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RESEARCH NOTE 20

ON NON-ADIABATIC FLAME

PROPAGATION

by

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ON NON-ADIABATIC FLAME PROPAGATION

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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 tem-
perature 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_o. This requirement that $(du_o/d\theta) = 0$ implies that there exists a finite
distance, x_o, 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 $x = \infty$.

IIB. Mathematical Formulation:

The energy conservation equation may be written

$$T_0 \frac{d}{dx} \lambda \frac{dt}{dx} - c_p \rho_0 u_0 T_0 \frac{dt}{dx} + R_g - \mathcal{L}(t) = 0 \qquad (1.)$$

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

$$R = k_1 F_1 (\rho c) F_2 (t) \qquad (2.)$$

Then, by definition

$$\frac{dc}{d\theta} = - \frac{R}{\rho} = - k_1 \rho^{-1} F_1 (\rho c) F_2 (t) \qquad (3.)$$

Also, for constant mole flow

$$\frac{dc}{d\theta} = u \frac{dc}{dx} = u_0 t \frac{dc}{dx} \qquad (4.)$$

Thus, from equations (3) and (4)

$$\int_{c_0}^{c} \frac{dc}{F_1(\rho c)} = - \frac{k_1}{\rho_0 M_0} \int_{-x_0}^{x} F_2(t) dx \qquad (5.)$$

For the case $F_1 (\rho c) = \rho^2 c^2$, equation (5) yields

$$\mathcal{L} = \frac{\mathcal{L}_0}{1 + \frac{\mathcal{L}_0 k_1 \rho_0}{\mu_0} \int_{-x_0}^{x} \frac{F_2(t)}{t^2} dx} \qquad (6)$$

The heat loss term, $\mathcal{L}$ (t) will be of the form

$$\mathcal{L}(t) = \ell_\lambda(t) + \ell_\lambda(t) + \ell'_\lambda \left[(dt/dx)_{x=-x_0} \right] \qquad (7)$$

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

$$x = -x_0: \quad T = T_0, \quad c = c_0, \quad dT/dx = \xi$$

$$(8)$$

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

Neither the conditions at $x = -x_0$ nor those at $x = +\infty$ by themselves guarantee the existence of a flame in the region $-x_0 \le x \le +\infty$. 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 $-x_0 \leq x \leq 0$.

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

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 $0 \leq x \leq x_0 \beta$.

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

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, α, is determined by β. βx_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, αt_m is quite close to t_m. The linear approximation of equation (10) is thus justified. These conditions then permit the rewriting of equation (1) for the third interval, where $x_o \beta \leq x \leq +\infty$,

$$\frac{d}{dx} \lambda \frac{dt_3}{dx} - \rho_o c_f \mu_o \frac{dt_3}{dx} - \frac{1}{T_o} \mathcal{L}(t_3) = 0 \tag{11.}$$

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

$$\mathcal{R} = k_1 \rho^2 c^2 exp\left(-\frac{E}{RT_o} \cdot \frac{1}{t}\right) \tag{12.}$$

and, over a limited range, approximated by

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

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

$$c_1 = \frac{c_o}{1 + \frac{c_o \rho_o k_2}{\mu_o} \int_{-x_o}^{0} t_1^{m-2} dx} \tag{14}$$

and for $0 \leq x \leq x_o \beta$

$$c_2 = \frac{c_1}{1 + \frac{c_1 \rho_0 k_2}{\mu_0} \int_0^{\beta x_0} t_2^{m-2} \, dx} \qquad (15).$$

There then results

$$c_1 = \frac{1}{\frac{1}{c_0} + \frac{x_0}{\mu_0} \, \psi_1(t_m)} \qquad (16.)$$

where for even n-values:

$$\psi_1(t_m) = \rho_0 k_2 \left[\left(\frac{t_m+1}{2}\right)^{m-2} + \frac{(m-2)(m-3)}{(2!)(2)}\left(\frac{t_m+1}{2}\right)^{m-4}\left(\frac{t_m-1}{2}\right)^2 + \cdots \right.$$
$$\left. \cdots + \frac{(m-3)(m-5)\cdots 3}{(m-2)(m-4)\cdots 2}\left(\frac{t_m-1}{2}\right)^{m-2} \right] \qquad (17A.)$$

and for odd n-values

$$\psi_1(t_m) = \rho_0 k_2 \left[\left(\frac{t_m+1}{2}\right)^{m-2} + \frac{(m-2)(m-3)}{(2!)(2)}\left(\frac{t_m+1}{2}\right)^{m-4}\left(\frac{t_m-1}{2}\right)^2 + \cdots \right.$$
$$\left. \cdots + \frac{(m-2)(m-4)\cdots 3}{(m-3)(m-5)\cdots 2}\left(\frac{t_m+1}{2}\right) \right] \qquad (17B.)$$

A similar expression results for c_2,

$$c_2 = \frac{1}{\frac{1}{c_0} + \frac{x_0}{\mu_0} \, \psi_2(\beta, t_m)} \qquad (18.)$$

where

$$\psi_2(\beta, t_m) = \psi_1(t_m) + \frac{\ell_0 k_2 \beta t_m^{m-2}}{m-1}(1 + \alpha + \cdots + \alpha^{m-1}) \quad (19.)$$

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_o, u_o, t_m.

Integration of equation (1), subject to the boundary conditions $T = T_o$, $c = c_o$, and $(dT/dx) = 0$ yields:

$$g \int_{-x_o}^{\tilde{\infty}} R\, dx = \int_{-x_o}^{\tilde{\infty}} \mathcal{L}\, dx \quad (20.)$$

For the approximation model, this equation may be written as

$$g \int_{-x_o}^{x_o \beta} R\, dx = \int_{-x_o}^{\infty} \mathcal{L}\, dx \quad (21.)$$

Now, the left hand side of equation (21) may be written

$$g \int_{-x_o}^{x_o \beta} R\, dx = \ell_0 \beta \, u_o g \left(1 - \frac{\ell_2}{\ell_0}\right) \quad (22.)$$

and the right hand side of equation (21) may be written

$$\int_{-x_0}^{\infty} \mathcal{L}\, dx = \int_{-x_0}^{\beta x_0} \mathcal{L}\, dx + \int_{\beta x_0}^{\infty} \mathcal{L}\, dx \qquad (23.)$$

where

$$\int_{-x_0}^{\beta x_0} \mathcal{L}\, dx = \int_{-x_0}^{\beta x_0} \frac{G \bar{\lambda} T_0}{2 d^2} (t-1)\, dx + \int_{-x_0}^{\beta x_0} \ell_n\, dx \qquad (24.)$$

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

$$\frac{d^2 t}{dx^2} - H \frac{dt}{dx} - \frac{G}{2 d^2} (t-1) = 0 \qquad (25.)$$

Solution of equation (25) yields

$$\int_{x_0 \beta}^{\infty} \mathcal{L}\, dx = -\bar{\lambda} T_0 \left(\frac{dt}{dx}\right)_{x_0 \beta} + \; \bar{i}_0 \rho_0 M_0 (\alpha t_m - 1) \qquad (26)$$

where

$$\left(\frac{dt}{dx}\right)_{x_0\beta} = \left[\frac{H-\sqrt{H^2+(2G/d^2)}}{2}\right](\alpha t_m - 1) \qquad (27.)$$

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.

$$\mathcal{L}_0 \rho_0 u_0 q\left[1- \frac{1}{1+\mathcal{L}_0 \frac{x_0}{u_0}\Psi_2}\right] = x_0 T_0\left[\frac{G\bar\lambda}{4d^2}(t_m-1)+\frac{G\lambda_m}{4d^2}\beta\left\{\left(\frac{1+\alpha}{2}\right)t_m-1\right\}\right]+$$

$$+x_0(l_{r,1}+\beta l_{r,2})+\bar\lambda T_0\left[\frac{H+\sqrt{H^2+2G/d^2}}{2}\right](\alpha t_m-1) \qquad (28.)$$

and for $-x_0 \leq x \leq 0$:

$$\mathcal{L}_0 \rho_0 u_0 q\left[1-\frac{1}{1+\mathcal{L}_0(\frac{x}{u_0})\Psi_1}\right] = x_0 T_0\left[\frac{G\bar\lambda}{4d^2}(t_m-1)\right]+$$

$$+x_0 l_{r,1}+\mathcal{L}_{g}\rho_0 u_0 T_0(t_m-1) \qquad (29.)$$

It is now necessary to determine β in such a way that

$$(dt_2/dx)_{\beta x_0} = (dt_3/dx)_{\beta x_0} \qquad (30.)$$

and

$$1 \gg (c_2/c_o) \leq 0.01 \qquad (31.)$$

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

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

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:

$$\int_{-x_0}^{\infty} \delta^2 dx = \int_{-x_0}^{\infty} \left[T_0 \frac{d}{dx}\lambda\frac{dt}{dx} - c_p \rho u_0 T_0 \frac{dt}{dx} + Rq - \mathcal{L}(t)\right]^2 dx \qquad (33.)$$

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

$$\frac{\partial}{\partial u_0} \int_{-x_0}^{\infty} \delta^2 dx = 0 \tag{34.}$$

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

IIIB. 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 = 5cm.) 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 atm. include $\rho_0 = 1.3 \times 10^{-3}$; k_2 and n values were calculated from the data of reference (11). $\bar{\lambda}$ 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_o/u_o) value. One may consider this critical value of (x_c/u_o) 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 illus-
trated in Table (1) is that critical (x_o/u_o) values decrease with increasing
$0_2/N_2$ 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_o) is small.

It is of interest to note the relation of equation (29) to previously pro-
posed 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

$$d^2 = \frac{(G)\left(\frac{\lambda}{\rho_o c_p}\right)\left(\frac{x_o}{u_o}\right)}{\left(\frac{T_\lambda - T_o}{T_m - T_o}\right) - 1} \qquad (35.)$$

	p	d	$C_3H_8/O_2/N_2$	t_m	c_1/c_o	x_o/u_o	Exp. Ref.		k_2	n	$\bar{\lambda}$
A	1	0.037	$1/5O_2$	8.0	0.104	0.23×10^{-3}		Theory	2.07×10^3	8	$.1726 \times 10^{-3}$
	1	0.034	$1/5O_2$				5.	Expt.			
B	1	0.35	$1/5O_2/18.8N_2$	5.5	0.170	9.3×10^{-3}		Theory	6.68	11	$.1425 \times 10^{-3}$
	1	0.31	$1/5O_2/18.8N_2$				9.	Expt.			
C	0.060	5.00	$1/5O_2/18.8N_2$	5.7	0.124	0.12		Theory	5.68	11	$.1452 \times 10^{-3}$
	0.046	5.00	$1/5O_2/18.8N_2$				12.	Expt.			
D	1	5.00	$1/5O_2/28.0N_2$	4.5	0.052	0.73		Theory	0.862×10^{-2}	15	$.825 \times 10^{-4}$
	1	5.00	$1/5O_2/32.2N_2$				13.	Expt.			

TABLE 1   THEORETICAL AND EXPERIMENTAL
EXTINCTION LIMITS FOR VARIOUS STOICHIOMETRIC FLAMES
OF $C_3H_8/O_2/N_2$

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_o and diameter, d, and two porous surfaces of separation x_1 and temperature T_1. In the region $0 \le x \le x_1$ 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 $0 \leqq x \leqq x_1$.

It then follows that there exists a range of instantaneous temperature and concentration distributions, on the interval $0 \leqq x \leqq x_1$, 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 $0 \leqq x \leqq x_1$.

$$\overline{R}\,(d\theta) = A\,\overline{c}^{\,2}(d\theta) = (c_0 - c_1)\rho \tag{36.}$$

As before,

$$\frac{dc}{d\theta} = -\frac{R}{\rho} = -\frac{A c^2}{\rho} \tag{37.}$$

Yields

$$A = \left(\frac{c_0 - c_1}{c_0\, c_1}\right) \cdot \frac{c}{(d\theta)} \tag{38.}$$

thus

$$\overline{c} = \sqrt{c_0 c_1} \tag{39.}$$

Now, proceeding as in the previous section, one obtains

$$c_1 = \frac{c_0}{1 + (t_1^2 \mu_0)^{-1} x_1 \sqrt{c_0 c_1}\, \rho_0 k_1\, exp\left(-\frac{E}{RT_0 t_1}\right)} \tag{40.}$$

The conservation equation may then be written

$$c\rho_0 u_0 \frac{d}{dz}\left[\frac{S_1}{\mu_0 + S_1}\right] = \frac{G\bar{\lambda}}{2d^2}(t_1 - 1)T_0 x +$$

$$+ \bar{\lambda}_2 T(t_1 - 1)\sqrt{H^2 + 2G/d^2} + \left(\frac{x_1 \epsilon_{\pm}}{2} + \epsilon_{wr}\right)\sigma T_1^4 \qquad (4.1)$$

where $\epsilon_g \ll 1$, 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 $T_0 = 300°K$ and $p = 1$ atm. results in the allowed values of u_0 and (c_{x_1}/c_0) 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 gm(fuel)/(cm^3)(sec) and $t_1 = 6.67$ 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 7.9×10^3 cm/sec (for a c_1 corresponding to 81% completion within the reactor) approximately corresponds to the same <u>high temperature</u> reaction time available in the reaction zone of a laminar flame, where $x_1 \sim 0.05$ cm and $u_0 \sim 40$ cm/sec.

For the non adiabatic case, a knowledge of $\bar{\lambda}_1$ as well as the emissive properties of the reacting medium are needed. To illustrate the effect of heat losses, consider the following case. $\bar{\lambda}_1$ must be associated with <u>non-laminar</u> transport processes of very high order; thus a value of

$\overline{\lambda}_{,} \sim 1 \times 10^{-3}$ cal/(cm)(sec)($^{\circ}$K) 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 = 1cm.

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

$$\mathcal{V}_j = \frac{1}{h^2} \frac{(kT)^3}{\alpha_a \mathcal{V}_a^2} \, exp\left(- \frac{E_a}{RT}\right) \tag{42.}$$

Then, the number of jumps per $(cm^3)(sec)$ is $\nu c' N_o$. Assuming that $E_s \gg E_r$, and taking the probability of finding a similar free radical at an adjacent site to be $c' \alpha_\lambda$ yields

$$R_\lambda \simeq \left(\frac{M_I}{M_R}\right)\left(\frac{2}{h^3}\frac{c'}{\nu_\lambda^3}\right)(c')^2 (kT)^3 \exp\left(-\frac{E_\lambda}{RT}\right) \tag{43.}$$

for the reaction rate.

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

$$R_\lambda = k_i' \, F_1(\rho' c') \, F_2'(t) \tag{44.}$$

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, x_o/u_o.

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

A	constant
c	mass fraction of fuel
c_o	initial mass fraction of fuel
c_1	mass fraction of fuel at $x = 0$
c_2	mass fraction of fuel at $x = \beta x_o$
c_p	specific heat at constant pressure cal/(gm)(deg)
$\bar{c}$	average concentration in the highly stirred reactor
c'	free radical species fraction in solid inert
d	cylinder diameter, cm.
E	Activation Energy, kcal/mole
E_r	Atom-Atom recombination rate activation energy
E_s	Activation Energy necessary for a diffusing atom to jump across a solid lattice saddle point
$F_1(c)$	dimensionless function of fuel concentration
$F_2(t)$	dimensionless function of temperature
G	Geometric factor involved in channel quenching (reference 9)
H	$(1/\bar{\lambda}) (c_p \rho_o u_o)$
h	characteristic lattice constant, cm.
k	Boltzman Constant
k_1	a constant, $gm/(cm^3)(sec)$
k_1'	a constant, $(2M_I k^3)/(M_R h^3 \nu_s^2)$
k_2	a constant, $gm/(cm^3)(sec)$
$\mathcal{L}(t)$	Heat loss function, $cal/(cm^3)(sec)$

1_λ	conduction heat loss
$1'_\lambda$	axial conduction heat loss at $x = -x_o$
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_o	numerical concentration of inert species, cm^{-3}
p	pressure, atmospheres
q	heat of combustion, cal/gm
R	reaction rate, gms(of fuel)/(cm^3)(sec)
R_s	reaction rate in the solid, gm(of recombining atoms)/(cm^3)(sec)
r	reaction rate order constant
S_1	$(1/t_1^2)(\bar{c}x_1\rho_o k_1) \exp\left[-\dfrac{E}{RT_o} \cdot \dfrac{1}{t_1}\right]$
T	Temperature, ^oK
t	T/T_o, dimensionless temperature
$\bar{t}$	time average value of t, stirred reactor case
t_1	temperature in the region $-x_o \le x \le 0$
t_2	temperature in the region $0 \le x \le \beta x_o$
t_m	temperature at $x = 0$
u	flow velocity, cm/sec
u_o	burning velocity, cm/sec
x	longitudinal coordinate, cm
x_o	distance defined in Figure 1, cm.

Subscripts

a	adiabatic
o	initial conditions, except as noted
r	radiation
λ	conduction

Greek Symbols

α_s	number of saddle points (of molar energy E_s) about a given free radical equilibrium position
αt_m	a post t_m temperature at which the flame properties are insensitive to the existence of a small reaction rate
βx_o	point in space at which αt_m occurs
γ	radiant heat loss equation constant
δ	error function
ϵ_g	radiative emmissivity of gas
ϵ_w	radiative emmissivity of stirred reactor permeable membranes at $x = 0$, $x = x_1$
Θ	time, sec
λ	Thermal conductivity, cal/(cm)(°K)(sec)
$\bar{\lambda}$	$\lambda_o \int_{\gamma}^{\tau} (t)^{3/4} \cdot dt/(t-1)$
ν_j	jump frequency of a diffusing atom in an inert lattice, sec^{-1}
ν_s	characteristic vibrational frequency of an interstitial atom, sec^{-1}
ξ	(dT/dx) at $x = -x_o$
ρ	gas density, gm/cm^3

ρ' crystal density, gm/cm^3

σ Stefan-Boltzmann constant

ψ_1 defined by equations 17

ψ_2 defined by equation 19

ω_1 $(1/2)(H + \sqrt{H^2 + (2G/d^2)}\,)$

ω_2 $(1/2)(H - \sqrt{H^2 + (2G/d^2)}\,)$

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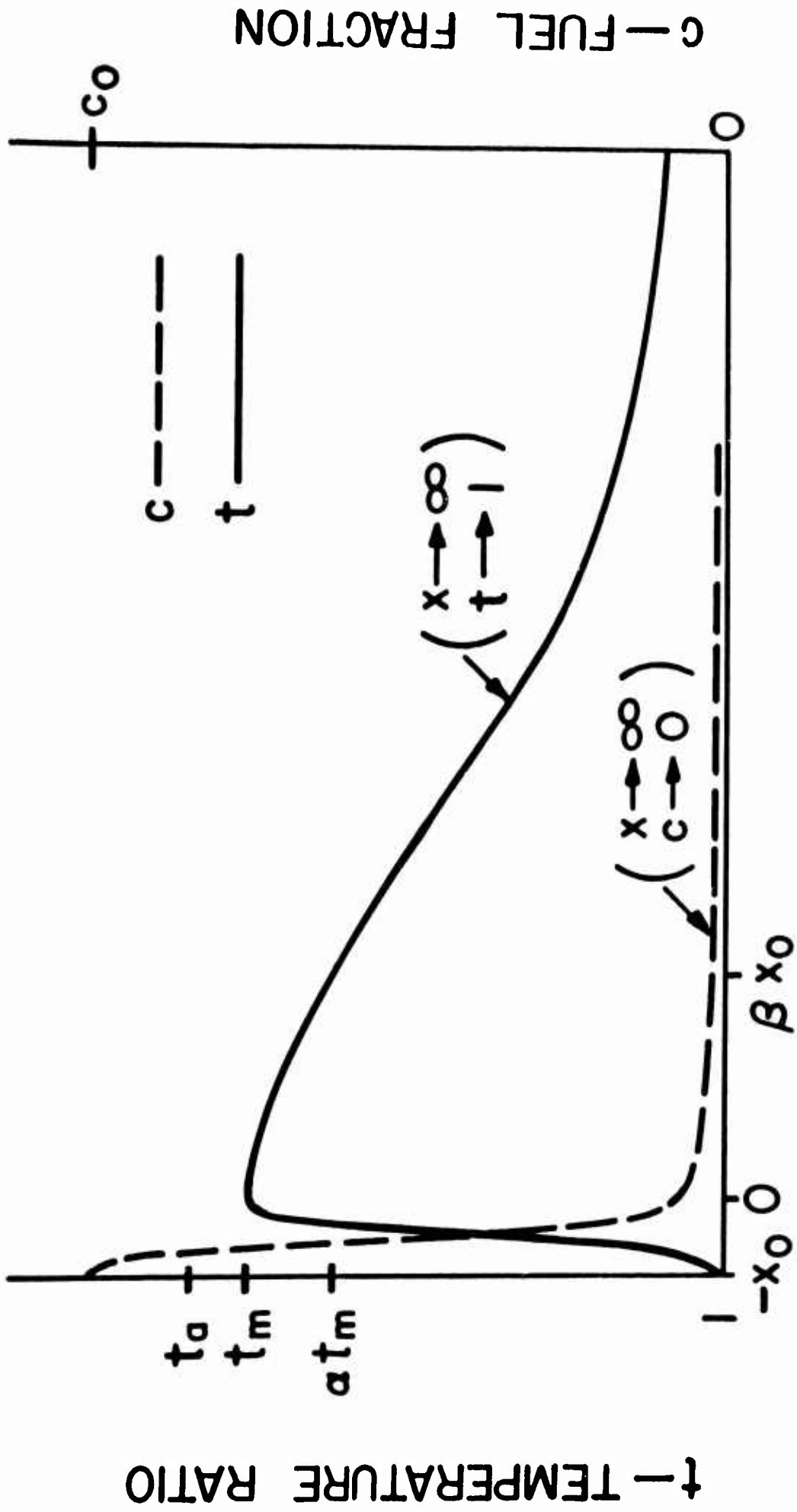
FIGURE LEGENDS

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

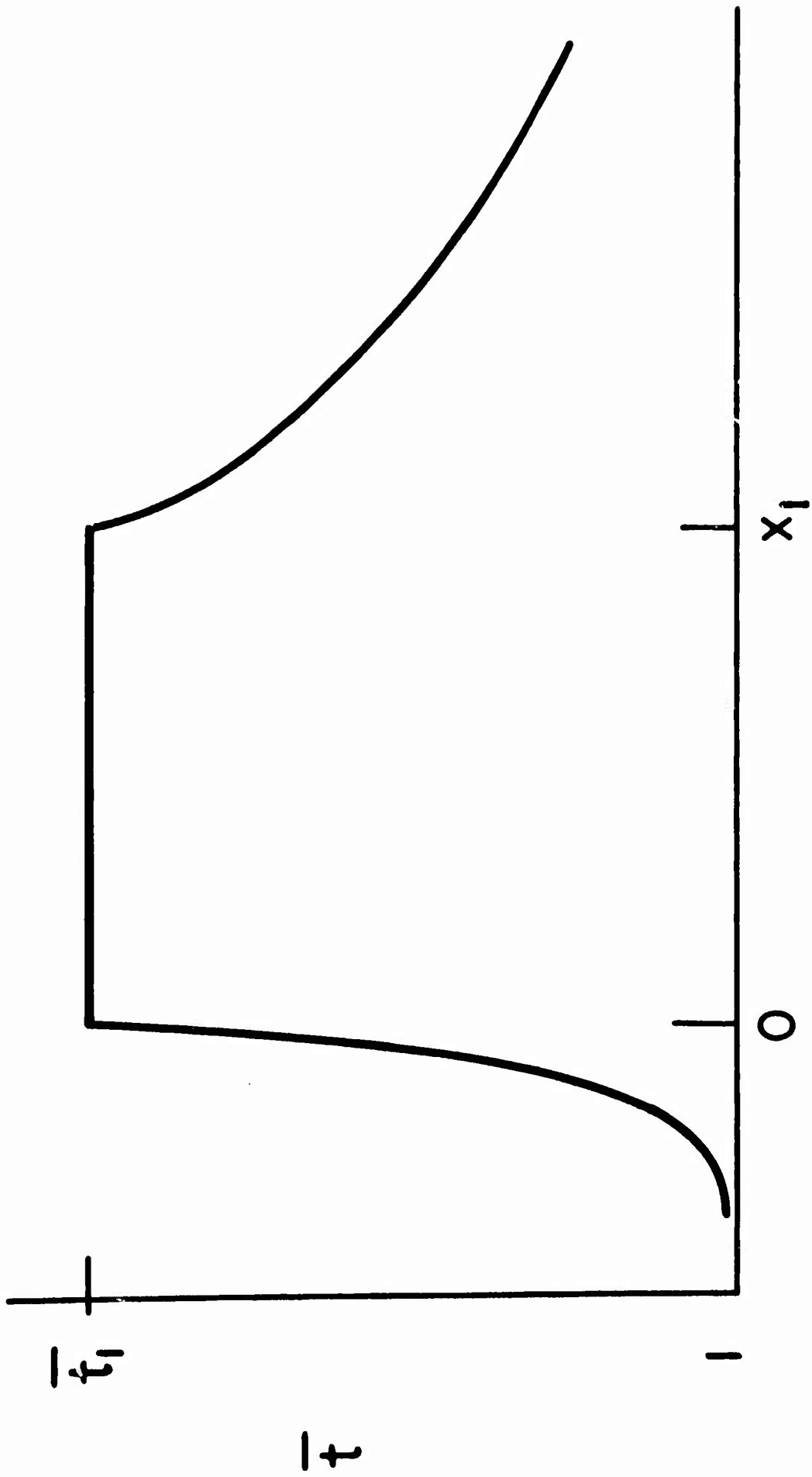Figure (2)   Highly-Stirred Reactor, One Dimensional Average Temperature
Profile

Figure (3)   Highly-Stirred Reactor, Velocity Limits

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Table (1)   Theoretical and Experimental Extinction Limits For Various
Stoichiometric Flames of $C_3H_8/O_2/N_2$

FIG.1 NON-ADIABATIC FLAME STRUCTURE (QUALITATIVE)
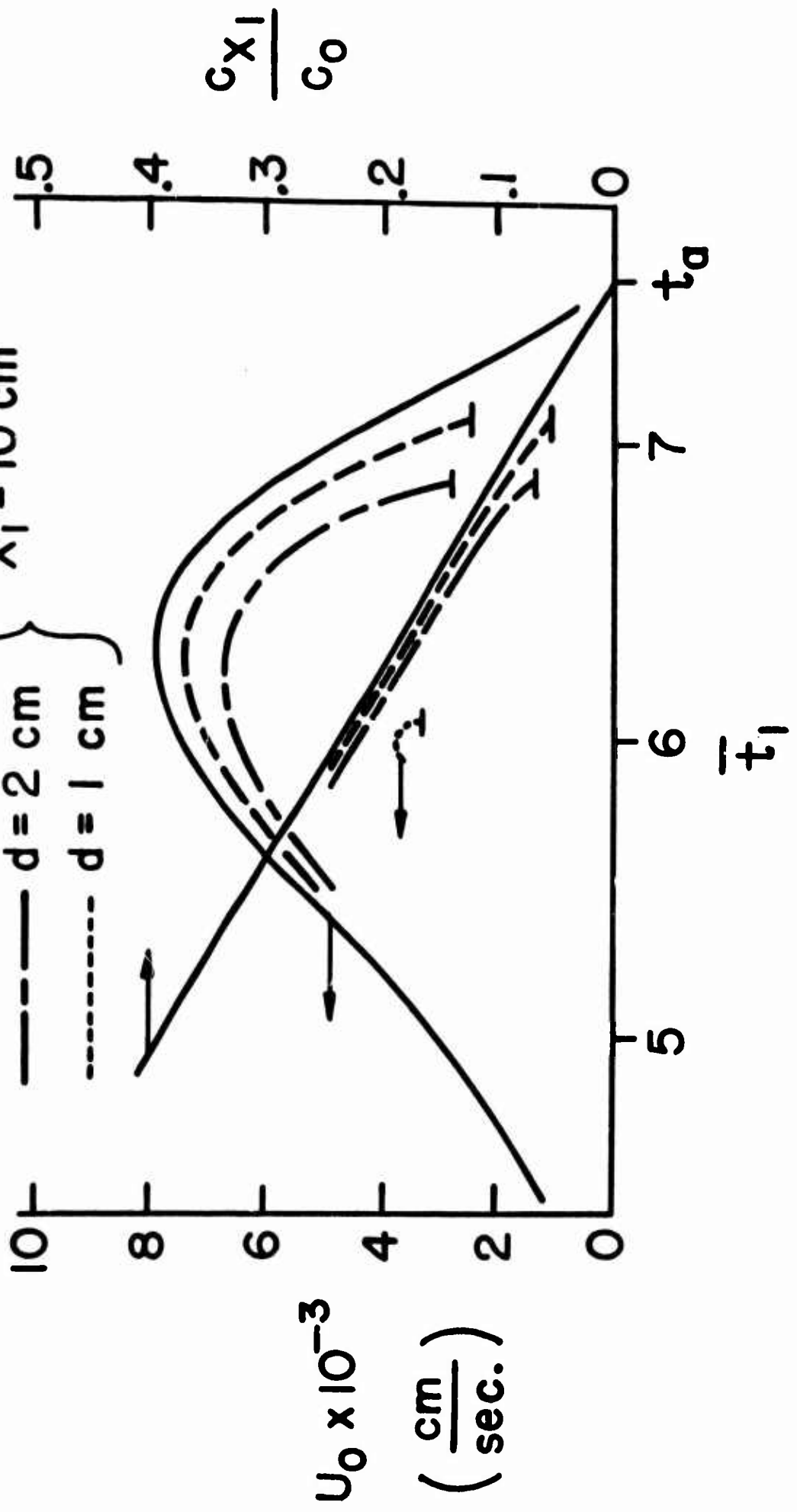
FIG. 2   HIGHLY-STIRRED REACTOR, ONE DIMENSIONAL

AVERAGE TEMPERATURE PROFILE

FIG. 3 HIGHLY STIRRED REACTOR, VELOCITY LIMITS