

# THE THERMAL THEORY OF CONSTANT-PRESSURE DEFLAGRATION FOR FIRST-ORDER GLOBAL REACTIONS

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## 1. INTRODUCTION

THE one-dimensional thermal theory of constant-pressure deflagration has been discussed in a recent publication by the senior author and G. Millán. In this paper an explicit relation was given for the linear burning velocity in flames supported by first-order global reactions.<sup>1</sup> It is the purpose of the present analysis to extend this work by dropping the assumptions (a) that the average molecular weight of the gas mixture remains constant, and (b) that the thermal conductivity is constant. As the result, the one-dimensional theory of constant-pressure deflagration described in this paper is complete except in so far as the following reasonable approximations are concerned: (a) a constant average specific heat equal to the ratio of heat release per gram of reactant to total temperature rise may be used; (b) the ideal gas law constitutes a satisfactory equation of state for reacting gas mixtures.

In section 2, we present general expressions for the rate of formation of reaction products by an arbitrary irreversible global reaction. The general relation is then applied to reactions of the type  $nC \rightarrow n'D$ .

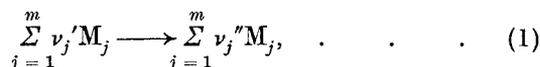
In Section 3, the appropriate equations for one-dimensional, constant-pressure deflagration are solved for flames supported by global reactions of the type  $C \rightarrow 2D$ . The method of solution follows along the lines of the treatment given in Ref. 1.

The results obtained in Section 3 are applied to the hydrazine decomposition flame in Section 4. This application is based on the assumption that the global reaction corresponds to the rate-controlling step used by Hirschfelder *et al.*,<sup>2</sup> *i.e.* to the unimolecular N-N bond splitting:  $N_2H_4 \rightarrow 2NH_2$ . The numerical value for the linear burning velocity obtained from

our thermal theory is then compared with results obtained<sup>2</sup> by numerical calculations. In order to facilitate a comparison of the results, we are using in our analytical method the values for the physico-chemical parameters given by Hirschfelder *et al.*, with the exception that the diffusion coefficient is put equal to zero. It is found that the calculated values are consistent with the principle that diffusion of reaction products decreases the laminar burning velocity.

## 2. RATE OF FORMATION OF REACTION PRODUCTS FOR AN ARBITRARY IRREVERSIBLE GLOBAL REACTION

An arbitrary irreversible global reaction may be represented by the relation



where  $\nu_j'$  and  $\nu_j''$  denote, respectively, the stoichiometric coefficients of species  $M_j$  in the global reaction. The total number of chemical species involved in the global reaction is  $m$  and the overall order of the (forward) reaction is  $n = \sum_{j=1}^m \nu_j'$ .

Application of the "law of mass action" to Eq. (1) leads to the following expression for the net rate of production of species  $M_i$  in moles per unit volume per unit time:

$$Dc_i/Dt = (\nu_i'' - \nu_i') k_f \prod_{j=1}^m (c_j)^{\nu_j'} \quad . \quad . \quad (2)$$

Here  $k_f$  is the specific reaction rate for the global reaction and  $c_j$  represents the concentration of species  $M_j$  (in moles per unit volume). We proceed by transforming Eq. (2) to the form used in Ref. (1), which is particularly well-suited to the study of chemical reactions in flow systems.

The weight fraction  $y_j$  is related to the mole concentration  $c_j$  by the expression

$$c_j = \frac{\rho y_j}{W_j}, \quad . \quad . \quad . \quad . \quad (3)$$

where  $\rho$  is the density of the gas mixture and  $W_j$  represents the molecular weight of  $M_j$ . Let  $w_i = W_i (Dc_i/Dt)$  represent

the net rate of production of mass of species  $M_i$  per unit volume. Combining Eqs. (2) and (3) leads to the result

$$w_i = (\nu_i'' - \nu_i') k_f W_i \rho^n \prod_{j=1}^m \left( \frac{y_j}{W_j} \right)^{\nu_j'} \quad (4)$$

The specific reaction rate is customarily expressed by a relation of the form

$$k_f = B e^{-\frac{A}{RT}} \quad (5)$$

where the "frequency factor"  $B$  has the dimension of  $\text{sec}^{-1} (\text{volume/mole})^{n-1}$ . The activation energy  $A$  is assumed to be independent of temperature. It is now convenient to introduce a parameter  $K_i$  of dimension  $\text{sec}^{-1}$  by the relation

$$K_i = (\nu_i'' - \nu_i') B W_i (\rho_s)^{n-1} \prod_{j=1}^m (W_j)^{\nu_j'} \quad (6)$$

where  $\rho_s$  is a conveniently chosen reference density. From Eqs. (4), (5) and (6) it follows that

$$w_i = K_i \left( \frac{\rho}{\rho_s} \right)^{n-1} \rho \prod_{j=1}^m (y_j)^{\nu_j'} e^{-\frac{A}{RT}} \quad (7)$$

For ideal gases the density of the gas mixture is given by the equation of state

$$\rho = \frac{\bar{W} p_o}{RT} \quad (8)$$

In Eq. (8)  $R$  is the molar gas constant,  $p_o$  is the constant pressure and  $\bar{W}$  equals the average molecular weight of the gas mixture, which is defined as

$$\bar{W} = \frac{\sum_{j=1}^m W_j c_j}{\sum_{j=1}^m c_j}$$

or

$$\bar{W} = \frac{1}{\sum_{j=1}^m (y_j/W_j)} \quad (9)$$

From Eqs. (7), (8) and (9) the desired general expression for the mass rate of production per unit volume of species  $M_i$  is obtained, viz.

$$w_i = \frac{K_i p_o^n}{\rho_s^{n-1} R^n T^n} \prod_{j=1}^m \frac{(y_j)^{\nu_j'}}{\left[ \sum_{j=1}^m (y_j/W_j) \right]^n} e^{-\frac{A}{RT}} \quad (10)$$

As a simple illustration for the use of Eq. (10) we consider the reaction



It is then evident that if  $y_D = \epsilon$  then  $y_C = 1 - \epsilon$ , and Eq. (10) becomes

$$w_D = \frac{K_D p_o^n}{\rho_s^{n-1} R^n T^n} \frac{(1-\epsilon)^n}{\left(\frac{\epsilon}{W_D} + \frac{1-\epsilon}{W_C}\right)^n} e^{-\frac{A}{RT}} \quad . \quad . \quad (10a)$$

For steady flow the quantity  $w_D$  can be expressed as

$$w_D = \rho \frac{d\epsilon}{dt} = \rho u \frac{d\epsilon}{dx},$$

where  $t$  represents time,  $u$  is the linear flow velocity, and  $x$  is the length coordinate across the flame. For the special case where  $n = 1$ ,  $n' = 2$ ,  $W_C = 2W_D$ , Eq. (10a) becomes

$$m \frac{d\epsilon}{dx} = \frac{K p_o}{R_g T} \frac{1-\epsilon}{1+\epsilon} e^{-\frac{A}{RT}}, \quad . \quad . \quad (11)$$

where  $R_g = R/W_C$ ,  $K = K_D$  and  $m = \rho u$  is the mass flow rate for steady burning.

### 3. LAMINAR BURNING VELOCITY FOR FLAMES SUPPORTED BY THE GLOBAL REACTION $C \longrightarrow 2D$

#### A. Formulation of the Eigenvalue Problem for the Reaction Zone

It has been shown in Ref. (1) that the equation for conservation of energy can be written in the form

$$\lambda \frac{dT}{dx} = mc_p [(T - T_o) - \epsilon(T_f - T_o)], \quad . \quad . \quad (12)$$

if  $\lambda$  equals the thermal conductivity,  $c_p$  is a constant average specific heat defined as the ratio of the heat of reaction per unit mass of reactant to  $(T_f - T_o)$ , and the subscripts  $o$  and  $f$  identify initial conditions and equilibrium conditions after reaction, respectively. But  $dT/dx = (dT/d\epsilon)(d\epsilon/dx)$ ; hence, using Eqs. (11) and (12)

$$\frac{\lambda}{m^2 c_p} \frac{K p_o}{R_g T} \frac{1-\epsilon}{1+\epsilon} e^{-\frac{A}{RT}} \frac{dT}{d\epsilon} = (T - T_o) - \epsilon(T_f - T_o). \quad . \quad (13)$$

We introduce the non-dimensional parameters

$$\theta = \frac{T}{T_f}, \theta_a = \frac{A}{RT_f}, \theta_o = \frac{T_o}{T_f}, \theta_i = \frac{T_i}{T_f}. \quad (14)$$

where  $T_i$  is an "ignition temperature", *i.e.* a temperature below which the rates of chemical reaction are negligibly small. As in the treatment given in Ref. (1), it will be shown that the laminar burning velocity is substantially independent of  $\theta_i$  for all reasonable values of  $\theta_i$ . With this result in mind, there can be no logical objection to the use of the concept of an "ignition temperature" on the grounds that the chemical reaction rates are always non-zero.

In terms of the parameters introduced through Eq. (14) the eigenvalue problem for the "reaction zone" reduces to the solution of the following differential equation :

$$\frac{\lambda T_f}{m^2 c_p T} \frac{K p_o}{R_g T_f} \frac{1-\epsilon}{1+\epsilon} e^{-\frac{\theta_a}{\theta}} \frac{d\theta}{d\epsilon} = (\theta-1) + (1-\theta_o)(1-\epsilon).$$

The boundary conditions are

$$\theta = \theta_i \text{ at } \epsilon = 0 \quad \text{and} \quad \theta = 1 \text{ at } \epsilon = 1.$$

We assume that the thermal conductivity is, approximately, a linear function of the temperature, *i.e.*,

$$\lambda_f = \lambda \frac{T_f}{T}. \quad (15)$$

Let

$$\Lambda = \frac{\lambda_f \rho_o K}{m^2 c_p} \frac{T_o}{T_f} = \frac{\lambda_f}{m^2 c_p} \frac{K p_o}{R_g T_f} \quad (16)$$

where use has been made of the relation

$$\rho_o = \frac{p_o}{R_g T_o}.$$

Using the notations introduced by Eqs. (15) and (16), the problem of laminar flame propagation reduces to the solution of the following eigenvalue problem for  $\Lambda$  :

$$\left. \begin{aligned} \Lambda \frac{1-\epsilon}{1+\epsilon} e^{-\frac{\theta_a}{\theta}} \frac{d\theta}{d\epsilon} &= (\theta-1) + (1-\theta_o)(1-\epsilon); \\ \text{with the boundary conditions} & \\ \theta = \theta_i \text{ for } \epsilon = 0; \quad \theta = 1 \text{ for } \epsilon = 1. & \end{aligned} \right\} \quad (17)$$

As in Ref. (1) the temperature distribution is determined solely by thermal conduction for  $\theta < \theta_i$ .

### B. Solution of the Eigenvalue Problem

The following solution of the eigenvalue problem is patterned after the procedure described in Ref. 1. Briefly, asymptotic solutions are found for the regions near  $\epsilon = 0$  and near  $\epsilon = 1$ . The solutions are then joined by requiring that both  $\theta(\epsilon)$  and  $d\theta/d\epsilon$  are continuous at the point at which the asymptotic solutions have been joined. It turns out that the end result is independent of the point at which the two solutions are joined.

From Eq. (17) it is apparent that in the singular point  $\epsilon = 1$ ,  $\theta = 1$

$$\lim_{\theta, \epsilon \rightarrow 1} \frac{d\theta}{d\epsilon} = \frac{1 - \theta_o}{1 + \frac{\Lambda}{2} e^{-\theta_a}}, \quad . \quad . \quad . \quad (18)$$

and for small values of  $\epsilon$

$$\frac{d\theta}{d\epsilon} = \frac{\theta - \theta_o}{\Lambda e^{-\frac{\theta_a}{\sigma}}} (1 + \epsilon). \quad . \quad . \quad . \quad (19)$$

Introducing Eq. (18) on the right hand side of Eq. (17) for  $\theta$  and  $\epsilon$  close to unity leads to the following approximation for the  $\theta$  versus  $\epsilon$  curve :

$$1 - \theta = (1 - \theta_o)(1 - \epsilon) \left\{ 1 - \frac{\frac{\Lambda}{2} e^{-\theta_a}}{1 + \frac{\Lambda}{2} e^{-\theta_a}} \right\} . \quad . \quad . \quad (20)$$

Eq. (20) is now used on the right hand side of Eq. (17) to give a better approximation to  $d\theta/d\epsilon$  than is provided by Eq. (18) for  $\theta$  and  $\epsilon$  close to unity. The result is

$$e^{-\frac{\theta_a}{\sigma}} d\theta = (1 - \theta_o) \frac{\frac{1}{2} e^{-\theta_a}}{1 + \frac{\Lambda}{2} e^{-\theta_a}} (1 + \epsilon) d\epsilon. \quad . \quad . \quad . \quad (21)$$

Let  $(\theta_i, \epsilon_i)$  represent the point at which  $\theta$  and  $d\theta/d\epsilon$

(obtained from Eqs. (19) and (21)) are to be joined. We then integrate Eq. (19) from  $\theta = \theta_i$ ,  $\epsilon = 0$  to  $\theta = \theta_t$ ,  $\epsilon = \epsilon_t$ . The result is

$$-\frac{1}{4} + \frac{(1+\epsilon_t)^2}{4} = \frac{\Lambda}{2} \int_{\theta_i}^{\theta_t} \frac{e^{-\frac{\theta_a}{\theta}}}{\theta - \theta_o} d\theta.$$

The quantity  $\exp(-\theta_a/\theta)$  decreases rapidly with decreasing  $\theta$  so that the following approximation is justified, as in Ref 1, provided that  $\theta_i$  is somewhat greater than  $\theta_o$  :

$$\int_{\theta_i}^{\theta_t} \frac{e^{-\frac{\theta_a}{\theta}}}{\theta - \theta_o} d\theta \simeq \frac{1}{\theta_t - \theta_o} \int_{\theta_i}^{\theta_t} e^{-\frac{\theta_a}{\theta}} d\theta.$$

This last integral can be evaluated readily by setting  $z = \theta/\theta_a$  and integrating by parts. In this manner it is found that

$$-\frac{1}{4} + \frac{(1+\epsilon_t)^2}{4} = \frac{\Lambda}{2(\theta_t - \theta_o)} \times \left\{ \left( \theta_t e^{-\frac{\theta_a}{\theta_t}} - \theta_i e^{-\frac{\theta_a}{\theta_i}} \right) + \theta_a \left[ \text{Ei} \left( -\frac{\theta_a}{\theta_t} \right) - \text{Ei} \left( -\frac{\theta_a}{\theta_i} \right) \right] \right\} \quad (22)$$

where the exponential logarithm is defined as

$$-\text{Ei}(-x) = \int_x^\infty \frac{e^{-t}}{t} dt > 0. \quad (23)$$

The functions  $\text{Ei}(-x)$  have been tabulated.

Integration of Eq. (21) between the limits  $(\theta_t, \epsilon_t)$  and  $(1, 1)$  leads to the equation

$$1 - \frac{(1+\epsilon_t)^2}{4} = \frac{1 + \frac{\Lambda}{2} e^{-\theta_a}}{(1-\theta_o)e^{-\theta_a}} \times \left\{ \left( e^{-\theta_a} - \theta_i e^{-\frac{\theta_a}{\theta_i}} \right) + \theta_a \left[ \text{Ei}(-\theta_a) - \text{Ei} \left( -\frac{\theta_a}{\theta_i} \right) \right] \right\} \quad (24)$$

Similarly, from Eq. (19),

$$\left( \frac{d\theta}{d\epsilon} \right)_{\theta_t, \epsilon_t} = \frac{(1+\epsilon_t)(\theta_t - \theta_o)}{\Lambda e^{-\frac{\theta_a}{\theta_t}}},$$

and, from Eq. (21),

$$\left( \frac{d\theta}{d\epsilon} \right)_{\theta_t, \epsilon_t} = \frac{(1+\epsilon_t)(1-\theta_o)}{2e^{-\frac{\theta_a}{\theta_t}}} \frac{e^{-\theta_a}}{1 + \frac{\Lambda}{2} e^{-\theta_a}},$$

whence

$$\frac{\Lambda}{2(\theta_i - \theta_o)} = \frac{1 + \frac{\Lambda}{2} e^{-\theta_a}}{(1 - \theta_o) e^{-\theta_a}} \quad (25)$$

Addition of Eqs. (22) and (24), noting Eq. (25), now yields the result

$$\frac{3}{4} \frac{(1 - \theta_o) e^{-\theta_a}}{1 + \frac{\Lambda}{2} e^{-\theta_a}} = \left[ e^{-\theta_a} - \theta_i e^{-\frac{\theta_a}{\theta_i}} \right] + \theta_a \left[ \text{Ei}(-\theta_a) - \text{Ei}\left(-\frac{\theta_a}{\theta_i}\right) \right],$$

$$\Lambda = 2e^{\theta_a} \left\{ \frac{\frac{3}{4}(1 - \theta_o)}{\left[ 1 - \theta_i e^{\theta_a} e^{-\frac{\theta_a}{\theta_i}} \right] + \theta_a e^{\theta_a} \left[ \text{Ei}(-\theta_a) - \text{Ei}\left(-\frac{\theta_a}{\theta_i}\right) \right]} - 1 \right\} \quad (26)$$

Eq. (26) can be used to evaluate  $\Lambda$  as a function of  $\theta_i$  for fixed values of  $\theta_a$  and of  $\theta_o$ . For all reasonable values of  $\theta_i$ , i.e. if  $\theta_i$  is somewhat larger than  $\theta_o$  and somewhat less than 1, Eq. (26) reduces to the relation

$$\Lambda = 2e^{\theta_a} \left\{ \frac{\frac{3}{4}(1 - \theta_o)}{1 + \theta_a e^{\theta_a} \text{Ei}(-\theta_a)} - 1 \right\} \quad (27)$$

For many chemical reactions  $\theta_a \gg 1$ . In this case, it is convenient to integrate Eq. (23) repeatedly by parts to obtain the following semi-convergent series:

$$\text{Ei}(-\theta_a) = - \frac{1 - \frac{1!}{\theta_a} + \frac{2!}{\theta_a^2} - \dots}{\theta_a e^{\theta_a}};$$

hence, for  $\theta_a \gg 1$ , Eq. (27) becomes

$$\Lambda = 2e^{\theta_a} \left\{ \frac{3}{4} \theta_a (1 - \theta_o) \left( 1 + \frac{2!}{\theta_a} - \dots \right) - 1 \right\} \quad (27a)$$

Explicit relations for the laminar burning velocity,  $u_o$ , are obtained by using Eq. (16) with  $m = \rho_o u_o$ .

#### 4. APPLICATION TO THE HYDRAZINE DECOMPOSITION FLAME

The detailed reaction kinetics of the hydrazine decomposition flame are not known. However, Hirschfelder and

collaborators<sup>2</sup> have assumed that the slow and rate-controlling chemical reaction step is the unimolecular breaking of the N—N bond, viz.  $\text{N}_2\text{H}_4 \longrightarrow 2\text{NH}_2$  with the rate constant (in  $\text{sec.}^{-1}$ )<sup>3</sup>

$$k_f = 4 \times 10^{12} e^{-\frac{60,000}{RT}}. \quad (28)$$

The slow reaction step in a chain reaction is to be identified with the global reaction. Hence  $K = 4 \times 10^{12}$  and  $A = 60,000$  cal./mole. Also<sup>2</sup>  $T_o = 423^\circ \text{K}$ ,  $T_f = 1933^\circ \text{K}$  whence  $\theta_o = 0.22$ ,  $\theta_a = 15.6$ ,  $C_p = 0.6623$  cal./gm.<sup>o</sup> K,  $\lambda_f = 6.7 \times 10^{-3}$  cal./cm.<sup>o</sup> K sec.<sup>2</sup>

Introduction of the numerical values given above into Eq. (27a) leads to the result

$$\Lambda = 1.1 \times 10^8$$

whence

$$u_o = \sqrt{\frac{\lambda_f K R_g T_o^2}{\Lambda c_p p_o T_f}} = 300 \text{ cm./sec.}$$

The value for  $u_o$  obtained by Hirschfelder *et al.*, using numerical calculations and including diffusion of the reaction product  $\text{NH}_2$ , is 93 or 127 cm./sec. depending on the value chosen for the diffusion coefficient. Comparison of this result with our estimate emphasises the well-known fact that the laminar burning velocity decreases as the upstream transport of reaction product by diffusion increases.

The experimentally determined value<sup>2</sup> of  $\phi$  is 200 cm./sec. which is roughly 33 per cent. smaller than the result obtained from our thermal theory but is 57 per cent. larger than the value calculated by including the diffusion transport<sup>2</sup> and using the value of the diffusion coefficient indicated by Hirschfelder as "his best choice". This observation is in line with expectations since it is clearly incorrect to assume that all of the  $\text{NH}_2$  formed by a slow chemical reaction step, *e.g.* the breaking of the N—N bond in  $\text{NH}_2$ , should be included in estimating diffusion transport. Some of the  $\text{NH}_2$  must be removed by rapid chemical reactions and hence a "best estimate" of diffusion of  $\text{NH}_2$  must be too high. For this reason, it appears that the use of the normal equation for diffusion transport in calculations of the burning velocity is probably not justified when the idealisation of a global or

rate-controlling reaction step is introduced in the treatment of flames supported by chain reactions.

## REFERENCES

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