CORRELATION OF LAMINAR FLAME VELOCITIES FOR HYDROCARBON-OXYGEN-INERT GAS MIXTURES

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ABSTRACT

A thermal theory of laminar flame propagation for hydrocarbon-oxygen flames is described. The method of analysis follows the earlier work of von Kármán and his collaborators. The problem is greatly simplified by the introduction of several approximations and assumptions.

In Section III the problem is formulated and approximate solutions are given for hydrocarbon-oxygen flames, assuming a second order rate-controlling step. Approximate analytic solutions have been obtained for all mixture ratios.

Hydrocarbon-oxygen-inert gas mixtures are considered in Section IV. A second order rate-controlling step is again assumed and solutions are given for various initial gas compositions.

An attempt is made to correlate experimentally determined burning velocity data in Section V. Reference to Section V shows that a good correlation was obtained only for lean mixtures. Absolute values for the laminar burning velocity cannot be estimated because of the lack of data concerning reaction mechanism and specific reaction rate constants.

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SYMBOLS

Subscript	f	property at flame temperature
Subscript	o	property at initial temperature
Subscript	i	property at ignition temperature
Subscript	F	property of fuel
Subscript	O_2	property of oxygen
Subscript	P	property of combustion products
Subscript	I	property of inert gases
Subscript	light	property of initial mixture with $r < 1$
Subscript	heavy	property of initial mixture with $r > 1$
Subscript	balanced	property of initial mixture with $r = 1$
Superscript	f	property at flame temperature
	λ	effective thermal conduction coefficient
	ρ	density
	c_p	specific heat
	σ	overall order of a chemical reaction
	W	molecular weight
	n_j	moles of j'th chemical species
	ξ	moles of oxygen or fuel which have reacted
	Y_j	weight fraction of j'th chemical species
	ε	weight fraction of products of combustion
	r	ratio of the initial number of moles of fuel to oxygen
	m	mass flow rate of mixture per unit area
	h_j	specific enthalpy of j'th chemical species

T	temperature
x	linear distance
δ_j	standard heat of formation of j'th chemical species
θ	reduced temperature = T/T_f
γ_P	net rate of production of combustion products in moles per unit volume
k_1	specific reaction rate for a chemical process
β_1	"effective frequency factor"
A_1	"effective activation energy"
R_g	gas constant per gram
ω_P	net rate of production of combustion products in grams per unit volume
θ_a	characteristic reduced temperature = A/RT_f
Λ'	dimensionless parameter defined by Eq. (16)
u_o	laminar burning velocity = m/ρ_o
Λ''	dimensionless parameter defined by Eq. (38)
α	dimensionless parameter defined by Eq. (72)
Λ^I	dimensionless parameter defined by Eq. (79)
Λ^{II}	dimensionless parameter defined by Eq. (88)
z', z	computational parameters occurring in Eq. (58)

I. INTRODUCTION

The problem of laminar flame propagation has been considered by many investigators. Extensive references to the published literature on this subject may be found in the well-known books by Lewis and von Elbe(1) and by Jost(2) as well as in a survey report prepared by Evans(3). In view of our obvious lack of detailed knowledge concerning chemical reaction rates in regions of active combustion, we shall not be interested in obtaining rigorous solutions to the complete set of differential equations, a task which has been tackled particularly by Hirschfelder and his collaborators(4). Instead we shall content ourselves with a simplified formulation of the problem of laminar flame propagation with attempts to develop a phenomenological description of flame velocities for hydrocarbon-oxygen-inert gas systems.

The methods of analysis used in this paper are applications of the procedures introduced by Th. von Kármán and his collaborators(5-7).

Before discussing hydrocarbon flames, summary remarks concerning approximations used in some of the published theories of laminar flame propagation will be given (Section II). A phenomenological theory of laminar flame propagation in hydrocarbon-oxygen mixtures is developed in Section III. The corresponding analysis for hydrocarbon-oxygen inert gas mixtures is given in Section IV. Attempts at correlating experimentally determined burning velocities with the theoretical equations are described in Section V.

II. SUMMARY REMARKS CONCERNING LAMINAR FLAME THEORIES*

The published theories on laminar flame propagation may be classified as comprehensive theories, thermal theories, and diffusion theories. In the comprehensive theories an attempt is made to deduce a complete description of the flame, including expressions for the velocities and concentrations of all chemical species as functions of distance or temperature, without assuming that energy and mass transport, either by conduction or by diffusion, are of dominant importance. Mass transport of atoms and free radicals by diffusion is of primary importance in the diffusion theories; the burning rate is largely controlled by heat conduction in the thermal theories.

Typical approximations and assumptions made in various published(3) theoretical studies (of course, not all at the same time) of laminar flame propagation are:

(a) All quantities depend only on a single space coordinate, that is, the problem is one dimensional.

(b) All quantities are independent of time, that is, a steady state is assumed to exist.

(c) Velocity gradients are small; hence viscous forces may be neglected.

(d) The pressure is constant across the flame front.

(e) A single rate-controlling reaction is assumed as a basis for the reaction rate law.

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* For references to the original literature concerning the summary statements made in this Section II, the survey paper by Evans should be consulted.

(f) All molecules are taken to have the same mass and dimensions.

(g) An ignition temperature concept is often used, that is, the initial mixture is prepared for combustion by conduction of heat to the unburned gas until the ignition temperature is reached, at which time chemical reactions begin to occur.

(h) In some diffusion theories it is postulated that the initial mixture is prepared for combustion by diffusion of atoms and free radicals from the hot burned gases. In these theories the energy equation is neglected and a simplified temperature profile may be used.

(i) In some diffusion theories the instantaneous concentrations of active particles are assumed to be determined everywhere in the flame by an equilibrium between active particles and the initial gas mixture. In other treatments, equilibrium concentrations of active particles are assumed for the completely burnt gas and the active particles diffuse back into the unburnt mixture.

(j) If chain-branching occurs, the velocity of the chain-branching reaction is sometimes taken as the limiting factor which determines the flame velocity.

(k) The heat capacity, coefficient of heat conductivity, and diffusion coefficients are assigned average values or else are represented by simple functional forms.

(l) Thermal diffusion is neglected.

(m) The ideal gas law is assumed to be valid.

Some of the assumptions and approximations are not justified and are made only in order to simplify the problem and make it tractable by ordinary means (e.g., f, h, i, j); some approximations are introduced because exact data or relationships between variables are unknown (e, k), and others because experience has shown that they lead to valid first approximations (a, b, c, d, g, k, ℓ, m).

The validity of approximations and assumptions in any given case depends upon the particular problem which is being investigated. Theorists in the field of laminar flame propagation agree that both thermal and diffusional processes play a part in flame propagation. However, the relative importance of the two processes is not known until a complete description of the chemical reaction mechanism, as well as accurate methods for calculating the diffusion coefficients and thermal conductivities, are available.

It should be noted that most thermal theories yield results which indicate that flame velocities are proportional to some function of $\frac{\lambda}{c_p \rho} \frac{T_f - T_i}{T_i - T_o}$, where T_f is the final temperature, T_i the ignition temperature, T_o the initial temperature, λ a thermal conductivity, c_p the average specific heat, and ρ the density. Diffusion theories generally yield results which indicate that flame velocities are proportional to a function of the diffusion coefficients and an average temperature.

Our approach to the problem of laminar flame propagation in hydrocarbon-oxygen-inert gas mixtures involves the reasonable approximations expressed in (a), (b), (c), (d), (g), (k), (ℓ), and (m).

In addition, we discuss only a thermal theory for a one-step chemical reaction (assumption e) using constant molecular weights (assumption f). We shall find that our simplified analysis leads to an acceptable correlation of burning velocities, at least for lean mixtures (Section V).

Although the idea of a single "effective" rate-controlling reaction step for a flame-reaction is not unreasonable, the particular functional form of the relation used by us cannot be justified in general(7, 8). For free radical and chain mechanisms, the overall rate law may well be complicated as it is, for example, in the steady-state treatment for the hydrogen-bromine reaction. About the best that can be said for our particular choice for the overall reaction-rate law is that detailed treatments (see, for example, the book by Lewis and von Elbe(1), Chapters IV and VII,) show that, neglecting surface reactions, the fuel and oxygen concentrations enter sometimes to the first power. An attempt at empirical correlation of laminar burning velocities, without detailed theoretical analysis, has been made previously by D. L. Ritter(9).

III. DEVELOPMENT OF THEORETICAL EQUATIONS FOR CORRELATING BURNING VELOCITIES IN HYDROCARBON-OXYGEN MIXTURES

The detailed chemical reaction steps in hydrocarbon-oxygen-inert gas mixtures are understood only incompletely(1, 2, 3). Furthermore, neither the specific reaction rates nor the transport coefficients can be estimated with any degree of accuracy. For this reason it is of obvious interest to attempt a phenomenological overall description of the chemical processes involved, and to assess the utility of the simplified theory by the success of the resulting equations in correlating observed experimental data. With this objective in mind we may consider the overall reaction

$$F + O_2 \longrightarrow 2P \qquad (1)$$

as a first approximation to the rate-controlling reaction step in hydrocarbon-oxygen-inert gas flames. Equation (1) represents a second-order chemical reaction, which is in accord with the observation that the linear burning velocity for some hydrocarbon flames is nearly independent of pressure. As has been pointed out repeatedly before, the linear burning velocity for laminar flames described by a single rate-controlling chemical reaction varies as the pressure raised to the $(\sigma/2)-1$ power, where σ is the reaction order of the slow chemical process. Thus for $\sigma = 2$ the burning velocity for a one-step process is independent of pressure.

For the sake of simplicity we assume that the molecular weights and the specific heats of the reactants and of the reaction products are constant and equal to W and c_p, respectively. Let n_F, n_{O_2}, and n_P represent the number of moles of F, O_2, and P, respectively, the initial number of moles being n_F^o, $n_{O_2}^o$, and $n_P^o = 0$. Let ξ represent the number of moles of F and O_2 which have reacted and 2ξ the number of moles of P formed. The total number of moles, n_T, is evidently constant and equal to $n_{O_2}^o + n_F^o$. Since the molecular weights of the chemical species F, O_2, and P are equal, it follows that the mole fractions and weight fractions are equal. Hence

$$Y_F = (n_F^o - \xi)/(n_{O_2}^o + n_F^o), \qquad Y_{O_2} = (n_{O_2}^o - \xi)/(n_{O_2}^o + n_F^o)$$

$$Y_P = 2\xi/(n_{O_2}^o + n_F^o).$$

Let

$$Y_P = \varepsilon, \tag{2}$$

whence

$$\xi = (\varepsilon/2)(n_{O_2}^o + n_F^o).$$

Also let

$$r = n_F^o/n_{O_2}^o. \tag{3}$$

Hence

$$Y_F = r/(1 + r) - (\varepsilon/2), \tag{4}$$

and

$$Y_{O_2} = 1/(1 + r) - (\varepsilon/2). \tag{5}$$

We now distinguish several cases for different mixture compositions, "light" mixtures for $r < 1$ with $\varepsilon_f = 2r/(1 + r)$, and "heavy" mixtures for $r > 1$ with $\varepsilon_f = 2/(1 + r)$. For the "balanced" mixture ratio $r = 1$, $\varepsilon_f = 1$.*

The definitions given in Eqs. (2) to (5) are useful for the development of a simplified set of differential equations for the description of laminar burning velocities. Accordingly we turn our attention now to a discussion of the basic equations.

A. Basic Equations for a Thermal Theory

The momentum equation need not be included in a discussion of the basic equations for laminar flame propagation, since it is easily shown that it leads only to the conclusion that the pressure drop across a laminar flame front is negligibly small. In view of the crudeness of our assumptions about the chemical processes, it is not warranted to include diffusive transport of chemical species in the discussion. Accordingly, we shall content ourselves with the development of a thermal theory and consider only the equations of conservation of energy and mass.

1. Energy Equation

For a one-dimensional flow process the expression for conservation of energy can be written in the form

$$\frac{\lambda}{m} \frac{dT}{dx} = (\sum_i h_i Y_i) - (\sum_i h_i Y_i)_{T_f} , \qquad (6)$$

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* It is, of course, clear that the terms "light", "heavy", and "balanced" mixtures as used here bear no relation to the terms "lean", "rich", and "stoichiometric" used ordinarily. For practical combustion flames r is considerably less than unity, i.e., practical flames are "light" flames.

where λ is the thermal conductivity; m equals the mass flow rate (in grams per unit area per unit time) which, as will be shown presently, is the desired eigenvalue of the boundary value problem corresponding to one-dimensional laminar flame propagation; T represents the temperature; x equals linear distance; h_i is the (specific) enthalpy per gram of the i'th chemical species.

Introduction of Eqs. (2) to (5) into Eq. (6) leads to the following expression for conservation of energy:

$$\frac{\lambda}{m}\frac{dT}{dx} = h_F\left(\frac{r}{1+r} - \frac{\varepsilon}{2}\right) + h_{O_2}\left(\frac{1}{1+r} - \frac{\varepsilon}{2}\right) + h_P\,\varepsilon$$

$$- h_{F,f}\left(\frac{r}{1+r} - \frac{\varepsilon_f}{2}\right) - h_{O_2,f}\left(\frac{1}{1+r} - \frac{\varepsilon_f}{2}\right)$$

$$- h_{P,f}\,\varepsilon_f$$

where the subscript f identifies conditions when the reaction has gone to completion. The preceding relation may be rewritten in the form

$$\frac{\lambda}{m}\frac{dT}{dx} = c_p\,(T - T_f) - (\varepsilon_f - \varepsilon)\left(\delta_P - \frac{\delta_{O_2}}{2} - \frac{\delta_F}{2}\right),$$

since $h_F = \delta_F + c_p T$, $h_{O_2} = \delta_{O_2} + c_p T$, $h_P = \delta_P + c_p T$, with δ_F, δ_{O_2}, and δ_P representing, respectively, the standard heats of formation of the chemical species involved. But the heat evolved by the chemical reaction per gram of reacting mixture is

$$\left(\delta_P - \frac{\delta_{O_2}}{2} - \frac{\delta_F}{2}\right)\varepsilon_f = -c_p\,(T_f - T_o),$$

since ε_f grams of product have been formed per gram of mixture when the reaction is completed and the temperature has been raised from T_o to T_f. Therefore the energy equation takes the form

$$\frac{\lambda}{m}\frac{dT}{dx} = c_p\left[(T - T_f) + \left(1 - \frac{\varepsilon}{\varepsilon_f}\right)(T_f - T_o)\right].$$

It is now apparent that dT/dx vanishes as $T \rightarrow T_f$, $\varepsilon \rightarrow \varepsilon_f$ or as $T \rightarrow T_o$, $\varepsilon \rightarrow 0$. Introduction of the reduced temperature $\theta = T/T_f$ transforms the energy equation to the form in which it will be used subsequently, viz.,

$$\frac{\lambda}{m}\frac{d\theta}{dx} = c_p\left[(\theta - 1) + \left(1 - \frac{\varepsilon}{\varepsilon_f}\right)(1 - \theta_o)\right], \tag{7}$$

where $\theta_o = T_o/T_f$.

2. Continuity Equation

For a one-step chemical process, the conservation of mass equations for the chemical species involved are not independent and, therefore, the conservation equation for one chemical species determines the conservation equations for the others. In the present discussion we choose the reaction product P as the chemical species in terms of which the continuity equation is to be expressed. It follows from Eq. (1) and the law of mass action that the net rate of production of moles of P per unit volume at the temperature T, γ_P, is

$$\gamma_P = 2k_1(F)(O_2), \tag{8}$$

where k_1 is the specific reaction rate for the process described in Eq. (1) and is assumed to be represented by the functional expression

$$k_1 = \beta_1 \exp(-A_1/RT) , \tag{9}$$

with β_1 (the "effective frequency factor") and A_1 (the "effective activation energy") constants which will be determined by correlation of empirical burning velocities with the final theoretical equation derived from the present treatment. The parentheses around a chemical symbol identify molar concentrations and R equals the molar gas constant.

The molar concentrations are related to the weight fractions through the expressions

$$(F) = \frac{\rho}{W} Y_F, \quad (O_2) = \frac{\rho}{W} Y_{O_2} . \tag{10}$$

Introducing Eqs. (4), (5), (9), and (10) into Eq. (8) it is readily seen that

$$\gamma_P = \frac{2\beta_1 \rho^2}{W^2} e^{-A_1/RT} \left(\frac{r}{1+r} - \frac{\varepsilon}{2}\right)\left(\frac{1}{1+r} - \frac{\varepsilon}{2}\right). \tag{11}$$

The net rate of production of reaction products in grams per unit volume per unit time, ω_P, is related to $d\varepsilon/dx$ and to γ_P through the relation

$$\omega_P = m \frac{d\varepsilon}{dx} = W \gamma_P . \tag{12}$$

Furthermore,

$$\frac{d\theta}{dx} = \frac{d\theta}{d\varepsilon} \frac{d\varepsilon}{dx} ;$$

whence

$$\gamma_P = \frac{m}{W}\ \frac{d\,\varepsilon}{dx} = \frac{m}{W}\ \frac{d\,\theta\,/dx}{d\,\theta/d\,\varepsilon}\ ;$$

and Eq. (11) becomes

$$\frac{2\beta_1\,\rho^2}{mW}\ e^{-\,\theta_a/\theta}\left(\frac{r}{r+1}-\frac{\varepsilon}{2}\right)\left(\frac{1}{r+1}-\frac{\varepsilon}{2}\right)\frac{d\,\theta}{d\,\varepsilon}=\frac{d\,\theta}{dx}\,, \quad (13)$$

where

$$\theta_a = A_1/RT_f\ .$$

3. Basic Differential Equation for One-Dimensional Laminar Flame Propagation

It is convenient in problems on laminar flame propagation to eliminate the distance x as independent variable. By dividing Eq. (7) by Eq. (13) the following differential equation is obtained

$$\frac{2\beta_1\,\rho^2\,\lambda}{c_p\,m^2W}\ e^{-\,\theta_a/\theta}\left(\frac{r}{1+r}-\frac{\varepsilon}{2}\right)\left(\frac{1}{1+r}-\frac{\varepsilon}{2}\right)\frac{d\,\theta}{d\,\varepsilon}=(\theta-1)+(1-\frac{\varepsilon}{\varepsilon_f})\,(1-\ \theta_o). \quad (14)$$

Finally, if λ is taken to be a linear function of the temperature, we may write

$$\lambda\ =\ \lambda_f\,\theta\ ,$$

and Eq. (14) becomes

$$\frac{\Lambda'}{\theta}\ e^{-\,\theta_a/\theta}\Big[2r-\varepsilon(1+r)\Big]\Big[2-\varepsilon(1+r)\Big]\ \frac{d\,\theta}{d\,\varepsilon}=(\theta-1)+(1-\theta_o)\,(1-\frac{\varepsilon}{\varepsilon_f}), \quad (15)$$

with

$$\Lambda' = \frac{2\beta_1 \lambda_f p_o^2}{R_g^2 T_f^2 m^2 c_p W} \frac{1}{4(1 + r)^2} , \qquad (16)$$

where use has been made of the ideal gas equation of state,

$$\frac{p_o}{\rho} = R_g T . \qquad (17)$$

The parameter Λ' depends on the mass flow rate m and serves as an eigenvalue of the transformed basic differential equation. The laminar burning velocity, u_o, which is defined as

$$u_o = m/\rho_o , \qquad (18)$$

may be expressed in terms of Λ' as follows:

$$u_o = \frac{\theta_o}{2(1 + r)} \left(\frac{2\beta_1 \lambda_f}{c_p W \Lambda'} \right)^{1/2} . \qquad (19)$$

4. Boundary Conditions

In order to complete the formulation of the eigenvalue problem, suitable, physically meaningful, boundary conditions should be introduced. As the reactions go to completion, $\theta \rightarrow 1$ and $\varepsilon \rightarrow \varepsilon_f$. Reference to Eq. (15) shows that the point $\theta = 1$, $\varepsilon = \varepsilon_f$ is a singular point since

$$\varepsilon_f = \frac{2r}{1+r} , \quad \text{for} \quad r < 1 ;$$

$$\varepsilon_f = \frac{2}{1+r} , \quad \text{for} \quad r > 1 ;$$

and (20)

$$\varepsilon_f = 1 , \quad \text{for} \quad r = 1 .$$

The boundary conditions specified by Eq. (20) lead to no essential difficulties in the solution of the flame equations. However, as has been emphasized particularly by von Kármán and Emmons, imposition of the cold boundary condition, $\theta = \theta_o$ for $\varepsilon = 0$, leads to infinite values for the mass flow rate. Since it is known that the mass flow rate is substantially independent of the value of an assumed ignition temperature, θ_i, for all reasonable values of θ_i in the range $\theta_o < \theta_i < 1$, we may choose the following limiting values at the cold boundary:

$$\theta = \theta_i, \quad \text{for} \quad \varepsilon = 0, \text{ with } \theta_i \text{ appreciably larger than } \theta_o \text{ and appreciably smaller than unity.} \tag{21}$$

The formulation of the cold boundary condition expressed in Eq. (21) is known to lead to results which are equivalent to those obtained through the use of Hirschfelder's porous-plug flame holder which acts as a heat sink$^{(4)}$.

B. Solution of the Boundary-Value Problem

1. "Heavy" Mixtures

For "heavy" (as well as for "light") mixtures, the eigenvalue for the mass burning rate can be obtained by a straightforward application of the von Kármán - Millán technique, which is illustrated in detail in the following analysis.

As has been noted in the preceding Section, for "heavy" mixtures, $\varepsilon_f = 2/r + 1$, with $r > 1$. Hence the basic differential equation

$$\frac{\Lambda'}{\theta} \cdot e^{-\theta_a/\theta}\left[2r - \varepsilon(1 + r)\right]\left[2 - \varepsilon(1 + r)\right]\frac{d\theta}{d\varepsilon} = (\theta - 1) + (1 - \theta_o)(1 - \frac{\varepsilon}{\varepsilon_f}) \tag{22}$$

becomes at the hot boundary

$$\lim_{\substack{\theta \to 1 \\ \varepsilon \to \varepsilon_f}} \frac{d\theta}{d\varepsilon} = \frac{(1 - \theta_o)\ (1/\varepsilon_f)}{1 + 2\Lambda'\left[\exp(-\theta_a)\right](r^2 - 1)}, \quad r > 1 . \tag{23}$$

Introduction of Eq. (23) for $\theta \sim 1$ on the left-hand side of Eq. (22) shows that

$$(\theta - 1) + (1 - \theta_o)(1 - \frac{\varepsilon}{\varepsilon_f}) =$$

$$\Lambda' e^{-\theta_a}\left[2 - \varepsilon(1 + r)\right]\left[2r - \varepsilon(1 + r)\right]\frac{(1 - \theta_o)(1/\varepsilon_f)}{1 + 2\Lambda' e^{-\theta_a}(r^2 - 1)} .$$

The use of this last expression on the right-hand side of Eq. (22) yields the following:

$$\theta^{-1}\left[\exp(-\theta_a/\theta)\right]\frac{d\theta}{d\varepsilon} = \frac{\left[\exp(-\theta_a)\right](1 - \theta_o)(1/\varepsilon_f)}{1 + 2\Lambda'\left[\exp(-\theta_a)\right](r^2 - 1)} . \tag{24}$$

It is clear that Eq. (24) represents a useful approximation to the differential equation in the vicinity of the hot boundary only for $r \gg r_1 > 1$. We shall determine the value of r_1 later on by comparing the solutions for "light" and "heavy" mixtures with an approximation solution for "balanced" proportions of the reactants (compare

Section III, B4).

Equation (24) may be integrated from θ_t, $\mathcal{E}_t$ to $\theta = 1$, $\mathcal{E}_f = 2/(1 + r)$, viz.,

$$2/(1 + r) - \mathcal{E}_t = \frac{1 + 2\Lambda'(r^2 - 1)\left[\exp(-\theta_a)\right]}{\left[\exp(-\theta_a)\right](1 - \theta_o)(1/\mathcal{E}_f)} \int_{\theta_t}^{1} \theta^{-1}\left[\exp(-\theta_a/\theta)\right] d\theta. \tag{25}$$

From Eq. (22) the limiting slope at the cold boundary is found to be

$$\lim_{\substack{\theta \to \theta_i \\ \mathcal{E} \to 0}} (d\theta/d\mathcal{E}) = \frac{(\theta - 1) + (1 - \theta_o)}{(\Lambda'/\theta)\left[\exp(-\theta_a/\theta)\right] 4r} .$$

Hence

$$\mathcal{E}_t \simeq \frac{4r\Lambda'}{(\theta_t - 1) + (1 - \theta_o)} \int_{\theta_i}^{\theta_t} \theta^{-1}\left[\exp(-\theta_a/\theta)\right] d\theta . \tag{27}$$

where we have replaced θ by θ_t in the term $(\theta - 1)^{(5)}$.

Continuity of slopes of the two asymptotic solutions at the point $(\theta_t, \mathcal{E}_t)$ leads to the requirement

$$\frac{(\theta_t - 1) + (1 - \theta_o)}{(\Lambda'/\theta_t)\exp\left[(-\theta_a/\theta_t)\right]4r} = \frac{\left[\exp(-\theta_a)\right](1 - \theta_o)(1/\mathcal{E}_f)}{\left[\exp(-\theta_a/\theta_t)\right](1/\theta_t)\left\{1 + 2\Lambda'\left[\exp(-\theta_a)\right](r^2 - 1)\right\}},$$

or

$$\frac{4r\Lambda'}{(\theta_t - 1) + (1 - \theta_o)} = \frac{1 + 2\Lambda'\left[\exp(-\theta_a)\right](r^2 - 1)}{\left[\exp(-\theta_a)\right](1 - \theta_o)(1/\mathcal{E}_f)} . \tag{28}$$

Addition of Eqs. (25) and (27), in view of Eq. (28), leads to the conclusion

$$2/(1 + r) = \frac{1 + 2\,\Lambda'\left[\exp(-\theta_a)\right](r^2 - 1)}{\left[\exp(-\theta_a)\right](1 - \theta_o)\,(1/\mathcal{E}_f)} \int_{\theta_i}^{1} \theta^{-1}\left[\exp(-\theta_a/\theta)\right|\, d\theta\,,$$

whence, after integrating$^{(5,6)}$,

$$\Lambda' = \frac{\left[\exp(\theta_a)\right]}{2\,(r^2 - 1)}\left\{\frac{\left[\exp(-\theta_a)\right](1 - \theta_o)}{E_i(-\theta_a/\theta_i) - E_i(-\theta_a)} - 1\right\}, \quad r \geq r_1 > 1\,, \qquad (29)$$

where E_i represents the exponential integral. For θ_i appreciably smaller than unity we have

$$\Lambda' \simeq \frac{\exp(\theta_a)}{2(r^2 - 1)}\left\{\frac{(1 - \theta_o)\left[\exp(-\theta_a)\right]}{-\,E_i(-\theta_a)} - 1\right\}, \quad r \geq r_1 > 1; \qquad (30)$$

and, for sufficiently large values of θ_a,

$$\Lambda' \simeq \frac{\exp(\theta_a)}{2(r^2 - 1)}\left[\frac{(1 - \theta_o)\,\theta_a^2}{\theta_a - 1} - 1\right], \quad r \geq r_1 > 1\,. \qquad (31)$$

2. "Light" Mixtures

For "light" mixtures $\mathcal{E}_f = 2r(1 + r)$, $r < 1$, and it is seen from Eq. (22) that

$$\lim_{\substack{\theta \to 1 \\ \mathcal{E} \to \mathcal{E}_f}} (d\theta/d\mathcal{E}) = \frac{(1 - \theta_o)\,(1/\mathcal{E}_f)}{1 + 2\,\Lambda'\left[\exp(-\theta_a)\right](1 - r^2)}\,. \qquad (32)$$

As before, it is clear that routine application of the von Kármán - Millán technique will lead to useful results only if $r \leq r_2 < 1$. We shall determine the value of r_2 later on by comparing the solutions for "light" and "heavy" mixtures with an approximate solution for "balanced" proportions of the reactants (compare Section III, B4).

Following the precedure described in the preceding Section III, B1 it is readily shown that

$$\Lambda' = \frac{\exp(\theta_a)}{2(1-r^2)} \left\{ \frac{\left[\exp(-\theta_a)\right](1-\theta_o)}{E_i(-\theta_a/\theta_i) - E_i(-\theta_a)} - 1 \right\}, \quad r \leq r_2 < 1; \qquad (33)$$

for θ_i appreciably smaller than unity,

$$\Lambda' \simeq \frac{\exp(\theta_a)}{2(1-r^2)} \left\{ \frac{(1-\theta_o)\exp(-\theta_a)}{-E_i(-\theta_a)} - 1 \right\}, \quad r \leq r_2 < 1; \qquad (34)$$

and, for θ_a sufficiently large,

$$\Lambda' \simeq \frac{\exp(\theta_a)}{2(1-r^2)} \left[\frac{(1-\theta_o)\,\theta_a^2}{\theta_a - 1} - 1 \right], \quad r \leq r_2 < 1 . \qquad (35)$$

3. "Balanced" Mixtures

For "balanced" proportions of reactants ($r = 1$ and $\mathcal{E}_f = 1$) it is no longer possible to apply the von Kármán - Millán technique without modification since the point $\theta = 1$, $\mathcal{E} = 1$ becomes a singular point. A useful procedure, proposed by von Kármán, for removing the singular point is described below.

For $\mathcal{E}_f = 1$ and $r = 1$ the energy equation takes the form

$$(\lambda/m)(d\theta/dx) = c_p \left[(\theta - 1) + (1 - \theta_o)(1 - \mathcal{E}) \right| . \qquad (36)$$

The net rate of production of reaction product is

$$\omega_p = m(d\mathcal{E}/x) = (2\beta_1\rho^2/W)\left|(1-\mathcal{E})^2/4\right| \exp(-\theta_a/\theta) .$$

Hence the boundary-value problem becomes

$$(\Lambda''/\theta)\ \left[\exp(-\theta_a/\theta)\right](1-\varepsilon)^2(d\theta/d\varepsilon) = (\theta-1)+(1-\theta_o)(1-\varepsilon), \tag{37}$$

$$\theta = \theta_i \text{ at } \varepsilon = 0 \quad \text{and} \quad \theta = 1 \text{ at } \varepsilon = 1,$$

with

$$\Lambda'' = (\beta_1 \lambda_f\ p_o{}^2/2R_g{}^2\ T_f{}^2\ m^2\ c_p\ W), \tag{38}$$

and

$$u_o = \theta_o(\beta_1 \lambda_f/2c_p\ W\Lambda'')^{(1/2)}. \tag{39}$$

Comparison of Eqs. (16) and (38) shows that

$$\Lambda'' = 4\ \Lambda', \qquad \text{for} \qquad r = 1. \tag{40}$$

We next replace the singular point ($\theta = 1$, $\varepsilon = 1$) by the boundary condition ($\theta = 1$, $\varepsilon = \varepsilon_1 < 1$). This choice is plausible in view of the results obtained for "unbalanced" mixture ratios which show that ($d\theta/d\varepsilon$) is close to zero as the hot boundary is approached, at least for reasonable values of $\Lambda''\exp(-\theta_a)$. In the vicinity of the point ($\theta = 1$, $\varepsilon = \varepsilon_1$) we may neglect the quantity ($\theta - 1$) on the right-hand side of Eq. (37), with the result

$$\left[\Lambda''(1-\varepsilon)^2/\theta\right]\left[\exp(-\theta_a/\theta)\right](d\theta/d\varepsilon) = (1-\theta_o)(1-\varepsilon). \tag{41}$$

From Eqs. (23) and (32) one obtains formally

$$\lim_{\substack{\theta\to 1\\ \varepsilon\to 1\\ r=1}} (d\theta/d\varepsilon) = (1-\theta_o). \tag{42}$$

We shall now join the curve of Eq. (41) to the straight-line determined by Eq. (42) at the point $(\theta', \mathcal{E}')$. In order to accomplish this objective we integrate Eq. (41) from $(\theta', \mathcal{E}')$ to $(1, \mathcal{E}_1)$ with the result

$$(1 - \theta_o)\, \ln \frac{(1 - \mathcal{E}')}{(1 - \mathcal{E}_1)} = \Lambda'' \left[E_i(-\theta_a/\theta') - E_i(-\theta_a) \right], \tag{43}$$

or, since θ' is very close to unity,

$$(1 - \theta_o) \quad \ln \frac{(1 - \mathcal{E}')}{(1 - \mathcal{E}_1)} \simeq \Lambda'' (1 - \theta') \exp(-\theta_a) . \tag{44}$$

The equation of the straight line with slope $(1 - \theta_o)$ passing through the point $(\theta', \mathcal{E}')$ is

$$(1 - \theta') = (1 - \theta_o)(1 - \mathcal{E}') . \tag{45}$$

In order to join the curve of Eq. (41) to the line of slope $(1 - \theta_o)$ at $(\theta', \mathcal{E}')$ it is necessary to combine Eqs. (44) and (45) and to equate $(d\theta/d\mathcal{E})$ in Eq. (41) to $(1 - \theta_o)$ at $(\theta', \mathcal{E}')$. In this manner it is found that

$$\ln \left[(1 - \mathcal{E}')/(1 - \mathcal{E}_1)\right] = \Lambda'' \left[\exp(-\theta_a)\right](1 - \mathcal{E}') \tag{46}$$

and, since $\theta' \sim 1$,

$$\Lambda'' \left[\exp(-\theta_a)\right] (1 - \mathcal{E}') \simeq 1 . \tag{47}$$

From Eqs. (46) and (47) we obtain an interesting explicit expression for $\mathcal{E}'$, viz.,

$$(1 - \mathcal{E}') \simeq (1 - \mathcal{E}_1)\, e \tag{48}$$

Similarly, from Eqs. (45) and (47) it is apparent that

$$(1 - \theta') \simeq (1 - \theta_o)/\left[\Lambda'' \exp(-\theta_a)\right] \tag{49}$$

It is clear from Eq. (49) that we must expect values of $\Lambda'' \exp(-\theta_a)$ which are appreciably greater than unity.

As a first approximation it will now be assumed that Eq. (41) holds over the entire integration interval from $(\theta_i, 0)$ to $(1, \varepsilon_1)$. Hence, similarly to Eq. (43),

$$-(1 - \theta_o)\left[\ln(1 - \varepsilon_1)\right]\exp(-\theta_a) = \Lambda''\left[\exp(-\theta_a)\right]\left[E_i(-\theta_a/\theta_i) - E_i(-\theta_a)\right]. \tag{50}$$

But from Eqs. (47) and (48)

$$\Lambda'' \exp(-\theta_a) = 1/(1 - \varepsilon') = 1/(1 - \varepsilon_1)\, e\,;$$

whence

$$(1 - \varepsilon_1) \ln(1 - \varepsilon_1) = -\frac{E_i(-\theta_a/\theta_i) - E_i(-\theta_a)}{e\,(1 - \theta_o)\left[\exp(-\theta_a)\right]}. \tag{51}$$

But from Eq. (50)

$$\ln(1 - \varepsilon_1) = \frac{\Lambda''\left[E_i(-\theta_a/\theta_i) - E_i(-\theta_a)\right]}{-(1 - \theta_o)} \tag{52}$$

or, for θ_i appreciably less than unity,

$$\ln(1 - \varepsilon_1) = \Lambda'' E_i(-\theta_a)/(1 - \theta_o), \tag{53}$$

and

$$(1 - \mathcal{E}_1) = \exp\left\{- \Lambda''\left[- E_i(- \theta_a)/(1 - \theta_o)\right]\right\}. \tag{54}$$

In view of Eq. (52), Eq. (51) becomes

$$\Lambda''\left[\exp(- \theta_a)\right] \exp\left\{\frac{- \Lambda''\left[E_i(- \theta_a/\theta_i) - E_i(- \theta_a)\right]}{1 - \theta_o}\right\} = 1/e ,$$

or

$$- \Lambda'' \frac{E_i(- \theta_a/\theta_i) - E_i(- \theta_a)}{1 - \theta_o} + \ln\left[\Lambda'' \exp(- \theta_a)\right] = - 1. \tag{55}$$

For θ_i appreciably smaller than unity, Eq. (55) becomes

$$\frac{- \Lambda''\left[- E_i(- \theta_a)\right]}{1 - \theta_o} + \ln\left[\Lambda'' \exp(- \theta_a)\right] = - 1 . \tag{56}$$

For θ_a appreciably larger than unity the following approximation is obtained from Eq. (56):

$$- \frac{\Lambda'' \exp(- \theta_a)}{\theta_a(1 - \theta_o)} + \ln\left[\Lambda'' \exp(- \theta_a)\right] = - 1 . \tag{57}$$

The eigenvalue Λ'' can be found from Eq. (57) conveniently by writing $z = \Lambda'' \exp(- \theta_a)$ and $z' = \theta_a(1 - \theta_o)$ whence Eq. (57) becomes

$$z' = \frac{z}{1 + \ln z} . \tag{58}$$

The quantity z' is plotted in Fig. 1 as a function of z .

4. Limits of Validity of the Solutions for "Unbalanced" Mixtures

We shall now determine the parameters r_1 and r_2, which define the limits of validity of the solutions for "unbalanced" mixture ratios, by the requirement that the burning velocities calculated for "unbalanced" mixtures must appraoch the known value for the "balanced" mixture as r approaches r_1 or r_2. Here it is assumed that θ_a is independent of mixture ratio.

Comparison of Eqs. (19) and (39) shows that the condition given in Eq. (40), viz.,

$$\Lambda'' = 4\Lambda'$$

is sufficient to assure that the burning velocities for "light" and "heavy" mixtures are equal as r approaches unity. In terms of Λ', Eq. (57) becomes

$$-\frac{4\Lambda' \exp(-\theta_a)}{\theta_a(1-\theta_o)} + \ln\left[4\Lambda' \exp(-\theta_a)\right] = -1 . \qquad (59)$$

For "heavy" mixtures we may apply the following expression, which is obtained from Eq. (31):

$$\Lambda' \simeq \frac{\left[\exp(\theta_a)\right](1-\theta_o)\theta_a}{2(r_1^2-1)} ; \qquad (60)$$

for "light" mixtures, from Eq. (35),

$$\Lambda' \simeq \frac{\left[\exp(\theta_a)\right](1-\theta_o)\theta_a}{2(1-r_2^2)} . \qquad (61)$$

Introduction of the value of Λ' given in Eq. (60) into Eq. (59) leads to the result

$$\ln\left(\frac{2(1-\theta_o)\theta_a}{r_1^2-1}\right) = \frac{2}{r_1^2-1} - 1 . \tag{62}$$

From Eqs. (61) and (59):

$$\ln\left(\frac{2(1-\theta_o)\theta_a}{1-r_2^2}\right) = \frac{2}{1-r_2^2} - 1 . \tag{63}$$

From the preceding relations we find, for example, for $(1-\theta_o)\theta_a = 10$, the results, $r_1 = 1.18$ and $r_2 = 0.76$.

It should be noted that the preceding method for the determination of r_1 and r_2 involves the assumption that θ_a is independent of mixture ratio, which has not yet been verified. Perhaps a more satisfactory procedure for the determination of r_1 and r_2 involves utilization of the experimental fact that u_o is a continuous function of r. Thus we can calculate u_o as a function of r for small values of r and for large values of r and connect the resulting pair of curves.

The burning velocity for the most rapidly burning composition, which generally differs from the stoichiometric mixture ratio, can be obtained by calculating the maximum value of $(u_o^2)_{light}$ as a function of r for fixed values of θ_o. From Eqs. (19) and (35) it follows that

$$(u_o^2)_{light} = c_1 \frac{1-r}{1+r} \frac{1}{\theta_a \exp(\theta_a)} , \tag{64}$$

where

$$c_1 = \frac{\beta_1 \lambda_f \theta_o^2}{c_p W (1 - \theta_o)} , \tag{65}$$

From Eq. (64) it is apparent that the condition $d(u_o^2)_{light}/dr = 0$ leads to the relation

$$\frac{d \, \ell n \left[\theta_a \exp(\theta_a)\right]}{dr} = 2/(1 - r^2) , \tag{66}$$

i. e., at the most rapidly burning mixture composition, for which the value of $r = r_o$ is known,

$$\left(\frac{1}{T_f} + \frac{(A_1)_{light}}{RT_f^2}\right)\left(\frac{-dT_f}{dr}\right) = \frac{2}{(1 - r_o^2)} , \tag{67}$$

provided the activation energy $(A_1)_{light}$ is independent of mixture ratio r .

For the unusual case where the maximum value of $(u_o^2)_{light}$ corresponds to $r > 1$, it can similarly be shown that

$$\left(\frac{1}{T_f} + \frac{(A_1)_{heavy}}{RT_f^2}\right)\left(\frac{-dT_f}{dr}\right) = \frac{2}{(r_o^2 - 1)} \tag{68}$$

5. Determination of Activation Energies for the Rate-Controlling Reaction in Hydrocarbon - Oxygen Combustion

One of the problems in combustion, which has not yet been answered satisfactorily with regard to the concept of a rate-controlling reaction step in hydrocarbon-air flames, is the existence of a unique value for the activation energy in "heavy", "balanced", and in "light" mixtures. This question can be answered conveniently for $\theta_a >> 1$. In this case we obtain the following results:

(a) For "heavy" mixtures, $r > 1$, whence from Eqs. (19) and (31),

$$\frac{\partial \ln \left[\dfrac{u_{o\,heavy} (1 + r)^{(1/2)}}{(r - 1)^{(1/2)} (T_f)^{(1/2)}} \right]}{\partial (1/T_f)} = - (A_1)_{heavy}/2R , \qquad (69)$$

for fixed values of θ_o and λ_f.

(b) For "light" mixtures, $r < 1$, and from Eqs. (19) and (35),

$$\frac{\partial \ln \left[\dfrac{(u_o)_{light} (1 + r)^{(1/2)}}{(1 - r)^{(1/2)} (T_f)^{(1/2)}} \right]}{(1/T_f)} = - (A_1)_{light}/2R , \qquad (70)$$

for fixed values of θ_o and λ_f.

Practically all of the available experimental data on hydrocarbon-oxygen flames correspond to very "light" mixtures, i.e., $r << 1$. If T_o rather than θ_o is fixed, λ_f is taken to be proportional to T_f, and $1 - \theta_o$ is treated as a constant, then the terms in square brackets in Eqs. (69) and (70) are multiplied by $T_f^{(1/2)}$. This change does not materially affect the computed correlations of experimental data because the temperature variation of the burning velocity is controlled primarily by the exponential term.

IV. DEVELOPMENT OF THEORETICAL EQUATIONS FOR CORRELATING BURNING VELOCITIES IN HYDROCARBON - OXYGEN - INERT GAS MIXTURES

The results of the present section constitute a straightforward extension of the material given in Section III and are of particular interest in connection with the discussion of hydrocarbon-air flames.

A. Basic Equations

As in Section III let ξ represent the number of moles of F and O_2 which have reacted to form 2ξ moles of reaction product P. The total number of moles is constant and equal to $n^o_{O_2} + n^o_F + n^o_I$, where n^o_I is the total number of moles of inert gas present. If the molecular weights of all chemical species are all equal, the weight fractions and mole fractions may again be equated. Hence

$$Y_F = (n^o_F - \xi)/(n^o_{O_2} + n^o_F + n^o_I), \qquad Y_{O_2} = (n^o_{O_2} - \xi)(n^o_{O_2} + n^o_F + n^o_I),$$

$$Y_P = 2\xi/(n^o_{O_2} + n^o_F + n^o_I).$$

Let

$$Y_P = \varepsilon, \tag{71}$$

whence

$$\xi = (\varepsilon/2)(n^o_{O_2} + n^o_F + n^o_I).$$

As before, letting

$$r = n^o_F/n^o_{O_2},$$

and introducing the new parameter α through the relation

$$\alpha = n^o_{O_2}/(n^o_{O_2} + n^o_I), \qquad \alpha < 1, \tag{72}$$

we find

$$Y_F = \frac{r}{1 + r + (1 - \alpha)/\alpha} - \frac{\varepsilon}{2}, \tag{73}$$

$$Y_{O_2} = \frac{1}{1 + r + (1 - \alpha)/\alpha} - \frac{\varepsilon}{2}, \tag{74}$$

and

$$Y_I = \frac{(1 - \alpha)/\alpha}{1 + r + (1 - \alpha)/\alpha}. \tag{75}$$

For "light" mixtures, $r < 1$, and

$\varepsilon_f = \dfrac{2r}{1 + r + (1 - \alpha)/\alpha}$; for "heavy" mixtures, $r > 1$, and

$$\varepsilon_f = \frac{2}{1 + r + (1 - \alpha)/\alpha}.$$

Introduction of the preceding expressions into the energy equation given in Eq. (6) leads to the result

$$
\begin{aligned}
(\lambda/m)(dT/dx) = {} & h_F \left[\frac{r}{1 + r + (1-\alpha)/\alpha} - \frac{\varepsilon}{2} \right] \\
& + h_{O_2} \left[\frac{1}{1 + r + (1-\alpha)/\alpha} - \frac{\varepsilon}{2} \right] \\
& + h_I \left[\frac{(1-\alpha)/\alpha}{1 + r + (1-\alpha)/\alpha} \right] \\
& + h_P \, \varepsilon \\
& - h_F^f \left[\frac{r}{1 + r + (1-\alpha)/\alpha} - \frac{\varepsilon_f}{2} \right] \\
& - h_{O_2}^f \left[\frac{1}{1 + r + (1-\alpha)/\alpha} - \frac{\varepsilon_f}{2} \right] \\
& - h_I^f \left[\frac{(1-\alpha)/\alpha}{1 + r + (1-\alpha)/\alpha} \right] \\
& - h_P^f \, \varepsilon_f \, . \qquad (76)
\end{aligned}
$$

Setting $h_F = \delta_F + c_p T$, $h_{O_2} = \delta_{O_2} + c_p T$, $h_I = \delta_I + c_p T$, and $h_P = \delta_P + c_p T$, it is readily shown that

$$(\lambda/m)(dT/dx) = c_p (T - T_f) - (\varepsilon_f - \varepsilon)\left[\delta_P - (\delta_{O_2}/2) - (\delta_F/2)\right].$$

Proceeding as before it is found that

$$(\lambda/m)(d\theta/dx) = c_p\left\{(\theta - 1) + \left[1 - (\varepsilon/\varepsilon_f)\right](\theta - \theta_o)\right\}. \qquad (77)$$

Following the procedure described in Section III it is easily shown that Eq. (22) is replaced by the expression

$$(\Lambda^I/\theta)\left[\exp(-\theta_a/\theta)\right]\left[2r - \varepsilon(1 + r + (1-\alpha)/\alpha)\right]\left[2 - \varepsilon(1 + r + (1-\alpha)/\alpha)\right](d\theta/d\varepsilon) =$$

$$(\theta - 1) + \left[1 - (\varepsilon/\varepsilon_f)\right](1 - \theta_o), \qquad (78)$$

where

$$\Lambda^I = \frac{2\beta_1 \lambda_f p_o^2}{R_g^2 T_f^2 m^2 c_p W} \quad \frac{1}{4(1 + r + (1-\alpha)/\alpha)^2} \qquad (79)$$

The boundary conditions are

$$\theta = \theta_i \quad \text{at} \quad \varepsilon = 0, \quad \theta = 1 \quad \text{at} \quad \varepsilon = \varepsilon_f, \quad \theta_i > \theta_o, \qquad (80)$$

with

$$\varepsilon_f = \frac{2r}{1 + r + (1-\alpha)/\alpha}, \qquad r < 1;$$

$$\varepsilon_f = \frac{2}{1 + r + (1-\alpha)/\alpha}, \qquad r > 1; \qquad (81)$$

and

$$\varepsilon_f = \frac{2}{2 + (1-\alpha)/\alpha}, \qquad r = 1.$$

Equation (79) may be solved for the linear burning velocity, with the

$$u_o = \frac{\theta_o}{2(1 + r + (1 - \alpha)/\alpha)} \left(\frac{2\beta_1 \lambda_f}{c_p W \Lambda^1} \right)^{(1/2)} \qquad (82)$$

B. Solution of the Boundary - Value Problem

1. "Heavy" Mixtures

Following the procedure described in Section III it is easily shown that the term $(r^2 - 1)$ is to be replaced by $(r - 1)\left[r + 1 + (1 - \alpha)/\alpha\right]$ all other terms remaining unchanged. Hence

$$\Lambda^I = \frac{\exp(\theta_a)}{2(r - 1)\left[r + 1 + (1 - \alpha)/\alpha\right]} \left\{ \frac{\left[\exp(-\theta_a)\right](1 - \theta_o)}{E_i(-\theta_a/\theta_i) - E_i(-\theta_a)} - 1 \right\}, \quad r \geq r_1 > 1; \qquad (83)$$

for θ_i appreciably smaller than unity we have

$$\Lambda^I = \frac{\exp(\theta_a)}{2(r - 1)(r + 1 + (1 - \alpha)/\alpha)} \left\{ \frac{(1 - \theta_o)\exp(-\theta_a)}{-E_i(-\theta_a)} - 1 \right\}, \quad r \geq r_1 > 1; \qquad (84)$$

for sufficiently large values of θ_a,

$$\Lambda^I \simeq \frac{\exp(\theta_a)}{2(r - 1)\left[r + 1 + (1 - \alpha)/\alpha\right]} \left\{ \frac{(1 - \theta_o)\theta_a^2}{\theta_a - 1} - 1 \right\}, \quad r \geq r_1 > 1. \qquad (85)$$

2. "Light" Mixtures

Proceeding in the usual manner it is found that

$$\Lambda^I = \frac{\exp(\theta_a)}{2(1 - r)\left[1 + r + (1 - \alpha)/\alpha\right]} \left\{ \frac{(1 - \theta_o)\theta_a^2}{(\theta_a - 1)} - 1 \right\}, \quad r \leq r_2 < 1, \qquad (86)$$

for θ_i appreciably less than unity and θ_a sufficiently large.

3. "Balanced" Mixtures

For the "balanced" mixture ratio, $r = 1$, the boundary-value problem becomes simply

$$(\Lambda^{II}/\theta)\left[\exp(-\theta_a/\theta)\right]\left[1-(\varepsilon/\varepsilon_f)\right]^2 (d\theta/d\varepsilon) =$$

$$(\theta - 1) + \left[1-(\varepsilon/\varepsilon_f)\right](1-\theta_o), \tag{87}$$

where

$$\Lambda^{II} = 4\,\Lambda^{I}, \tag{88}$$

and the boundary conditions are $\theta = \theta_i$ at $\varepsilon = 0$, $\theta = 1$ at $\varepsilon = \varepsilon_f = 2\alpha/(1+\alpha)$. If we replace $\varepsilon/\varepsilon_f$ by ε in Eq. (87), it is evident that the present problem reduces to that treated in Section III with Λ'' replaced by $\Lambda^{II}/\varepsilon_f$. Hence an approximate solution to the present problem is given by the relation

$$-\frac{(\Lambda^{II}/\varepsilon_f)\exp(-\theta_a)}{\theta_a(1-\theta_o)} + \ln\left[(\Lambda^{II}/\varepsilon_f)\exp(-\theta_a)\right] = -1\,. \tag{89}$$

The plot given in Fig. 1 may now be used with $z = (\Lambda^{II}/\varepsilon_f)\exp(-\theta_a)$.

4. Limits of Validity of the Solutions for "Unbalanced" Mixtures

A discussion similar to that presented in Section III, B4 may be used to define the limits of validity of the solutions for "unbalanced" mixture ratios. The results are similar to those given in Section III, B4.

5. Determination of Activation Energies for the Rate-Controlling Reaction in the Combustion of Hydrocarbon-Oxygen-Inert Gas Mixtures

For $\theta_a >> 1$ it is readily shown that

(a) for "heavy" mixtures, $r > 1$,

$$\frac{\partial \ln \left\{ \dfrac{(u_o)_{heavy} \left[1 + r + (1 - \alpha)/\alpha\right]^{(1/2)}}{(r - 1)^{(1/2)} \ (T_f)^{(1/2)}} \right\}}{\partial (1/T_f)} = - (A_1')_{heavy}/2R \qquad (90)$$

for fixed values of θ_o and λ_f;

(b) for "light" mixtures, $r < 1$, and

$$\frac{\partial \ln \left\{ \dfrac{(u_o)_{light} \left[1 + r + (1 - \alpha)/\alpha\right]^{(1/2)}}{(1 - r)^{(1/2)} \ (T_f)^{(1/2)}} \right\}}{\partial (1/T_f)} = - (A_1')_{light}/2R \qquad (91)$$

for fixed values of θ_o and λ_f.

Equations (90) and (91) will be used in the following Section V in order to correlate the experimental burning velocity measurements for hydrocarbon-air combustion. Practically all available experimental data refer to very "light" mixtures for which r is appreciably less than unity. If T_o rather than θ_o is fixed, λ_f is taken to be proportional to T_f, and $1 - \theta_o$ is assumed to be constant, then the terms in braces appearing in Eqs. (90) and (91) are multiplied by $T_f^{(1/2)}$. This change in the form of the basic equations does not affect significantly correlation of the experimental data.

V. CORRELATION OF EXPERIMENTALLY OBTAINED RESULTS FOR HYDROCARBON-OXYGEN-INERT GAS FLAMES

Experimental data on laminar flame velocities for mixtures of oxygen (with varying amounts of inert diluent) and methane, ethane, propane, pentane, ethylene, propyne, acetylene, benzene, and trimethyl pentane from various sources were used in the correlation equations developed in Sections III and IV, Eqs. (90) and (91). The references(10-19) from which the data were taken are listed in Tables I through XI, which also give the results of computations using the experimental data. The adiabatic flame temperatures, T_f, were calculated by using the methods and data given in Refs. 20 and 21.

The results given in Tables I through IX refer to hydrocarbon-air flames and are plotted in Fig. 2. A constant has been added to the calculated value of the logarithmic function for each system in order to plot the curves on the same figure. Figure 2 shows that it is possible, at least for "light" mixtures, to correlate measured burning velocities on the assumption that a second order rate-controlling reaction exists. The change of slope of the curves in Fig. 2 occurs, approximately, at the "balanced" mixture ratios. No universal correlation appears to be possible for "heavy" mixtures.

An improved correlation was obtained by drawing a mean reference line on Fig. 2 for "light" mixtures of methane, pentane, ethylene, and propyne and adding a constant to the logarithmic function to shift these curves as closely as possible to the reference line. The results obtained after using this procedure are given in Fig. 3. The effective activation energy for mixtures appreciably leaner than stoichiometric, as given by the slope of the curve of Fig. 3, is 26 Kcals per mole.

Tables X and XI give results of computations for propane-oxygen and ethylene-oxygen systems with varying amounts of inert diluent. The mixture ratios for these computations are nearly stoichiometric. The results for the propane-oxygen system are plotted in Fig. 4. The slope of this curve gives an effective activation energy for propane of 53 Kcals per mole. The results for the ethylene-oxygen system are plotted in Fig. 5. The slope of the correlation curve for near-stoichiometric ethylene-oxygen mixtures gives an effective activation energy of 36 Kcals per mole.

In a recent paper(19), Fenn and Calcote suggest that the activation energy for stiochiometric mixtures of various compounds with oxygen might be related to the lean limit blow-out temperature, $T_{f(lean)}$, i.e.,

$$A = cT_{f(lean)} \tag{92}$$

where c is a constant. Substituting this into the correlation equations, Eqs. (90) and (91), results in

$$\frac{\partial \ln \left[\dfrac{u_o \left(1 + r + \dfrac{1 - \alpha}{\alpha}\right)^{1/2}}{\left|1 - r\right|^{1/2} T_f^{\ 1/2}} \right]}{\partial \left[T_{f(lean)} / T_f \right]} = - \frac{c}{2R} \quad . \tag{93}$$

Data from Ref. 19 were used in Eq. (93). The results of these computations are given in Table XII and plotted in Fig. 6. The value of c given by the slope of the curve of Fig. 6 is 17.4 Kcals per mole per ^{o}K. Fenn and Calcote, using a modified Semenoff equation, calculated values of 16-18 Kcals per mole per ^{o}K for c.

VI. CONCLUSIONS

In the present analysis explicit analytical expressions have been obtained for the laminar burning velocity in hydrocarbon-oxygen-inert gas mixtures for a one-step rate-controlling reaction, neglecting diffusion. The results of this study have been found to be useful in correlating burning velocities for lean combustible mixtures. It appears, however, that the simplified kinetic model used here does not apply to stoichiometric and fuel-rich mixtures. A significant improvement over the present study must await a more complete understanding of hydrocarbon combustion than we have at the present time.

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Table I. Results of Computations for Methane-air Flames (Experimental Data taken from Reference 10, $\alpha = .21$).

u_o (cm/sec)	T_f (°K)	r	$10^4/T_f$	$\ln\left[\frac{u_o\left(1+r+\frac{1-\alpha}{\alpha}\right)^{1/2}}{\lvert 1-r\rvert^{1/2}\,T_f^{1/2}}\right]$
5.9	1665	.299	6.006	-0.95
6.3	1667	.303	5.963	-0.88
10.5	1781	.335	5.615	-0.368
11.1	1811	.344	5.522	-0.322
10.8	1828	.348	5.470	-0.365
18.4	2005	.402	4.488	0.191
20.0	2045	.415	4.890	0.274
22.6	2127	.445	4.701	0.406
24.9	2137	.450	4.679	0.500
24.7	2206	.486	4.533	0.458
27.2	2213	.454	4.519	0.582
26.9	2234	.508	4.476	0.615
26.7	2231	.528	4.482	0.642
27.2	2230	.531	4.484	0.659
26.8	2214	.547	4.517	0.662
24.9	2183	.571	4.581	0.631
23.6	2160	.587	4.630	0.610
22.6	2130	.606	4.695	0.592
19.2	2082	.637	4.803	0.500
14.3	2028	.671	4.931	0.251

Table I. Continued

u_0 (cm/sec)	T_f (°K)	r	$10^4/T_f$	$\ln\left[\dfrac{u_0\left(1+r+\frac{1-\alpha}{\alpha}\right)^{1/2}}{\lvert 1-r\rvert^{1/2}\;T_f^{1/2}}\right]$
10.9	1997	.694	5.008	0.030
9.1	1970	.708	5.076	-0.111
5.8	1908	.748	5.241	-0.476

Table II. Results of Computations for Ethane-air Flames (Experimental Data taken from Reference 11, $\alpha = .21$).

u_o (cm/sec)	T_f (°K)	r	$10^4/T_f$	$\ln\left[\frac{u_o\left(1+r+\frac{1-\alpha}{\alpha}\right)^{1/2}}{\|1-r\|^{1/2}\ T_f^{1/2}}\right]$
33.1	2140	.450	4.673	.829
35.0	2175	.461	4.598	.855
37.5	2232	.485	4.480	.938
38.9	2270	.509	4.405	.989
39.8	2255	.532	4.435	1.040
40.1	2220	.555	4.505	1.081
39.9	2190	.580	4.566	1.119
38.5	2170	.603	4.608	1.112
36.9	1780	.627	5.618	1.200

Table III. Results of Computations for Propane-air Flames (Experimental Data taken from References 12 and 13, $\alpha = .21$).

u_0 (cm/sec)	T_f (°K)	r	$10^4/T_f$	$\ln\left[\dfrac{u_0\left(1+r+\frac{1-\alpha}{\alpha}\right)^{1/2}}{\lvert 1-r\rvert^{1/2}\ T_f^{1/2}}\right]$
33.23	1940	.367	5.155	.784
36.0	2028	.393	4.931	.860
38.67	2107	.418	4.746	.935
41.17	2175	.444	4.598	1.003
44.0	2250	.482	4.444	1.085
44.92	2270	.507	4.405	1.120
44.83	2258	.504	4.429	1.115
44.0	2237	.550	4.470	1.115
42.46	2210	.586	4.525	1.150
40.39	2183	.612	4.581	1.140
37.54	2152	.639	4.647	1.110
33.69	2118	.665	4.721	1.080

Table IV. Results of Computations for Pentane-air Flames (Experimental Data taken from Reference 14, $\alpha = .21$).

u_0 (cm/sec)	T_f (°K)	r	$10^4/T_f$	$\ln\left[\frac{u_0\left(1+r+\frac{1-\alpha}{\alpha}\right)^{1/2}}{\lvert 1-r\rvert^{1/2}\, T_f^{1/2}}\right]$
7.1	1513	.250	6.609	-.74
10.8	1670	.290	5.988	-.345
23.7	2013	.382	4.968	.418
35.0	2262	.488	4.421	.858
35.6	2278	.506	4.390	.890
36.7	2284	.535	4.378	.950
37.0	2277	.540	4.398	.968
36.6	2226	.588	4.492	1.030
35.1	2173	.623	4.602	1.046
33.8	2148	.645	4.655	1.048
30.0	2091	.682	4.782	1.011

Table V. Results of Computations for Ethylene-air Flames (Experimental Data taken from Reference 15, $\alpha = .21$).

u_0 (cm/sec)	T_f(°K)	r	$10^4/T_f$	$\ln\left[\frac{\left(u_0 \; 1+r+\frac{1-\alpha}{\alpha}\right)^{1/2}}{\lvert 1-r\rvert^{1/2} \; T_f^{1/2}}\right]$
33.6	1880	.313	5.319	.746
36.5	2000	.345	5.000	.824
43.0	2110	.376	4.739	.985
49.2	2215	.408	4.515	1.130
49.5	2232	.416	4.480	1.138
61.1	2867	.497	4.225	1.400
65.5	2391	.538	4.182	1.512
67.8	2380	.579	4.202	1.598
68.2	2367	.605	4.225	1.640
67.5	2355	.621	4.246	1.660
64.0	2310	.664	4.329	1.680
56.9	2262	.707	4.421	1.640
52.3	2215	.750	4.515	1.650
39.9	2150	.794	4.651	1.500
32.7	2105	.838	4.751	1.440
27.3	2155	.883	4.866	1.430
23.9	2005	.928	4.988	1.555
17.5	1906	1.021	5.247	1.895
15.2	1755	1.163	5.698	.784
11.2	1575	1.361	6.349	.187

Table VI. Results of Computations for Propyne-air Flame (Experimental Data taken from Reference 14, $\alpha = .21$).

u_0 (cm/sec)	T_f (°K)	r	$10^4/T_f$	$\ln \left[\dfrac{u_0 \left(1 + r + \frac{1-\alpha}{\alpha}\right)^{1/2}}{\lvert 1-r \rvert^{1/2} \quad T_f^{1/2}} \right]$
23.2	1860	.289	5.376	.361
35.4	2030	.340	4.926	.780
47.8	2235	.396	4.474	1.082
56.9	2350	.443	4.255	1.280
63.0	2439	.500	4.100	1.420
66.9	2460	.553	4.065	1.540
67.4	2480	.602	4.032	1.602
63.0	2450	.672	4.082	1.645

Table VII. Results of Computations for Acetylene-air Flames (Experimental Data taken from Reference 16, $\alpha = .21$).

u_o (cm/sec)	T_f (°K)	r	$10^4/T_f$	$\ln \left[\frac{u_o \left(1 + r + \frac{1-\alpha}{\alpha}\right)^{1/2}}{\lvert 1-r \rvert^{1/2} \; T_f^{1/2}} \right]$
120.0	2460	.448	4.065	2.01
138.0	2570	.518	3.891	2.20
145.0	2555	.589	3.914	2.34
145.0	2535	.662	3.945	2.44
141.0	2515	.736	3.976	2.55
122.0	2475	.812	4.040	2.59
100.0	2400	.889	4.165	2.68
146.2	2480	.455	4.032	2.18
159.6	2570	.500	3.891	2.32
169.2	2560	.555	3.906	2.42
169.2	2545	.624	3.929	2.54
155.7	2524	.715	3.960	2.60

Table VIII. Results of Computations for Benzene-air Flames (Experimental Data taken from Reference 11, $\alpha = .21$).

u_o(cm/sec)	T_f(°K)	r	$10^4/T_f$	$\ln\left[\frac{u_o\left(1+r+\frac{1-\alpha}{\alpha}\right)^{1/2}}{\lvert 1-r\rvert^{1/2}\ T_f^{1/2}}\right]$
37.3	2500	.520	4.000	.904
39.3	2500	.553	4.000	.968
39.8	2490	.572	4.016	1.033
40.5	2485	.571	4.024	1.077
40.7	2480	.620	4.032	1.121
40.6	2480	.629	4.032	1.135
40.1	2470	.648	4.049	1.152
39.6	2460	.667	4.065	1.170

Table IX. Results of Computations for Tri-methyl Pentane Flames (Experimental Data taken from Reference 17, $\alpha = .21$).

u_0(cm/sec)	T_f(°K)	r	$10^4/T_f$	$\ln\left[\frac{u_0\left(1+r+\frac{1-\alpha}{\alpha}\right)^{1/2}}{\lvert 1-r\rvert^{1/2}\;T_f^{1/2}}\right]$
30.70	2180	.450	4.587	.709
32.57	2240	.475	4.464	.775
34.28	2270	.500	4.405	.845
34.64	2285	.525	4.376	.891
34.00	2250	.550	4.444	.895
32.43	2218	.575	4.509	.895

Table X. Results of Computations for Propane-Oxygen-Nitrogen Flames (Experimental Data taken from Reference 18).

u_0 (cm/sec)	T_f (°K)	r	α	$10^4/T_f$	$\ln\left[\frac{u_0\left(1+r+\frac{1-\alpha}{\alpha}\right)^{1/2}}{\lvert 1-r\rvert^{1/2}\ T_f^{1/2}}\right]$
16.1	2009	.53	.166	4.97	.266
42.9	2293	.53	.210	4.36	1.10
67.3	2441	.52	.250	4.09	1.43
94.1	2561	.515	.294	3.90	1.66
127.0	2670	.515	.348	3.74	1.87
217.1	2896	.50	.496	3.51	2.215

Table XI. Results of Computations for Ethylene-Oxygen-Nitrogen Flames (Experimental Data taken from Reference 18).

u_0 (cm/sec)	T_f (°K)	r	α	$10^4/T_f$	$\ln\left[\frac{u_0\left(1+r+\frac{1-\alpha}{\alpha}\right)^{1/2}}{\lvert 1-r\rvert^{1/2}\ T_f^{1/2}}\right]$
42.6	2100	.58	.166	4.76	1.305
81.3	2401	.57	.210	4.16	1.76
116.6	2550	.55	.250	3.92	1.995
156.3	2665	.54	.295	3.75	2.18
203.0	2766	.54	.348	3.62	2.35

Table XII. Results of Computations for Combustion of Stoichiometric Mixtures of Various Substances and Oxygen (Experimental Data taken from Reference 19).

Compound	u_0(cm/sec)	T_f(°K)	$T_{f(\text{lean})}/T_f$	r	$\ln\left[\frac{u_0\left(1+r+\frac{1-\alpha}{\alpha}\right)^{1/2}}{\lvert 1-r\rvert^{1/2}\;T_f^{1/2}}\right]$
Acetaldehyde	41.4	2300	.729	.4	.928
Acetone	42.6	2210	.771	.25	.849
Acetylene	144.0	2580	.495	.4	2.118
Acrolein	65.9	2340	.656	.286	1.285
Allyl chloride	32.4	2270	.839	.25	.554
Benzene	47.8	2340	.735	.133	.855
Butadiene 1, 3	49.6	2365	.671	.182	.918
n Butane	44.8	2280	.771	.154	.813
n Butyl chloride	31.6	2225	.779	.200	.482
Carbon disulfide	58.8	2250	.457	.333	1.231

Table XII. Continued

Compound	u_o(cm/sec)	T_f (°K)	$T_{f(lean)}/T_f$	r	$\ln\left[\frac{u_o\left(1+r+\frac{1-\alpha}{\alpha}\right)^{1/2}}{\lvert 1-r\rvert^{1/2}\ T_f^{1/2}}\right]$
Cyclohexane	43.5	2225	.750	.111	.769
Cyclopentane	45.3	2235	.745	.133	.844
Cyclopropane	54.2	2350	.701	.222	1.042
Diethyl ether	48.0	2305	.700	.167	.887
2, 2 Dimethyl butane	39.9	2220	.769	.105	.655
2, 2 Dimethyl propane	34.8	2220	.784	.125	.571
Ethane	44.5	2195	.730	.285	.926
Ethyl acetate	37.0	2125	.800	.25	.728
Ethylene	74.2	2340	.630	.333	1.443
Ethylene oxide	88.8	2425	.610	.4	1.661
Furan	62.5	2390	.645	.222	1.171

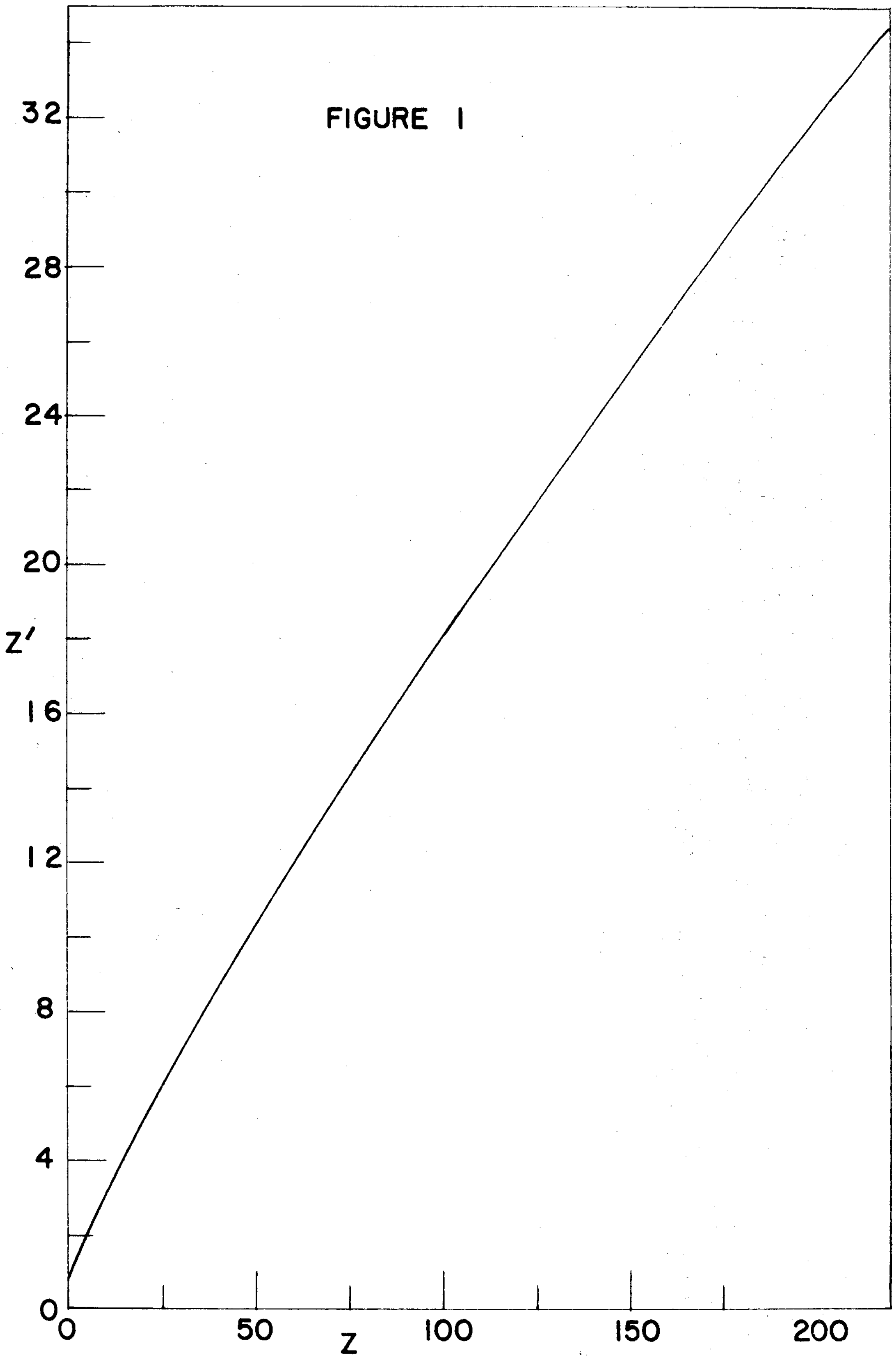
Table XII. Continued

Compound	u_o (cm/sec)	T_f (°K)	$T_{f(lean)}/T_f$	r	$\ln\left[\frac{u_o\left(1+r+\frac{1-\alpha}{\alpha}\right)^{1/2}}{\lvert 1-r\rvert^{1/2}\ T_f^{1/2}}\right]$
Hydrogen	170.0	2345	.421	2.0	2.213
Isopentane	40.0	2250	.735	.125	.681
Isopropyl chloride	27.4	2205	.840	.222	.389
Isopropyl ether	38.3	2250	.771	.111	.636
Isopropyl mercaptan	33.0	2250	.790	.167	.521
Methane	38.9	2200	.760	.5	.988
Methyl acetylene	70.8	2450	.653	.25	1.308
Methyl sulfide	33.0	2330	.720	.222	.546
n Pentane	43.6	2275	.716	.182	.809
n Pentane, 2	47.8	2320	.713	.182	.892
Propionaldehyde	49.5	2310	.678	.25	.980

Table XII. Continued.

Compound	u_0 (cm/sec)	T_f(°K)	$T_{f(lean)}/T_f$		$\ln\left[\frac{u_0\left(1+r+\frac{1-\alpha}{\alpha}\right)^{1/2}}{\lvert 1-r\rvert^{1/2}\ T_f^{1/2}}\right]$
Propane	44.0	2260	.732	.200	.836
n Propyl chloride	27.5	2205	.840	.222	.393
Propylene	51.2	2320	.694	.222	.951
Propylene oxide	66.5	2360	.658	.25	1.262

FIGURE 1



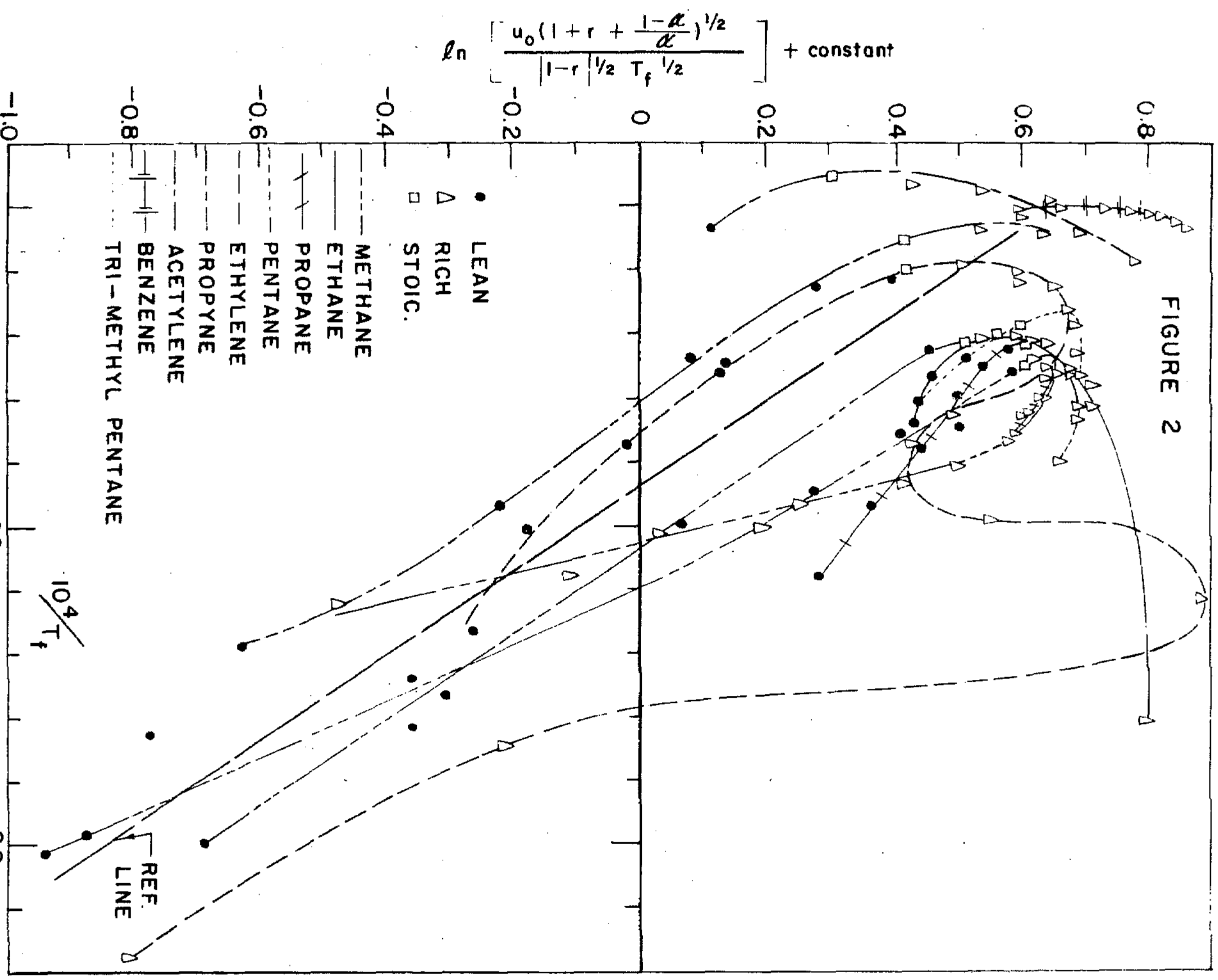


FIGURE 2

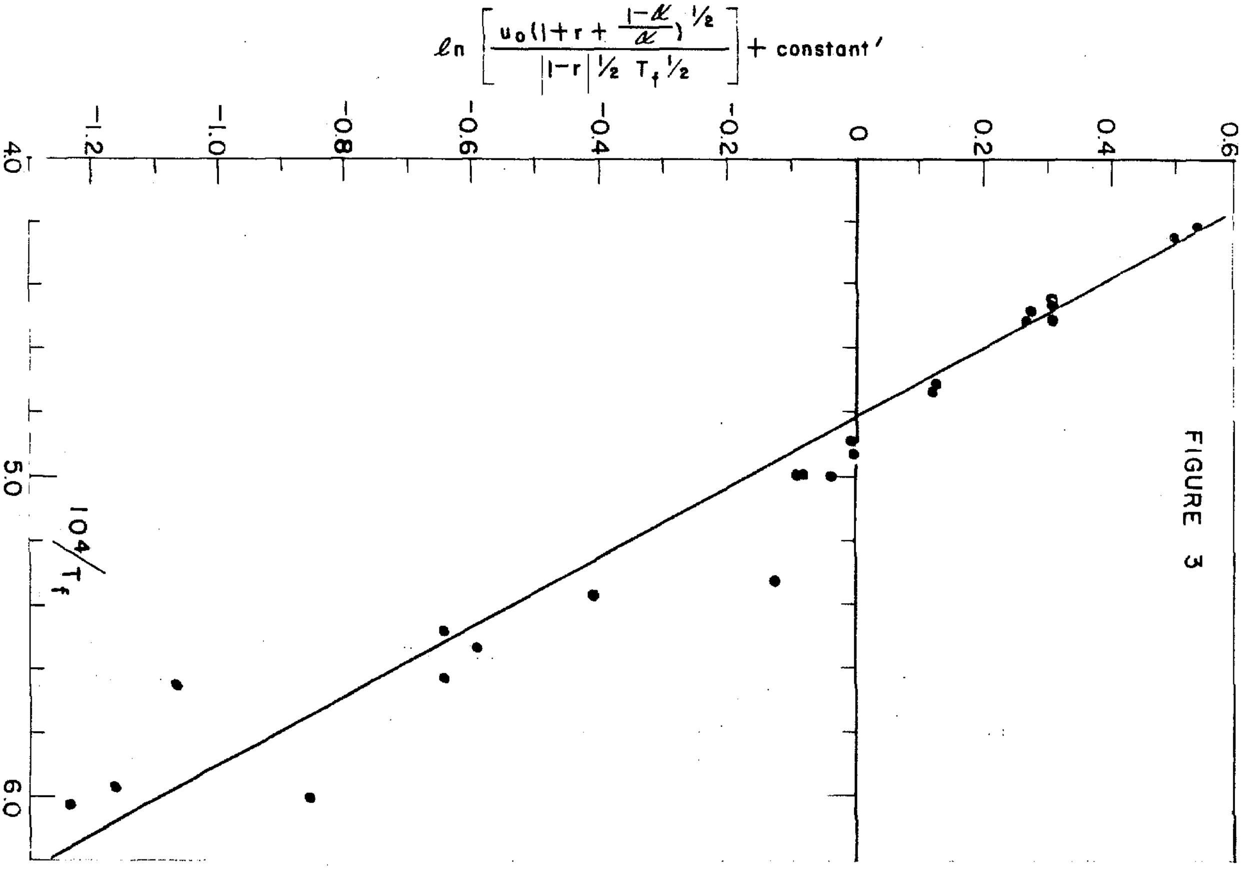


FIGURE 3

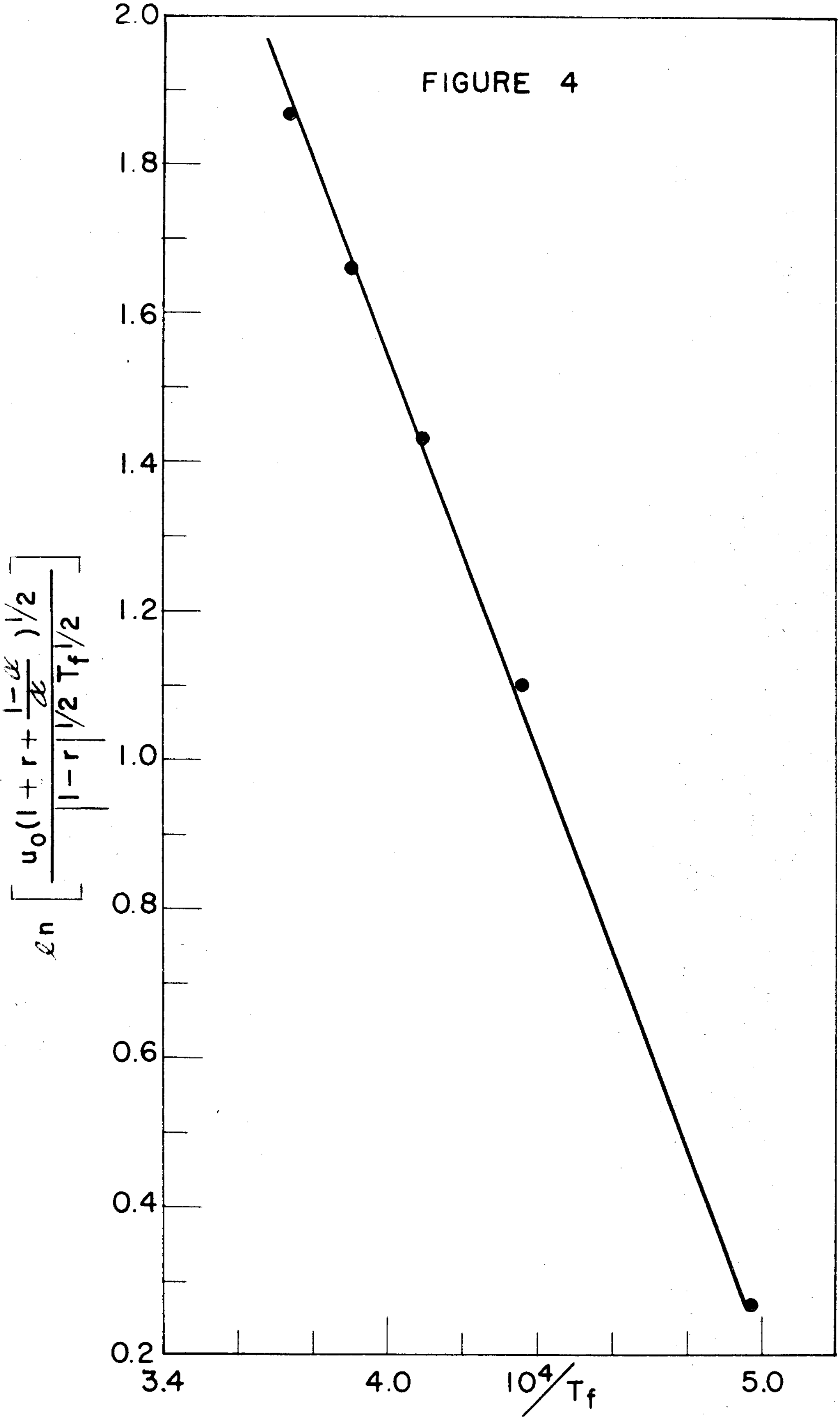
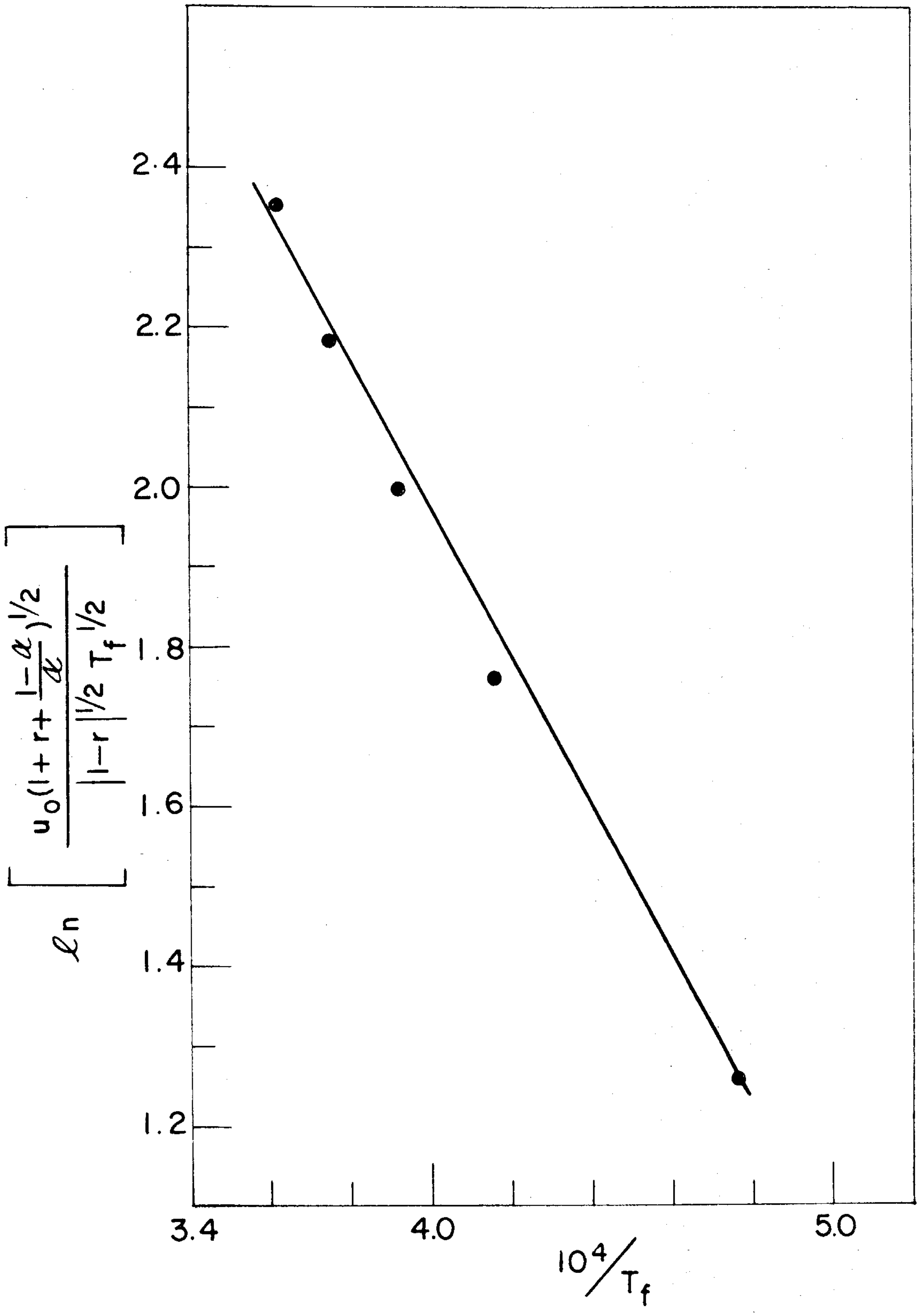


FIGURE 4

2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
3.4
4.0
5.0
$10^4/T_f$
$\ln\left[\dfrac{u_0\left(1+r+\frac{1-\alpha}{\alpha}\right)^{1/2}}{|1-r|^{1/2}\,T_f^{1/2}}\right]$

FIGURE 5


2.4
2.2
2.0
1.8
1.6
1.4
1.2
$\ell n \left[\frac{u_o(1+r+\frac{1-\alpha}{\alpha})^{1/2}}{|1-r|^{1/2} T_f^{1/2}} \right]$
3.4
4.0
5.0
$10^4/T_f$

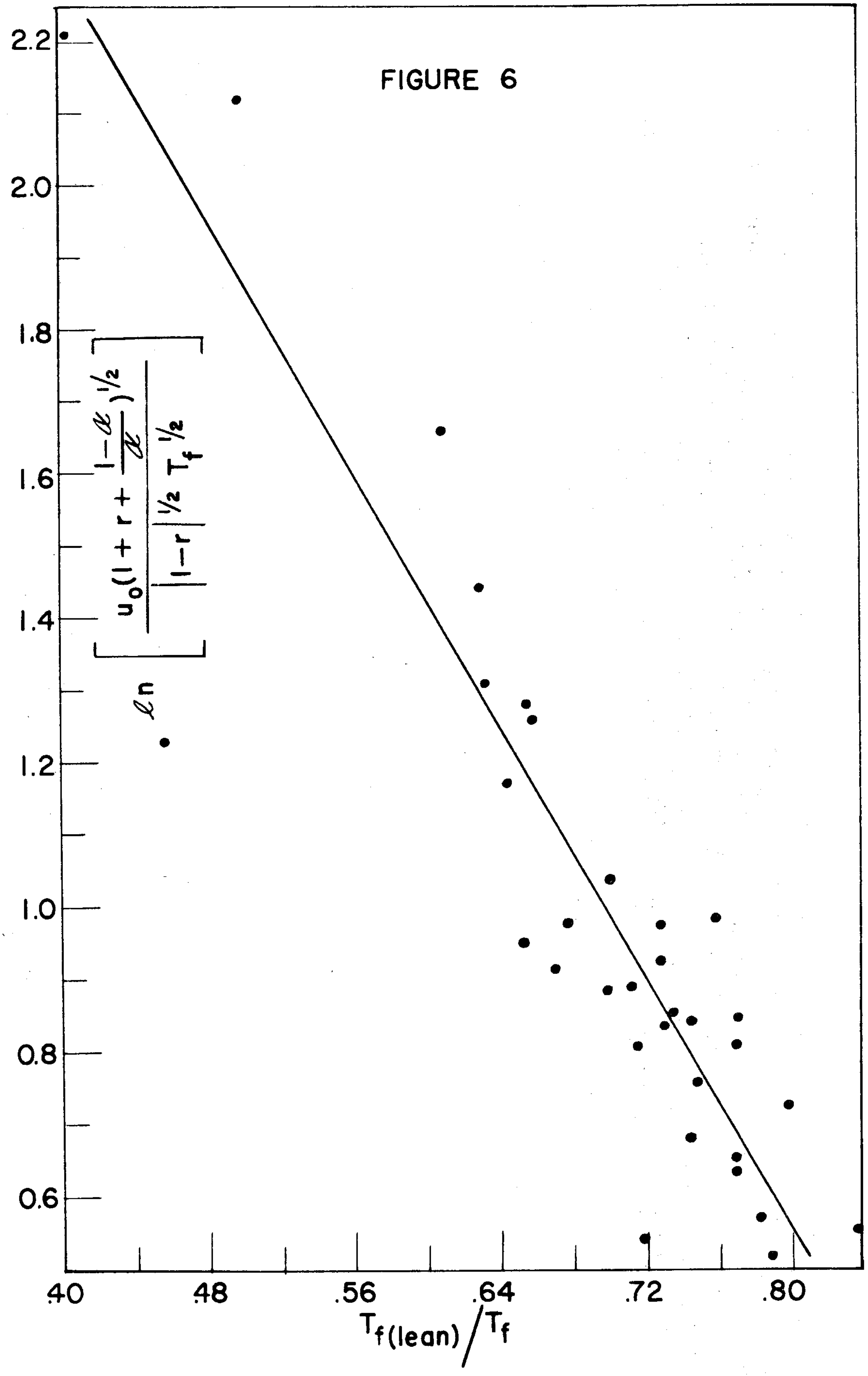


FIGURE 6

2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
ℓn [u_o(1 + r + ((1−α)/α)^{1/2}) / |1−r|^{1/2} T_f^{1/2}]
.40
.48
.56
.64
.72
.80
T_f(lean) / T_f