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### AUTHORITY

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ON NON-ADIABATIC FLAME PROPAGATION

by

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July 1958
I. INTRODUCTION

Well defined existence limits as well as burning velocities are general characteristics of flame systems. Experimentally, it has been noted that:

1. Abstraction of heat from flames reduces the burning velocity (references 1, 2).

2. Sufficiently large heat abstraction from normally vigorous flames causes flame extinction or quenching (references 3, 4, etc.).

3. Well defined fuel-oxidant mixture ratio limits exist outside of which stable flame propagation does not appear to be possible (reference 5).

4. For systems studied so far, the chemical nature of solid, cold heat sinks does not seem to affect any of the flame properties under consideration - the burning velocity, the quenching conditions, or the concentration limits.

It thus appears that flame quenching and flammability limit phenomena, and burning velocity variations with heat abstraction are interrelated quantities and that a theoretical treatment of these phenomena must simultaneously account for all these phenomena.
Recent contributions to the theory of non-adiabatic flame propagation (references 6, 7) have considered these phenomena for the case of laminar, premixed, gaseous flames. This paper represents another approach to a non-adiabatic flame theory which is consistent with the previously stated general characteristics of flame systems. Non-adiabatic, one-dimensional, flame propagation through cylinders is considered for premixed gaseous fuel-oxidant mixtures. The theory is then extended to also include flames in "a free radical-containing solid inert" as well as "a gaseous highly stirred reactor".

Although there are necessary differences among the flame models chosen for the latter two cases the concepts employed for gaseous premixed flames are basic to all three cases.

II. NON-ADIABATIC LAMINAR FLAMES
IN PREMIXED GASEOUS MEDIA

IIA. The Model:

In the case of adiabatic flames in laminar, premixed gaseous media, the following treatment is customary. Final temperature and the final equilibrium compositions are determined by equilibrium adiabatic calculations. These hot boundary conditions are then used, together with the conservation and reaction rate laws and the conditions at the cold boundary to determine the eigenvalue for the problem, the burning velocity (reference 8).
Real flames are non-adiabatic and the picture is quite different. Consider a non-adiabatic reacting medium to be contained in an infinitely long cylinder of diameter, \( d \). The cylinder axis is taken to be coincident with the X-axis. The reacting medium is in a gaseous, homogeneously premixed state. The following assumptions are made concerning the system:

(a) Heat generation in the medium occurs as a result of a chemical reaction which is non-zero wherever reactant concentration and absolute temperature are both non-zero.

(b) A quasi-steady flame propagation state exists. That is, there exists a combustion wave (Figure 1) which travels in the \(-x\) direction with velocity \( u_0 \). This requirement that \((\frac{du_0}{d\theta}) = 0\) implies that there exists a finite distance, \( x_0 \), between the maximum flame temperature and a "cold boundary" characterizing "unburned" conditions.

(c) Processes governing the behavior of the system include radiative and conductive heat transfer to boundaries as well as chemical reaction within the medium. It is assumed that there exists at every value of \( x \), an average temperature (average over the tube cross-section) which may be used in characterizing radial and axial heat transfer and local reaction rates.

(d) \( T_w = T_o > 0 \) for all \( x \).

(e) "Burned" conditions exist at \( x = \infty \).
II B. Mathematical Formulation:

The energy conservation equation may be written

\[ T_0 \frac{d}{dx} \frac{dT}{dx} - c_p \rho u_0 \frac{dT}{dx} + R - L(t) = 0 \]  (1)

where the chemical rate, \( R \), is taken to be of the form

\[ R = k, F_1(\rho c)F_2(t) \]  (2)

Then, by definition

\[ \frac{dc}{dt} = - \frac{R}{\rho} = -k, \rho F_1(\rho c)F_2(t) \]  (3)

Also, for constant mole flow

\[ \frac{dc}{dt} = u \frac{dc}{dx} = u_0 x \frac{dc}{dx} \]  (4)

Thus, from equations (3) and (4)

\[ \int_{f_0}^{x} \frac{dc}{h(\rho c)} = - \frac{k,}{\rho_0 u_0} \int_{-\infty}^{F_2(t)} dx \]  (5)
For the case $F_1 (p, c) = p^2 c^2$, equation (5) yields

$$L = \frac{L_0}{1 + \frac{L_0 k_1 c}{\mu_0} \int_{-\chi_0}^{\chi} \frac{F_2 (t)}{t^2} \, dt}$$  \hspace{1cm} (6)

The heat loss term, $L(t)$ will be of the form

$$L(t) = L_0 (t) + L_1 (t) + L_2 \left[ (dT/dx)_{x=-\chi_0} \right]$$  \hspace{1cm} (7)

Examination of the above system of equations shows that the conservation equation can be combined with one other, say equation (6), to yield a third order nonlinear differential equation subject to the boundary conditions

$$x = -\chi_0: \quad T = T_0, \quad c = c_0, \quad dT/dx = \xi$$  \hspace{1cm} (8)

$$x = +\infty: \quad T = T_0, \quad c = 0, \quad dT/dx = 0$$

Neither the conditions at $x = -\chi_0$ nor those at $x = +\infty$ by themselves guarantee the existence of a flame in the region $-\chi_0 \leq x \leq +\infty$. It is the satisfaction of the conservation equation, point by point, in conjunction with the boundary conditions which allow this point by point satisfaction which prescribes the characteristic $u_0$ value. It then appears that the existence of a single value of $u_0$, rather than a band of $u_0$ values, can result only from the circumstance that all but one of these seemingly allowed $u_0$ values are inconsistent with the conditions of the problem.
III. FLAME PROPERTIES - NON-ADIABATIC FLAMES
IN PREMIXED GASEOUS MEDIA

In order to examine the exact behavior of a given non-adiabatic flame, a point by point integration of equation (1) must be carried out for the case considered. However, it is instructive to consider an approximate approach which does not compromise the essential features of the problem but which does yield a very good, general picture of the basic structure and properties of non-adiabatic flames.

IIIA. Approximation Model:

Assume that the temperature profile on the interval $-x_0 \leq x \leq +\infty$ can be approximated by a three segment continuous temperature profile. The first segment, $t_1$, approximately describes the temperature profile on the interval $-x_0 \leq x \leq 0$.

$$t_1 = (t_m-1) \left[ \frac{1 + \cos \left( \frac{\pi x}{x_0} \right)}{2} \right] + 1 \quad (9.)$$

Thus, $t_1$ is represented in terms of two parameters ($t_m$ and $x_0$) which are to be so evaluated that the conservation equation (1) is satisfied. The second segment, $t_2$, approximately describes the temperature on the interval $0 \leq x \leq x_0\beta$.

$$t_2 = t_m \left[ 1 - \left( \frac{1 - \beta x_0}{x_0} \right)^\frac{x}{x_0} \right] \quad (10.)$$

$t_2$ is so chosen that it approximately describes the temperature in a region where some heat release occurs even though the temperature is declining.
Here again, equation (1) is to be satisfied. The parameter, $\alpha$, is determined by $\beta$. $\beta x_o$ is so chosen that the third interval, $\beta x_o \leq x \leq +\infty$ is one in which virtually no heat release occurs (e.g. less than 1 percent). Thus, the region $0 \leq x \leq \beta x_o$ is a region of low heat release and, in general, $t_m$ is quite close to $t_m^o$. The linear approximation of equation (10) is thus justified. These conditions then permit the rewriting of equation (1) for the third interval, where $x_0 \beta \leq x \leq +\infty$,

$$\frac{d}{dx} \lambda \frac{d^3 t}{dx^3} - \rho R_i M_o \frac{dt}{dx} - \frac{1}{t_0} \xi(t_3) = 0 \tag{11}$$

For a hydrocarbon-oxygen-nitrogen flame, the overall reaction rate, equation (2), may be written

$$R = k_1 \rho^2 c^2 \exp \left( -\frac{E}{RT_0} \cdot \frac{1}{T} \right) \tag{12}$$

and, over a limited range, approximated by

$$R = k_2 \rho^2 c^2 t^n \tag{13}$$

$k_2$ and $n$ are so chosen that both $R$ and $dR/dt$ match at the mid-point of the temperature interval of interest. Thus, equation (6) becomes, for $-x_0 \leq x \leq 0$

$$C_1 = \frac{C_0}{1 + \frac{C_0 k_2}{M_0} \int_{-x_0}^{0} t^{-2} \, dx} \tag{14}$$

and for $0 \leq x \leq x_0 \beta$
\[ L_2 = \frac{C_1}{1 + \frac{C_{0} \beta_{k}}{M_{0}} \int_{0}^{\infty} \frac{\beta_{2}}{\text{d}y} } \]  

(5)

There then results

\[ L_1 = \frac{1}{\lambda_0 + \frac{k_x}{M_0} \Psi_1(x_m)} \]  

(6)

where for even values:

\[ \Psi_1(x_m) = \rho k_2 \left[ \frac{(t_{m+1})^{m-2}}{2} + \frac{(n-2)(n-3)(t_{m+1})}{(2)(2)} \left( \frac{t_m}{2} \right)^2 \right. \]

\[ \left. + \frac{(n-3)(n-5) \cdots 3}{(n-2)(n-4) \cdots 2} \left( \frac{t_m}{2} \right)^{m-2} \right] \]  

(17A)

and for odd values

\[ \Psi_1(x_m) = \rho k_2 \left[ \frac{(t_{m+1})^{m-2}}{2} + \frac{(n-3)(n-3)(t_{m+1})}{(2)(2)} \left( \frac{t_m}{2} \right)^2 \right. \]

\[ \left. + \frac{(n-3)(n-5) \cdots 3}{(n-2)(n-4) \cdots 2} \left( \frac{t_m}{2} \right)^{m-2} \right] \]  

(17B)

A similar expression results for \( c_2 \).

\[ L_2 = \frac{1}{\lambda_0 + \frac{k_x}{M_0} \Psi_2(\beta, t_m)} \]  

(18)
where
\[ \psi_2(\beta t_m) = \psi_1(t_m) + \frac{\beta t_m^{m-2}}{m-1}(1 + \alpha + \cdots + \alpha^{m-1}) \] (19)

Thus, equations (16) and (18) enable us to determine the concentrations at \( t = t_m \) and at \( t = \alpha t_m \), respectively, in terms of the parameters \( x_0, u_0, t_m \).

Integration of equation (1), subject to the boundary conditions \( T = T_o, c = c_o \), and \( (dT/dx) = 0 \) yields:
\[ \int_{x_0}^{x} R \, dx = \int_{x_0}^{y} L \, dx \] (20)

For the approximation model, this equation may be written as

\[ \int_{x_0}^{x} R \, dx = \int_{x_0}^{y} L \, dx \] (21)

Now, the left hand side of equation (21) may be written
\[ \int_{x_0}^{x} R \, dx = c_0 \rho_0 u_0 \beta (1 - \frac{c_2}{c_0}) \] (22)
and the right hand side of equation (21) may be written

\[
\int_{-\infty}^{\infty} L \, dx = \int_{-\infty}^{\infty} L \, dx + \int_{-\infty}^{\infty} L \, dx
\]  

(2.3)

where

\[
\int_{-\infty}^{\infty} L \, dx = \int_{-\infty}^{\infty} \frac{G}{2} \left( T - T_{\infty} \right) \, dx + \int_{-\infty}^{\infty} L \, dx
\]  

(2.4)

The conduction loss term results from solution of the radial heat conduction equation (reference 9). The radiation loss term is based on the \( H_2O \) and \( CO_2 \) partial pressures and is evaluated by use of the methods and data of reference (10). For the afterburning region, equation (11) may be employed to evaluate the conduction heat loss. Equation (11) becomes

\[
\frac{d^2 T}{dx^2} + \frac{dT}{dx} - \frac{G}{2a^2} (T - 1) = 0
\]  

(2.5)

Solution of equation (25) yields

\[
\int_{-\infty}^{\infty} L \, dx = -\int_{-\infty}^{\infty} T_0 \left( \frac{dT}{dx} \right) + \int_{-\infty}^{\infty} T_0 \left( \frac{d^2 T}{dx^2} - \frac{G}{2a^2} (T - 1) \right)
\]  

(2.6)
If it is necessary to consider the radiation loss in this afterburning region, equation (11) becomes nonlinear, but a linear approximation can be made by modification of \( G \).

The conservation equation, (21), may now be evaluated.

\[
\lambda_0 \beta \left[ \frac{1}{x + \lambda_0 \beta \gamma} \right] = \chi_0 T_0 \left[ \beta \frac{G}{4 \lambda_2} (x_m - 1) + \beta \frac{G}{4 \lambda_2} \left( \frac{1 + \alpha}{2} \right) x_m - 1 \right] + \\
+ \chi_0 \left( \lambda_{n_1} + \beta \lambda_{n_2} \right) + \lambda_0 \beta \gamma \left[ \frac{H + 1 + \beta^2 G}{\lambda_2} \right] (x_m - 1) \tag{28}
\]

and for \(-x_0 \leq x \leq 0:\)

\[
\lambda_0 \beta \left[ 1 - \frac{1}{x + \lambda_0 \beta \gamma} \right] = \chi_0 T_0 \left[ \beta \frac{G}{4 \lambda_2} (x_m - 1) \right] + \\
+ \chi_0 \left( \lambda_{n_1} + \beta \lambda_{n_2} \right) + \lambda_0 \beta \gamma \left[ \frac{H + 1 + \beta^2 G}{\lambda_2} \right] (x_m - 1) \tag{29}
\]

It is now necessary to determine \( \beta \) in such a way that

\[
\left( \frac{dt_2}{dx} \right)_{\beta \chi_0} = \left( \frac{dt_3}{dx} \right)_{\beta \chi_0} \tag{30}
\]
and

\[ 1 \gg \left( \frac{\alpha_2}{\alpha_0} \right) \leq 0.01 \quad (31) \]

A value of \((c_2/c_0) \leq 0.01\) assures a close approximation to the true behavior of the flame. Equation (30) then yields

\[
\frac{(\alpha-1)t_m}{\beta x_0} = (\alpha x_m - 1) \left[ \frac{H - \sqrt{H^2 + 2G/d^2}}{2} \right] \quad (32)
\]

We now have a flame system described by five parameters \((x_0, u_0, t_m, \alpha, \beta)\) with four equations, (28), (29), (31), (32). The fifth equation for the determination of the five parameters is obtained in the following way. It should be recalled that the temperature profile specified by equation (1) is not satisfied, point by point, by the approximate temperature profiles assumed in the use of equations (9), (10), (11). Consider the integrated square error of the conservation equation at every point. This error results from the differences between the actual and assumed temperature profiles:

\[
\int_{-x_0}^{x_0} \left[ \frac{1}{\rho_0} \frac{d}{dx} (\lambda_0 \frac{dt}{dx} - \lambda_0 \rho_0 u_0 \frac{dx}{dt} - R_0 - L(x)) \right] dx \quad (33)
\]

where the \(t\)-values to be employed are, of course, those prescribed by the profiles developed in this approximate model. In order to determine the \(u_0\)
value which minimizes the square error represented by equation (33), one may impose the condition

$$\frac{2}{\mu_0} \int_{-\infty}^{\infty} \delta^2 d\chi = 0$$

(34.)

Thus, equations (28), (29), (31), (32) and (34) define the five parameters \((x_0, u_0, t_m, \alpha, \beta)\).

III B. Flame Quenching and Flammability Limits:

Equations (28) and (29) represent the energy balance within the most important portions of the flame. Energy conservation must be satisfied if the flame is to exist. Thus, limits of applicability of either equations (28) or (29) define existence limits for the flame system under consideration. It is generally considered that the minimum \(c_0\) value which will allow a flame to propagate through a large \((d = 5\text{cm.})\) tube at a pressure of 1 atm. defines a flammability limit; the minimum tube size which will allow the propagation of a flame of fixed \(c_0\) defines a quenching distance. Both, "flammability limits" and wall "quenching distances", are predictable from the limits of applicability of the conservation equation. Consider these limits of applicability of equation (29) for the case of various stoichiometric, propane-oxygen-nitrogen flames. Parameters employed in the calculations for propane-air at \(p = 1\text{ atm.}\) include \(\rho_o = 1.3 \times 10^{-3}\); \(k_2\) and \(n\) values were calculated from the data of reference (11). \(\overline{\mu}\) and \(c_p\) values appropriate for the proper \(t_m\) values were used. The \(c_p\) values were chosen to give
the proper adiabatic flame temperatures. Results of these calculations are given in Table (1).

It is significant that extinction conditions are associated with a critical \( (x_0/u_0) \) value. One may consider this critical value of \( (x_0/u_0) \) to be a critical reaction time for extinction. Further, it is to be noted that the radiation loss is relatively insensitive to tube diameter variations, whereas the radial conduction loss varies as \( d^{-2} \). Consequently, the radiation term predominates in determining the flammability limits; the conduction term predominates in determining quenching distances. An important fact illustrated in Table (1) is that critical \( (x_0/u_0) \) values decrease with increasing \( O_2/N_2 \) ratios and increasing \( t_m \) values. This explains why a propane-oxygen flame quenches at a much higher \( t_m \) than does a propane-air flame. Further, it is important to note that significant quantities of reactants are still unburned at \( t = t_m \), particularly under quenching conditions. For normal, near-adiabatic flame propagation, \( (c_1/c_0) \) is small.

It is of interest to note the relation of equation (29) to previously proposed semi-empirical quenching equations. Equation (29) reduces to a form similar to those proposed in references (12) and (14) if it is assumed that, (a) radiation losses are negligible and (b) all the fuel is burned prior to \( t = t_m \). For these simplifying assumptions

\[
d^2 = \frac{(G)(\frac{x_0}{P_0}) \frac{(x_0)}{u_0}}{\left(\frac{T_a - T_0}{T_m - T_0}\right) - 1} \tag{35}
\]
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**TABLE 1** THEORETICAL AND EXPERIMENTAL EXTINCTION LIMITS FOR VARIOUS STOICHIOMETRIC FLAMES OF C₃H₈/O₂/N₂
Thus, one should not expect equation (35) to present a completely acceptable description of extinction phenomena.

IV. OTHER NON-ADIABATIC FLAMES

The approach employed in the description of the structure, behavior and stability of a premixed laminar flame may be extended to other flame systems. In this section, abbreviated discussions of such approaches are presented for the cases of "Flames in a Highly Stirred Reactor" and "Flames in a Free Radical Containing Solid Inert".

IVA. Highly Stirred Reactor:

The combustion behavior of a highly stirred reactor consisting of the volume contained between concentric spherical shells has been investigated experimentally and theoretically (references 11, 15, 16). The assumption of temperature and concentration homogeneity as well as negligible heat loss is generally made in describing the reactor behavior. In this work, a one dimensional reactor is considered in which the restriction of homogeneity of temperature and concentration is relaxed. In addition, the effects of heat losses on the stability limits are examined.

Consider the stirred reactor to be a section of a long cylinder, defined by the cylinder of temperature $T_0$ and diameter, $d$, and two porous surfaces of separation $x_1$ and temperature $T_1$. In the region $0 \leq x \leq x_1$ non-laminar mixing is taken to be very vigorous and of such a nature as to assure:
(a) Volumetric scales of temperature inhomogeneities which are very small compared to $\pi x_1 d^2$.

(b) A time average temperature, $T_1$ which is uniform throughout $0 \leq x \leq x_1$.

It then follows that there exists a range of instantaneous temperature and concentration distributions, on the interval $0 \leq x \leq x_1$, which will satisfy the requirements listed above as well as the requirement that $t = t_1$ and $c = c_{x_1}$ at $x = x_1$. Consider the average rate in the region $0 \leq x \leq x_1$.

$$\bar{R} \left( d\Theta \right) = \frac{A \rho^2 (d\Theta)}{\rho} = (\rho_0 - \rho_1) \rho$$  \hspace{1cm} (36.)

As before,

$$\frac{dC}{d\Theta} = - \frac{R}{\rho} = - \frac{A \rho^2}{\rho}$$  \hspace{1cm} (37.)

Yields

$$A = \left( \frac{\rho_0 - \rho_1}{\rho_0 \rho_1} \right) \frac{\rho}{d\Theta}$$  \hspace{1cm} (38.)

thus

$$\bar{c} = \sqrt{c_0 c_1}$$  \hspace{1cm} (39.)

Now, proceeding as in the previous section, one obtains

$$C_1 = \frac{\rho_0}{1 + \left( \frac{z}{\rho_0} \right) x_1 / \rho_0 \rho_1 \rho \kappa_1 \exp \left( - \frac{E}{RT_0 x_1} \right)}$$  \hspace{1cm} (40.)
The conservation equation may then be written

$$\rho \mu_\eta \left[ \frac{S}{u_\eta + \xi_\eta} \right] = \frac{G \lambda}{2d^2} \left( \xi_\eta - \xi_\omega \right) T_0 \kappa +$$

$$+ \frac{\alpha_2 T \left( \xi_\eta - \xi_\omega \right) \lambda}{\left( H^2 + 2\xi_\omega \right)} + \left( \xi_\omega - \xi_\eta \right) \sigma T_0^4$$

(4.1)

where $\xi_\eta \ll 1$, permitting neglect of reabsorption effects.

In general, a temperature profile similar to that shown in Figure (2) may be expected. First, consider the behavior of the adiabatic case:

Neglect of heat loss processes for the case of stoichiometric propane air reaction at $T_0 = 300^\circ K$ and $p = 1$ atm. results in the allowed values of $u_\eta$ and $(c_{x_\eta} / c_o)$ shown by the solid curves of Figure (3). The value $k_1 = 1.455 \times 10^{14}$ is deduced from the data of reference (11) where a rate of $0.124 \text{ gm(fuel)} / (\text{cm}^3) \text{ (sec)}$ and $t_1 = 4.67$ are used. This is the same value used as a starting point in the calculations of section IIIB. Interestingly enough, the maximum blow out velocity of $7.9 \times 10^3$ cm/sec (for a $c_{x_\eta}$ corresponding to $81\%$ completion within the reactor) approximately corresponds to the same high temperature reaction time available in the reaction zone of a laminar flame, where $x_\eta \sim 0.05 \text{ cm}$ and $u_\eta \sim 40$ cm/sec.

For the non adiabatic case, a knowledge of $\lambda$ as well as the emissive properties of the reacting medium are needed. To illustrate the effect of heat losses, consider the following case. $\lambda$ must be associated with non-laminar transport processes of very high order; thus a value of
\[ \bar{\lambda}_1 \sim 1 \times 10^{-3} \text{ cal/(cm)(sec)(^0K)} \text{ is not unreasonable. It is supposed that purely molecular transport prevails outside of the regime } 0 \leq x \leq x_1. \] The data and methods of reference (10) are again employed to calculate the emissive properties of the hot gases. The calculated \( u_0 \) and \( c_{x_1}/c_0 \) values as a function of \( t_1 \) for the non-adiabatic cases treated are given by the broken curves of Figure (3). Of particular interest is the existence of critical values of \( u_0 \) below which this reactor cannot operate. As expected, velocity limits exist. In addition, as the reactor diameter is reduced from 5cm to 1cm, it becomes apparent that a quenching limit exists; that is, there exists a critical diameter below which this reactor will not operate. In theory, the low temperature branch of the \( u_0 \) vs. \( t_1 \) curve may exist - however, it's existence under the conditions considered has not been demonstrated experimentally. If the low temperature branch is unstable then, for the hypothetical case considered, quenching occurs for a tube diameter just below \( d = 1 \)cm.

IVB. Flames in Free Radical Containing Solid Inerts

Consider a long cylinder enclosing a free-radical containing solid inert (for example, H-atoms in Argon). Radical recombination may occur either in the volume or at the walls. As in the case of flame propagation in premixed gases, the boundary conditions, the transport properties, the heat loss mechanisms and reaction rates will determine the flame's existence, structure and behavior. Flame phenomena in such systems have been qualitatively observed (reference 17). Of utmost importance to the flame behavior of such a system is the form of the reaction rate law. There exists little information on the kinetics of diffusion controlled reactions of the sort under consideration. However, the general form of the rate law may be deduced. Seitz (reference 18) has proposed that the jump frequency of a diffusing atom in an inert lattice be given by

\[ \nu_j = \frac{1}{h^2} \frac{(RT)^3}{\alpha_n \nu_n^2} \exp\left(-\frac{E_n}{RT}\right) \]  

(42)
Then, the number of jumps per \( \text{cm}^3/\text{sec} \) is \( \nu \lambda' N_0 \). Assuming that \( E_s \gg E'_r \), and taking the probability of finding a similar free radical at an adjacent site to be \( \lambda' \lambda_\alpha \), yields

\[
\mathbf{R}_\lambda = \left( \frac{M_s}{kR} \right)^2 \left( \frac{2\lambda' \lambda_\alpha}{2kR} \right)^2 (kT)^3 \exp \left( -\frac{E_s}{kT} \right) \quad \text{(4.3,)}
\]

for the reaction rate.

In view of the fact that we may write equation (43) in the form

\[
\mathbf{R}_\lambda = k' F_1 (\rho' \lambda') F_2' (t) \quad \text{(4.4)}
\]

it follows that the above form for the reaction rate law implies no changes in the basic flame model developed for the case of premixed gases. It may be necessary, however, to account for radical-radical wall recombination rates, where the diffusion coefficient has the form given by Seitz and where the method of reference (19) may be used to calculate the influence of walls on radical lifetimes. Some data (reference 20) exist on thermal conductivities of molecular crystals. In addition, the high energy release per reacting pair suggests a high photon yield per reaction. This, coupled with the fact that systems of interest are generally cryogenic implies that the dominant heat loss parameter in the reaction zone of the flame may be radiative.
Evaluation of these relations awaits detailed examination of the existence limits as well as burning velocities associated with the systems of interest. In addition to the above considered flame phenomena, there exists the usual phenomenon of a space distributed slow reaction with the attendant possibility of an explosion (reference 19).

Thus, for the case of flame propagation in free radical containing solid inerts it is clear that the boundary conditions, conservation equations and rate laws, can be simply incorporated into the non-adiabatic flame theory developed for the case of flames in premixed gases. Burning velocity measurements under varying conditions of temperature and concentration are then capable of yielding activation energies and diffusion coefficients pertinent to processes involved.

V. CONCLUDING REMARKS

1. The above treatment can be generalized to take account of diffusion processes, changing molar flow rates, more realistic chemical rate laws, etc. Simplifications made in the above treatment were for purposes of convenience and do not compromise the essential features of the flame system.

2. One may derive an adiabatic flame theory as a special case of the non-adiabatic theory treated herein.

3. Extinction limits associated with a given flame are characterized by a critical reaction time, \( \frac{x_0}{u_0} \).
4. Near extinction, significant quantities of unburned reactants may exist at \( t = t_m \).

5. The tedious calculation of the burning velocity is indicated, but not included in this paper.

6. The success of this model in predicting the extinction limits for flames covering a wide spectrum of reactivities, tube sizes and pressures argues for its validity.

7. This model can easily be extended to treat the behavior, structure and stability limits of a gas phase flame supported by the evaporation of premixed solid reactants.
VI NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>constant</td>
</tr>
<tr>
<td>c</td>
<td>mass fraction of fuel</td>
</tr>
<tr>
<td>c₀</td>
<td>initial mass fraction of fuel</td>
</tr>
<tr>
<td>c₁</td>
<td>mass fraction of fuel at x = 0</td>
</tr>
<tr>
<td>c₂</td>
<td>mass fraction of fuel at x = βx₀</td>
</tr>
<tr>
<td>c_p</td>
<td>specific heat at constant pressure (cal/(gm)(deg))</td>
</tr>
<tr>
<td>c̄</td>
<td>average concentration in the highly stirred reactor</td>
</tr>
<tr>
<td>c'</td>
<td>free radical species fraction in solid inert</td>
</tr>
<tr>
<td>d</td>
<td>cylinder diameter, cm.</td>
</tr>
<tr>
<td>E</td>
<td>Activation Energy, kcal/mole</td>
</tr>
<tr>
<td>E_r</td>
<td>Atom-Atom recombination rate activation energy</td>
</tr>
<tr>
<td>E_s</td>
<td>Activation Energy necessary for a diffusing atom to jump across a solid lattice saddle point</td>
</tr>
<tr>
<td>F₁(c)</td>
<td>dimensionless function of fuel concentration</td>
</tr>
<tr>
<td>F₂(t)</td>
<td>dimensionless function of temperature</td>
</tr>
<tr>
<td>G</td>
<td>Geometric factor involved in channel quenching (reference 9)</td>
</tr>
<tr>
<td>H</td>
<td>(1/λ)(c_p₀u₀)</td>
</tr>
<tr>
<td>h</td>
<td>characteristic lattice constant, cm.</td>
</tr>
<tr>
<td>k</td>
<td>Boltzmann Constant</td>
</tr>
<tr>
<td>k₁</td>
<td>a constant, gm/(cm³)(sec)</td>
</tr>
<tr>
<td>k₁'</td>
<td>a constant, (2M₁k²)/(M₉h³v_s²)</td>
</tr>
<tr>
<td>k₂</td>
<td>a constant, gm/(cm³)(sec)</td>
</tr>
<tr>
<td>L(t)</td>
<td>Heat loss function, cal/(cm³)(sec)</td>
</tr>
</tbody>
</table>
1. conduction heat loss

1' conduction heat loss at \( x = -x_0 \)

1\_r radiation heat loss (hot gas to cold walls)

1\_r, w radiation heat loss (hot walls to surroundings)

\( M_I \) atomic weight of inert species

\( M_R \) atomic weight of radical species

\( N_0 \) numerical concentration of inert species, \( \text{cm}^{-3} \)

\( p \) pressure, atmospheres

\( q \) heat of combustion, \( \text{cal/gm} \)

\( R \) reaction rate, \( \text{gms(of fuel)}/(\text{cm}^3)(\text{sec}) \)

\( R_s \) reaction rate in the solid, \( \text{gm(of recombining atoms)}/(\text{cm}^3)(\text{sec}) \)

\( r \) reaction rate order constant

\( \xi_1 \) 

\( (1/t_1^2)(\varepsilon x_Ip_0k_1) \exp \left[ -\frac{E}{RT_0} \frac{1}{t_1} \right] \)

\( T \) Temperature, \( ^{\circ}\text{K} \)

\( t \) \( T/T_0 \), dimensionless temperature

\( \bar{t} \) time average value of \( t \), stirred reactor case

\( t_1 \) temperature in the region \( -x_0 \leq x \leq 0 \)

\( t_2 \) temperature in the region \( 0 \leq x \leq \beta x_0 \)

\( t_m \) temperature at \( x = 0 \)

\( u \) flow velocity, \( \text{cm/sec} \)

\( u_0 \) burning velocity, \( \text{cm/sec} \)

\( x \) longitudinal coordinate, \( \text{cm} \)

\( x_0 \) distance defined in Figure 1, \( \text{cm} \)
Subscripts

- \( a \): adiabatic
- \( o \): initial conditions, except as noted
- \( r \): radiation
- \( \lambda \): conduction

Greek Symbols

- \( \alpha \): number of saddle points (of molar energy \( E_s \)) about a given free radical equilibrium position
- \( \alpha t_m \): a post \( t_m \) temperature at which the flame properties are insensitive to the existence of a small reaction rate
- \( \beta_{x_0} \): point in space at which \( \alpha t_m \) occurs
- \( \gamma \): radiant heat loss equation constant
- \( \delta \): error function
- \( \varepsilon_g \): radiative emissivity of gas
- \( \varepsilon_w \): radiative emissivity of stirred reactor permeable membranes at \( x = 0, \ x = x_1 \)
- \( \Theta \): time, sec
- \( \lambda \): Thermal conductivity, cal/(cm)(K)(sec)
- \( \overline{\lambda} \): \( \lambda_o \int (t)^{3/4} \cdot dt/(t-1) \)
- \( \nu_j \): jump frequency of a diffusing atom in an inert lattice, sec\(^{-1}\)
- \( \nu_s \): characteristic vibrational frequency of an interstitial atom, sec\(^{-1}\)
- \( \xi \): \( (dT/dx) \) at \( x = -x_0 \)
- \( \rho \): gas density, gm/cm\(^3\)
\( \rho' \)  
crystal density, gm/cm\(^3\)  

\( \sigma \)  
Stefan-Boltzmann constant  

\( \psi_1 \)  
defined by equations 17  

\( \psi_2 \)  
defined by equation 19  

\( \omega_1 \)  
\((1/2)(H + \sqrt{H^2 + (2G/d^2)})\)  

\( \omega_2 \)  
\((1/2)(H - \sqrt{H^2 + (2G/d^2)})\)
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FIGURE LEGENDS

Figure (1)        Non-Adiabatic Flame Structure (Qualitative)

Figure (2)        Highly-Stirred Reactor, One Dimensional Average Temperature Profile

Figure (3)        Highly-Stirred Reactor, Velocity Limits

Table (1)        Theoretical and Experimental Extinction Limits For Various Stoichiometric Flames of C₃H₈/O₂/N₂
FIG. 1 NON-ADIABATIC FLAME STRUCTURE (QUALITATIVE)
CONDUCTION / RADIATION ABSENT

CONDUCTION / RADIATION LOSSES

\[ \text{--- } d = 5 \text{ cm} \]
\[ \text{--- } d = 2 \text{ cm} \]
\[ \text{--- } d = 1 \text{ cm} \]

\( X_1 = 10 \text{ cm} \)

\[ U_0 \times 10^{-3} \]

\[ \left( \frac{\text{cm}}{\text{sec.}} \right) \]

\[ \frac{c_{X_1}}{c_0} \]

FIG. 3 HIGHLY STIRRED REACTOR, VELOCITY LIMITS