



Nonadiabatic frontal polymerization

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Received 17 June 1997; accepted in revised form 15 May 1998

Abstract. Frontal polymerization is a process in which a spatially localized reaction zone propagates into a monomer, converting it into a polymer. In the simplest case of free-radical polymerization, a mixture of a monomer and initiator is placed into a test tube. Upon reaction initiation at one end of the tube a self-sustained thermal wave, in which chemical conversion occurs, develops and propagates through the tube. In a previous paper, a perfectly insulated tube (*i.e.*, an adiabatic polymerization process) was considered. In reality, it is nearly impossible to eliminate heat losses completely, and an accurate model must take this into account. Extinction of polymerization waves and difficulties initiating the wave, both as a result of heat losses, are often encountered in experiments. This paper will therefore concentrate on *nonadiabatic* frontal polymerization.

The propagation of nonadiabatic free-radical polymerization fronts is studied by methods originally developed in combustion theory, and employed in a previous paper. This analysis is accomplished by examination of the structure of the polymerization wave, its propagation velocity, degree of conversion of the monomer and maximum temperature, and how these quantities are affected by changes in initial temperature, concentrations and kinetic parameters. The values of these quantities near the extinction limit (beyond which traveling-wave solutions will no longer exist) are compared to those in the adiabatic case.

Keywords: combustion, polymerization, thermal wave, mathematical model, activation energy.

1. Introduction

Frontal polymerization is a process in which a spatially localized reaction zone propagates into a monomer, converting it into a polymer [1], [2]. In the simplest case of free-radical polymerization a mixture of a monomer and initiator is placed into a test tube. Upon reaction initiation at one end of the tube a self-sustained thermal wave, in which chemical conversion occurs, develops and propagates through the tube. This unusual method of polymerization holds promise as a method of producing currently available materials in a more energy-efficient process, and of producing superior thermoset materials [3]. Before any of these advantages can be achieved, a better understanding of the factors that affect frontal polymerization is necessary. In our previous paper [4] we considered a perfectly insulated tube (*i.e.*, an adiabatic polymerization process). In reality, it is nearly impossible to eliminate heat losses completely, and an accurate model must take this into account.

The effects of heat loss on reaction-wave propagation have been studied in the context of combustion problems. Classical results [5] concerning nonadiabatic combustion waves with narrow reaction zones and one-step overall idealized kinetics state that, if the heat loss coefficient α exceeds a critical value, the combustion wave cannot propagate. The propagation velocity u_α decreases as α increases. At the extinction limit, the propagation velocity was found to satisfy the relation $u_{\text{ext}} = e^{-1/2}u_{\text{ad}}$, where u_{ad} is the propagation velocity for the adiabatic case. This result cannot be directly applied to the frontal polymerization process

in which case the kinetics are much more complicated, but may be useful for the sake of comparison.

Extinction of polymerization waves as well as difficulties with initiating the wave are often encountered in experiments. Thus, the study of nonadiabatic frontal polymerization would be of great practical importance.

In this paper we model and study the propagation of nonadiabatic free-radical polymerization fronts. We examine the structure of the polymerization wave, its propagation velocity, degree of conversion of the monomer, maximum temperature, and how these quantities are affected by changes in initial temperature, concentrations and kinetic parameters. Also, comparisons are made between the values of these quantities near the extinction limit and those in the adiabatic case.

2. Mathematical model

The propagation of free-radical polymerization fronts involves the usual free-radical mechanism [6] consisting of decomposition, initiation, propagation and termination reactions. For the process studied in this paper, the characteristic scale of the polymerization wave is much smaller than the vessel through which it propagates, so that a traveling wave coordinate (x) may be introduced. At one side of the vessel ($x = -\infty$) there is a fresh mixture of monomer and initiator, and on the other side ($x = \infty$) there is the inactive polymer, or products, that are left behind in the wave's wake. The kinetic equations describing this system are written as

$$uI' + k_d I = 0, \quad (2.1)$$

$$uR' - 2fk_d I + k_p RM + k_t R\dot{P} = 0, \quad (2.2)$$

$$uM' + k_p RM + k_p M\dot{P} = 0, \quad (2.3)$$

$$u\dot{P}' - k_p RM + k_t R\dot{P} + k_t \dot{P}^2 = 0, \quad (2.4)$$

$$uP' - k_t R\dot{P} - k_t \dot{P}^2 = 0, \quad (2.5)$$

where u is the propagation velocity of the wave which must be determined in the course of solution of the problem. Here I , R , M , and P denote the concentrations in mol/L of the initiator, free radicals, monomer, and inactive polymer, \dot{P} is the concentration of the polymer radicals, and prime denotes the derivative with respect to x . Next, k_d , k_p , and k_t are the rate constants for the decomposition, propagation, and termination reactions, respectively, that are all taken in the form of Arrhenius exponentials

$$k_d(T) = k_d^0 \exp(-E_d/R_g T), \quad k_p(T) = k_p^0 \exp(-E_p/R_g T),$$

$$k_t(T) = k_t^0 \exp(-E_t/R_g T),$$

where R_g is the gas constant, k_d^0 , k_p^0 , and k_t^0 are the pre-exponential factors, and E_d , E_p , and E_t the activation energies for the corresponding reactions, and T is the temperature.

Equation (2.1) describes the consumption of the initiator occurring in the decomposition reaction. Equation (2.2) describes both the production (the $2fk_d I$ term) and consumption (the $k_p RM$ and $k_t R\dot{P}$ terms) of the free radicals. These radicals are produced in the initiator

decomposition reaction and consumed in the propagation and termination reactions. In the decomposition reaction, f is an efficiency factor which is necessary to account for the fact that not all of the radicals produced survive to initiate polymer chains. In a similar way, various terms in the remaining Equations (2.3)–(2.5) describe the production and/or consumption of the monomer, polymer radicals and inactive polymer, respectively. Note that (2.5) decouples from the remaining equations.

These kinetic equations must be supplemented by the energy balance in the system, which accounts for thermal diffusion, heat release, and heat loss in the polymerization process. Since the heat release occurs mainly in the propagation step [7], the energy balance takes the form

$$\kappa T'' - uT' - quM' - \alpha(T - T_0) = 0, \quad (2.6)$$

where T_0 is the ambient temperature, κ is the thermal diffusivity of the mixture (assumed to be constant), α is the heat loss coefficient and q is the increase in temperature associated with converting 1 mol/L of monomer into polymer. We will study a simplified kinetic system by using a steady-state assumption regarding the total concentration of the radicals. Under this fairly common assumption, employed in many texts and papers on polymerization (see, for example, [4], [6], [8], and [9]), the rate of change of the combined concentration of the radicals, R and \dot{P} , is much smaller than the rates of their production and consumption, so that there is a simple algebraic balance between the amounts of radical and initiator. This assumption reduces Equations (2.2)–(2.4) to a single equation

$$uM' + k_{\text{eff}}\sqrt{I}M = 0, \quad (2.7)$$

where the effective rate constant, k_{eff} , pre-exponential factor, k_{eff}^0 , and activation energy, E_{eff} , are given by

$$k_{\text{eff}} = k_{\text{eff}}^0 \exp(-E_{\text{eff}}/R_g T), \quad k_{\text{eff}}^0 = k_p^0 \sqrt{\frac{2fk_d^0}{k_t^0}}, \quad E_{\text{eff}} = E_p + \frac{E_d - E_t}{2}. \quad (2.8)$$

Thus, our model consists of the mass and energy balances (2.1), (2.6), and (2.7), and the boundary conditions at the left ($x = -\infty$) and right ($x = \infty$) ends of the tube. For calculational simplicity, we make a change of variables for the initiator, $I = J^2$, and for convenience rewrite the modified equations as

$$uJ' + Jk_1(T) = 0, \quad (2.9)$$

$$uM' + JMk_2(T) = 0, \quad (2.10)$$

$$\kappa T'' - uT' - \alpha(T - T_0) = quM'. \quad (2.11)$$

The boundary conditions at the left ($x = -\infty$) and right ($x = +\infty$) boundaries are

$$x = -\infty : M = M_0, T = T_0, J = J_0, \quad x = +\infty : T = T_0. \quad (2.12)$$

Here J_0 and M_0 are the concentration of initiator and monomer present in the initial mixture, and

$$k_1(T) = \frac{1}{2}k_d(T) = k_{01} e^{-E_1/R_g T}, \quad k_{01} = \frac{1}{2}k_d^0, \quad E_1 = E_d,$$

$$k_2(T) = k_{\text{eff}}(T) = k_{02} e^{-E_2/R_g T}, \quad k_{02} = k_{\text{eff}}^0, \quad E_2 = E_{\text{eff}}.$$

At points far behind the propagating front ($x \rightarrow \infty$) the temperature will reach a constant value, namely the ambient temperature, T_0 . At this point, the temperature will not be high enough to cause appreciable decomposition of the initiator. If decomposition does not occur, then neither will initiation or propagation. Thus, both $J(x)$ and $M(x)$ will take on constant values far behind the front. These values will be called J_f and M_f . In the adiabatic case, J_f was zero because the temperature far behind the front was sufficiently high for the decomposition reaction to come to completion. For the nonadiabatic problem that we discuss in this paper, the maximum temperature, T_m , will be reached at a certain point in space, x_m , but as Figure 1 shows, the temperature drops immediately after this due to heat losses. The maximum temperature, T_m , as well as the quantities J_f and M_f are important characteristics of the polymerization process and must be determined.

Though frontal polymerization is much slower and significantly less exothermic than combustion processes, nondimensional parameters, such as $R_g T_m / E_1$ and $R_g T_m / E_2$, that determine the structure of the wave are of the same order as the corresponding small parameters in combustion problems. Thus, the methods developed in combustion theory, which are based on various modifications of the large activation energy asymptotics, can be used to attack the frontal polymerization problem. A technique used with great success in both our previous work [4], and a number of combustion studies (see, for example, [10] and [11]) which yields correct qualitative, as well as quantitative, results is to replace the usual Arrhenius dependence of the reaction rate, $k_n(T)$ ($n = 1, 2$), with the step function

$$\hat{k}_n(T) = \begin{cases} 0, & T < T_n \\ A_n, & T > T_n \end{cases} \quad (n = 1, 2), \quad (2.13)$$

where

$$T_n = T_m(1 - \epsilon_n), \quad A_n = k_n(T_m), \quad \epsilon_n = R_g T_m / E_n \quad (n = 1, 2). \quad (2.14)$$

Here, T_n ($n = 1, 2$) are the temperatures at which the first and second reactions begin, ϵ_n are small dimensionless parameters, A_n are the heights of the step functions, and $k_n(T_m)$ are the reaction rates evaluated at the maximum temperature, T_m . Thus, the actual Arrhenius temperature dependence is replaced by the step function with height equal to the maximum of the Arrhenius function. The integral values of the two over the range from T_0 to T_m are approximately equal. This approximation is motivated by the fact that the reactions occur in such a narrow zone that they can be considered as nearly instantaneous or localized, making the reaction rates behave quite similarly to Dirac delta functions [12]. The use of a step function will be further justified in the Appendix where we examine the simpler case of a single chemical reaction and compare known results with Arrhenius temperature dependence to those with a step function approximation.

For the parameter values used in our model, the activation energy for the decomposition reaction (E_1) is almost double that of the polymerization reaction (E_2), so that the temperature required for the polymerization reaction to begin (T_2) is actually *less* than that required for the decomposition reaction to begin (T_1). Thus, with Equations (2.9)–(2.11) and the step function in place of the Arrhenius dependence (2.13), it is possible for the polymerization reaction to occur prior to the decomposition reaction. To correct this inconsistency, we need to modify our

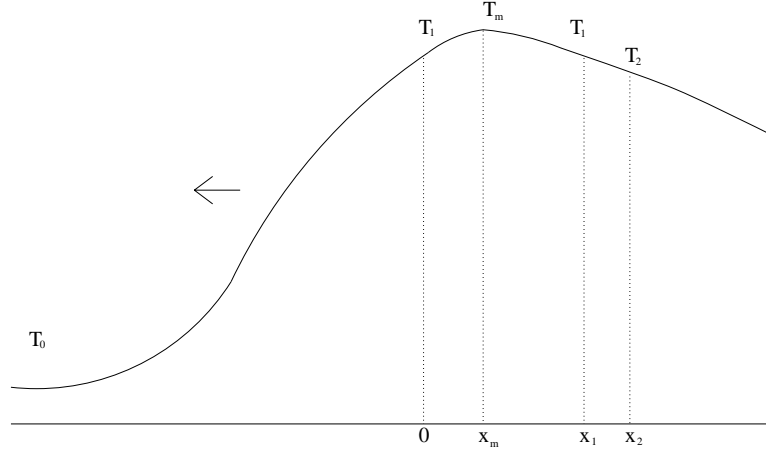


Figure 1. Schematic of nonadiabatic polymerization front.

model slightly. We can do this by introducing a Heaviside function, χ , in the polymerization reaction. We rewrite Equation (2.10) as

$$uM' + \chi(J_0 - J)JMk_2(T) = 0. \quad (2.15)$$

Thus, the polymerization cannot begin, unless $J < J_0$ (*i.e.*, the decomposition reaction has already begun).

Since the set of equations is invariant under spatial translation, we let the point in space where the temperature reaches the value T_1 (and thus both reactions begin) be $x = 0$. Similarly, we label the points in space where the temperature increases to T_m (its maximum), decreases to T_1 , and then drops to T_2 as x_m , x_1 , and x_2 , respectively (see Figure 1). Thus, the spatial region from $x = -\infty$ to $x = +\infty$ can be divided into four regions: $(-\infty, 0)$, $(0, x_1)$, (x_1, x_2) , and (x_2, ∞) . In the first of these regions, neither reaction has begun ($x < 0$, $k_1(T) = k_2(T) = 0$), in the second both reactions have occurred ($0 < x < x_1$, $k_1(T)k_2(T) \neq 0$), in the third the first reaction is completed, but the second is not ($x_1 < x < x_2$, $k_1(T) = 0$, $k_2(T) \neq 0$), and in the final region neither reaction occurs because of the low temperature ($x > x_2$, $k_1(T) = k_2(T) = 0$). Thus, we can state Equations (2.9)–(2.11) for each of the four regions as

$$uJ' = 0, \quad uM' = 0, \quad \kappa T'' - uT' - \alpha(T - T_0) = 0 \quad (x < 0), \quad (2.16)$$

$$\begin{aligned} uJ' + JA_1 &= 0, & uM' + JMA_2 &= 0, \\ \kappa T'' - uT' - \alpha(T - T_0) &= quM' \quad (0 < x < x_1), \end{aligned} \quad (2.17)$$

$$\begin{aligned} uJ' &= 0, & uM' + JMA_2 &= 0, \\ \kappa T'' - uT' - \alpha(T - T_0) &= quM' \quad (x_1 < x < x_2), \end{aligned} \quad (2.18)$$

$$uJ' = 0, \quad uM' = 0, \quad \kappa T'' - uT' - \alpha(T - T_0) = 0 \quad (x > x_2). \quad (2.19)$$

The boundary conditions are given in (2.12). In addition, there are matching conditions at $x = 0$, x_1 , and x_2 that constitute continuity of the mass, temperature and temperature gradient

distributions in the polymerization wave, and the condition that the temperature attains a maximum at $x = x_m$, where its derivative must be zero:

$$\begin{aligned} J(0^-) &= J(0^+), & M(0^-) &= M(0^+), \\ T(0^-) &= T(0^+) = T_1, & T'(0^-) &= T'(0^+), \end{aligned} \quad (2.20)$$

$$\begin{aligned} J(x_1^-) &= J(x_1^+), & M(x_1^-) &= M(x_1^+), \\ T(x_1^-) &= T(x_1^+) = T_1, & T'(x_1^-) &= T'(x_1^+), \end{aligned} \quad (2.21)$$

$$\begin{aligned} J(x_2^-) &= J(x_2^+), & M(x_2^-) &= M(x_2^+), \\ T(x_2^-) &= T(x_2^+) = T_2, & T'(x_2^-) &= T'(x_2^+), \end{aligned} \quad (2.22)$$

$$T(x_m) = T_m, \quad T'(x_m) = 0. \quad (2.23)$$

3. Solution

We found solutions of the Equations (2.16)–(2.19) subject to the boundary conditions (2.12) and matching conditions (2.20)–(2.22) by first solving the equations for $J(x)$ and $M(x)$, and then substituting the results in the equation for $T(x)$. Solving for $J(x)$ and $M(x)$ over all of space yields

$$J(x) = \begin{cases} J_0, & x < 0, \\ J_0 e^{-A_1 x/u}, & 0 < x < x_1, \\ J_0 e^{-A_1 x_1/u} \equiv J_f, & x > x_1, \end{cases} \quad (3.1)$$

and

$$M(x) = \begin{cases} M_0, & x < 0, \\ M_0 \exp[a(e^{-B \frac{u}{\kappa} x} - 1)], & 0 < x < x_1, \\ M_0 \exp[a(e^{-B \xi_1} - 1) + Ba e^{-B \xi_1} (\xi_1 - \frac{u}{\kappa} x)], & x_1 < x < x_2, \\ M_0 \exp[a(e^{-B \xi_1} - 1) + Ba e^{-B \xi_1} (\xi_1 - \xi_2)] \equiv M_f, & x > x_2, \end{cases} \quad (3.2)$$

where J_f and M_f are the amounts of initiator and monomer remaining after both reactions have ceased, and

$$a = \frac{A_2 J_0}{A_1}, \quad B = \frac{\kappa A_1}{u^2}, \quad \xi_n = \frac{u}{\kappa} x_n \quad (n = 1, 2). \quad (3.3)$$

Solving the equations for $T(x)$ yields

$$T(x) = T_0 + e^{\mu_1 x} \frac{q}{d} \int_{x_2}^x M'(\tau) e^{-\mu_1 \tau} d\tau - e^{\mu_2 x} \frac{q}{d} \int_0^x M'(\tau) e^{-\mu_2 \tau} d\tau, \quad (3.4)$$

which is valid over the entire spatial region. Here, M is given by Equation (3.2). In addition, we introduced the following quantities

$$d = \sqrt{1 + 4 \frac{\kappa \alpha}{u^2}}, \quad \mu_{1,2} = \frac{u}{2\kappa} (1 \pm d). \quad (3.5)$$

This solution satisfies the boundary conditions given in Equations (2.12), and is continuous, along with its first derivative, over all space. Applying the remaining conditions in Equations (2.20)–(2.23) we obtain five equations

$$T_1 - T_0 = -\frac{q}{d} \int_0^{x_2} M'(\tau) e^{-\mu_1 \tau} d\tau, \quad (3.6)$$

$$T_1 - T_0 = -e^{\mu_1 x_1} \frac{q}{d} \int_{x_1}^{x_2} M'(\tau) e^{-\mu_1 \tau} d\tau - e^{\mu_2 x_1} \frac{q}{d} \int_0^{x_1} M'(\tau) e^{-\mu_2 \tau} d\tau, \quad (3.7)$$

$$T_2 - T_0 = -e^{\mu_2 x_2} \frac{q}{d} \int_0^{x_2} M'(\tau) e^{-\mu_2 \tau} d\tau, \quad (3.8)$$

$$T_m - T_0 = -e^{\mu_1 x_m} \frac{q}{d} \int_{x_m}^{x_2} M'(\tau) e^{-\mu_1 \tau} d\tau - e^{\mu_2 x_m} \frac{q}{d} \int_0^{x_m} M'(\tau) e^{-\mu_2 \tau} d\tau, \quad (3.9)$$

$$0 = -\mu_1 e^{\mu_1 x_m} \int_{x_m}^{x_2} M'(\tau) e^{-\mu_1 \tau} d\tau - \mu_2 e^{\mu_2 x_m} \int_0^{x_m} M'(\tau) e^{-\mu_2 \tau} d\tau \quad (3.10)$$

for five unknown quantities x_1 , x_2 , x_m , u , T_m . We can rewrite the integrals in the right-hand sides of (3.6)–(3.10) as

$$\int_0^{x_1} M'(\tau) e^{-\mu_n \tau} d\tau = -a M_0 \int_0^{\eta_1} e^{a(e^{-\eta}-1)-\eta-\frac{1}{B}v_n \eta} d\eta \quad (n = 1, 2), \quad (3.11)$$

$$\int_0^{x_m} M'(\tau) e^{-\mu_n \tau} d\tau = -a M_0 \int_0^{\eta_m} e^{a(e^{-\eta}-1)-\eta-\frac{1}{B}v_n \eta} d\eta, \quad (3.12)$$

$$\int_{x_1}^{x_2} M'(\tau) e^{-\mu_n \tau} d\tau = M_0 e^{a(\zeta-1)+a\zeta\eta_1} \frac{\zeta Ba}{\zeta Ba + v_n} (e^{(-a\zeta+\frac{1}{B}v_n)\eta_2} - e^{-(a\zeta+\frac{1}{B}v_n)\eta_1}), \quad (3.13)$$

where

$$v_n = \frac{\kappa}{u} \mu_n, \quad \eta_n = B\xi_n, \quad \eta_m = B\xi_m, \quad \zeta = e^{-B\xi_1} \quad (n = 1, 2). \quad (3.14)$$

To simplify the integrals in the right-hand sides of (3.11)–(3.13), we assume that

$$B \equiv \frac{\kappa A_1}{u^2} = O\left(\frac{1}{\epsilon}\right) \gg 1.$$

The validity of this assumption lies in the fact that we expect the major quantities which comprise the parameter B (*i.e.*, T_m and u) to have values very close to their adiabatic counterparts (these expectations are shown below to indeed be true), coupled with the knowledge that, in the adiabatic case, B was shown to be an $O(1/\epsilon)$ quantity. In addition, this assumption is motivated by our study of the propagation of an exothermic reaction wave in which one overall reaction occurs [4], where we showed that

$$B = \frac{Eq}{RT_m^2}.$$

This parameter is also known as the Zeldovich number, and it is large due to a large activation energy of the reaction. Knowing that B is large, and using (3.11)–(3.13), we can show that Equations (3.6)–(3.9) yield identical results to leading order. Thus, instead of studying these equations in their present form, we can examine a new set of equations given by the differences (3.9)–(3.6), (3.8)–(3.6), and (3.7)–(3.6) (all taken to the leading order in small ϵ). These will be supplemented by the $O(1)$ terms in Equation (3.10), which gives us five equations

$$d \frac{T_m - T_0}{qM_0} = 1 - e^{a(\zeta-1)+a\zeta(\eta_1-\eta_2)}, \quad (3.15)$$

$$ad e^{-a} I(\eta_1) = v_1 \eta_1 e^{a(\zeta-1)+a\zeta(\eta_1-\eta_2)} - d \eta_1 e^{a(\zeta-1)} - \eta_2 v_1, \quad (3.16)$$

$$dB \frac{T_2 - T_1}{qM_0} = ad e^{-a} I(\eta_1) - d e^{a(\zeta-1)} \left(\frac{e^{a\zeta(\eta_1-\eta_2)} - 1}{a\zeta} + \eta_2 e^{a\zeta(\eta_1-\eta_2)} - \eta_1 \right) + \eta_2 v_2 (1 - e^{a(\zeta-1)+a\zeta(\eta_1-\eta_2)}), \quad (3.17)$$

$$dB \frac{T_m - T_1}{qM_0} = -v_1 \eta_m e^{a(\zeta-1)+a\zeta(\eta_1-\eta_2)} + d \eta_m e^{a(e^{-\eta_m}-1)} + \eta_2 v_m + ad e^{-a} I(\eta_m), \quad (3.18)$$

$$v_1 e^{a(\zeta-1)+a\zeta(\eta_1-\eta_2)} - d e^{a(e^{-\eta_m}-1)} - v_2 = 0, \quad (3.19)$$

where

$$I(w) \equiv \int_0^w e^{ae^{-\eta}-\eta} d\eta. \quad (3.20)$$

Next we want to consider the case of a nearly adiabatic process. Our motivation for examining this particular case is the knowledge (*c.f.* the Appendix below) that, in the case of one overall reaction, extinction occurs for very small values of α (specifically, α is inversely proportional to the Zeldovich number), and that past this point (the extinction limit), there will be no traveling wave solutions. A similar behavior is expected in the frontal polymerization problem. For very small values of α the quantities ξ_1 , ξ_2 , and ξ_m will no longer be small, in fact they are $O(1)$ in small α . This is the case because for smaller values of α , the reaction zone gets somewhat ‘stretched out,’ increasing the values of these quantities. With ξ_1 , ξ_2 , and ξ_m no longer being small and B remaining large, η_1 , η_2 , and η_m will all be large, and ζ will now be exponentially small. In addition, we can approximate the first part of Equation (3.5) as

$$d \approx 1 + 2\delta$$

where

$$\delta = \frac{\kappa\alpha}{u^2} \quad (3.21)$$

is a small dimensionless quantity.

Under these assumptions (which turn out to be self-consistent), the above five equations can be reduced to the following four nondimensional expressions

$$e^{-\eta_m} = 1 + \frac{1}{a} \log [e^{-a} + \delta(1 - e^{-a_0})], \quad (3.22)$$

$$a = a_0 e^{Z\sigma}, \quad (3.23)$$

$$\delta = \frac{\sigma + e^{-a_0} - e^{-a}}{2(1 - e^{-a_0})}, \quad (3.24)$$

$$\frac{1}{\alpha} = \frac{2nZ e^{-a} (1 - e^{-a_0}) a^{n+1}}{A_1(T_m) a_0^n (\sigma + e^{-a_0} - e^{-a})} I(\eta_m), \quad (3.25)$$

where

$$\begin{aligned} a_0 &= \frac{A_2(T_{\text{ad}})}{A_1(T_{\text{ad}})} J_0, & \theta &= \frac{T_m - T_0}{qM_0}, & \sigma &= \frac{T_{\text{ad}} - T_m}{qM_0}, \\ Z &= \frac{E_1 - E_2}{RT_{\text{ad}}^2} qM_0, & n &= \frac{E_1}{E_1 - E_2} \end{aligned} \quad (3.26)$$

were introduced as nondimensional parameters. Here T_{ad} is the burning temperature in the adiabatic case.

It is important to notice that Equation (3.25) gives α as a function of only one variable, σ . This may not be immediately apparent, but by using equations (3.22)–(3.24), we can express all the variables in Equation (3.25) in terms of σ .

Now that we have α as a function of σ only, we can find (in terms of σ) the critical value of α (*i.e.*, where the extinction limit will be) and how it is affected by changes in certain parameters of the problem. The graph of α as a function of σ was found to be a curve with a maximum. Using elementary methods, we may find the maximum value of α by simply differentiating α with respect to σ and finding the zero of the derivative. After computation and simplification, we have the following implicit equation for σ_{ext}

$$\begin{aligned} n &= \frac{a(\sigma_{\text{ext}} + e^{-a_0})}{\sigma_{\text{ext}} + e^{-a_0} - e^{-a}} + I(\eta_m)^{-1} \\ &\times \left[\frac{e^a}{a} \left(\frac{\sigma_{\text{ext}} + e^{-a_0} + e^{-a}}{2} - 1 \right) + \frac{1}{2} \eta_m (\sigma_{\text{ext}} + e^{-a_0}) e^a + \eta_m e^a \frac{e^{-Z\sigma_{\text{ext}}}}{a_0 Z} \right] \\ &+ \frac{a}{\sigma_{\text{ext}} + e^{-a_0} - e^{-a}} \frac{e^{-Z\sigma_{\text{ext}}}}{a_0 Z}, \end{aligned} \quad (3.27)$$

where η_m , a , and δ are given by (3.22)–(3.24) with σ replaced by σ_{ext} .

4. Results

Examining Equation (3.27) numerically, we were able to observe how variation of either the initial temperature of the monomer or the values of certain kinetic parameters affect the maximum temperature in the front, the final degree of conversion of the monomer, the propagation velocity, and other quantities of interest at the extinction limit.

Unless otherwise noted, we used the following parameter values [4]:

$$\begin{aligned}
 k_d^0 &= 4 \times 10^{12} \text{ 1/s}, & k_p^0 &= 5 \times 10^6 \text{ L/(s}\cdot\text{mol)}, & k_t^0 &= 3 \times 10^7 \text{ L/(s}\cdot\text{mol)}, \\
 E_d &= 27 \text{ kcal/mol}, & E_p &= 4.7 \text{ kcal/mol}, & E_t &= 0.7 \text{ kcal/mol} \\
 q &= 33.24 \text{ L}\cdot\text{K/mol}, & M_0 &= 6 \text{ mol/L}, & \kappa &= 0.0014 \text{ cm}^2/\text{s}
 \end{aligned} \tag{4.1}$$

Figures 2–5 show the effects that changes in the activation energy of the decomposition reaction (E_d), the initial temperature of the system (T_0) and the initial concentration of initiator (I_0) have on the following quantities at the extinction limit: the ratio of the propagation velocity of the front at the extinction limit to the velocity in the adiabatic case ($u_{\text{ext}}/u_{\text{ad}}$), the nondimensional maximum temperature of the system (σ_{ext}), the quantity $\kappa\alpha_{\text{ext}}/u_{\text{ad}}^2$, which characterizes the heat-loss coefficient at the extinction limit, the ratios of monomer remaining once the reactions have been completed ($M_{\text{ext}}/M_{\text{ad}}$), and the heat-loss coefficient (α_{ext}).

The reason that we chose the activation energy from the decomposition reaction as a parameter to vary was that this corresponds to the experimental situation where numerous initiators can be used for the same monomer. Similarly, the initial temperature and initiator concentration are the parameters that can be experimentally controlled.

It has been customary to assume that the kinetic parameters E_{eff} and k_{eff} given by (2.8) are the actual effective kinetic parameters of the process, *i.e.*, in many cases the behavior of the polymerization process is accurately described by one overall reaction with these effective kinetic parameters. In particular, we have shown in [4] that if the amount of initiator initially present in the mixture is sufficiently high, the propagation velocity of the wave is indeed given by the usual formula [5] for a one-step chemical process with the activation energy E_{eff} and the pre-exponential factor k_{eff} . Thus, it is interesting to see how the nonadiabatic polymerization process compares with one-step nonadiabatic reaction with the effective kinetic parameters. The quantities that we will compare are $u_{\text{ext}}/u_{\text{ad}}$, σ_{ext} and $\kappa\alpha_{\text{ext}}/u_{\text{ad}}^2$. In case of one reaction (*c.f.* the Appendix) with $T_0 = 300 \text{ K}$

$$\begin{aligned}
 \frac{u_{\text{ext}}}{u_{\text{ad}}} &= e^{-1/2} \approx 0.61, & \sigma_{\text{ext}} &= \frac{R_g(T_0 + qM_0)^2}{E_{\text{eff}} qM_0} \approx 0.14, \\
 \frac{\kappa\alpha_{\text{ext}}}{u_{\text{ad}}^2} &= \frac{R_g(T_0 + qM_0)^2}{2E_{\text{eff}} qM_0} e^{-1} \approx 0.026,
 \end{aligned}$$

where the parameter values (4.1) have been used to compute $E_{\text{eff}} = 17.85 \text{ kcal/mol}$.

The plots in Figures 2a, b, show how $u_{\text{ext}}/u_{\text{ad}}$ is affected by changes in I_0 , T_0 , and E_d . For all the plots the value of $u_{\text{ext}}/u_{\text{ad}}$ is sufficiently close to 0.61. Thus, in this respect the polymerization process is well described by a single exothermic reaction with effective kinetic parameters. As I_0 increases, the magnitude of u_{ext} increases for all values of T_0 . This occurs because the more initiator is present, the more free radicals will be produced, and if there

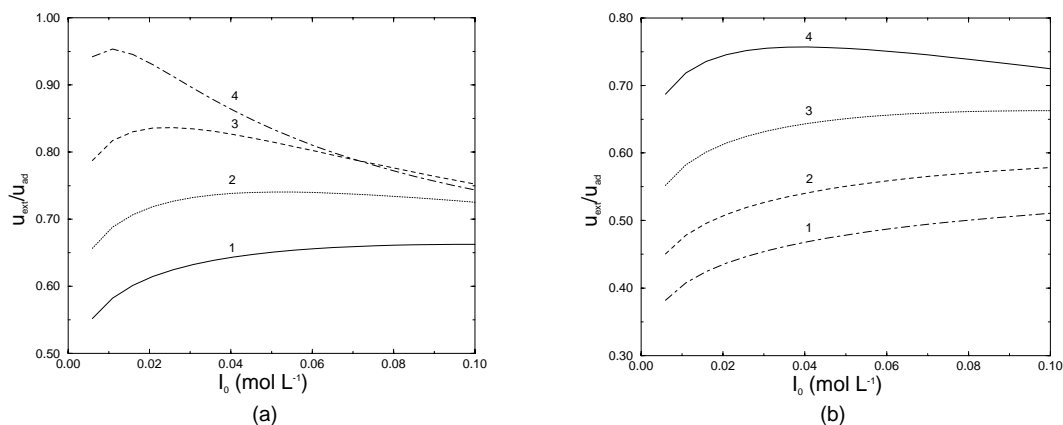


Figure 2. Effects of changes in (a) the initial temperature, and (b) the activation energy (for the decomposition reaction) on the ratio of the propagation velocity at the extinction limit to that for the adiabatic case. Curve 1 in (a) corresponds to $T_0 = 300$ K, curve 2 – $T_0 = 280$ K, curve 3 – $T_0 = 260$ K, curve 4 – $T_0 = 240$ K. Curve 1 in (b) corresponds to $E_d = 25$ kcal/mol, curve 2 – $E_d = 26$ kcal/mol, curve 3 – $E_d = 27$ kcal/mol, curve 4 – $E_d = 28$ kcal/mol.

are more free radicals present for the propagation reactions, there will be more heat produced (because they are the most exothermic reactions in the process). The decrease in $u_{\text{ext}}/u_{\text{ad}}$ for $T_0 = 240$ K and $T_0 = 260$ K (curves 3 and 4 in Figure 2a) is explained by the fact that u_{ad} increases with I_0 for these ranges of initial temperatures at a faster rate than u_{ext} .

Similarly, increases in E_d will cause slower decomposition (because the reaction constant contains E_d as a negative exponent) and therefore a slower speed of propagation. This is true for both the adiabatic and extinction cases, with u_{ad} being more affected by an increase in E_d than u_{ext} , which results in an increase in $u_{\text{ext}}/u_{\text{ad}}$ with E_d (Figure 2b).

The plots in Figures 3a, b show how σ_{ext} is affected by changes in I_0 , T_0 , and E_d , where

$$\sigma_{\text{ext}} = \frac{T_{\text{ad}} - T_{\text{ext}}}{qM_0}$$

is the nondimensionalized difference between the maximum temperature T_{ad} achieved in the adiabatic case and that at the extinction limit (T_{ext}). For the case of one overall reaction with the effective parameters this quantity is somewhat lower (0.14). Thus, nonadiabatic polymerization fronts can exist at maximum temperatures lower than those of a single-step reaction wave. We can give a simple physical explanation for this by comparing the mechanisms of extinction for the two types of waves. For a single-step reaction wave, heat losses slow down the wave, and when this occurs, even more heat is removed to the environment, which retards the wave even further, leading to extinction. In the case of frontal polymerization the same mechanism also works, but in addition to that there is a mechanism preventing extinction: when the wave slows down, the monomer has more time to react, less monomer is left behind the wave (*c.f.* Figure 5 below), and more heat is released in the polymerization reactions. This additional heat release stabilizes the process.

Increases in σ_{ext} with the initial concentration of the initiator for sufficiently small concentration of I_0 occur because the initiator limits the polymerization process. For larger concentrations of the initiator σ_{ext} no longer depends on I_0 . We also observe that σ_{ext} increases with

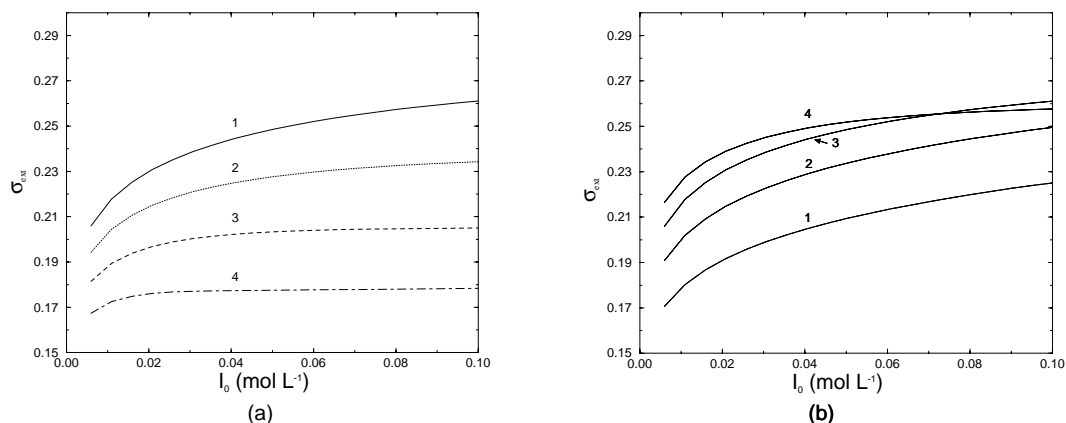


Figure 3. Effects of changes in (a) the initial temperature, and (b) the activation energy (for the decomposition reaction) on σ_{ext} , the difference between the maximum (nondimensional) temperatures in the adiabatic and extinction cases. Curve 1 in (a) corresponds to $T_0 = 300$ K, curve 2 – $T_0 = 280$ K, curve 3 – $T_0 = 260$ K, curve 4 – $T_0 = 240$ K. Curve 1 in (b) corresponds to $E_d = 25$ kcal/mol, curve 2 – $E_d = 26$ kcal/mol, curve 3 – $E_d = 27$ kcal/mol, curve 4 – $E_d = 28$ kcal/mol.

T_0 . In fact, both T_{ad} and T_{ext} increase with T_0 , but T_{ext} does so at a slower rate, due to the aforementioned stabilizing mechanism.

Figure 4 provides an additional confirmation of the stability of the polymerization front to heat losses. It is seen here that the maximum allowed values of the heat-loss coefficient for which the wave still exists are well above the corresponding quantity for a single reaction. Finally, Figure 5 shows that the amount of monomer left in nonadiabatic fronts at the extinction limit is significantly smaller than that in the adiabatic case.

5. Concluding remarks

In this paper, we were able to examine the ways in which heat-loss affects free-radical polymerization fronts. We showed that, in many ways, this nonadiabatic frontal polymerization process can be fairly accurately described – both qualitatively and quantitatively – by one overall reaction with effective kinetic parameters. The exception to this is the aforementioned mechanism indigenous to frontal polymerization, which allows for greater amounts of heat-loss and higher conversion than predicted by the single-reaction model.

It would be interesting to see some experimental data concerning nonadiabatic frontal polymerization, which, to the best of our knowledge does not exist at this point. An efficient way to perform such experiments seems to be to change the diameter of the test tube, since the heat-loss coefficient α is typically inversely proportional to this diameter.

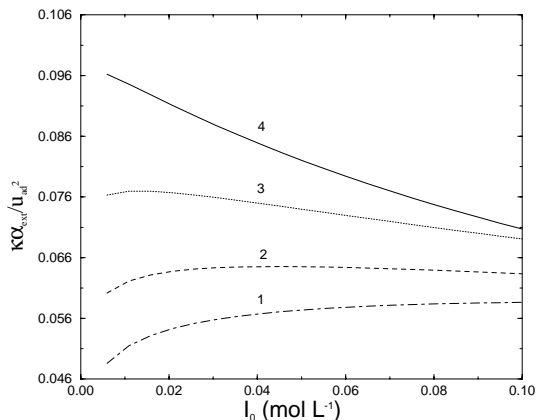


Figure 4. Effects of changes in the activation energy (for the decomposition reaction) on the quantity $\kappa\alpha_{\text{ext}}/u_{\text{ad}}^2$. Here curve 1 corresponds to $E_d = 25$ kcal/mol, curve 2 – $E_d = 26$ kcal/mol, curve 3 – $E_d = 27$ kcal/mol, curve 4 – $E_d = 28$ kcal/mol.

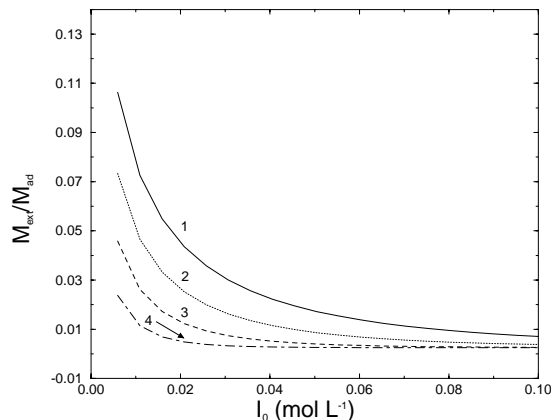


Figure 5. Effects of changes in the initial temperature on the ratio of the monomer remaining in the nonadiabatic cases after completion of the reactions to the amount remaining in the adiabatic cases. Curve 1 corresponds to $T_0 = 300$ K, curve 2 – $T_0 = 280$ K, curve 3 – $T_0 = 260$ K, curve 4 – $T_0 = 240$ K.

Appendix: One-step exothermic reaction wave

In order to justify the use of a step function in place of the usual Arrhenius-type temperature dependence, we consider a simpler problem: a general first-order exothermic reaction. Propagation of the wave in this case is described by the system of two equations

$$\kappa T'' - uT' + qk(T)a - \alpha(T - T_0) = 0, \quad (\text{A.1})$$

$$-ua' - k(T)a = 0, \quad (\text{A.2})$$

where T is the temperature, κ is the thermal diffusivity, u is the propagation velocity, q is the temperature increase in the reaction, a is the concentration of the deficient reactant in the initial mixture, α is the heat-loss coefficient, and $k(T)$ is the temperature dependence of the reaction rate,

$$k(T) = k_0 e^{-E/R_g T}. \quad (\text{A.3})$$

Here E is the activation energy, and k_0 is the pre-exponential factor. The system of equations is considered on the entire x -axis subject to the boundary conditions

$$x \rightarrow -\infty : T = T_0, \quad a = 1, \quad (\text{A.4})$$

$$x \rightarrow \infty : T = T_0, \quad (\text{A.5})$$

where T_0 is the ambient temperature.

Similarly to the system discussed in the body of this paper, we replace the usual Arrhenius temperature dependence by a step function

$$\hat{k}(T) = \begin{cases} 0, & T < T_{\text{ig}}, \\ A, & T > T_{\text{ig}}, \end{cases} \quad (\text{A.6})$$

where

$$T_{\text{ig}} = T_m(1 - \epsilon), \quad A = k(T_m), \quad \epsilon = \frac{R_g T_m}{E}. \quad (\text{A.7})$$

Here, T_{ig} is the temperature above which the reaction occurs, T_m is the maximum temperature attained, and ϵ is a small dimensionless parameter. Because we have replaced the Arrhenius temperature dependence by a step function, the spatial region from $x = -\infty$ to $x = +\infty$ can be divided into three distinct regions: one where the reaction has not yet begun because the temperature is less than T_{ig} , one where the reaction occurs ($T > T_{\text{ig}}$), and one where the reaction has ceased because the temperature drops below T_{ig} due to heat loss. Because the system is invariant under spatial translation, we can name the points in space separating these three regions as $x = 0$ and $x = x_s$, so that the system reduces to

$$\kappa T'' - uT' - \alpha(T - T_0) = 0, \quad -ua' = 0 \quad (x < 0), \quad (\text{A.8})$$

$$\kappa T'' - uT' + qaA - \alpha(T - T_0) = 0, \quad -ua' - Aa = 0 \quad (0 < x < x_s), \quad (\text{A.9})$$

$$\kappa T'' - uT' - \alpha(T - T_0) = 0, \quad -ua' = 0 \quad (x > x_s), \quad (\text{A.10})$$

with the matching conditions

$$T(0^-) = T(0^+) = T_{\text{ig}}, \quad T'(0^-) = T'(0^+), \quad a(0^-) = a(0^+), \quad (\text{A.11})$$

$$T(x_s^-) = T(x_s^+) = T_{\text{ig}}, \quad T'(x_s^-) = T'(x_s^+), \quad a(x_s^-) = a(x_s^+), \quad (\text{A.12})$$

$$T(x_m) = T_m, \quad T'(x_m) = 0, \quad (\text{A.13})$$

where x_m , $0 < x_m < x_s$, is the point in space where the temperature reaches its maximum value, T_m .

Solving equations (A.8)–(A.10) and applying matching and boundary conditions we have

$$T(x) = T_0 + (T_{\text{ig}} - T_0) e^{\mu_1 x}, \quad a(x) = 1 \quad (x < 0), \quad (\text{A.14})$$

$$T(x) = T_0 + [T_{\text{ig}} - T_0 - (\nu_2 + B)\Delta] e^{\mu_1 x} + (\nu_1 + B)\Delta e^{\mu_2 x} - d\Delta e^{-\frac{A}{u}x}, \\ a(x) = e^{-(A/u)x} \quad (0 < x < x_s), \quad (\text{A.15})$$

$$T(x) = T_0 + (T_{\text{ig}} - T_0) e^{\mu_2(x-x_s)}, \quad a(x) = e^{-(A/u)x_s} \equiv a_f \quad (x > x_s), \quad (\text{A.16})$$

where a_f is the concentration of the reactant after the reaction has run to completion. The following parameters were introduced

$$\delta = \frac{\kappa\alpha}{u^2}, \quad d = \sqrt{1 + 4\delta}, \quad \mu_{1,2} = \frac{u}{2\kappa}(1 \pm d), \\ B = \frac{\kappa A}{u^2}, \quad \nu_{1,2} = \frac{\kappa}{u}\mu_{1,2}, \quad \Delta = \frac{q}{d(1 + B - \frac{\delta}{B})}. \quad (\text{A.17})$$

We now use the remaining matching conditions to derive the four equations necessary to determine the four remaining unknowns: x_m , x_s , u , and T_m . Applying these conditions we obtain

$$[T_{\text{ig}} - T_0 - (\nu_2 + B)\Delta] e^{\nu_1 \xi_s} + (\nu_1 + B)\Delta e^{\nu_2 \xi_s} - d\Delta e^{-B\xi_s} = T_{\text{ig}} - T_0, \quad (\text{A.18})$$

$$\begin{aligned} & \nu_1 [T_{\text{ig}} - T_0 - (\nu_2 + B)\Delta] e^{\nu_1 \xi_s} + \nu_2(\nu_1 + B)\Delta e^{\nu_2 \xi_s} + Bd\Delta e^{-B\xi_s} \\ & = (T_{\text{ig}} - T_0)\nu_2, \end{aligned} \quad (\text{A.19})$$

$$[T_{\text{ig}} - T_0 - (\nu_2 + B)\Delta] e^{\nu_1 \xi_m} + (\nu_1 + B)\Delta e^{\nu_2 \xi_m} - d\Delta e^{-B\xi_m} = T_m - T_0, \quad (\text{A.20})$$

$$\nu_1 [T_{\text{ig}} - T_0 - (\nu_2 + B)\Delta] e^{\nu_1 \xi_m} + \nu_2(\nu_1 + B)\Delta e^{\nu_2 \xi_m} + Bd\Delta e^{-B\xi_m} = 0, \quad (\text{A.21})$$

where

$$\xi_s = \frac{u}{\kappa} x_s, \quad \xi_m = \frac{u}{\kappa} x_m. \quad (\text{A.22})$$

In order to simplify (A.18)–(A.21) further, we consider the limit $\epsilon \ll 1$. In this limit, we can make the following assertions

$$B = O\left(\frac{1}{\epsilon}\right), \quad \xi_s = O(\epsilon), \quad \xi_m = O(\epsilon), \quad \delta = O(1). \quad (\text{A.23})$$

In addition to this, we introduce the following nondimensional temperature

$$\theta = \frac{T_m - T_0}{q}, \quad (\text{A.24})$$

where θ is an $O(1)$ quantity. Taking Equations (A.18)–(A.21) to leading order and simplifying we arrive at the following four equations

$$1 + \theta \nu_1 B \xi_s - B \xi_s - e^{-B \xi_s} = 0, \quad (\text{A.25})$$

$$1 + \theta \nu_1 B \xi_m - B \xi_m - e^{-B \xi_m} = \epsilon B T_m / q, \quad (\text{A.26})$$

$$d\theta - 1 + e^{-B \xi_s} = 0, \quad (\text{A.27})$$

$$\nu_1 \theta - 1 + e^{-B \xi_m} = 0. \quad (\text{A.28})$$

Eliminating ξ_s by using Equations (A.25) and (A.27), and ξ_m by using Equations (A.26) and (A.28) we obtain two equations implicitly involving two unknowns (T_m and u)

$$\exp\left[-\frac{d\theta}{1 - \theta \nu_1}\right] = 1 - d\theta, \quad (\text{A.29})$$

$$\exp\left[-\frac{\theta \nu_1 - \epsilon B T_m / q}{1 - \theta \nu_1}\right] = 1 - \theta \nu_1. \quad (\text{A.30})$$

Similarly to what was done in the body of the paper, we examine the case of small values of α . Under this assumption,

$$\delta \ll 1, \quad d \approx 1 + 2\delta, \quad v_1 \approx 1 + d, \quad \sigma \equiv 1 - \theta = \frac{T_{ad} - T_m}{q} \ll 1, \quad (\text{A.31})$$

where $T_{ad} = T_0 + q$ is the maximum temperature in the adiabatic case. With these approximations, Equations (A.29) and (A.30) can be rewritten as

$$\exp \left[-\frac{1 + 2\delta - \sigma - 2\delta\sigma}{\sigma - \delta + \sigma\delta} \right] = \sigma - 2\delta + 2\delta\sigma, \quad (\text{A.32})$$

$$\exp \left[-\frac{1 - \epsilon T_m B/q + \delta - \sigma - \delta\sigma}{\sigma - \delta + \sigma\delta} \right] = \sigma - \delta + \sigma\delta. \quad (\text{A.33})$$

Since the exponent in Equation (A.32) is very large (and thus the term itself will be exponentially small), the right-hand side of that equation can be approximated, to exponentially small error, as zero,

$$\sigma - 2\delta + 2\delta\sigma = 0.$$

But because the quantity $\epsilon T_m B/q$ may be close to 1, the same cannot be said about Equation (A.33). Thus, neglecting *only* exponentially small terms, we can rewrite Equations (A.32) and (A.33) as

$$\sigma = \frac{2\delta}{1 + 2\delta}, \quad (\text{A.34})$$

$$\exp \left[1 - \frac{1 + 2\delta}{\delta} \left(1 - \frac{\epsilon T_m B}{q} \right) \right] = \frac{\delta}{1 + 2\delta}. \quad (\text{A.35})$$

From the definitions of ϵ , δ , and B given in Equations (A.7) and (A.17),

$$\frac{\epsilon T_m B}{q} = \frac{R_g T_m^2 A \delta}{E q \alpha}.$$

Substituting this expression in Equation (A.35) and solving for α , we have

$$\alpha = \left(1 - \frac{\delta}{1 + 2\delta} + \frac{\delta}{1 + 2\delta} \log \frac{\delta}{1 + 2\delta} \right)^{-1} \delta \frac{R_g T_m^2}{E q} A(T_m). \quad (\text{A.36})$$

Using the expressions for σ given in Equations (A.31) and (A.34), we can rewrite T_m as

$$T_m = T_{ad} - \frac{2\delta q}{1 + 2\delta}.$$

Substituting this expression in the definition of A given by Equations (A.3) and (A.7) and realizing that $\delta \ll 1$ and $E/(R_g T_{ad}) \gg 1$, we may write

$$\begin{aligned} A(T_m) &= k_0 \exp \left[-\frac{E}{R_g T_{ad} (1 - 2\delta q / [T_{ad} (1 + 2\delta)])} \right] \\ &\approx k_0 \exp \left[-\frac{E}{R_g T_{ad}} \left(1 + \frac{2q\delta}{T_{ad}} \right) \right]. \end{aligned} \quad (\text{A.37})$$

Taking Equation (A.36) to leading order in small δ and replacing $A(T_m)$ with the approximation from Equation (A.37), we have

$$\alpha = \delta \frac{R_g T_{\text{ad}}^2}{Eq} k_0 \exp\left(-\frac{E}{R_g T_{\text{ad}}}\right) \exp\left(-2\delta \frac{Eq}{R_g T_{\text{ad}}^2}\right). \quad (\text{A.38})$$

Using an expression for the propagation velocity in the adiabatic case [4],

$$u_{\text{ad}}^2 = \kappa A(T_{\text{ad}}) \frac{R_g T_{\text{ad}}^2}{Eq}$$

we can rewrite (A.38) as

$$\alpha = u_{\text{ad}}^2 \frac{1}{\kappa} \delta \exp\left(-2\delta \frac{Eq}{R_g T_{\text{ad}}^2}\right) \equiv F(\delta). \quad (\text{A.39})$$

The function $F(\delta)$ has a global maximum at

$$\delta = \delta_{\text{ext}} = \frac{1}{2} \frac{R_g T_{\text{ad}}^2}{Eq} \quad (\text{A.40})$$

with the corresponding maximum value being

$$\alpha_{\text{ext}} = F(\delta_{\text{ext}}) = u_{\text{ad}}^2 \frac{1}{\kappa} \delta_{\text{ext}} e^{-1}. \quad (\text{A.41})$$

For $\alpha > \alpha_{\text{ext}}$ equation (A.38) has no solutions α , which means that the original problem has no solutions in the form of a traveling wave. Using (A.17) and (A.41), we find

$$u_{\text{ext}}^2 = \frac{\alpha_{\text{ext}} \kappa}{\delta_m} = u_{\text{ad}}^2 e^{-1}$$

which recovers the result in [5]. The derivation of this result seems to support the use of a step function in place of the usual Arrhenius-dependence.

Acknowledgement

This research was supported under NSF Grant DMS-9600103.

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