Homogeneous branched-chain explosion: Initiation to completion⋆

A. K. KAPILA

Department of Mathematical Sciences, Rensselaer Polytechnic Institute, Troy, New York 12181, USA

SUMMARY

This paper traces the complete time history of a spatially homogeneous model of a branched-chain reaction through asymptotic methods and develops (i) a subcritical solution (fizzle) where the state variables change by small amounts, and (ii) a supercritical solution (explosion) where extremely rapid transients occur. Three distinct time scales are seen to govern the explosion: a long induction period exhibiting a very slow change of state (as in a thermal explosion), a very brief period characterized by a rapid increase in the chain-carrier concentration but a small increase in temperature (unlike a thermal explosion), followed by a longer period in which most of the chemical heat is released.

1. Introduction

In the literature of chemistry and combustion, the term "explosion" refers to the event in which a series of chemical reactions is continually accelerated at a rate such that most of the chemical activity is completed in a time interval of utmost brevity. Emission of light, momentary attainment of high temperature and rapid variation of pressure may or may not accompany the process.
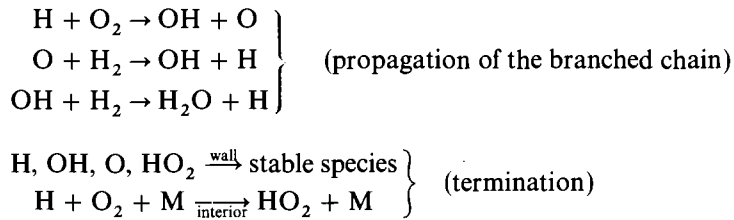
Spontaneous explosions, i.e. those that occur without the aid of external initiating devices such as an electric spark, a hot wire or a subsidiary flame, are of two types. They may be due either to the exothermicity of the reaction (thermal explosion) or to its chain character (branched-chain explosion). In the former the overall exothermic reaction increases the temperature of the reacting gas, thereby accelerating the rate of reaction and thus the heat-release rate. This buildup leads to an explosion unless heat is abstracted from the system sufficiently rapidly so that the resulting reaction is a "fizzle", characterized by a gradual change of state.

A branched-chain explosion can occur when the reaction proceeds by a chain mechanism, i.e. the reactants are transformed into products through so-called propagation reactions with active intermediaries called chain carriers. Consider, for example, the combusion of Hydrogen and Oxygen. The overall reaction $2H_2 + O_2 \rightarrow 2H_2O$ is believed to occur in the following steps (see Semenov [1], p. 153, 189):
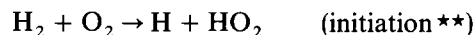
$$H_2 + O_2 \rightarrow H + HO_2 \qquad \text{(initiation⋆⋆)}$$

⋆⋆ There is a lack of unanimity on the initiation step; see Dainton [2], p. 150.

$$H + O_2 \rightarrow OH + O$$
$$O + H_2 \rightarrow OH + H \quad \text{(propagation of the branched chain)}$$
$$OH + H_2 \rightarrow H_2O + H$$

$$H, OH, O, HO_2 \xrightarrow{\text{wall}} \text{stable species}$$
$$H + O_2 + M \underset{\text{interior}}{\longrightarrow} HO_2 + M \quad \text{(termination)}$$

Here the atoms H and O and the hydroxyl radical OH act as chain carriers. A single H atom generated in the initiation step swells to a total of 3H atoms at the end of one propagation cycle. In fifty cycles of such a chain, each original H atom would have grown to 3^{50}, or approximately, 10^{24} atoms. It is this Malthusian growth of the branching chain which makes it possible for it to provoke an explosion.

The rise in the concentration of the chain carriers is, of course, retarded by the termination steps which occur either through absorption at the vessel walls or through three-body collisions in the interior (M, the third body, is any one of the other species present). The competition between the propagation rate and the termination rate determines the eventual outcome of the reaction.

In a study of a potentially explosive event, the following questions may be asked:

(i) Given a set of experimental conditions, what is the criterion for an explosion to occur?

(ii) If an explosion results, what is the time elapsed prior to its occurrence, i.e. what is the induction period?

(iii) What is the time history of the temperature and reactant concentrations from initiation to completion?

Although such questions were first considered fifty years ago by Semenov [3] and later by several authors, including Frank–Kamenetskii [4], a complete solution for the thermal explosion problem was developed only recently by Kassoy* [5], who carried out an asymptotic analysis in the realistic limit of large activation energy. The purpose of the present work is to develop an analogous theory for the branched-chain explosion. In particular, the non-isothermal character of the chemical reactions is taken into account; a feature missing from previous studies (Semenov [1], chapter IX). We present a mathematical model that retains the essentials but contains several simplifications based upon the actual features of a chain-branching reaction such as the Hydrogen-Oxygen system discussed above. First a criticality criterion is given, and then a complete time history of the supercritical event is developed. The analysis in the text is carried out only to leading order in order to emphasize the physical aspects of the development. Higher-order calculations, which are essential for a complete determination of the leading-order solution, are relegated to the Appendix.

2. Mathematical model

Consider a vessel filled with a potentially reactive mixture containing a single reactant A. We make the following assumptions:

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* See [5] for a detailed bibliography.

(i) The reactant A is converted into products through reaction with a single active intermediary C according to the second-order chain-branching step

$$A + C \to (1 + n)C + \text{products} \tag{2.1}$$

(ii) The sole recombination process occurs at the walls of the vessel according to first-order kinetics, i.e.

$$C \xrightarrow{\text{wall}} \text{stable species.} \tag{2.2}$$

As mentioned in the Introduction, chains may also be terminated, in general, through three-body collisions in the gas. However, their effect is ignored here; a valid assumption if the pressure is not excessive (Strehlow [6], p. 104) or if the vessel is not too large★ (Dainton [2], p. 103).

(iii) Rather than postulate an initiation reaction, which is usually far slower than the other two steps (Semenov [1], p. 111) and therefore unlikely to influence the overall reaction rate, we assume that a small concentration of chain carriers is already present in the starting mixture. Experimentally the assumption corresponds to the injection into the system of chain carriers produced externally, or their generation within the gas by a short radiation burst (Dainton [2], pp. 60–67).

(iv) The propagation step (2.1) is assumed to have a strongly temperature-dependent rate, i.e. a large activation energy, but is considered to be thermally neutral. (In the Hydrogen-Oxygen system, only five percent of the total heat release occurs in the propagation steps.)

(v) The overall reaction is assumed exothermic with the entire heat being liberated in the termination step (2.2). In practice the rate of this step is weakly dependent upon temperature, and either weakly or inversely proportional to the pressure (Semenov [1], p. 118). Our model assumes the rate constant of the termination reaction to be independent of temperature (zero activation energy) and pressure.

(vi) The system is assumed to be spatially homogeneous. This appears to be a strong assumption because in reality the effect of wall termination can be rigorously represented only by a diffusive term. However it is a useful approximation (Dainton [2], p. 103) to model it by a spatially uniform term, much like the replacement of the heat conduction effect by a uniform heat sink in the thermal explosion problem [5].

The mathematical equations governing the reactive system are those of species and heat conservation (Williams [7]):

$$\rho \, dY_A/d\tau = - W_A B_1 (pX_A/RT)(pX_C/RT) \exp(-E_1/RT),$$

$$\rho \, dY_C/d\tau = W_C n B_1 (pX_A/RT)(pX_C/RT) \exp(-E_1/RT) - W_C B_2 (pX_C/RT),$$

$$\rho c_p \, dT/d\tau = Q W_C B_2 (pX_C/RT),$$

★ Gas termination, being a volume effect, is more pronounced in large vessels than wall termination, a surface effect.

where Y_i is the mass fraction, X_i the mole fraction and W_i the molecular weight of species i; p is the pressure, ρ the density and T the temperature of the mixture; and B_1, B_2 are the pre-exponential factors and E_1, E_2 the activation energies of the reaction steps (2.1) and (2.2) respectively (E_2 is taken to be zero in accordance with assumption (v) above). Finally, Q is the heat release per unit mass, R the universal gas constant, c_p the specific heat at constant pressure and τ the time. For simplicity of the analysis, we shall assume c_p and the B_i to be constant.

Elimination of p and X_j through the relations

$$p = \rho R T \sum_i Y_i/W_i, \tag{2.3}$$

$$X_j = (Y_j/W_j)/\sum_i (Y_i/W_i), \quad (i \text{ summed over } all \text{ species})$$

reduces the governing equations to

$$dY_A/d\tau = -(B_1\rho/W_C)Y_A Y_C \exp(-E_1/RT), \tag{2.4a}$$

$$dY_C/d\tau = (nW_C/W_A)(B_1\rho/W_C)Y_A Y_C \exp(-E_1/RT) - B_2 Y_C, \tag{2.4b}$$

$$(c_p/Q)dT/d\tau = B_2 Y_C. \tag{2.4c}$$

Appropriate initial conditions are

$$T(0) = T_0, \; Y_A(0) = Y_{A0}, \; Y_C(0) = Y_{C0}, \tag{2.4d}$$

where the initial chain-carrier concentration Y_{C0} is assumed small in accordance with assumption (iii) above. Nondimensionalization via the relations

$$\tau = t/B_2, \; T = T_0\theta, \; (B_1\rho T_0 c_p)/(B_2 W_C Q) = \lambda, \; RT_0/E_1 = \varepsilon,$$

$$Y_A = (T_0 c_p/Q)(W_A/nW_C)y, \; Y_C = (T_0 c_p/Q)z$$

reduces the set (2.4) to

$$dy/dt = -\Omega, \tag{2.5}$$

$$dz/dt = \Omega - z, \tag{2.6a}$$

$$d\theta/dt = z, \tag{2.6b}$$

with

$$\theta(0) = 1, \; y(0) = \alpha \text{ and } z(0) = \varepsilon\beta, \tag{2.6c}$$

and the chemical term

$$\Omega = \lambda yz \exp(-1/\varepsilon\theta). \tag{2.6d}$$

The quantities

$$\alpha = (Q/T_0 c_p)(nW_C/W_A)Y_{A0}, \quad \beta = (Q/T_0 c_p)(nW_C/W_A)(E_1/RT_0)Y_{C0}$$

are considered $O(1)$. It may be noted that in eqn. (2.6d), λ is a measure of the propagation-reaction rate relative to the termination-reaction rate.

We seek to solve the above system asymptotically in the limit $\varepsilon \to 0$. It is worth noting that the exact integral

$$\theta + y + z = 1 + \alpha + \varepsilon\beta \tag{2.6e}$$

may be thought of as defining y and replacing equation (2.5). Also, it shows that the maximum temperature attainable in the system (corresponding to $y = z = 0$) is given by

$$\theta_{max} = 1 + \alpha + \varepsilon\beta. \tag{2.7}$$

3. Induction regime and criticality criterion

Equations (2.6) pose an initial-value problem which must have a solution for all values of λ when the remaining parameters are specified. However, if the solution is constrained to have a specified character, λ must be appropriately restricted. On defining the quantity $\bar{\theta}$ by $\lambda = \exp(\bar{\theta}/\varepsilon)$, it is clear that $\bar{\theta}$ must be unity for a well-defined explosion preceded by a finite induction period to occur. For $\bar{\theta} < 1$ the chemical term Ω is exponentially small as $\varepsilon \to 0$ [cf. eqn. (2.6d)], showing that the propagation reaction is too slow relative to the termination reaction to result in anything but a "frozen" state. For $\bar{\theta} > 1$, Ω is exponentially large, i.e. the propagation reaction is so fast as to cause an "instantaneous" explosion. We do not consider the last two possibilities.

More precisely, we let λ have the expansion

$$\lambda = (\lambda_0 + \ldots) \exp(1/\varepsilon), \tag{3.1}$$

where λ_0 is $O(1)$, so that from (2.6d),

$$\Omega = (\lambda_0 + \ldots)yz \exp[(\theta - 1)/\varepsilon\theta]. \tag{3.2}$$

Here λ_0 is an assignable quantity which measures the speed of the propagation reaction relative to that of the termination reaction on an $O(\exp(1/\varepsilon))$ scale.

The appropriate expansion for θ, suggested by the exponent in the expression (3.2), is

$$\theta = 1 + \varepsilon\theta_1 + \ldots \tag{3.3a}$$

and correspondingly, the expansions for y and z are

$$y = \alpha(1 + \varepsilon y_1 + \ldots), \quad z = \varepsilon z_1 + \ldots. \tag{3.3b}$$

Substitution into (2.6) yields the leading-order equations

$$dz_1/dt = \alpha\lambda_0 z_1 e^{\theta_1} - z_1, \quad d\theta_1/dt = z_1, \tag{3.4a}$$
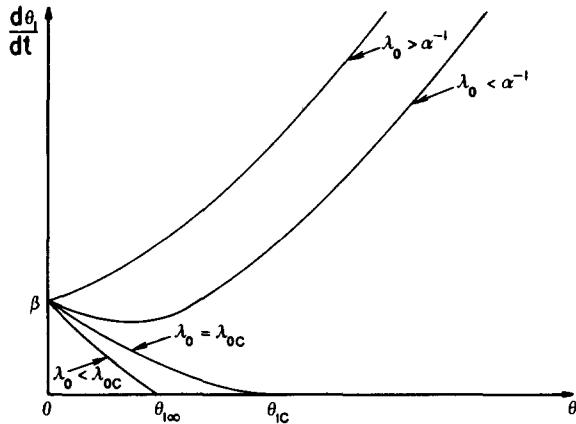
$$\theta_1 + \alpha y_1 + z_1 = \beta, \tag{3.4b}$$

Figure 1. Graph of $d\theta_1/dt$ for various λ_0.

TABLE 1
Data used in the construction of graphs

$\alpha = 1.0$	$\beta = 0.5$	$\lambda_0 = 0.5$	$\varepsilon = 0.05$

with

$$\theta_1(0) = 0, \quad z_1(0) = \beta. \tag{3.4c}$$

The above problem has a first integral given by

$$d\theta_1/dt = \alpha\lambda_0(e^{\theta_1} - 1) + \beta - \theta_1, \tag{3.5}$$

which may be integrated again to yield

$$\int_0^{\theta_1} [\alpha\lambda_0(e^x - 1) + \beta - x]^{-1} dx = t. \tag{3.6}$$

The nature of this solution can be ascertained by considering Fig. 1 which shows the graph of $d\theta_1/dt$ as a function of θ_1. (The numerical data used in constructing this graph as well as those to follow is displayed in Table 1.) For $\alpha\lambda_0 > 1$ the graph is monotone increasing, while for $\alpha\lambda_0 < 1$ it has a minimum value $1 + \beta - \alpha\lambda_0 + \ln(\alpha\lambda_0)$ at $\theta_1 = -\ln(\alpha\lambda_0)$. This minimum vanishes at the critical value λ_{0C} of λ_0, given by the smaller of the two roots of the equation★

$$\exp[\alpha\lambda_{0C}]/\alpha\lambda_{0C} = \exp(1 + \beta), \tag{3.7}$$

the corresponding value of θ_1 being

$$\theta_{1C} = -\ln[\alpha\lambda_{0C}].$$

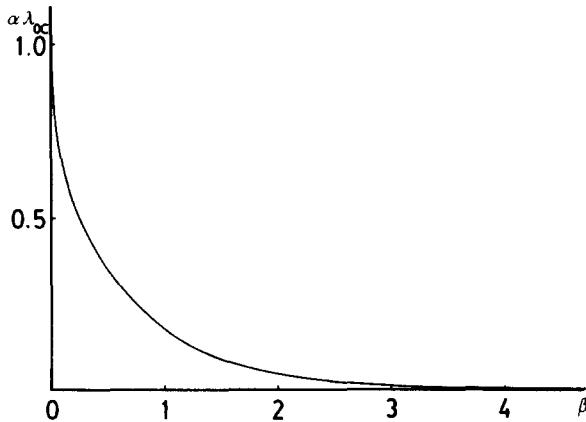★ For $\beta > 0$ eqn. (3.7) has two positive roots, one each on either side of $1/\alpha$.

Figure 2. Graph of $\alpha \lambda_{0C}$ versus β.

Thus we find that for fixed β, λ_{0C} is inversely proportional to α. For fixed α, the plot of $\alpha \lambda_{0C}$ against β (Fig. 2) shows that λ_{0C} falls off rapidly with increasing β, indicating that even for small λ_0 the system may become critical at moderate values of β. (We recall that moderate values of β correspond to $O(\varepsilon)$ values of initial chain-carrier concentration.)

3.1. *Subcritical theory*

If $\lambda_0 < \lambda_{0C}$, $d\theta_1/dt$ vanishes at a finite value $\theta_{1\infty}$ of θ_1 where $\theta_{1\infty} < \theta_{1C}$ and is given by the smaller zero of the right hand side of (3.5). Equation (3.6) then shows that θ_1 decays to $\theta_{1\infty}$ exponentially, i.e.

$$\theta_1 \sim \theta_{1\infty}[1 - \exp\{(1 - \alpha\lambda_0 e^{\theta_{1\infty}})(t_0 - t)\}] \quad \text{as } t \to \infty,$$

where

$$t_0 = \int_0^{\theta_{1\infty}} [\{\alpha\lambda_0(e^\theta - 1) + \beta - \theta\}^{-1} - (1 - \alpha\lambda_0 e^{\theta_{1\infty}})^{-1}(\theta_{1\infty} - \theta)^{-1}]d\theta.$$

Eqns. (3.3) and (3.4) then show the ultimate state of the system to be an $O(\varepsilon)$ perturbation of the original, i.e.

$$\theta \sim 1 + \varepsilon\theta_{1\infty}, \quad z \sim 0 \quad \text{and} \quad y \sim \alpha - \varepsilon(\theta_{1\infty} - \beta) \quad \text{as } t \to \infty.$$

Physically, the propagation step is too slow for the chain-carriers to be generated in large quantities. Instead, their concentration decays, resulting in a fizzle reaction. A typical time history appears in Fig. 3.

3.2. *Supercritical theory*

If $\lambda_0 > \lambda_{0C}$, the induction-period solution (3.6) develops a singularity at a finite value of t given by

$$t_\infty = \int_0^\infty [\alpha\lambda_0(e^x - 1) + \beta - x]^{-1} dx. \tag{2.15}$$
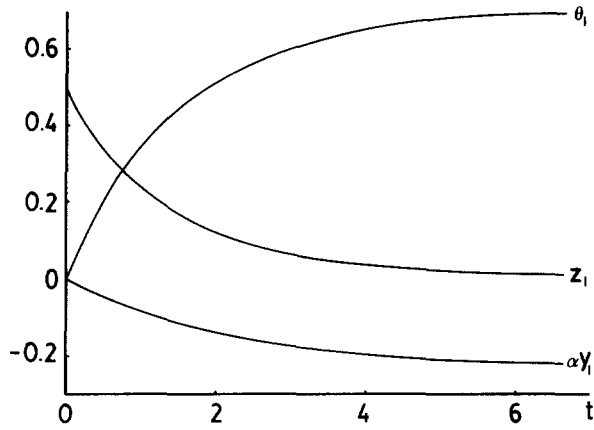
Figure 3. Histories of the perturbation quantities θ_1, αy_1 and z_1 for the subcritical case.
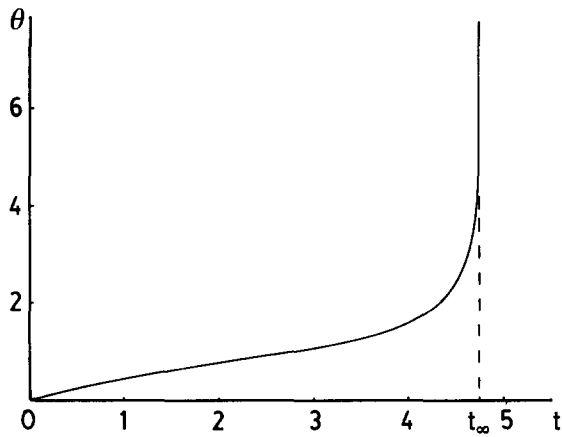

Figure 4. History of perturbation temperature θ_1 for the supercritical case.

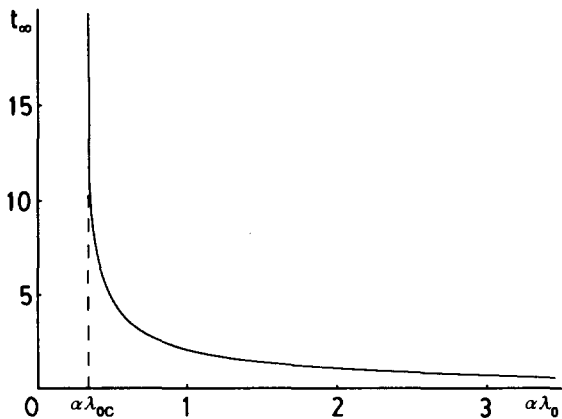

Figure 5. Graph of t_∞ versus $\alpha\lambda_0$ at fixed β.

In fact, it can be shown that

$$\theta_1 \sim -\ln[\alpha\lambda_0(t_\infty - t)] \quad \text{as} \quad t \to t_\infty,$$

while y_1 and z_1 are singular like $(t_\infty - t)^{-1}$. A typical time history of θ_1 is shown in Fig. 4. This singularity in the perturbation solution characterizes a rapid reaction event (explosion) and the time t_∞ which signals the onset of explosion is known as the induction period. Fig. 5 is a plot of t_∞ against $\alpha\lambda_0$ for fixed β and shows, as expected, that t_∞ becomes unbounded as λ_0 approaches λ_{0C} from above.

4. Explosion regime

The singular behavior of the induction solution exhibited above demonstrates the need for new asymptotics near time t_∞. Therefore we employ the stretching

$$t_\infty - t = \varepsilon\sigma, \tag{4.1}$$

rewrite equations (2.6a, b) as

$$dz/d\sigma = -\varepsilon\lambda yz \exp(-1/\varepsilon\theta) + \varepsilon z, \quad d\theta/d\sigma = -\varepsilon z, \tag{4.2}$$

and seek the expansions

$$\theta = 1 + \varepsilon(-\ln\varepsilon + \phi_0) + \ldots, \quad y = \eta_0 + \ldots, \quad z = \zeta_0 + \ldots, \tag{4.3}$$

the expansion for λ being (3.1) as before. We note that while z has grown to become $O(1)$ in the explosion zone, θ is still a small perturbation of the original temperature unity. This is in marked contrast to a thermal explosion [5], where the temperature grows to an $O(1)$ departure away from its initial value. Substitution of (4.3) and (3.1) into (4.2) and (2.6e) yields the leading-order equations

$$d\zeta_0/d\sigma = -\lambda_0\eta_0\zeta_0 \exp(\phi_0), \quad d\phi_0/d\sigma = -\zeta_0, \tag{4.4a}$$

and

$$\eta_0 = \alpha - \zeta_0, \quad -\infty < \sigma < \infty. \tag{4.4b}$$

These equations integrate to

$$\int_\mu^{\phi_0} [\exp(-\lambda_0 e^x) - 1]^{-1} dx = \alpha\sigma \tag{4.5}$$

where the constant $\mu = \phi_0(0)$ is determined by higher-order matching with the induction solution (3.3) (see eqn. (A.15) in the Appendix). The expressions for ζ_0 and η_0 can then be written down by using eqns. (4.4).

The solution for ϕ_0 is displayed in Fig. 6. It has the asymptotic behavior

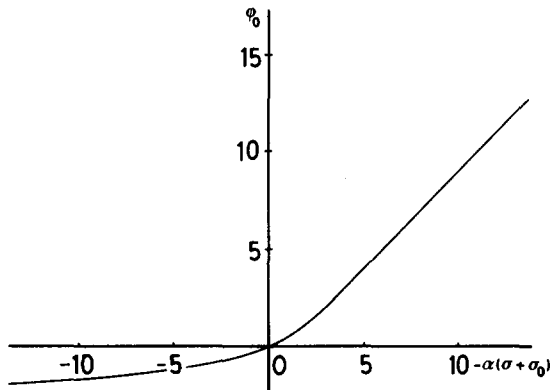$$\phi_0 = -\alpha\sigma + K_4 + \text{a.e.s.}, \tag{4.6a}$$

Figure 6. Graph of $\phi_0(\alpha)$ versus $\alpha(\sigma + \sigma_0)$, where $\sigma_0 = \alpha^{-1} \int_0^\mu (\exp(-\lambda_0 e^x) - 1)^{-1} dx$.

$$\zeta_0 = \alpha + \text{a.e.s. and } \eta_0 = \text{a.e.s. as } \sigma \to -\infty \qquad (4.6b)$$

where a.e.s. stands for quantities asymptotically exponentially small and K_4 is a constant defined by eqn. (A.16) of the Appendix. Thus the entire reactant A is consumed in the explosive regime, while the concentration of the chain carriers rises to the $O(1)$ value α. The temperature perturbation ϕ_0 becomes unbounded, suggesting the breakdown of the explosion-zone asymptotics.

5. Thermal regime

The singularity in the solution for the temperature in the explosion zone suggests that in the post-explosion period, θ is $O(1)$ away from its initial value of unity. Then from (2.6d) Ω is exponentially large unless y is exponentially small (exponentially small z would not match the explosion-zone solution). Therefore, from (2.5) and (2.6), the reduced equations valid in this regime are

$$y = 0, \quad dz/dt = -z \text{ and } d\theta/dt = z, \qquad (5.1)$$

leading to the solution

$$y = 0, \quad z = A(\varepsilon)\exp(t_\infty - t), \quad \theta = B(\varepsilon) - A(\varepsilon)\exp(t_\infty - t). \qquad (5.2)$$

Here B and A are determined by matching with the explosion-zone solution (see Appendix). The result is

$$A = \alpha + \varepsilon \ln \varepsilon + \varepsilon(\beta - K_4) + \dots, \qquad (5.3a)$$

$$B = 1 + \alpha + \varepsilon\beta, \qquad (5.3b)$$

where K_4 is the constant appeared in eqn. (4.6a). Thus, $z \sim 0$ and $\theta \sim \theta_{\max} = 1 + \alpha + \varepsilon\beta$ as $t \to \infty$.
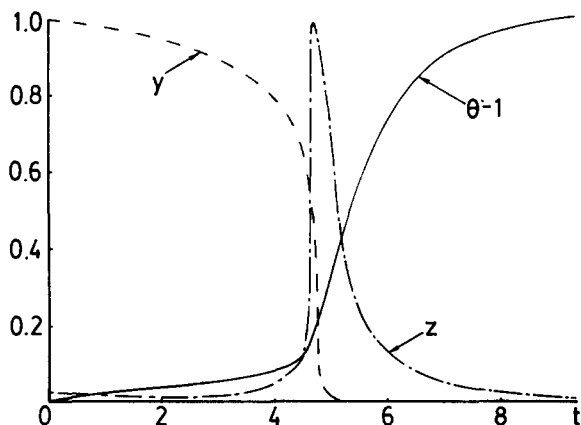
Figure 7. Histories of θ, y and z for the supercritical case.

6. Conclusions

Large activation-energy asymptotics have been employed to derive complete solutions for a spatially homogeneous model of the branched-chain reaction process. The critical parameter governing the nature of the solution is found to be λ_0, a suitably scaled version of the propagation-step rate relative to the termination-step rate. If λ_0 is below a critical value λ_{0C} the ultimate state of the system is but a small perturbation of the initial state, i.e. a fizzle reaction occurs. If λ_0 exceeds λ_{0C} an explosion takes place. The system may go critical at a smaller value of λ_0 if the initial concentration of either the reactant or the chain carrier is increased.

The explosion phenomenon occurs over three distinct temporal zones. The induction process occurs over a time scale $t = O(1)$ which, physically, is representative of the time characterizing the termination reaction. During this period the temperature and the chain-carrier concentration rise while the reactant concentration falls, all changes being small. The explosion regime which follows next is extremely rapid, characterized by an $O(\varepsilon)$ time scale, in which all the reactant is consumed and the chain-carrier concentration reaches a maximum value. Unlike a purely thermal explosion, however, the temperature rise is still small. Most of the heat release occurs subsequent to explosion, again on an $O(1)$ time scale, when all the chain-carriers are claimed by the exothermic termination reaction and the temperature reaches a maximum.

While only leading-order terms were treated in the text, the analysis has been carried out to higher orders in the Appendix. Fig. 7 depicts the complete time histories of the temperature and concentrations calculated by using composite expansions based on the higher-order (upto $O(\varepsilon^2)$) results.

Once the temperature and species concentrations are known, the pressure in the system can be calculated from eqn. (2.3). We note that if the molecular weights of all the species are equal, pressure is directly proportional to temperature. In any event, since the quantity $\sum_i Y_i/W_i$ lies between zero and unity, pressure variations are of the same order as temperature variations. In particular, the pressure remains essentially constant through the explosive regime and almost the entire rise in pressure occurs in the thermal regime.

Appendix A: Higher-order supercritical analysis

The essential purpose of this Appendix is to provide additional details and to determine, in particular, the yet unknown constant μ appearing in equation (4.5).

A.1. Induction Regime
We begin again with eqns. (2.6) but for brevity, treat the system as a second-order problem in θ:

$$d^2\theta/dt^2 + d\theta/dt = \lambda(1 + \alpha + \varepsilon\beta - \theta - d\theta/dt)(d\theta/dt)\exp(-1/\varepsilon\theta), \ 0 \le t < \infty,$$

with $\theta = 1$, $d\theta/dt = \varepsilon\beta$ at $t = 0$. Once θ is known, z and y can be calculated from eqns. (2.6b) and (2.6e) respectively.

The appropriate expansions for λ and θ are★

$$\lambda = \exp(1/\varepsilon)(\lambda_0 + \varepsilon \ln \varepsilon \lambda_1 + \varepsilon \lambda_2 + \ldots), \tag{A.1}$$

$$\theta = 1 + \varepsilon\theta_1 + \varepsilon^2 \ln \varepsilon \theta_2 + \varepsilon^2 \theta_3 + \ldots, \tag{A.2}$$

where, as we shall see, λ_0 is assignable but the remaining λ_i ($i = 1, 2, \ldots$) are determined as parts of the solution. The appearance of logarithms in the gauge-function sequence is not evident a priori; we have anticipated matching requirements that will occur later.

The leading-order problem, already discussed in the text, has the solution $\theta_1(t; \alpha, \beta, \lambda_0)$ given implicitly by eqn. (3.6). Its asymptotic behavior in the limit $t \to t_\infty$ will be needed for matching later. With

$$p = \alpha\lambda_0(t_\infty - t),$$

we find that

$$\theta_1 = -\ln p - \frac{1}{2\alpha\lambda_0} p \ln p + \frac{1}{2\alpha\lambda_0}(\alpha\lambda_0 - \beta + \tfrac{1}{2})p + O[p^2(\ln p)^2] \text{ as } p \to 0. \tag{A.3}$$

The problems for θ_2 and θ_3 are, respectively,

$$L(\theta_2) = \alpha\lambda_1 e^{\theta_1}(d\theta_1/dt), \quad 0 \le t < \infty,$$

$$\theta_2 = d\theta_2/dt = 0 \text{ at } t = 0, \tag{A.4}$$

and

$$L(\theta_3) = \alpha\lambda_2 e^{\theta_1}(d\theta_1/dt)$$
$$+ \alpha\lambda_0 e^{\theta_1}(d\theta_1/dt)[-\theta_1^2 + \alpha^{-1}(\beta - \theta_1 - d\theta_1/dt)], \quad 0 \le t < \infty,$$

★ A referee has suggested that λ, being a physically assignable quantity, should be treated as fixed, and that rather than (A.1), an expansion for the explosion time t_∞ should be derived. While such an approach may be more attractive physically, it was found that the mathematically equivalent procedure adopted here was more convenient.

$$\theta_3 = d\theta_3/dt = 0 \text{ at } t = 0, \tag{A.5}$$

where L is a linear differential operator with variable coefficients, given by

$$L \equiv d^2/dt^2 + (1 - \alpha\lambda_0 e^{\theta_1})d/dt - \alpha\lambda_0 e^{\theta_1}(d\theta_1/dt).$$

It can be shown that

$$\theta_2 = -\frac{\lambda_1}{\lambda_0} + \lambda_1 C_1 \left[p^{-1} + \frac{1}{2\alpha\lambda_0}\ln p - \frac{1}{2\alpha\lambda_0}(\alpha\lambda_0 - \beta - \tfrac{1}{2}) \right] + O(p\ln p) \text{ as } p \to 0, \tag{A.6}$$

and

$$\theta_3 = \frac{\lambda_0}{2}p^{-1}\ln p + C_2\lambda_2 p^{-1} + \left(1 + \frac{1}{4\alpha}\right)(\ln p)^2$$

$$+ \left[\frac{C_2\lambda_2}{2\alpha\lambda_0} - \frac{1}{4\alpha}(\alpha\lambda_0 - \beta + \tfrac{5}{2})\right]\ln p + \left[2 - \frac{\lambda_2}{\lambda_0} - \frac{1}{4\alpha}(\alpha\lambda_0 + 3\beta - \tfrac{7}{2})\right.$$

$$\left. - \frac{C_2\lambda_2}{2\alpha\lambda_0}(\alpha\lambda_0 - \beta - \tfrac{1}{2})\right] + O[p(\ln p)^2] \text{ as } p \to 0, \tag{A.7}$$

where the constants C_1 and C_2 depend upon α, β and λ_0 only, and can be determined by solving the problems (A.4) and (A.5) numerically. Henceforth we shall treat these constants as being known.

A.2. Explosion Regime

The independent variable is now σ, defined by the stretching (4.1), and the appropriate expansion for θ is

$$\theta = 1 + \varepsilon(-\ln \varepsilon + \phi_0) + \varepsilon^2[(\ln \varepsilon)^2 + \ln \varepsilon \phi_1 + \phi_2] + \dots. \tag{A.8}$$

The expansion for λ is, of course, given by (A.1) as before. Equation (4.5) provides the solution for ϕ_0, which can be shown to have the asymptotic behavior

$$\phi_0 \sim -\ln(\alpha\lambda_0\sigma) + \frac{1}{2\alpha}\sigma^{-1}\ln(\alpha\lambda_0\sigma) + \frac{K_3}{\alpha\lambda_0}\sigma^{-1}$$

$$+ \frac{1}{8\alpha^2}\sigma^{-2}[\ln(\alpha\lambda_0\sigma)]^2 + \frac{1}{\alpha^2}\left(\frac{K_3}{2\lambda_0} - \frac{1}{4}\right)\sigma^{-2}\ln(\alpha\lambda_0\sigma)$$

$$+ \frac{1}{\alpha^2}\left(\frac{K_3^2}{2\lambda_0^2} - \frac{K_3}{2\lambda_0} - \frac{1}{12}\right)\sigma^{-2} \text{ as } \sigma \to \infty. \tag{A.9}$$

Here,

$$K_3 = -e^{-\mu} + \frac{\mu\lambda_0}{2} + \frac{\lambda_0^2}{12}e^{\mu} + \lambda_0\int_{\lambda_0 e^\mu}^0 F(y)dy \tag{A.10}$$

and

$$F(y) \equiv \frac{1}{y(e^{-y} - 1)} + \frac{1}{y^2} + \frac{1}{2y} + \frac{1}{12}.$$

The constant μ now appears in K_3 above and is yet to be determined. The equations for ϕ_1 and ϕ_2 are, respectively,

$$L(\phi_1) = -\lambda_0 e^{\phi_0} \phi_0'[(\alpha + \phi_0')(\lambda_1/\lambda_0) + 1 + 2\phi_0(\alpha + \phi_0')], \quad -\infty < \sigma < \infty, \tag{A.11}$$

and

$$L(\phi_2) = -\lambda_0 e^{\phi_0} \phi_0'[(\alpha + \phi_0')(\lambda_1/\lambda_0) + \beta - \phi_0 - (\alpha + \phi_0')\phi_0^2] + \phi_0',$$
$$-\infty < \sigma < \infty, \tag{A.12}$$

where primes denote differentiation with respect to σ and L is the differential operator

$$L \equiv d^2/d\sigma^2 + \lambda_0 e^{\phi_0}(\alpha + 2\phi_0')d/d\sigma + \lambda_0 e^{\phi_0}\phi_0'(\alpha + \phi_0').$$

The general solutions ϕ_1 and ϕ_2 of (A.11) and (A.12) respectively can be shown to have the expansion

$$\phi_1 \sim P_1\sigma + \left(2 - \frac{P_1}{2\alpha}\right)\ln\alpha - \frac{\lambda_1}{\lambda_0} - \frac{P_1}{\alpha}\left(\frac{K_3}{\lambda_0} + \frac{1}{2}\right) - \frac{1}{\alpha}, \quad \text{as } \sigma \to \infty, \tag{A.13}$$

and

$$\phi_2 \sim -\tfrac{1}{2}\sigma \ln(\alpha\lambda_0\sigma) + P_2\sigma + \left(1 + \frac{1}{4\alpha}\right)[\ln(\alpha\lambda_0\sigma)]^2 + Q_2 \ln(\alpha\lambda_0\sigma) + R_2,$$
$$\text{as } \sigma \to \infty, \tag{A.14}$$

where P_1, P_2, Q_2, R_2 are yet unknown. We now match the 3-term induction solution (A.2) with the 3-term explosion solution (A.8). Details are omitted because matching is straight-forward. It is found that

$$\lambda_1 = -\frac{\lambda_0}{2C_1}, \quad \lambda_2 = \frac{K_3}{C_2} = 0, \quad P_1 = -\tfrac{1}{2}, \quad P_2 = \tfrac{1}{2}(\alpha\lambda_0 - \beta + \tfrac{1}{2}),$$

$$Q_2 = -\frac{1}{4\alpha}(\alpha\lambda_0 - \beta + \tfrac{5}{2}), \quad R_2 = 2 - \frac{1}{4\alpha}(\alpha\lambda_0 + 3\beta - \tfrac{7}{2})$$

and the constant μ is given by the implicit relation

$$K_3 \equiv -e^{-\mu} + \frac{\mu\lambda_0}{2} + \frac{\lambda_0^2}{12}e^{\mu} + \lambda_0 \int_{\lambda_0 e^{\mu}}^{0} F(y)dy = 0. \tag{A.15}$$

Matching involves the use of the asymptotic expressions (A.3), (A.6), (A.7), (A.9), (A.13) and (A.14).

In order to match with the post-explosion (thermal regime) solution (5.2) developed in the text, we shall need the asymptotic expressions for ϕ_0, ϕ_1 and ϕ_2 as $\sigma \to -\infty$. The behavior of ϕ_0 is given by (4.6a) while the expressions for ϕ_1 and ϕ_2 are found to be

$$\phi_1 \sim -\sigma + O(1), \quad \phi_2 \sim -\tfrac{1}{2}\alpha\sigma^2 - (\beta - K_4)\sigma + O(1), \quad \text{as} \quad \sigma \to -\infty,$$

where

$$K_4 = \int_{\lambda_0 e^\mu}^\infty \frac{e^{-y}dy}{y(e^{-y} - 1)} + \mu. \tag{A.16}$$

Matching of the 2-term thermal solution (5.2) with the 3-term explosion solution (A.8) then leads to (5.3).

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