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Observations on the Nature of Reaction Runaway in Reaction-Diffusion Systems

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Introduction:

The evolution equation combining linear conduction and nonlinear production of heat

$$\phi_t = \nabla^2\phi + F(\phi) \tag{1}$$

has been studied for some time [1–3]. In chemically reacting systems, the function $F(\phi)$, representing the rate of reaction, introduces a feedback mechanism by virtue of which a self-sustained acceleration of the chemical reaction can arise. The process generally continues until equilibrium is approached and the rate of reaction F finally decreases towards zero at relatively high temperatures. Much of what happens subsequently depends in more detail on the way in which the reaction runaway has taken place.

There are essentially three possibilities. In the somewhat contrived circumstance that reaction runaway is simultaneously accompanied by external or boundary conditions which act to quench the reaction, then an ignition of the system may be prevented altogether—in the sense that the reaction runaway does not lead to further rapid combustion. More normally, however, some form of ignition will ensue, and either a laminar deflagration flame or a detonation wave will be produced. To properly describe such processes, a fuller model than equation (1) must be used, including gasdynamic, chemical and transport effects. Such an analysis may be found in reference [4] and will not be pursued here. It suffices to say that equations of the form of (1) play a key role in determining the overall generation and evolution of self-ignition.

The equation can be recast into a different form by making use of the transformation

$$w(\underline{\mathbf{r}},t) = \mathcal{W}(\phi) = \int_{\phi}^{\phi_I} \frac{d\phi}{F(\phi)} \tag{2}$$

(for a suitable constant ϕ_I) in terms of which, spatially uniform solutions would take the simple form $w = t_I - t$. The equation for w is

$$w_t = \nabla^2 w - 1 - \frac{(\nabla w)^2}{\mu w}$$

in which $$\mu^{-1} = wF'(\phi) = \frac{dF}{d\phi}\int_{\phi}^{\phi_I} \frac{d\phi}{F(\phi)}. \tag{3}$$

The latter definition is such that wide classes of the function F can be found to give constant values of μ. For example, if $\phi_I = \infty$ and $F = e^{\phi}$ or $F = \phi^{\nu}$ with $\phi \geq 0$ and $\nu > 1$, then it is easily seen that $\mu = 1$ or $\mu = (\nu - 1)/\nu$, respectively. In more general problems, it may often be considered that the constant ϕ_I is chosen such that the parameter μ remains at least very nearly constant [5] over much of the evolution of ϕ. At any rate, it is clear that equation (3) is relevant to a wide variety of cases if μ is taken to be a constant in the range $0 < \mu \leq 1$. The problem is

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considered to be normalised such that $F(\phi)$ varies as an order one function of ϕ (when ϕ is of order one) and that order one boundary–initial conditions are specified.

The existence of a reaction runaway then corresponds to the condition that $w \to 0$ in a finite time t_I. If the runaway does not take place uniformly in space, then the origin may be chosen such that

$$w(\underline{0}, t_I) = 0, \quad \text{with} \quad w(\underline{r}, t) > 0 \quad \text{for all} \quad t < t_I. \tag{4}$$

The main questions that need to be asked are: what types of behaviour are possible for w as $t \to t_I$, and with what forms of boundary–initial conditions would they be consistent? In this spirit, it is most natural to anticipate some manner of self-similar behaviour for w as $t \to t_I$.

Exactly Self-similar Behaviour:

In the sense of Barenblatt [6], equation (3) admits only one exactly self-similar form of behaviour which is consistent with the condition (4):

$$w = (t_I - t) h\left(\frac{\underline{r}}{\sqrt{t_I - t}}\right). \tag{5}$$

Concentrating attention on symmetric cases, so that one can define the scalar self-similarity variable $\zeta = |\underline{r}|/\sqrt{t_I - t}$, the equation satisfied by the function $h(\zeta)$ is

$$h'' + \left(\frac{n}{\zeta} - \frac{\zeta}{2} - \frac{h'}{\mu h}\right) h' = 1 - h \tag{6}$$

where $1 + n$ is now the number of dimensions of symmetry. Identifying the integrating factor $\zeta^n \exp(-\zeta^2/4)/h^{1/\mu}$, this differential equation for h can be transformed into the integral equation

$$\int_\gamma^h \frac{dh}{h^{1/\mu}} = \int_0^\zeta \frac{e^{\zeta^2/4}}{\zeta^n} \int_0^\zeta \zeta^n e^{-\zeta^2/4} \frac{1-h}{h^{1/\mu}} \, d\zeta^2 \tag{7}$$

in which it has been assumed that $h'(0) = 0$ (the condition for non-singular symmetry) and that $h(0) = \gamma > 0$ so that γ, n and μ parameterise the full range of possible non-singular symmetric solutions.

The most useful interpretation of the constant γ is found by recognising that it is simply the coefficient in the rate of decrease of w at the point of symmetry: $w(0) = \gamma(t_I - t)$. If $\gamma = 1$, then the spatially uniform solution $w \equiv t_I - t$ is recovered, so that γ^{-1} is a measure of the time taken for reaction runaway to occur relative to the time for homogeneous reaction runaway. Values in the range $\gamma > 1$ require that $w(0)$ decreases faster than it would do without conduction. This is a somewhat pathological situation requiring that the decrease in $w(0)$ be enhanced by heat conducting inwards from some hotter region away from $\zeta = 0$.

The left side of equation (7) integrates to give

$$\int_\gamma^h \frac{dh}{h^{1/\mu}} = \begin{cases} \ln(h/\gamma) & : \quad \mu = 1 \\[2ex] \dfrac{\gamma^{-(1-\mu)/\mu} - h^{-(1-\mu)/\mu}}{(1-\mu)/\mu} & : \quad \mu < 1. \end{cases} \tag{8}$$

Noting that the second of these forms (for $\mu < 1$) tends to a finite upper limit as $h \to \infty$, it becomes clear that, unless the second integral on the right side of (7) tends to zero as $\zeta \to \infty$, then the function w behaves as follows

$$w \sim \begin{cases} (t_I - t) \exp\left[B^2 \left(\dfrac{t_I - t}{r^2}\right)^{\frac{1+n}{2}} \exp\left(\dfrac{r^2/4}{t_I - t}\right)\right] & : \quad \mu = 1 \\[2ex] (t_I - t) B'^2 \left(\zeta_\infty - |r|/\sqrt{t_I - t}\right)^{-\mu/(1-\mu)} & : \quad \mu < 1 \end{cases} \tag{9}$$

as $\zeta \to \infty$ or $\zeta \to \zeta_\infty$, for positive constants B^2, B'^2 and ζ_∞. As a result, the limit of w as $t \to t_I$ is indeed zero at $r = 0$, but it is infinity for all $r \neq 0$ in the case $\mu = 1$; for $\mu < 1$, w becomes infinite at the finite boundary $|r| = \zeta_\infty (t_I - t)^{1/2}$ which moves towards $r = 0$ as

$t \to t_I$. Applying boundary conditions which would be consistent with such behaviour (in order to maintain these forms of self-similar solution) is more-or-less equivalent to a failed attempt to quench the reaction runaway by increasingly rapid cooling (or, if necessary, somehow reducing the effective size) of some container of the reactants.

In the absence of such conditions, the exactly self-similar form (5) can only be of relevance if the second integral on the right side of (7) tends to zero as $\zeta \to \infty$. One way of investigating this condition is by considering the behaviour of the function $B_\infty(\gamma, \mu, n)$ defined to represent the integral

$$B_\infty^2 = \int_0^{\zeta_\infty} \zeta^n e^{-\zeta^2/4} \frac{1-h}{h^{1/\mu}} \, d\zeta. \tag{10}$$

In this, ζ_∞ is interpreted as representing the position at which $h(\zeta)$ becomes infinite, or if this does not happen for finite values of ζ, then $\zeta_\infty = \infty$. Only where $B_\infty = 0$ can the exactly self-similar form of behaviour for w be of relevance without any artificial attempts at quenching the reaction.

The behaviour of B_∞ in up to four dimensions of symmetry is illustrated in figure 1. The diagrams cover a wide range of variation of the parameters μ and γ. It is clear that B_∞ is zero, as it must be, for $\gamma = 1$; this is the case which leads to the trivial spatially-uniform solution $h \equiv 1$. For $\gamma > 1$, it seems that B_∞ decays in some exponential way as μ decreases towards zero. There is no firm indication, however, that B_∞ will actually be zero for $\mu > 0$ and $1 < \gamma < \infty$. This is the range of γ identified earlier as requiring somewhat abnormal behaviour, and so is not of particular interest.

Otherwise, in dimensions of one and two $(n \leq 1)$, it can be seen that B_∞ increases as $\gamma \to 0$. Only in dimensions of three or more $(n \geq 2)$, does B_∞ actually decrease as $\gamma \to 0$ for some values of μ, raising the possibility that B_∞ may actually become zero for small enough values of γ. It may also be noted that equation (6) possesses the degenerate solution $h = \frac{1}{2}\zeta^2/(1 + n - 2/\mu)$ which can only be positive for $\zeta \neq 0$ (as w must be, before $t = t_I$) if $n \geq 2$. Based on the existence of this solution, it has in fact been proven recently that countably infinite numbers of exactly self-similar solutions, having $h/\zeta^2 \to$ constant as $\zeta \to \infty$, exist in the cases, $F = e^\phi$ for $n \geq 2$ and $F = \phi^\nu$ for $n > (\nu + 3)/(\nu - 1)$ (see review by Bebernes and Kassoy [7]). In terms of μ, this shows that infinite numbers of zeros of B_∞ should be found for $\mu > 4/(3 + n)$.

Examining the behaviour of B_∞ for small values of γ, these zeros are indeed found. Using γ_i $(i = 1, 2, \ldots)$ to denote the successive values of γ at which $B(\gamma_i, \mu, n) = 0$, table 1 shows the pattern of these zeros for $\mu = 1$. It can be seen that zeros are found for ratios of γ_{i+1}/γ_i which seem to approach a constant value as i increases. In the case of spherical symmetry, figure 2 shows the way in which the values of γ_i vary with μ. As μ is decreased below unity, the values of γ_i decrease and approach zero when μ approaches the limit $4/(3 + n)$.

In the physically meaningful case of three dimensional symmetry, the first zero is found for γ equal to about $1/248$. This is a very small value indeed, so that the corresponding self-similar solution represents a case in which the reaction and diffusion terms of equation (1) are only very slightly out of balance. Successive values of γ_i are reduced further by a factor of less than 10^{-2} at each stage. It follows that successive solutions are yet closer still to a reactive–diffusive balance. The situation is reminiscent of the well-known occurrence of an infinite number of steady-state symmetric solutions of equation (1) in dimensions of three or more (see [8,9], for example). Indeed, for small values of γ_i, the time-dependent term of (1) will be correspondingly small—thus ensuring that the solutions will, in fact, have almost the same structure. Table 1 shows that, while the values of γ_1 are larger in cases of higher dimensional symmetry, they are nevertheless also still very small.

This property renders these exactly self-similar solutions of little practical use. Equations of the form of (1) are normally obtained by neglecting the consumption of chemical reactants in modelling exothermic chemistry [3]. This approximation can only be sustained for a relatively short time, the order of magnitude of which must generally be small compared to the nondimensional activation-energy ratio $E/(RT)$, which is rarely greater than about 50 in value (even at room temperatures). Since reaction runaway with this sort of self-similar behaviour should occur on a time-scale of the

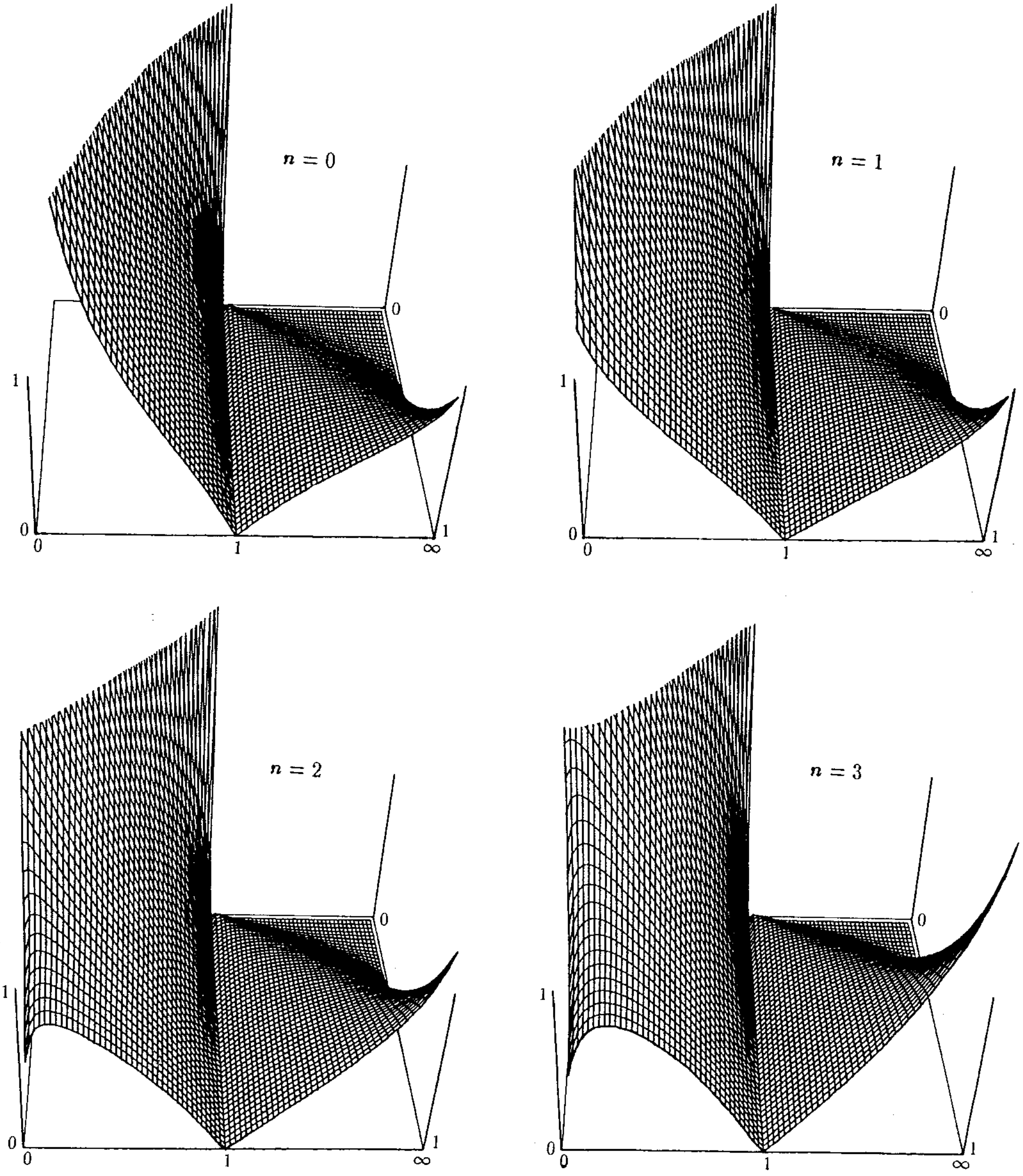

Figure 1. Perspective views of the function B_∞, numerically calculated for dimensions $1+n$ from 1 to 4. The γ axes are scaled in proportion to $2\gamma/(1+\gamma)$. Values of B_∞ are plotted for μ between 0.02 and 1, and for γ between 0.0127 and 79.

order of γ_i^{-1}, the model is likely to become invalid long before this can happen. In effect, the consumption of chemical reactants would prevent an exactly self-similar reaction runaway of this type from forming.

Table 1. The first few values of γ_i at which the zeros of B_∞ are found, for between three and six dimensional symmetry with $\mu = 1$.

n	γ_1	γ_2	γ_3	γ_4	γ_1/γ_2	γ_2/γ_3	γ_3/γ_4
2	4.026×10^{-3}	3.564×10^{-5}	3.040×10^{-7}	2.637×10^{-8}	113.0	117.3	115.3
3	1.043×10^{-2}	2.850×10^{-4}	7.53×10^{-6}	2.005×10^{-7}	36.6	37.9	37.6
4	1.322×10^{-2}	5.17×10^{-4}	2.01×10^{-5}	7.84×10^{-7}	25.6	25.7	25.6
5	1.277×10^{-2}	5.42×10^{-4}	2.34×10^{-5}	1.01×10^{-6}	23.5	23.2	23.1

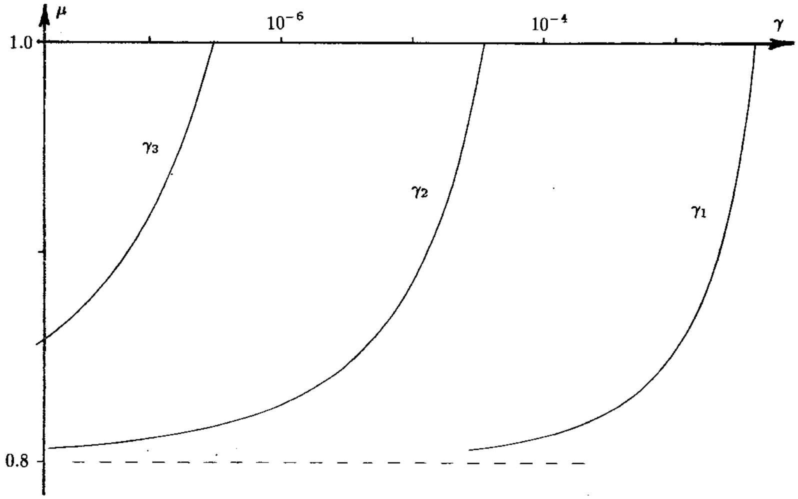

Figure 2. The dependence of γ_i on μ in the spherically symmetric case. The γ axis is scaled in proportion to $\log_{10}\gamma$.

Asymptotically Self-Similar Form:

A more fruitful approach to determining the nature of reaction runaway begins by using semi-qualitative arguments. Equation (3) contains only one nonlinear term. The reaction-rate $F(\phi)$ has been reduced to the constant negative forcing -1 on w. At a minimum value of w the diffusive term $\nabla^2 w$ will be positive (or at least non-negative), opposing the effects of the reaction. The nonlinear term is zero at the minimum (where ∇w must be zero), but negative elsewhere. Moreover, this term depends inversely on the value of w, so that it should become important as $w \to 0$. Also, because the negative forcing of this term on w increases to either side of the minimum, its overall effect should generally be to *flatten out* the spatial variation of w about its minimum, and thereby to reduce the immediate influence of the diffusive term $\nabla^2 w$. By contrast it may be noted that, apart from the spatially uniform case $\gamma = 1$, diffusive effects remain of primary importance in any exactly self-similar description—as seen, for example, in equation (6).

The argument can be made more formal by firstly considering symmetric cases, with the function w expanded about $r = 0$ in the manner $w = a(t) + r^2 b(t) + r^4 c(t) + r^6 d(t) + \ldots$. Equation (3) then requires that

$$\begin{aligned} a' &= -1 + [2(1+n)b] \\ b' &= -\frac{4b^2}{\mu a} + [4(3+n)c] \\ c' &= -\left(\frac{16bc}{\mu a} - \frac{4b^3}{\mu a^2}\right) + [6(5+n)d] \\ &\vdots \end{aligned} \tag{11}$$

where the final terms, in square brackets, arise because of the diffusive term $\nabla^2 w$.

If the effect of the nonlinear term is, indeed, to diminish the importance of diffusive effects, then it should be feasible to seek solutions in which these terms are negligible at the dominant order; accordingly, it can be assumed that as $t \to t_I^-$, the coefficients satisfy the asymptotic ordering:

$$b = o(a'), \quad c = o(b'), \quad d = o(c'), \quad \text{etc.} \tag{12}$$

As a result,

$$\begin{aligned} a' &\sim -1 & &\Rightarrow & a &\sim t_I - t \\ \mu b' &\sim -\frac{4b^2}{a} & &\Rightarrow & b &\sim \frac{\mu/4}{\alpha - \ln(t_I - t)} \\ \mu c' &\sim -\frac{16bc}{a} + \frac{4b^3}{a^2} & &\Rightarrow & c &\sim \mu^2 \frac{\beta + [\alpha - 1 - \ln(t_I - t)]/(t_I - t)}{16[\alpha - \ln(t_I - t)]^4} \\ & & &\vdots & & \end{aligned} \tag{13}$$

for constants α, β etc. These solutions satisfy the asymptotic ordering (12) and thus they provide a consistent asymptotic description of the reaction runaway close to $r = 0$.

To first-order, the analysis shows that the reaction-runaway process can possess solutions which behave asymptotically in the manner

$$\phi \sim \mathcal{W}^{-1}\left(t_I - t + \frac{\mu r^2/4}{\alpha - \ln(t_I - t)}\right) \tag{14}$$

or simply

$$\frac{w}{t_I - t} \sim 1 + \frac{\mu r^2/4}{(t_I - t)[\alpha - \ln(t_I - t)]} \tag{15}$$

regardless of the number of dimensions of symmetry. This result generalises on similar findings [10,11] for more specific examples of the function $F(\phi)$. Equation (15) provides an asymptotically self-similar description of the reaction runaway in terms of the self-similarity variable-grouping $\xi_\alpha = r/\sqrt{(t_I - t)[\alpha - \ln(t_I - t)]}$. More details about this solution, including its behaviour both at higher orders and in regions away from the hottest point, can be found in references [5,11].

The simplicity of this result also carries over into non-symmetric cases. Provided the rectangular coordinates of the system are chosen to lie along appropriate major and minor axes which characterise the reaction runaway, the series expansion for w can be taken in the form $w \sim t_I - t + x^2 b_1(t) + y^2 b_2(t) + z^2 b_3(t) + \dots$ (in, say, three dimensions); the axes of x, y and z are therefore chosen so that the coefficients of xy, xz and yz may be taken to be zero (or asymptotically smaller than b_i)—no generality is lost in doing this. In this case,

$$\mu b_1' \sim -\frac{4b_1^2}{t_I - t}, \quad \mu b_2' \sim -\frac{4b_2^2}{t_I - t} \quad \text{and} \quad \mu b_3' \sim -\frac{4b_3^2}{t_I - t} \tag{16}$$

so that

$$b_1 \sim \frac{\mu/4}{\alpha_1 - \ln(t_I - t)}, \quad b_2 \sim \frac{\mu/4}{\alpha_2 - \ln(t_I - t)}, \quad \text{and} \quad b_3 \sim \frac{\mu/4}{\alpha_3 - \ln(t_I - t)} \tag{17}$$

etc. It is thus seen that the reaction runaway can take the more general leading-order form,

$$\frac{w}{t_I - t} \sim 1 + \frac{\mu}{t_I - t}\left[\frac{x^2/4}{\alpha_1 - \ln(t_I - t)} + \frac{y^2/4}{\alpha_2 - \ln(t_I - t)} + \frac{z^2/4}{\alpha_3 - \ln(t_I - t)}\right] \tag{18}$$

which reduces to the simpler symmetric form if all α_i are either equal or infinite, with the coordinate r appropriately defined.

Discussion:

It can therefore be seen that non-uniform reaction runaway generally tends to develop in a way that involves a relative diminishing of the overall effects of diffusion or conduction in comparison with the effects of the chemical reaction. Exceptions to this occur when the reaction runaway has to compete with some externally applied cooling—this must vary in its strength so as to keep pace with the accelerating chemical activity in the reaction kernel. In a less contrived manner, it seems that diffusion may be able to maintain its relative importance in three (or more) dimensions in certain cases where diffusion and reaction remain only very slightly out of balance. The stability of self-similar descriptions of this type of runaway has not yet been analysed, but in physically realistic examples it is very unlikely that they would be able to develop significantly before chemical equilibrium is achieved.

The reason why diffusion adopts such a secondary role is connected with the nonlinear effects exhibited in equation (3). In terms of the original model (1), when the reaction-rate $F(\phi)$ is a nonlinearly increasing function of ϕ, it acts to increase higher temperatures faster than lower temperatures. This produces a tendency to progressively concentrate the growth of ϕ. For example, if diffusion were to be omitted from the model so that $\psi_t = F(\psi)$, then symmetric solutions would take the form

$$\frac{\mathcal{W}(\psi)}{t_I - t} = 1 + \epsilon\zeta^2 + O[(t_I - t)\zeta^4] \tag{19}$$

for some constant $\epsilon \geq 0$. Ironically, as $t \to t_I$ for $\epsilon \neq 0$, this result for a model *without diffusion* mimics the exactly self-similar behaviour postulated in equation (5) for the model with diffusion. Thus this behaviour can be seen to arise solely from the nonlinearly increasing reaction rate.

On the other hand, particularly in the absence of strong enough sources or sinks at boundaries of the system, diffusion generally acts to disperse any concentration of temperature. In equation (19), this would amount to reducing the value of the coefficient ϵ. This, in turn, reduces the relative effectiveness of diffusion in the system so that ϵ will decrease at a diminishing rate. This is precisely the behaviour found in the arguments leading to equation (15) which also shows that ϵ should vary in the manner $\epsilon = \frac{1}{4}\mu/[\alpha - \ln(t_I - t)]$.

The constant α must ultimately be dominated by the logarithm in this expression for ϵ, which therefore becomes remarkably independent of both the initial–boundary conditions, leading to reaction runaway, and the number of dimensions of symmetry. However, α should generally be large in situations where diffusion initially has only a weak effect [11]—a reaction runaway of this type resembles a more developed reaction runaway in which diffusive effects have *become* weak.

It is important to bear in mind the limitations of the model (1). The value of ϕ cannot generally grow without bound; at some stage, possibly for a fairly large value of ϕ, the chemical reaction must slow down as it approaches equilibrium. For systems satisfying an Arrhenius rate-law (in which $F(\phi) \approx e^{\phi}$), this will happen when ϕ and $-\ln(t_I - t)$ are of the order of $E/(RT)$. If α happens to be as large as this (or larger), then it will not be completely dominated in the expression for ϵ. Hence α will play an important role, throughout the evolution, in determining the size of the most vigorously reacting region.

Compressibility effects should also be borne in mind. A large enough reacting region can develop a degree of inertial confinement of (say) hot expanding gases, leading to a significant local increase in absolute pressure [12]. In the case of gases reacting at an Arrhenius rate-law, a condition can be determined for pressure increases, accompanying the reaction runaway, to remain relatively minor [4]:

$$\mathbf{K\acute{a}} \gg \alpha + \frac{E}{RT} \tag{20}$$

in which **Ká** is the von Kármán number, defined as the ratio of the chemical time to the mean molecular collision time, under locally prevailing conditions. For sound physical reasons, this ratio has to be large [13] so that (with the possible exception of α) the inequality (20) is a comparison between large quantities. The inequality can certainly be violated if α becomes large enough. Under these circumstances, a detonation rather than a laminar deflagration may be the end result of the reaction runaway.

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