nabla T = \kappa \nabla^2 T + \frac{Qr}{\rho_o C_p} \quad (7)$$

for the conservation of energy, for when either the simple exothermic reaction $A \rightarrow B$ or $A \rightarrow B \rightarrow C$ occurs in a fluid inside a spherical batch reactor, whose walls are held at a constant temperature. The contributions of the convective, diffusive and reactive terms to Eq. (7) were computed; their variation with time at *e.g.* the centre of the vessel showed an induction period before natural convection became important. This is shown in Fig. 7 for the reactions $A \rightarrow B \rightarrow C$ under the conditions shown. Here it is clear that there is an early release of heat, which is followed by the onset of natural convection. The value of Ra is high enough (12060) for the diffusion (conduction) of heat inside the reactor to be negligible relative to heat transfer by natural convection. Likewise, accompanying calculations of the upward velocity at the centre of the reactor demonstrated a similarly delayed appearance of natural convection [14]. Results for the simple reaction $A \rightarrow B$ would give a better indication of τ'_{conv} as the moment, when either the convective contribution to Eq. (7) (as in Fig. 7), or the velocity at the centre of the vessel, acquires a point of inflexion, when plotted against time. There do not appear to have been any computations or measurements relating to similar reacting systems with laminar or turbulent flows and their development. The time-scale for the initiation of natural convection in these reacting systems thus merits further study.

Fig. 7 hereabouts

Exothermic reactions like $A \rightarrow B$ and $A \rightarrow B \rightarrow C$ can produce not only natural convection in a fluid, but also oscillations and time-dependent spatial variations of temperature and concentrations [13, 14, 35, 37, 45]. Even the chemical reaction with the simplest mechanism of $A \rightarrow B$ can produce complex aperiodic oscillations [46], so that, provided there is feed-back of heat, the resulting oscillations can in principle lead to self-mixing. It is also worth noting that Griffiths and co-workers [47] have done important computational and experimental work on low temperature reactions (oscillating cool flames) in unstirred batch reactors, in which transport was governed by diffusional fluxes of both enthalpy and species. The experiments were conducted under various gravitational conditions [47, 48] in parabolic flights by researchers at the NASA Glenn Research Center.

3. Critical mixing

Critical mixing was introduced in section 1c above for a substance near its critical point. Equally one might have in mind a mixture of two species, which may form two immiscible liquid layers near what is in effect a pseudo-critical point. These are practical situations, *e.g.* encountered with mixtures of hydrocarbons. Let us now consider a system experiencing some external influence, such as an applied field. Suppose the influence is independent of time and also that changes in the system are described by an autonomous set of equations. Among

solutions to the problem, there are, of course, stationary modes, *i.e.* steady states. If a stationary mode is stable, nearby trajectories in phase space converge on the so-called limit point, which is an “attractor”. Now imagine that the external field approaches zero. In that case the stationary mode can be called an “equilibrium state”. For our analysis, the key feature is that bifurcations of both equilibrium states and stationary modes in active systems (*i.e.* a system under some external influence, such as a field) have a common feature. In parameter space, the region close to a bifurcation point has a large susceptibility [23], as defined above. The result is the appearance of large fluctuations near a bifurcation point and the system behaves chaotically. A transition from a stationary mode to any other always occurs via chaos [23].

Chaos can be generated by weak random noise inherent in any real system. Far from a bifurcation, noise does not have a noticeable effect on the system’s behaviour. However, as parameters are changed in order that a bifurcation point is approached, any noise is amplified considerably, because of the growth in susceptibility. Modes with every frequency are amplified, but the amplification of low frequencies prevails. Consequently, the observed fluctuations in such a region of criticality do not reproduce the initial noise, but are characteristic of the system itself. When the parameters become such that the system becomes close to a bifurcation, a variable’s mean value and variance can be comparable to one another, so that turbulence is likely to develop fully.

Below we use the Langevin equations for a numerical simulation of this critical chaos. To the initial set of equations, small random functions of time are added as white noise, so that the set of equations is no longer autonomous. In a real system, noise isn’t normally white; in general, its statistics are unknown. However, near a bifurcation, the correlation times of fluctuations grow so much that by comparison any noise looks to be δ -correlated, *i.e.* it is white noise, independent of frequency. In the case of equilibrium states, the use of the Langevin equations is not necessary. Moreover, the susceptibility may be then calculated from thermodynamic formulae. We now first discuss the problem of critical mixing, as applied to transitions involving two different, but continuous, phases, in particular to solutions forming two layers. For chemically reacting systems, the cusp in parametric space for a CSTR will be treated.

3.1 Critical states and their susceptibility

Let a system with many degrees of freedom undergo a deviation from a limit point in phase space. Such a deviation leads to the appearance of a “restoring force”, so the system returns to the initial stable state after some relaxation time. The relaxation time is different, as a rule, for different degrees of freedom. When the limit point is close to a bifurcation, there is one degree of freedom, for which the restoring force is anomalously small and the relaxation time is

correspondingly large. In the theory [19] of continuous phase transitions, such a variable is named “the order parameter”. We will assume that every dependent variable, with the exception of the order parameter, has its steady state value, whilst the value of the order parameter changes.

We denote the deviation from the limit point as x , so that $\langle x \rangle = 0$. The linearised equation for x takes the form:

$$dx/dt = -\lambda x + y(t), \quad (8)$$

where $\lambda > 0$ and y constitutes the source of a deviation. Firstly, let us choose a periodic source, so that $y \propto e^{-i\omega t}$. In that case, one can determine the steady state susceptibility, $\sigma(\omega)$, to be the ratio of the periodic solution $x \propto e^{-i\omega t}$ to the value of y . Thus, we arrive at:

$$\text{Re } \sigma = \frac{\lambda}{\lambda^2 + \omega^2}; \quad \text{Im } \sigma = \frac{\omega}{\lambda^2 + \omega^2}. \quad (9)$$

If the limit point approaches a bifurcation, $\lambda \rightarrow 0$, so the susceptibility, σ , becomes very large at low frequencies. The correlator of fluctuations created by a random source, (*e.g.* producing white noise, independent of frequency) is given by:

$$\langle x(0)x(t) \rangle = \langle x^2 \rangle e^{-\lambda|t|} \quad (10)$$

and the variance $\langle x^2 \rangle$ is connected with the source by:

$$\langle y(0)y(t) \rangle = 2\lambda \langle x^2 \rangle \delta(t). \quad (11)$$

where $\delta(t)$ is Dirac’s δ -function. It will be seen that the correlator has the Fourier transform:

$$(x^2)_\omega = (y^2)_\omega \frac{\text{Im } \sigma}{\omega}, \quad (12)$$

where, according to Eq. (11), the spectral density $(y^2)_\omega$ is independent of frequency. This equality may be treated as a manifestation of the fluctuation-dissipation theorem [19]. The rôle of “temperature” is played by the intensity of the noise.

When we deal with thermal fluctuations, the variance $\langle x^2 \rangle$ in Eq. (11) is determined by thermodynamic formulae. Therefore, the intensity of the noise is not arbitrary and should be fitted to provide the correct value of the variance. In the case of active systems (*i.e.* those under some external influence, such as a field), the intensity of the noise is a specified parameter. The critical pulsating magnitude depends on the “seed” noise, fed into the system. However, the pulsating frequency spectrum and other statistical properties are independent of noise. Finally, for several quantities, x_i , relating to different degrees of freedom, the set of equations:

$$dx_i/dt = -\lambda_{ik} x_k + y_i(t); \quad i, k = 1, 2, \dots \quad (13)$$

must be studied. A summation is implied by twice conforming to the subscripts. In that case the susceptibility becomes the matrix:

$$\sigma_{ik}(\omega) = (\lambda_{ik} - i\omega\delta_{ik})^{-1}, \quad (14)$$

where the superscript “-1” denotes the inverse of a matrix and δ_{ik} is the Kronecker delta. It will be seen that σ_{ik} is the resolvent to the Jacobian matrix of the set of Eqs. (14).

3.2 Fluids near their critical point

The theory of continuous phase transitions (see *e.g.* [19]) is suitable for analysing the behaviour of fluids (and even those which are mixtures of *e.g.* two species) near their critical point. This theory operates with the order parameter, ζ and the Gibbs chemical potential for a species takes the form:

$$\mu = \mu_0 + aT'\zeta^2 + B\zeta^4 - FV\zeta. \quad (15)$$

Here μ_0 is the constant part of the chemical potential, a and B are positive parameters and T' is the temperature above the critical point. The symmetric [19] phase corresponds to positive values of T' ; the antisymmetric phase to $T' < 0$. The strength of the applied field is F ; V is the system's volume. We shall assume that F is constant, when studying stationary states. If $F = 0$, there is one minimum for μ at $T' > 0$ and there are three turning points at $T' < 0$, *viz.* two minima, as well as one maximum between them. The minimum at ζ_0 changes continuously with T and T' , but a jump in the derivative $d\zeta_0/dT'$ occurs. At small F , there is a transition of 1st order; the value of ζ_0 changes step-wise from zero to $\zeta_1 \propto F^{1/4}$. The susceptibility is:

$$\sigma \text{ (at } \omega = 0) = \left(\frac{\partial \zeta}{\partial F} \right)_{T', F \rightarrow 0} = \frac{V}{abT'}, \quad (16)$$

where b has one of two values, *i.e.* either $b(T' > 0) = 2$ or $b(T' < 0) = -4$. Near the critical point, the susceptibility becomes extremely large. Just as for low frequencies in Section 3.1, the long-wavelength modes prevail now. The medium becomes inhomogeneous due to large slow fluctuations. The susceptibility depends on the wave number, k . Instead of Eq. (14), we write [49]:

$$\sigma(\omega = 0, k) = \frac{1}{2(aT' + dk^2)}. \quad (17)$$

We find again that the susceptibility approaches infinity at $k, T' \rightarrow 0$. At the same time, a distance-scale, d , has appeared in Eq. (17), just as the time-scale, λ , appeared in Eq. (8). These two quantities are natural parameters for self-mixing.

One can apply these equations for a general theory to the “liquid-vapour” transition, using ζ as the deviation of density from its critical value. The equation of state can then be derived from Eq. (15) to be:

$$p = FT' + 2aT'\zeta + 4B\zeta^3, \quad (18)$$

in which the dimensionless pressure above the critical point is $p = (P - P_c)/P_c$, and P_c is the critical pressure. The straight line $p = FT'$ corresponds, when $T' < 0$, to phase equilibrium (the boiling curve), and it is the critical isochore at T' . The susceptibility in this particular case is the compressibility and is:

$$\sigma(\omega = 0, k = 0) = \left(\frac{\partial \zeta}{\partial p} \right)_{T'} = \frac{1}{2aT' + 12B\zeta_0^2}. \quad (19)$$

By analogy, the susceptibility of a solution with two immiscible layers can be determined, because it is the derivative of concentration with respect to temperature, provided that the critical values are both referred to. Very importantly, large pulsations will develop near this critical point, so that one then expects effective mixing.

4. Bifurcations in the behaviour of a chemical reactor

Let us return to considering again the single, first-order reaction $A \rightarrow B$ in a CSTR. In the plane (Da, Se) there is a region of bistability for the stationary states; the boundary of this domain includes a cusp. Near the cusp the susceptibility and fluctuations in both the concentration and temperature are large. Consequently near a bifurcation point, the properties of stationary states are similar to those of the critical state of matter, due to this high susceptibility. Instead of the two, first-order Eqs. (1) and (2) for the dimensionless concentration, η , and temperature, θ , we can consider one single second-order equation. For example, by expressing η in terms of θ and $(d\theta/d\tau)$ one obtains [7]:

$$\frac{d^2\theta}{d\tau^2} = -\frac{\partial V}{\partial \theta} - \xi \frac{d\theta}{d\tau}, \quad (20)$$

where

$$\xi = e^\theta + \frac{1}{\text{Da}} + \frac{1+\theta}{\text{Se}} - \frac{d\theta}{d\tau} \quad (21)$$

and the potential $V(\theta)$ is given by:

$$V = e^\theta \left(\frac{1+\theta}{\text{Se}} - \frac{Ze}{\text{Da}} \right) + \frac{1}{\text{DaSe}} \left(\frac{\theta^2}{2} + 2\theta \right) + \text{constant}, \quad (22)$$

Here $\theta = (E/RT_c^2)(T - T_c)$, where T_c is the temperature at the cuspidal point, which is taken as the reference temperature. Equation (20) for the CSTR is mathematically equivalent to the one-dimensional equation of motion of a particle of unit mass along the distance coordinate θ under the action, firstly, of the force defined by the potential in Eq. (22) and secondly by the frictional force $\xi d\theta/d\tau$. Given the initial values of η and θ , the initial “velocity” ($d\theta/d\tau$) can be found by using Eq. (2). Depending on the values of the relevant parameters, the “friction coefficient”, ξ , defined by Eq. (21) can change sign and interestingly become negative, *i.e.* there is apparently “energy growth”, fed by the inlet stream to the reactor. In this respect, Eq. (19) is analogous to van der Pol’s equation [50]. It is clear that the condition $\xi > 0$ can be established by adjusting the flow rate through the CSTR.

Inside a region of bistability, the potential $V(\theta)$, like the chemical potential above, has two minima separated by a maximum. Thus $T_l < T_m < T_u$ are the temperatures at the three steady state solutions to Eqs (1) and (2). The locus in the (Da, Se) plane defined by the equality of minimum potentials $V_l = V_u$ is analogous to the boiling line in the phase diagram for a liquid - gas system, when plotted as pressure against temperature. This line divides the bistable region into two parts, in which, respectively, the hot and the cold states of the reactor are metastable. At a given Da , the upper and lower boundaries of the bistable region (along the Se axis) correspond to the maximum with its “cold” and “hot” minima. The bistable region in the (Da, Se) plane is bounded by a cuspidal point (Da_c, Se_c) , where all three extrema merge.

The cuspidal point is analogous to the critical point of a (non-symmetry-breaking) phase transition [19]. A plot of $V(\theta)$ becomes “shallow” near the extrema, where $Da \rightarrow Da_c$ and $Se \rightarrow Se_c$. As the cuspidal point is approached, this must lead to an increase in susceptibility. The increase will be steepest in the low-frequency part of the susceptibility. Since the parameters of a real system always exhibit weak, random variations, irregular deviations from a stationary state must be observed near the cuspidal point. These deviations develop quickly and relax slowly; thus a state, which should be stationary as predicted by Eq. (20), is actually chaotic.

This behaviour differs from critical behaviour near a change of phase in that not only stationary, but also periodic solutions to Eq. (20) for a CSTR are possible. Such solutions have been found before [51, 52] and analyzed in detail by Vaganov *et al.* [11]. The threshold for an “oscillatory” instability is determined by the condition that ξ is zero at $T = T_{min}$, where $dT/d\tau = 0$ and T_{min} is the stationary temperature corresponding to a minimum in V . Furthermore, this condition for the onset of oscillations may pass through the cuspidal point, when parameters are changed in magnitude. In this case, these “critical” fluctuations strongly affect the dynamics of a transition to regular oscillations. Thus below an account is given of the changes in the dynamics

of a CSTR in the neighbourhood of a cusp, as revealed by Vaganova and Rumanov's [23] numerical simulation of a transition to periodic oscillations. They used “white noise” to seed the system.

Some results are shown in Fig. 8 for the changes in the frequency spectrum of a CSTR on altering the value of Ze . When $Ze = 7$, in this case we have $\xi_0 \gg \omega_0$, where, at a cuspidal point $\xi = \xi_0$, $\theta = \theta_0$, $d\theta/d\tau = 0$ and also the frequency

$$\omega_0 = \left[e^{\theta_0} \left(-\frac{Ze}{Da} + \frac{3 + \theta_0}{Se} \right) + \frac{1}{DaSe} \right]^{1/2}, \quad (23)$$

is the one which vanishes at the cuspidal point and also in its vicinity is low in amplitude. This is because, after a deviation, the “force”, restoring the reactor back to its stationary state is weak. In this case, the spectrum in Fig. 8 is found on analysis to behave approximately as $1/\omega$. However, when Ze is increased to move the system away from the cuspidal point, the low - frequency peak vanishes. This is in contrast to flicker (or $1/f$) noise. It should also be noted that the above numerical simulations were performed for a region of strongly non-linear behaviour, where approximations, *e.g.* Frank-Kamenetskii's discussed above, were necessary, but see [23] for a full discussion. The value of $Ze = 8$ (see Fig. 8) is close to the threshold of an oscillatory

Fig. 8 hereabouts

instability at: $Ze - 8 \approx 5 \times 10^{-9}$. In this case, $\xi_0 \ll \omega_0$, but no resonance is observed at the frequency of ω_0 ($\approx 0.1 \text{ s}^{-1}$). There may be a shallow maximum at $\omega \approx 0.2 \text{ s}^{-1}$ (the non-linear resonance frequency), but it is obscured by an intense background due to the high susceptibility and a low friction coefficient, ξ . The chaotic dynamics of a similar, resonantly driven, non-linear oscillator have been described by Huberman and Crutchfield [53]. When $Ze = 8.1$, the contrast between the peak and the background increases in Fig. 8, but the value of ξ corresponds to a periodic oscillation, because when $\xi < 0$ (as here, corresponding as seen above to “energy growth”), there is an unstable limit point. Also, $\xi = 0$ is the theoretical boundary for oscillatory instabilities, if fluctuations are ignored. The remaining power spectra in Fig. 8 for $Ra = 8.2, 8.5$ and 9.0 demonstrate how the peak amplitudes gradually increase at the fundamental and overtone frequencies at the expense of the background continuum. Thus, the picture observed, when Ze increases, has little in common with a transition from a stationary to a periodic oscillatory state. Instead, it should be interpreted as the emergence of a periodic oscillatory state from a chaotic one.

It is generally believed that reliable numerical results cannot be obtained for critical regions, near a bifurcation point. This is clearly due to the increase in the susceptibility of the stationary states of such a system, when its parameters approach their critical values. Vaganova

and Rumanov [23] have suggested that by introducing weak white noise into the governing equations, they become Langevin equations, which can be studied in detail. Of course, the intensity of the noise to simulate thermal fluctuations would have to be consistent with any thermodynamic variance. In the simulation of active systems, noise characteristics need not meet any requirement other than that of low intensity. It has been shown [23] that the variance of critical fluctuations driven by weak noise can be similar in magnitude to the expected value of the fluctuating variable, as in fully developed turbulence. In fact, a state, which is predicted to be stationary (and stable) by the system of governing equations, is actually chaotic. Moreover, the statistical characteristics of the resulting fluctuations are independent of the “seed” noise; instead, they are determined by the parameters of the system. Therefore, numerical integration of the Langevin equations in the critical region and subsequent statistical analysis of solutions can be used to refine the information obtained from physical experiments.

In many situations (particularly for lumped systems), the calculation of susceptibility is a huge task, since non-linear susceptibility should be taken into account very close to a bifurcation point. However, such characteristics are not required for describing critical phenomena. Solutions of Langevin’s equations provide “raw” data (actually for stochastic processes, like the variations in power examined in Fig. 8). These data can be used to calculate correlation functions, critical scaling exponents, and other characteristics, including the dimension of a chaotic attractor. Thus, numerical simulation can provide a comprehensive statistical description of the bifurcation under study. It should be noted that strong fluctuations in the critical region are due to the weakness of the “restoring force”, which appears when the system deviates from a stationary state. This behaviour is characteristic of all bifurcations of stationary states studied to date.

5. Self-mixing and chaotic modes induced by several chemical reactions

When the parameters of a system take it far from a bifurcation point, chaotic behaviour is possible under certain conditions. To understand them let us consider an autonomous set of equations. For the smallest number of equations, *i.e.* 1, chaotic solutions are impossible. On the other hand, when the number of equations is large enough, almost all solutions are chaotic. It would seem that a smooth transition from regular to chaotic behaviour occurs when the number of equations grows. The onset of chaos thus corresponds to the number of equations becoming much greater than unity. However, the picture appears to be more complicated.

5.1. Examples of chaotic modes

In chemical systems, several reactions often occur simultaneously. To describe the processes a mathematical model should include equations for both the concentrations of reagents and temperature. It is well known that chaotic solutions are possible for a system, provided the

number of equations is 3 or more. When the number of equations is as small as 3, the appearance of chaos had been revealed by Lorenz's study [54] of atmospheric turbulence generated by thermal convection. The solution to this fluid-dynamical problem was reduced to the following three equations:

$$dX / dt' = \alpha(Y - X), \quad (24)$$

$$dY / dt' = (r - Z)X - Y, \quad (25)$$

$$dZ / dt' = XY - \varphi Z. \quad (26)$$

In Eqs (24) – (26), X, Y and Z are the quantities sought, t' is now an appropriate dimensionless time and α, r and φ are governing parameters. Chaotic solutions to these equations exist if these parameters have values in the interval: $24.74 < r < 148.4$ at $\alpha = 10$, and $\varphi = 8/3$. However, a limit cycle also becomes an attractor at $r > 28$. Of course, in general the “chaotic” domain in parameter space may grow with the number of equations describing the system.

Equations (24) - (26) are *prima facie* similar to those of chemical kinetics. In fact, it is almost possible to devise *e.g.* a two-phase, isothermal CSTR (involving *e.g.* gaseous and liquid phases), whose dynamics are close to being described by these three equations, if X, Y and Z are dimensionless concentrations of reacting species, based on appropriate scales. Because X, Y and Z do not depend on any spatial coordinates, the system must be thought of as well-mixed. Now, as an exercise, let us replace X by the function:

$$f(X) = \frac{X}{1 + X}. \quad (27)$$

Such a change might occur because of diffusion becoming important. Thus, for example, the rate of reaction on unit surface area of a catalyst might be written as $k_s C_s X$, where k_s is a rate constant, C_s is the concentration of a reactant at the catalyst's surface and X is the fraction of the catalytic sites, which are unoccupied. If diffusion from the bulk fluid, adjacent to the catalyst's surface, is important, the rate of reaction per unit surface area is: $k_s C_s X = D(C_b - C_s)$. Here C_b is the concentration of reactant in the bulk fluid and D is its diffusivity. In such a case with diffusion, C_s becomes $C_s = DC_b / (k_s X + D)$ and the rate of reaction per unit surface area of catalyst is:

$$\frac{k_s C_b X}{1 + k_s X / D} \quad (28)$$

instead of $k_s C_s X$. Thus in effect X has been replaced by $C_b X / \{C_s(1 + k_s X/D)\}$ by introducing the above diffusional limitation. This means that by a suitable choice of scales, X can be replaced by $X/(1 + X)$.

Figure 9 gives plots of some trajectories for these two cases of (a) Lorenz's Eqns (24) – (26), which evidently behave chaotically, and (b) after the transformation (27), which results in stabilization of the chaos. Thus in this latter case, the stable stationary mode (steady state) has been established by introducing diffusion. It would thus appear that a chaotic dependence on time can be easily destroyed by introducing diffusion. Such a conclusion needs checking by solving *e.g.* the differential equations for flow and reaction inside *e.g.* a tubular reactor with and without the terms for diffusion. Nevertheless, Fig. 9 suggests that Eq. (4) is satisfied in this case, so that there is self-mixing with diffusion.

Fig. 9 hereabouts

Of course, other sets of equations have been proposed (*e.g.* [55 - 57]) for purely chemical systems to obtain chaotic solutions, which occur when the parameters are in restricted and sometimes narrow intervals. Occasionally chaos is developed *via* a series of period doublings. It should be noted that for an extended set of *pdes* with period doublings, the shift of the bifurcation parameter into a domain of instability is accompanied by alternating regular and chaotic intervals [58]. In fact, the deeper the shift into a domain of instability, the longer are the chaotic intervals. Such a change can result in there being eventually more chaotic intervals than non-chaotic ones. Thus, the picture of the eventual development of chaos [59, 60] is perhaps correct “on average”, but jumps between regular and chaotic behaviour can take place, if parameters are changed into a deeply unstable domain. It is also worth noting that chaotic solutions to all these systems give trajectories, which are locally smooth. Chaos is only seen during certain times.

A common property of chaotic solutions is of requiring a relatively narrow diapason of parameters for such solutions to exist. In this respect, systems based on a small number of equations are similar to systems with critical mixing, for which the parameters are very restricted for chaotic behaviour. Of course, a wider range of parameters gives chaos for systems with many degrees of freedom, including extended systems, *i.e.* those described by spatial variables, as well as time.

5.2 Temporal and spatial correlations

The break-down of a correlation will produce independent parameters and also mixing. As seen above in Eqs (8) and (13), chaotic modes are characterized by a scale, λ , with dimensions of s^{-1} . Under critical conditions, the correlation time grows. Nevertheless, even in these cases, the mixing time remains smaller than the residence time of fluid in the reactor. As

for spatial correlations, their scale (correlation length) may be estimated to be $\sqrt{\chi/\lambda}$, where χ is a suitable diffusivity, kinematic viscosity or thermal diffusivity. One can use these scales to estimate the quality of mixing.

5.3 The role of frequency locking

As seen above, examples of chaotic behavior are possible in small domains in parameter space. It is convenient to analyze the situation in terms of non-linear oscillations. As parameters shift into a region of instability, one can imagine the system's behaviour in terms of the superposition of the oscillations generated. Suppose the system has two frequencies, ω_1 and ω_2 , whose ratio is a rational number (*e.g.* $\omega_1/\omega_2 = 1/5$). Then the frequency $n_1\omega_1 + n_2\omega_2$ should also be an eigenmode of the system, provided n_1 and n_2 are integers. If this way of combining frequencies acted without limitation, a fast growth of the modes would occur. However, the opposite process of frequency-locking (discovered by Huygens [61]) does take place. Thus when two frequencies appear close to each other, one of them "catches up" the other and they merge. Thus, frequency locking decreases the number of frequencies and so prevents the development of chaos.

Suppose two independent exothermic reactions occur in a CSTR. In the case of either reaction, an oscillatory mode is possible at a frequency, which depends on the reaction's parameters. For two independent reactions proceeding in the same vessel, one can expect frequency-locking under certain conditions. If these conditions do not hold, complicated (quasi-periodic) oscillations should be observed. Such modes may well be suitable for generating "self-mixing".

6. Mixing by gas bubbles

It was noted in Fig. 2 that gas bubbles are capable of stirring a liquid and consequently also of mixing it. Many examples of such a use of gas bubbles are available, with the bubbles being either a reactant or product. One example worth considering is the deep shaft system for treating sewage. The principle is illustrated in Fig. 10. A huge U-tube, up to 100 m from top to bottom is buried in the ground, but both limbs (containing a liquid like sewage) protrude at ground level into a tank. Air is fed into one limb (the riser), so that the liquid circulates and bubbles are disengaged in the header-tank. When the velocity of the liquid in the downcomer tube exceeds the rise-velocity of single bubbles, air is also fed from a sparger into the downcomer, so that bubbles move downwards and later up the riser. The chemical reaction in this case is the oxidation of sewage by dissolved oxygen. Stirring of the liquid is achieved by rapid circulation of the liquid, together with the motion of the bubbles. A big advantage of such a design is that the high pressure caused by up to 100 m of liquid head increases the concentration of dissolved oxygen, so that rates of reaction are also accelerated. The process is

an offshoot of one originally conceived by ICI [62] for the production of artificial protein in an aqueous solution of methanol. The deep shaft process for treating sewage is very suitable for cities like Tokyo, where the price of land is high and a shaft can be sunk deep into the ground. In practice, two concentric pipes often replace the U-tube.

Fig. 10 heareabouts

This approach has recently been taken a step farther by Zimmermann *et al.* [63], who used microbubbles (diam. < 50 μm) generated by a novel fluidic oscillator in an airlift bioreactor, analogous to the U-tube in Fig. 10. These tiny bubbles have higher mass transfer rates than larger bubbles. Also, microbubbles can be inhibited from coalescing by stabilizing them hydrodynamically. One further advantage is that the fluidic oscillator disrupts boundary layers and so decreases the frictional losses in pipes, *etc*, thereby lowering the consumption of energy. These developments make the airlift reactor even more attractive.

Another reactor in which bubbles are crucially important is a fluidised bed. This involves a bed of particles (typically 0.5 to 5 mm in size), through which passes a flow of gas (or sometimes a liquid) sufficiently large for the pressure difference across the bed to be sufficient to lift and “fluidise” the particles. If the flowrate of gas exceeds the minimum for fluidisation, the excess gas passes through the mobilised and levitated solids as bubbles [64, 65]. These bubbles ensure that the solids are well stirred. However, there are two groups of gaseous bubbles: small, slow-moving, cloudless ones and large, fast, clouded bubbles. With the former, the gas percolating interstitially through and supporting the solids is moving upwards faster than a tiny bubble; the result is that gas enters the lower half of a small bubble and leaves via the top half. In fact, the leaving gas does not re-enter the bubble; instead it flows between the adjacent fluidised particles. This contrasts with the flow field of gas in and around a large, fast bubble. Here the gas percolating through the “particulate phase” rises more slowly than such a bubble does. Again, some gas enters the bottom of a bubble and leaves at the top. However, in this case the gas is swept through a “cloud” closely around the bubble to re-enter at the bottom of the bubble. Mixing between this re-circulating gas and that incipiently fluidising the particles is poor. In fact, most of the gas inside a very large bubble merely stays inside the bubble and circulates around its interior. The result is that the gas in the “bubble phase” is not at all mixed well with the gas in the particulate phase. Thus if a real fluidised bed were gasifying particles of coal char by reaction with CO_2 as the fluidising gas in the reaction: $\text{C} + \text{CO}_2 \rightarrow 2\text{CO}$, the result would be an increase in the flow rate of gas. The newly-formed CO enters the “bubble phase”, thereby leading to larger bubbles and poorer mixing of the CO_2 in rising bubbles with the fluidised carbon particles. The converse will occur whenever chemical reaction leads to a decrease in the overall flow rate of gas. One example is a fluidised bed of calcined limestone

(*i.e.* CaO) used to remove CO₂ from combustion gases [66] in the reaction $\text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3$. Another example is the use of the same sorbent to remove SO₂ from a fluidised bed combustor of coal or biomass [67] in the reaction $\text{CaO} + \text{SO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{CaSO}_4$. In both these examples, the chemical reaction promotes mixing of gas in the bubble and particulate phases by leading to a decreased flowrate of gas and smaller bubbles.

7. Conclusion

Our discussion has shown that random modes in chemical and mixing processes can influence each other. Sometimes the influence leads to feedback. Theoretical analysis, as well as numerical simulations, have given a satisfactory understanding of the main features of the phenomena, while experimental studies are as yet not developed to the same extent. The vicinity of the cusp in the (Da, Se)-plane for a CSTR does seem to be a useful location for experimentation. Likewise, optical methods (*e.g.* critical opalescence) could be useful for studying natural convection. A statistical study of bifurcations and chaotic modes might be expected to become the basis for a theory of self-mixing. Otherwise, the rôle of bubbles in effecting mixing in both liquids and fluidised beds of particles, is discussed.

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Fig.1. Plot (against the natural logarithm of the Rayleigh number) of the computed ratio of the critical value of the Frank-Kamenetskii number, δ , for an explosion and its value for $Ra = 0$. The four regions are as follows: 1, there is neither thermal explosion nor natural convection; 2, there is no explosion, but convection is observed; 3, there is an explosion, accompanied by convection, which prolongs the induction period for an explosion; 4, there is an explosion without convection, which has insufficient time to develop. Taken from Shtessel' *et al.* [27].

Fig. 2. The dependence of δ , for thermal explosion of the substance ‘Dina’ on the Rayleigh number: part *a* holds for the lower Ra and was measured in a laboratory experiment, when the release of gas caused bubbling in a melt; branch *b* was obtained during pilot-scale testing at relatively low temperatures and release rates of gas. Taken from Barzykin *et al.* [17].

Fig. 3. Velocity vectors in a vertical plane through the centre of a spherical reactor (radius 49.3 mm) for $Ra = 605$, $\tau_{\text{reac}} = 3.85$ s, $\tau_{\text{conv}} = 0.169$ s and $\tau_{\text{diff}} = 4.17$ s. The flow is vertically upwards near the axis of symmetry; adjacent to the walls fluid moves downwards. At the centre the velocity is 69 mm/s after 6 s. From Cardoso *et al.* [35].

(i)

(ii)

Fig. 4. Approximate streamlines showing the flow patterns in a vertical plane through the centre of symmetry after (i) 2 s and (ii) after 6 s. Here $Ra = 7.5 \times 10^5$, $\tau_{reac} = 3.85$ s, $\tau_{diff} = 25.0$, $\tau_{conv} = 0.0030$ s. From Cardoso *et al.* [35].

Fig.5. Sketch of the regime diagram for the exothermic reaction $A \rightarrow B$ occurring inside a spherical reactor without mechanical stirring. Between the grey surface and the origin the system explodes; at the other side of the grey surface no explosion occurs. From Liu *et al.* [25].

Fig. 6. The regime diagram for a spherical reactor without any consumption of reactant (*i.e.* $\tau_H / \tau_{\text{reac}} = 0$) for $RT_0/E = 0.027$, $Pr = 1$, order of reaction = 1.4 and $\gamma = 1.018$. The horizontal axis denotes the well-mixed limit where $Ra = \infty$; the vertical axis represents the purely diffusive limit for $g = 0$ and so for no natural convection. The straight lines for $Ra = 500$ and $Ra = 10^6$ are shown; they separate the space into three regions, where natural convection is either very weak, strong but laminar and, for $Ra > 10^6$, turbulent. From Liu *et al.* [18].

Fig. 7. Plots against real time of the three terms in Eq. (7) for the generation, convection and diffusion of heat at the centre of a spherical reactor. The conditions are: radius of reactor = 0.050 m, $g = 0.5 \text{ m s}^{-2}$, $\kappa = 0.5 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$, $Ra = 12060$. Other conditions are given by Campbell *et al.* [14].

Fig. 8. Power spectra of fluctuations inside a CSTR for $Ze = 7.0, 8.0, 8.1, 8.2, 8.5$, and 9.0 . The abscissa is the frequency (in s^{-1}), $\omega_n = 2\pi n/t_0$, where t_0 is the time for simulation and n is an integer. From Vaganova and Rumanov [23].

Fig. 9. Phase trajectories, plotted in 3-dimensional phase space, for (a) the Lorenz set of Eqs (24) – (26) and (b) after replacing X by $X/(1 + X)$ for $\alpha = 10$, $r = 28$ and $\varphi = 8/3$. With these parameters, there is a chaotic solution to the Lorenz system in Fig. 9(a). In Fig. 9(b) after the substitution (27), the phase trajectory, starting from $X = 10$, $Y = 40$, $Z = 0$, approaches the limit point $X = 19.9$, $Y = 19.9$, $Z = 7.1$.

Fig 10. Sketch of deep shaft system for reactions involving a gas and a liquid, taken from Davidson [62].