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DYNAMICS OF RAPID EXTINCTION IN A LUMPED SYSTEM WITH ARRHENIUS CHEMISTRY

D. D. DO AND R. H. WEILAND

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Abstract

Reacting systems with Arrhenius chemistry can exhibit multiple steady states for $\gamma > 4(1 + \beta)/\beta$ where γ is activation energy and β is the heat of reaction. We give a detailed analysis of the extremely rapid jump which takes place as catalyst activity slowly decays through criticality. Previous analyses are asymptotic in the limit $\gamma \to \infty$; here we relax the large γ assumption and only require that passage through criticality is slow.

1. Introduction

An intriguing feature of certain chemically reacting systems is a multiplicity of steady and stable oscillatory states. Oscillatory states are exemplified by the now famous Belusov-Zhabotinskii reaction. Multiple steady states are known to occur in systems obeying Arrhenius chemistry with large enough activation energy [3] and in isothermal systems with Langmuir-Hinshelwood kinetics [2].

Many solid-catalysed reactions are of the Langmuir-Hinshelwood (also termed substrate inhibited) type which results from a nonlinear relationship between reactant concentrations in the gas phase and in the sorbed form on the catalyst surface. Existence, uniqueness and stability have been discussed by De Vera and Varma [5] and we have recently investigated the dynamics of the jump or exchange of steady states which takes place when one of the parameters of the system passes through a critical value [6].

Multiplicity in systems with Arrhenius chemistry has been of interest for some time (see Aris [3]) and a good deal of work has been done in the context of combustion theory. For example, Liñán and Williams [16, 17] have determined ignition time for a combustible material exposed to constant energy flux and a sudden change in surface temperature. The analysis was asymptotic in the limit of large activation energy, γ. In the same limit, $\gamma \to \infty$, Kapila and Matkowsky [11] have obtained asymptotic solutions to the steady reaction-diffusion problem in nonisothermal porous catalyst pellets of slab and cylindrical geometries. Analytical expressions were obtained for all three branches of the S-curve characterising the response of the system.

Large activation energy asymptotics date from at least 1939 when Frank-Kamenetskii [7] used the concept, and it has since been discussed by Williams [20] and applied to flame phenomena [4, 15]. The dynamics of such systems on passage of a parameter through critical have begun to be analyzed only recently. The earliest work appears to be that of Kassoy [12] who gave a transient analysis of spatially homogeneous gaseous explosions in the subcritical, nearcritical and supercritical regions. For such lumped systems governed by nonlinear ordinary differential equations, the response caused by slow variation of a parameter through criticality has been treated by Haberman [8]. Very recently, Kapila [9] and Kassoy and Poland [13, 14] have examined the dynamics of ignition in distributed parameter systems and Kapila [10] has reported on the transition from the extinguished to the ignited state as the reaction rate parameter is slowly varied through critical in both lumped and distributed systems. All of these analyses are asymptotic in the limit $\gamma \to \infty$. From a practical viewpoint, such a limit is not nearly as relevant to chemical reactors as it is to combustion phenomena, although $\gamma \to \infty$ does allow one to get at higher order terms in the asymptotic expansions rather more easily.

In the current work, we analyse the dynamics of the response of a lumped parameter system when the catalyst activity slowly passes through a critical value but we relax the requirement that γ is large. We ask only that the rate of catalyst deactivation be sufficiently slow.

2. System equations

For the first-order reaction $A \to B$ in an adiabatic constant-flow stirred-tank reactor fed with product-free reactant at concentration C_0 and temperature T_0, the species and heat balance equations are

$$V\, dC_A/dt' = F(C_0 - C_A) - Vk_0 a C_A \exp\left[ER^{-1}\left(T_0^{-1} - T^{-1}\right)\right], \qquad (2.1a)$$

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$$V\,dC_B/dt' = -FC_B + Vk_0aC_A \exp\left[ER^{-1}\left(T_0^{-1} - T^{-1}\right)\right], \tag{2.1b}$$

$$V\rho C_p\,dT/dt' = \rho C_pF(T_0 - T) + (-\Delta H)Vk_0aC_A \exp\left[ER^{-1}\left(T_0^{-1} - T^{-1}\right)\right], \tag{2.1c}$$

where T is temperature, C_A and C_B are the reactant and product concentrations respectively, t' is time, a is catalyst activity, E is activation energy, $(-\Delta H)$ is the heat of reaction, V is reactor volume, F is feed rate, ρ is density and C_p is specific heat. We introduce the following nondimensional parameters and variables:

$$t = k_0t', \quad H = F/(Vk_0), \quad \gamma = E/(RT_0), \quad \beta = (-\Delta H)/(\rho C_p),$$
$$A = C_A/C_0, \quad B = C_B/C_0, \quad \theta = T/T_0,$$

so that (2.1) becomes

$$A_t = H(1 - A) - aA \exp\left[\gamma(1 - \theta^{-1})\right], \tag{2.2a}$$

$$B_t = -HB + aA \exp\left[\gamma(1 - \theta^{-1})\right], \tag{2.2b}$$

$$\theta_t = H(1 - \theta) + \beta aA \exp\left[\gamma(1 - \theta^{-1})\right]. \tag{2.2c}$$

The parameter H is the space velocity through the reactor and is essentially the inverse of the holdup time.

There are two types of self-poisoning: in the first the catalyst is deactivated by the reactant irreversibly bonding with active sites (parallel poisoning) while in the second, the product is responsible for loss-of-activity (series poisoning). We shall restrict our attention to series poisoning for which the nondimensional deactivation kinetics are

$$-a_t = \varepsilon aB \exp\left[\delta(1 - \theta^{-1})\right], \tag{2.2d}$$

where $\delta = E_d/(RT_0)$ is the activation energy associated with the poisoning process and $\varepsilon = k_dC_0/k$ is a small parameter measuring deactivation rate (constant k_d) relative to reaction rate.

The reactor is taken to be filled initially with only inert material at unit temperature but to contain fully active catalyst:

$$A(0) = B(0) = 0, \tag{2.2e}$$

$$\theta(0) = a(0) = 1. \tag{2.2f}$$

It can easily be shown that species concentrations and temperature are interrelated quite independently from reaction order, activation energy and any consideration of poisoning. This allows us to write the system equations solely in terms of temperature and catalyst activity:

$$\theta_t = H(1 - \theta) + a\left[(1 + \beta - \theta) - \beta \exp(-Ht)\right] \exp\left[\gamma(1 - \theta^{-1})\right], \tag{2.3a}$$

$$a_t = -\varepsilon\beta^{-1}a(\theta - 1) \exp\left[\delta(1 - \theta^{-1})\right], \tag{2.3b}$$

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subject to (2.2f). We are interested in the dynamic behaviour of θ as a slowly passes through a critical value, a_c. In the transition analysis we will take $\delta = 0$ but we will not impose any special restriction on γ except that it be sufficiently large for multiple solutions to exist. This is in sharp distinction to previous work on Arrhenius systems in which solutions were obtained only asymptotically in the limit $\gamma \to \infty$. We obtain leading order solutions valid in the limit $\varepsilon \to 0$, in which ε measures the rate of deactivation compared to the main reaction rate. The slow variation of a is characterized by a slow time τ, in which

$$\tau = \varepsilon t, \quad \varepsilon \ll 1, \tag{2.4}$$

so that (2.3) transforms to

$$\varepsilon\theta_\tau = H(1-\theta) + a\big[(1+\beta-\theta) - \beta\exp(-H\tau/\varepsilon)\big]\exp\big[\gamma(1-\theta^{-1})\big], \tag{2.5a}$$

$$a_\tau = -a\beta^{-1}(\theta-1)\exp\big[\delta(1-\theta^{-1})\big]. \tag{2.5b}$$

Initial conditions are

$$a(0) = 1, \quad \theta(0) = \theta^+, \tag{2.5c}$$

where θ^+ is the only real root of $g(\theta, 1, t \to \infty) = 0$ and

$$g(\theta, a, t) = H(1-\theta) + a\big[(1+\beta-\theta) - \beta\exp(-Ht)\big]\exp\big[\gamma(1-\theta^{-1})\big]. \tag{2.5d}$$

Thus, θ^+ represents the quasi-steady state attained immediately following reactor startup. We note that in the limit $\gamma \to \infty$, θ^+ becomes

$$\theta^+ \sim (1+\beta) - H\beta\exp\big[-\gamma\beta/(1+\beta)\big] + \ldots, \tag{2.5e}$$

and that the last term is transcendentally small.

3. Outer solutions

There are several regions which need to be considered separately. Away from criticality, τ is adequate to describe the slowly changing behaviour (except in the startup period when t is appropriate). As criticality is approached, the solution develops on a faster time scale; however this time fails to describe the dynamics of approach to the new steady state and an even faster time is needed. Here we examine the outer region, away from criticality.

We take advantage of the smallness of ε and assume asymptotic solutions of the form

$$\theta(\tau; \varepsilon) = \theta_0(\tau) + \varepsilon\theta_1(\tau) + O(\varepsilon^2), \tag{3.1a}$$

$$a(\tau; \varepsilon) = a_0(\tau) + \varepsilon a_1(\tau) + O(\varepsilon^2). \tag{3.1b}$$

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At leading order the equations are

$$H(1 - \theta_0) + a_0(1 + \beta - \theta_0) \exp\left[\gamma\left(1 - \theta_0^{-1}\right)\right] = 0, \tag{3.2a}$$

$$\frac{da_0}{d\tau} = a_0 \beta^{-1}(1 - \theta_0) \exp\left[\delta\left(1 - \theta_0^{-1}\right)\right], \tag{3.2b}$$

from which

$$a_0 = \left\{H(\theta_0 - 1) \exp\left[\gamma\left(\theta_0^{-1} - 1\right)\right]\right\} / (1 + \beta - \theta_0). \tag{3.3}$$

Using (3.3) in (3.2b), we obtain the dynamic equation for temperature θ_0 on the slowly varying manifold:

$$\frac{d\theta_0}{d\tau} = -\frac{\theta_0^2(1 + \beta - \theta_0)(\theta_0 - 1)^2 \exp\left[\delta\left(1 - \theta_0^{-1}\right)\right]}{\beta(\beta + \gamma)\left[\theta_0^2 - \dfrac{\gamma(2 + \beta)}{\beta + \gamma}\theta_0 + \dfrac{\gamma(1 + \beta)}{\beta + \gamma}\right]} \stackrel{\text{def}}{=} G(\theta_0). \tag{3.4}$$

The formal ordering which results from (3.1) is invalid when

$$\theta_0^2 - \frac{\gamma(2 + \beta)}{\beta + \gamma}\theta_0 + \frac{\gamma(1 + \beta)}{\beta + \gamma} = O(\varepsilon), \tag{3.5}$$

since then $\varepsilon d\theta_0/d\tau$ is not $O(\varepsilon)$. The solutions θ^* and θ_* of (3.5) with $\varepsilon = 0$ are

$$\theta^* = \frac{\gamma}{2}\left(\frac{\beta + 2}{\beta + \gamma}\right) + \left[\frac{\gamma^2}{4}\left(\frac{\beta + 2}{\beta + \gamma}\right)^2 - \frac{\gamma(1 + \beta)}{\beta + \gamma}\right]^{1/2}, \tag{3.6a}$$

$$\theta_* = \frac{\gamma}{2}\left(\frac{\beta + 2}{\beta + \gamma}\right) - \left[\frac{\gamma^2}{4}\left(\frac{\beta + 2}{\beta + \gamma}\right)^2 - \frac{\gamma(1 + \beta)}{\beta + \gamma}\right]^{1/2}, \tag{3.6b}$$

termed upper and lower branch points, respectively, and we see that a necessary condition for multiplicity is

$$\gamma > 4(1 + \beta)/\beta. \tag{3.7}$$

For non-first-order reaction, necessary conditions have been obtained by van den Bosch and Luss [19] and Tsotsis and Schmitz [18]. We note that in the limit $\gamma \to \infty$ expressions equivalent to (3.6) are

$$\theta^* \sim (1 + \beta) - (1 + \beta)^2/\gamma + (\beta^4 + 4\beta^3 - 4\beta - 2)/(2\beta\gamma^2) + O(\gamma^{-3}), \tag{3.8a}$$

$$\theta_* \sim 1 + \gamma^{-1} + (\beta^4 + 4\beta + 2)/(2\beta\gamma^2) + O(\gamma^{-3}). \tag{3.8b}$$

Thus, by comparing (2.5e) with (3.8) we see that $\theta^+ > \theta^* > \theta_* > 1$ and the necessary condition for multiplicity is always satisfied for $\gamma \to \infty$.

Only the upper branch point θ^* is of interest here since for extinction θ_* is unattainable by slowly decreasing a (see Figure 1). The other solution θ_0 varies smoothly from the initial quasi-steady level θ^+ to θ^* and then jumps (discontinuously on the τ-scale) to another quasisteady state $\bar{\theta}$, shown in Figure 1. The

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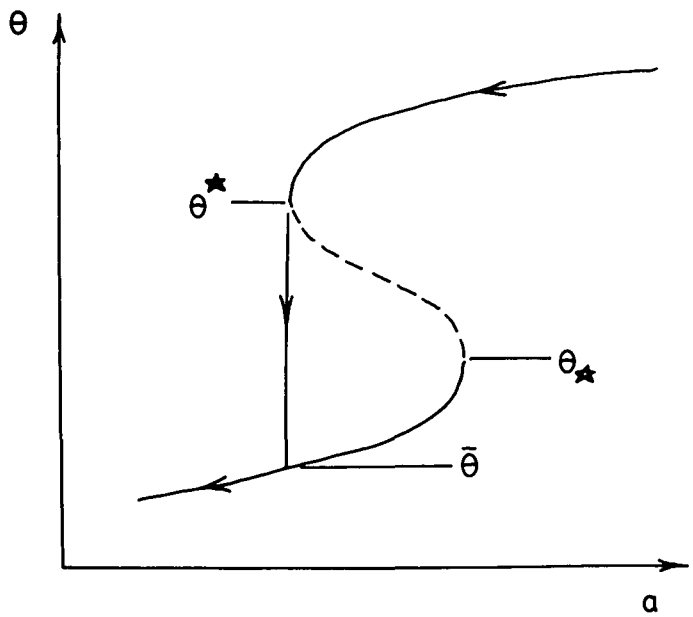

Figure 1. Solution trajectory in the phase plane.

other branch point, θ_*, could be reached only by increasing a along the branch containing $\bar{\theta}$ and it is noted that $\bar{\theta}$ is *not* a branch point.

The jump can be understood by linearized stability theory which in terms of the deviation variable

$$\omega = \theta - \theta_0, \tag{3.9}$$

gives

$$\frac{d\omega}{dt} = \frac{\partial g(\theta_0, a_0, \infty)}{\partial \theta}\omega + O(\omega^2), \tag{3.10a}$$

as the equation governing stability. Here

$$\frac{\partial g(\theta_0, a_0, \infty)}{\partial \theta} = -\frac{H(\beta + \gamma)}{\theta_0^2(1 + \beta - \theta_0)}\left[\theta_0^2 - \frac{\gamma(2 + \beta)}{\beta + \gamma}\theta_0 + \frac{\gamma(1 + \beta)}{\beta + \gamma}\right]. \tag{3.10b}$$

The solution θ_0 represents the entire solution given by the whole of the curve in Figure 1. The eigenvalue of (3.10a) is $\partial g/\partial\theta$; we have asymptotic stability in the limit $t \to \infty$ if $\partial g/\partial\theta < 0$, instability if it is positive and neutral stability if it is zero. In the precritical period, $\theta_0 \in (\theta^+, \theta^*)$ for which the eigenvalue is negative. As $\theta_0 \to \theta^*$, $\partial g/\partial\theta$ passes through zero and becomes positive as θ_0 passes through θ^*. It remains positive along the middle branch of the curve where

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$\theta_0 \in (\theta^*, \theta_*)$; the whole of this branch is globally unstable. Stability is regained on passage through θ_* and the entire lower branch is stable. Since $\partial g/\partial\theta$ is purely real, the new state $\bar{\theta}$ is approached monotonically and not through a limit cycle.

The solution of (3.4) with initial condition (2.5c) is implicit ($\theta_0 \notin (\theta^*, \bar{\theta})$)

$$\tau = \beta(\beta + \gamma)\int_{\theta_0}^{\theta^+} \frac{\exp\left[\delta(1 - x^{-1})\right]\left[x^2 - \dfrac{\gamma(2 + \beta)}{(\beta + \gamma)}x + \dfrac{\gamma(1 + \beta)}{(\beta + \gamma)}\right]}{(1 + \beta - x)(x - 1)^2 x^2}\, dx, \tag{3.11}$$

and since the time characteristic of the jump is too fast to permit a detectable change in a at leading order, the new steady state $\bar{\theta}$ is the only real solution (other than θ^*) of

$$\frac{(1 + \beta - \bar{\theta})\exp\left[\gamma(1 - \bar{\theta}^{-1})\right]}{(1 - \bar{\theta})} = \frac{(1 + \beta - \theta^*)\exp\left[\gamma(1 - \theta^{*-1})\right]}{(1 - \theta^*)}, \tag{3.12}$$

from (3.3). The branching time τ_0 is given by (3.11) with θ_0 replaced by θ^* as the lower limit of integration.

The behaviour of the upper and lower branches is needed for subsequent matching. At this juncture we put $\delta = 0$ to keep the analysis tractable and find that for, $(\tau - \tau_0) \to 0-$,

$$\theta_0 \sim \theta^* + \alpha(\theta^*)(\tau_0 - \tau)^{1/2} + O(\tau_0 - \tau) \tag{3.13a}$$

while for $(\tau - \tau_0) \to 0 +$,

$$\theta_0 \sim \bar{\theta} - G(\bar{\theta})(\tau - \tau_0) + O(\tau - \tau_0)^2, \tag{3.13b}$$

where $G(\bar{\theta})$ is as defined in (3.4) but with $\delta = 0$ and

$$\alpha^2(\theta^*) = \frac{2(1 + \beta - \theta^*)\theta^{*4}(\theta^* - 1)}{\beta\left\{\theta^*\left[\gamma^2 + 2\gamma(1 + \beta)\right] - \gamma^2(1 + \beta)\right\}}. \tag{3.13c}$$

4. Transition

The time appropriate to the initial stages of the jump is assumed to be of the form

$$\zeta = \frac{\tau - \tau_0 - \rho(\varepsilon)}{\nu(\varepsilon)}, \tag{4.1}$$

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in which $\nu(\varepsilon) \gg \varepsilon$ and $\rho(\varepsilon)$ is a time shift which could be found from higher order matching [6]. We examine the dynamics locally in the vicinity of the critical point (θ^*, a^*) using the following *local* expansions:

$$\theta = \theta^* + \sigma_1(\varepsilon)\theta_1(\zeta) + o(\sigma_1), \tag{4.2a}$$

$$a = a^* + \omega_1(\varepsilon)a_1(\zeta) + o(\omega_1). \tag{4.2b}$$

When the expansions (4.2) are used in (2.5) rewritten in terms of the new time ζ, a balance of the principal terms results from the choice

$$\nu(\varepsilon) = \varepsilon^{2/3}, \sigma_1(\varepsilon) = \varepsilon^{1/3}, \omega_1(\varepsilon) = \varepsilon^{2/3}, \tag{4.3}$$

and the leading order equations are

$$\frac{d\theta_1}{d\zeta} = \tfrac{1}{2}\left(\frac{\partial^2 g^*}{\partial\theta^2}\right)\theta_1^2 + \left(\frac{\partial g^*}{\partial a}\right)a_1, \tag{4.4a}$$

$$\frac{da_1}{d\zeta} = -\left[(\theta^* - 1)/\beta\right]a^*, \tag{4.4b}$$

with a^* given by

$$a^* = \left\{H(\theta^* - 1)\exp\left[\gamma(\theta^{*-1} - 1)\right]\right\}/(1 + \beta - \theta^*). \tag{4.5}$$

The notation g^* indicates that the derivatives are evaluated at θ^*, a^* with $t = \infty$.

The solution of (4.4b) is

$$a_1 = -\left(\left\{H(\theta^* - 1)^2\exp\left[\gamma\left(\theta_*^{-1} - 1\right)\right]\right\}/(1 + \beta - \theta^*)\right)\zeta, \tag{4.6}$$

in which the constant of integration has been absorbed into the time shift $\rho(\varepsilon)$. When this result is used in (4.4a), we obtain an equation which can be put ito Riccati form through the transformation

$$T = -\frac{1}{2}\left(\frac{\partial^2 g^*}{\partial\theta^2}\right)\zeta, \tag{4.7a}$$

$$K = 4\frac{\partial g^*/\partial a}{(\partial^2 g^*/\partial\theta^2)^2}\,\frac{H(\theta^* - 1)^2\exp\left[\gamma(\theta^{*-1} - 1)\right]}{\beta(1 + \beta - \theta^*)}. \tag{4.7b}$$

The resulting equation is

$$\frac{d\theta_1}{dT} + \theta_1^2 = -KT, \tag{4.8}$$

which can be solved through the transformation

$$\theta_1 = d(\ln V)/dT. \tag{4.9}$$

Putting $\eta = K^{1/3}T$ we obtain the well-known Airy equation

$$\frac{d^2V}{d\eta^2} + \eta V = 0, \tag{4.10}$$

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whose solution can be written in terms of the modified Bessel functions [1]:

$$V = \begin{cases} C(-\eta)^{1/2} K_{1/3}\left[\frac{2}{3}(-\eta)^{3/2}\right] & \text{for } \eta < 0, \\ \frac{C\pi\eta^{1/2}}{3^{1/2}}\left[J_{1/3}\left(\frac{2}{3}\eta^{3/2}\right) + J_{-1/3}\left(\frac{2}{3}\eta^{3/2}\right)\right] & \text{for } \eta > 0. \end{cases} \tag{4.11}$$

Thus, θ has the following asymptotic forms in the limits $\zeta \to \infty$ and $\zeta \to -\infty$, respectively:

$$\theta \sim \theta^* + \varepsilon^{1/3} C\left[\frac{2\beta(1+\beta-\theta^*)\theta^{*4}}{H^2(\theta^*-1)^3\{\theta^*[\gamma^2+2\gamma(1+\beta)]-\gamma^2(1+\beta)\}}\right]^{1/3}\zeta^{-1} + O(\zeta^{-2}) \quad \text{as } \zeta \to \infty, \tag{4.12a}$$

and

$$\theta \sim \theta^* + \varepsilon^{1/3} C\left[\frac{H^2(\theta^*-1)^3\{\theta^*[\gamma^2+2\gamma(1+\beta)]-\gamma^2(1+\beta)\}}{2\beta(1+\beta-\theta^*)\theta^{*4}}\right]^{1/6}(-\zeta)^{1/2} + O(\zeta) \quad \text{as } \zeta \to -\infty. \tag{4.12b}$$

It is the form (4.12b) which, when written in terms of $(\tau - \tau_0)$, matches the asymptotic form of the precritical solution in the limit $(\tau - \tau_0) \to 0-$ given by (3.13a); the integration constant must be

$$C = \left[\frac{2(1+\beta-\theta^*)\theta^{*4}}{\beta^{1/2}H^{1/2}\{\theta^*[\gamma^2+2\gamma(1+\beta)]-\gamma^2(1+\beta)\}}\right]^{2/3}, \tag{4.13}$$

The algebraic decay (ζ^{-1}) of (4.12a) does not permit matching with the lower branch of the outer solution. In view of the local nature of the expansions (4.2) this was to be expected. We therefore consider a second post-critical transition region.

5. Second transition

The time appropriate to the approach to a new quasi-steady level $\bar{\theta}$ is

$$\xi = \frac{\tau - \tau_0 - \delta(\varepsilon)}{\varepsilon}, \tag{5.1}$$

so that apart from the time shift $\delta(\varepsilon)$, which can be determined only by matching of terms higher order than the first, ξ is equivalent to the original fast time t. With the asymptotic expansion

$$\theta = \bar{\theta}_0(\xi) + \varepsilon\bar{\theta}_1(\xi) + O(\varepsilon^2), \tag{5.2a}$$

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$$a = \bar{a}_0(\xi) + \varepsilon\bar{a}_1(\xi) + O(\varepsilon^2), \tag{5.2b}$$

the leading order equations are

$$\frac{d\bar{\theta}_0}{d\xi} = g\left(\bar{\theta}_0, \bar{a}_0, \infty\right), \tag{5.3a}$$

$$\frac{d\bar{a}_0}{d\xi} = 0. \tag{5.3b}$$

The solution to (5.3b) is

$$\bar{a}_0(\xi) = a^*, \tag{5.4}$$

and when this is used in (5.3a) we obtain

$$\frac{d\bar{\theta}_0}{d\xi} = H\left(1 - \bar{\theta}_0\right) + H(\theta^* - 1)\left[\left(1 + \beta - \bar{\theta}_0\right)/\left(1 + \beta - \theta_0^*\right)\right] \exp\left[-\gamma\left(\left(\bar{\theta}_0\right)^{-1} - (\theta^*)^{-1}\right)\right]. \tag{5.5}$$

This can be solved in terms of a quadrature and the solution has the following asymptotic behaviour which we require for matching:

$$\xi \to \infty; \quad \bar{\theta}_0 \sim \bar{\theta} + \text{transcendentally small terms}, \tag{5.6a}$$

$$\xi \to -\infty; \quad \bar{\theta}_0 \sim \theta^* + \sigma/\xi, \tag{5.6b}$$

where

$$\sigma = \alpha^2/\left[H\beta(\theta^* - 1)^2\right], \tag{5.7}$$

and α^2 is given by (3.13c). The solution matches automatically with the lower branch, as can be seen from (5.6a), and a little algebra will show that it also matches with the first transition solution (see (4.12a)).

6. Concluding remarks

We have examined the dynamics of an adiabatically operated reactor as the catalyst activity passes through a critical value a^*. In the precritical period and in the period following the jump the system responds on a time scale εt but passes through criticality on the faster time scale $\varepsilon^{1/3}t$. The jump is completed on the even faster time t, which is basically time scaled on the space velocity through the reactor. Apart from (3.7) we have made no assumptions about the magnitude of γ, yet our results in many respects parallel those of Kapila [10] who examined the inverse problem of ignition but in the limit $\gamma \to \infty$. For the ignition problem he found that most of the jump took place on an exponentially

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fast time scale in γ; however this appears to be an artifact of the large activation energy asymptotics. When we relax the assumption of large γ such behaviour does not arise. The cost of relaxing this assumption is algebra so unwieldy that only $O(1)$ solutions can be found. However, we speculate that, just as in the case of a jump caused by the interaction of a slowly varying parameter with Langmuir-Hinshelwood kinetics [6], there will be two time shifts, one each on the $\varepsilon^{1/3}t$ and t-scales. The use of the approximation $\gamma \to \infty$ results in the shift on the $\varepsilon^{1/3}t$-scale being lost and only the t-scale need be time shifted [10].

The activity at which the transition will take place and the reactor will fail is given by (4.5) and in the limit of $\gamma \to \infty$ this is

$$a^* \sim \left[H\beta\gamma/(1+\beta)^2 \right] \exp\left[-\beta\gamma/(1+\beta)\right] \ll 1, \tag{6.1}$$

where we have had to use the first two terms in (3.8a). Thus, for $\gamma \to \infty$, Figure 1 must be replaced by Figure 2 and

$$a_* \sim \left[H/(\beta\gamma - 1) \right] \exp\left[-(1 + 1/\gamma)^{-1}\right]. \tag{6.2}$$

For very large γ, the reactor fails at *exponentially small* values of activity and the jump is most spectacular, being nearly β in magnitude.

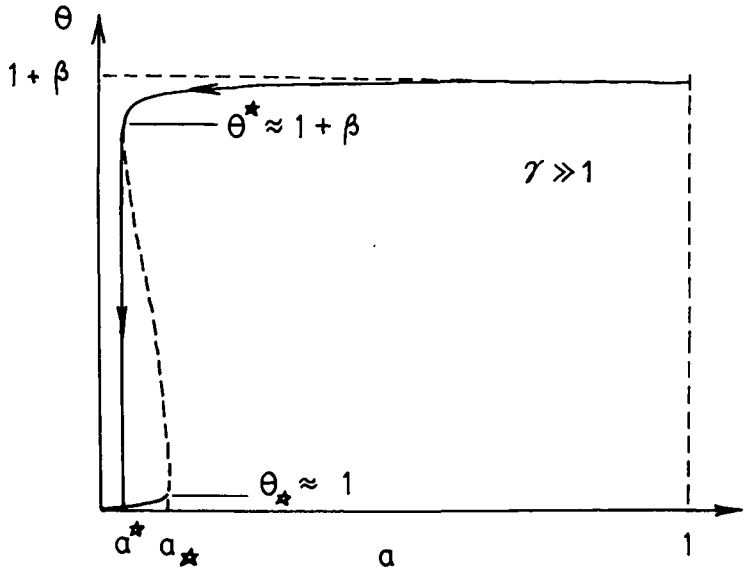

Figure 2. Solution trajectory for $\gamma \gg 1$ showing reactor failure when a is nearly zero.

In the transition region, for large γ, the solution (4.6) is asymptotically

$$a_1 \sim -\beta a^* \zeta, \tag{6.3}$$

with a^* given by (6.1). This implies that (4.2b) is

$$a/a^* \sim 1 - \varepsilon^{2/3}\beta\zeta, \tag{6.4a}$$

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or

$$a/a^* \sim 1 - \beta(\tau - \tau_0), \tag{6.4b}$$

and comparing with (2.24) of Kapila [10] we see that his small parameter δ plays the same role as ε here. In his analysis, $\delta \gg \gamma^{-1}$.

Perhaps the most important distinction between the work of Kapila [10] and the current analysis is that if one were to take $\gamma \to \infty$ in the present problem, then the reactor would not undergo sudden failure—it would merely die with slowly falling activity. Thus, from a practical standpoint the asymptotics of $\gamma \to \infty$ is probably not very relevant to the failure of chemical reactors, which in any case have rather modest values of γ. For ignition and explosion problems, however, large activation energy asymptotics allows calculations to be made in far greater detail.

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Department of Chemical Engineering
California Institute of Technology
Pasadena
California 91125
U.S.A.
and
Department of Chemical Engineering*
Clarkson College of Technology
Potsdam
New York 13676
U.S.A.

*Please address all correspondence to the second author at this address.