THE THERMAL THEORY OF LAMINAR FLAME PROPAGATION FOR HYDROGEN-BROMINE MIXTURES

Thesis by

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This thesis is a continuation of the theoretical studies on laminar flame propagation carried out by Dr. Theodore von Kármán and his collaborators. The calculations were carried out under the supervision of Dr. S. S. Penner. Throughout the course of the work the author has profited through direction and suggestions from Dr. von Kármán (indirectly) and from Dr. Penner (directly), without which this manuscript could not have been written.

ABSTRACT

The thermal theory of laminar flame propagation for hydrogen-bromine mixtures is described. The method of analysis follows the earlier work of von Kármán and Millán and of von Kármán and Penner. The problem is materially simplified by introducing the steady-state approximation of classical chemical kinetics for the concentrations of H- and Br-atoms.

The general formulation of the problem is presented in Section II.

Approximate solutions of the relevant mathematical problems, utilizing various procedures developed by von Kármán and his collaborators, are given in Sections III to V for bromine-rich, stoichiometric, and hydrogen-rich mixtures, respectively.

Numerical values for the physico-chemical parameters, which are required for the calculation of absolute values for the burning velocities, are considered in Section VI.

The calculated burning velocities are compared in Section VII with experimental results obtained by R. C. Anderson and his collaborators. Reference to Section VII shows that the variation of the observed burning velocities with mixture ratio is predicted correctly by the theoretical calculations. Absolute values for the laminar burning velocity cannot be estimated with certainty because of the possible existence of large errors resulting from extrapolation of low-temperature kinetics and heat conductivity data.

TABLE OF CONTENTS

PART	TITLE	PAGE
I	INTRODUCTION	1
II	GENERAL EQUATIONS FOR THE THERMAL THEORY OF LAMINAR FLAME PROPAGATION IN HYDROGEN-BROMINE FLAMES WITH THE STEADY STATE APPROXIMATION FOR H- AND Br-ATOMS	3
III	BROMINE-RICH FLAMES	9
IV	THE STOICHIOMETRIC MIXTURE	16
V	HYDROGEN-RICH FLAMES	21
	A. The Mixture Containing 43.3°/o of Bromine	21
	B. Hydrogen-rich Flames	26
VI	PHYSICO-CHEMICAL PARAMETERS	29
	A. Equilibrium Constant for the Reaction $Br_2 \rightleftarrows 2Br$.	29
	B. The Specific Rate Constant for the Reaction between Br and H_2.	30
	C. Ratio of the Reaction Rates k_4/k_3 for the Removal of Hydrogen Atoms.	31
	D. The Adiabatic Flame Temperatures and Equilibrium Compositions for H_2-Br_2 Mixtures.	32
	E. Thermal Conductivities in H_2-Br_2 Mixtures.	32
	F. The Average Specific Heat.	34
VII	COMPARISON OF CALCULATED AND OBSERVED BURNING VELOCITIES	36

LIST OF FIGURES

1. Plot of log (K_p/T) vs. 10^4/T for the reaction $Br_2 \rightleftharpoons 2Br$, where K_p is expressed in atmospheres. The data have been taken from a compilation prepared by the Bureau of Standards.

2. Adiabatic flame temperature T_f as a function of composition for H_2-Br_2 mixtures (p = 1 atmos., T_o = 323°K).

3. Equilibrium mole fractions as a function of gas composition for H_2 - Br_2 mixtures (p = 1 atmos., T_o = 323°K).

4. Thermal conductivity λ_f as a function of composition for H_2-Br_2 flames.

5. Average specific heat $\bar{c}_p$ as a function of composition for the H_2-Br_2 flame (p = 1 atmos., T_o = 323°K).

6. Comparison of observed and calculated values for the laminar burning velocity in H_2-Br_2 mixtures.

LIST OF TABLES

I. Logarithm of the equilibrium constants K_p, for the reaction $Br_2 \rightleftharpoons 2Br$, as a function of temperature, taken from Reference 13.

II. Ratio of reaction rates k_2 calculated from Eqs. (79) and (79a) as a function of temperature.

III. Adiabatic flame temperatures and equilibrium mole fractions as a function of composition (p = 1 atmos., T_o = 323°K).

IV. Thermal conductivities λ_f calculated from Eq. (82) and based on the data of Campbell and Hirschfelder(6) as a function of gas composition.

LIST OF TABLES (Cont'd)

V. Average specific heat $\bar{c}_p$ as a function of composition for H_2-Br_2 flames.

VI. Calculated laminar burning velocities, u_o, for H_2-Br_2 flames as a function of composition.

LIST OF SYMBOLS

SYMBOLS	INTERPRETATION
Subscript 1	property of HBr
Subscript 2	property of Br_2
Subscript 3	property of H_2
Subscript 4	property of H
Subscript 5	property of Br
Subscript j	property of j'th chemical species
Subscript o	property at initial conditions
Subscript f	property at flame temperature
Subscript t	property at arbitrary "transition" temperature
Subscript i	property at ignition temperature
Subscript ℓ	property of ℓ'th chemical reaction
X_j	mole fraction of j'th chemical species
Y_j	weight fraction of j'th chemical species
h_j^o	standard specific enthalpy of j'th chemical species
W_j	molecular weight of j'th chemical species
$\overline{W}$	average molecular weight of initial mixture
T	temperature in ^oK
T_f	adiabatic flame temperature in ^oK
θ	reduced temperature = T/T_f
p	pressure in atmospheres
R	molar gas constant
a	initial mole fraction of H_2
$\overline{c}_p$	average specific heat
λ	effective thermal conduction coefficient
m	mass flow rate of mixture per unit area = $\rho_o u_o$

LIST OF SYMBOLS (Cont'd)

u_o	burning velocity in cm/sec
Λ	dimensionless parameter defined by Eq. (21)
$\delta(a)$	dimensionless parameter defined by Eq. (29)
$b'(a, \theta_o)$	dimensionless parameter defined by Eq. (30)
$f(a)$	dimensionless parameter defined by Eq. (42)
$g(a)$	dimensionless parameter defined by Eq. (75)
ρ_o	initial mixture density = $p_o \overline{M}/R\,T_o$
k_ℓ	specific reaction rate constant for ℓ'th reaction $= B_\ell\, \theta^\alpha e^{-\theta_\ell/\theta}$
α	a fixed number
B_ℓ	frequency factor for ℓ'th reaction
θ_ℓ	a characteristic reduced temperature; if E_ℓ is the activation energy for the ℓ'th reaction then $\theta_\ell = E_\ell/R\,T_f$
θ_2'	dimensionless parameter defined by Eq. (20)
x	linear distance
E_2	error integral
K_c	equilibrium constant expressed in terms of concentration ratios
K_p	equilibrium constant expressed in terms of pressure ratios
X'	"third body"

I. INTRODUCTION

In recent years a large number of publications have appeared on experimental measurements and theoretical studies of laminar flame propagation in premixed gases. For a complete bibliography reference should be made to the books of Lewis and von Elbe(1) and of Jost(2) or to a survey paper by Evans(3). Experimental measurements on hydrogen-bromine flames have been described by Anderson and his collaborators(4,5). As yet incomplete theoretical studies on this flame have been published by J.O.Hirschfelder and his collaborators(6,7), who are attempting to carry out a rigorous numerical solution of the complete flame equations for the stoichiometric mixture ratio.

The method of approach which is followed in the present investigation differs in scope and purpose from the type of calculations carried out by Hirschfelder. We follow the work of von Kármán and Millán(8) and of von Kármán and Penner(9, 10) in that we shall content ourselves with an approximate solution of the flame equations for a thermal theory, on the grounds that the required physico-chemical parameters are not known with sufficient accuracy to justify numerical solutions. On the other hand, in order to obtain a reasonably severe empirical check of the physical model and of the mathematical approximations, complete calculations as a function of mixture ratio are carried out. In order to obtain the desired results, we shall utilize the steady-state approximation of classical reaction kinetics for the chain carriers, as suggested for flames by von Kármán and Penner(9); although the steady-state approximation cannot be justified for Br atoms at elevated temperatures, it appears that the calculated burning velocities are nevertheless approximately correct* .

There is a well-known cold boundary-value difficulty which enters into the solution of the one-dimensional laminar flame equations. We shall not discuss this problem except to note that a convenient method for avoiding complications is to utilize the concept of an ignition temperature(11).

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* This result can be established by an extended analysis comparing reaction rates with and without the steady-state approximation. The relevant analysis has been carried out by von Kármán and Millán.

II. GENERAL EQUATIONS FOR THE THERMAL THEORY OF LAMINAR FLAME PROPAGATION IN HYDROGEN-BROMINE FLAMES WITH THE STEADY-STATE APPROXIMATION FOR H AND Br

For the theoretical study of laminar flame propagation in hydrogen-bromine flames, we shall utilize the accepted reaction scheme for isothermal production of HBr in stationary systems at temperatures of the order of 500°K. The required equations are:(12)

$$X' + Br_2 \xrightarrow{k_1} 2Br + X' , \qquad (1)$$

$$Br + H_2 \xrightarrow{k_2} HBr + H , \qquad (2)$$

$$H + Br_2 \xrightarrow{k_3} HBr + Br , \qquad (3)$$

$$H + HBr \xrightarrow{k_4} H_2 + Br , \qquad (4)$$

$$2Br + X' \xrightarrow{k_5} Br_2 + X' . \qquad (5)$$

Here X' denotes the "third body", i.e. any of the chemical species H, Br, H_2, Br_2, or HBr. The specific reaction rate constants k_1 to k_5 for the five reaction steps are indicated above each of the arrows.

It is well-known that the steady-state approximation for H- and Br-atoms leads to the relation(12)

$$\frac{d(HBr)}{dt} = \frac{2k_2\left(\frac{k_1}{k_5}\right)^{1/2} (H_2)\,(Br_2)^{1/2}}{1 + \frac{k_4}{k_3}\,\frac{(HBr)}{(Br_2)}} \qquad (6)$$

where the chemical symbols in parentheses denote concentrations for the chemical species and $\underline{t}$ represents the time. For thermal flame theories it is convenient to introduce mole fractions, X; we identify HBr, Br_2, and H_2 by the subscripts 1, 2, and 3, respectively. Then

$$(H_2) = \frac{p}{RT} X_3 = \frac{p}{RT} (X_{3,o} - \frac{X_1}{2}) \tag{7}$$

and

$$(Br_2) = \frac{p}{RT} X_2 = \frac{p}{RT} (X_{2,o} - \frac{X_1}{2}) \tag{8}$$

where $\underline{p}$ denotes pressure, $\underline{R}$ is the molar gas constant, $\underline{T}$ is the temperature, and the subscript $\underline{o}$ identifies initial conditions.

For flames without inert diluents it is convenient to identify the initial composition by the parameter $\underline{a}$. Let $X_{3,o} = a$, $X_{2,o} = 1-a$. Then Eq. (6) becomes

$$\frac{p}{RT} \frac{d(X_1)}{dt} = \frac{2k_2(\frac{k_1}{k_5})^{1/2} (\frac{p}{RT})^{3/2} (a - \frac{X_1}{2})(1-a-\frac{X_1}{2})^{3/2}}{(1-a)-(\frac{1}{2} - \frac{k_4}{k_3}) X_1} . \tag{9}$$

If W_1, W_2, and W_3 denote the molecular weights of HBr, Br_2, and H_2, respectively, then

$$W_1 \frac{d(X_1)}{dt} \frac{p}{RT}$$

represents the rate of change of the mass of bromine per unit volume with time. But this quantity is also equal to

$$m \frac{W_1}{\overline{W}} \frac{dX_1}{dx}$$

if $\underline{m}$ is the mass flow rate per unit area of the mixture (i.e. the eigenvalue for the problem of laminar flame propagation), x equals distance, and

$$\overline{W} = \sum_i W_i X_i \tag{10}$$

is the average molecular weight of the gas mixture. Hence Eq. (9) becomes

$$\frac{m}{\overline{W}} \frac{dX_1}{dx} = \frac{2k_2\left(\frac{k_1}{k_5}\right)^{1/2} \left(\frac{p}{RT}\right)^{3/2} \left(a - \frac{X_1}{2}\right)\left(1-a-\frac{X_1}{2}\right)^{3/2}}{(1-a) - \left(\frac{1}{2} - \frac{k_4}{k_3}\right) X_1} \quad . \tag{11}$$

In the absence of diffusion the general energy equation for one-dimensional flow can be written in the form(9)

$$\frac{\lambda}{m\overline{c}_p} \frac{d\theta}{dx} = (\theta - 1) + \frac{\sum_j (Y_j - Y_{j,f}) h_j^o}{\overline{c}_p \, T_f} \tag{12}$$

where λ equals the thermal conductivity; the reduced temperature is $\theta = T/T_f$, with the subscript f identifying equilibrium conditions at the adiabatic flame temperature; Y_j is the weight fraction of the j'th chemical species; h_j^o equals the standard specific enthalpy of formation at temperature T_o of the j'th species; the average specific heat $\overline{c}_p$ is given by the expression (9)

$$\overline{c}_p = - \frac{1}{(1-\theta_o)T_f} \sum_j (Y_{j,f} - Y_{j,o}) h_j^o \ . \tag{13}$$

For the present approximate calculations we shall ignore the production of bromine and hydrogen atoms at the equilibrium conditions.* In this case it is found from Eqs. (12) and (13) that

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* This assumption is in line with the steady-state postulate but is not correct at elevated temperatures where appreciable concentrations of bromine atoms may form in bromine-rich mixtures. The required corrections have been worked out and have been found to be relatively small.

$$\frac{\lambda}{m\bar{c}_p}\ \frac{d\theta}{dx} = (\theta-1)-(1-\theta_o)\frac{\sum\limits_j (Y_j - Y_{j,f})h_j^o}{\sum\limits_j (Y_{j,f} - Y_{j,o})h_j^o}$$

$$= (\theta-1)-(1-\theta_o)\frac{(Y_1-Y_{1,f})h_1^o + (Y_2-Y_{2,f})h_2^o}{(Y_{1,f}-Y_{1,o})h_1^o + (Y_{2,f} - Y_{2,o})h_2^o}$$

$$= (\theta-1)-(1-\theta_o)\frac{(X_1-X_{1,f})W_1h_1^o+(X_2-X_{2,f})W_2h_2^o}{(X_{1,f}-X_{1,o})W_1h_1^o + (X_{2,f}-X_{2,o})W_2h_2^o}$$

since $h_3^o = 0$. But

$$(X_2 - X_{2,f}) = \frac{1}{2}(X_1-X_{1,f})$$

and

$$(X_{2,f} - X_{2,o}) = \frac{1}{2}(X_{1,f} - X_{1,o}) \ .$$

Hence

$$\frac{\lambda}{m\bar{c}_p}\ \frac{d\theta}{dx} = (\theta-1)-(1-\theta_o)(X_1-X_{1,f})\frac{(W_1h_1^o + \frac{1}{2}W_2h_2^o)}{(X_{1,f}-X_{1,o})(W_1h_1^o + 1/2\, W_2h_2^o)} \ .$$

We shall be interested only in flames for which $X_{1,o} = 0$. Hence the energy equation reduces to the following simple expression:

$$\frac{\lambda}{m\bar{c}_p}\ \frac{d\theta}{dx} = (\theta-1) + (1-\theta_o)\ (1 - \frac{X_1}{X_{1,f}}) \ . \qquad (14)$$

Following the conventional procedure for solving problems in laminar flame propagation, we now divide the continuity equation given in Eq. (11) by the energy equation given in Eq. (14) in order to eliminate the distance x as the independent variable. In this manner it is found that

$$\frac{m^2\bar{c}_p}{\lambda\,\bar{W}}\,\frac{dX_1}{d\theta} = 2k_2\left(\frac{k_1}{k_5}\right)^{1/2}\left(\frac{p}{RT}\right)^{3/2}\frac{\left(a-\frac{X_1}{2}\right)\left(1-a-\frac{X_1}{2}\right)^{3/2}}{\left[1-a-\left(\frac{1}{2}-\frac{k_4}{k_3}\right)X_1\right]\left[(\theta-1)+(1-\theta_o)(1-X_1/X_{1,f})\right]}\,. \qquad (15)$$

We now introduce the assumptions(9) that

$$\lambda = \lambda_f\,\theta^{1/2}\,, \qquad (16)$$

$$k_2 = B_2\,\theta^{1/2}\,e^{-\theta_2/\theta}\,, \qquad (17)$$

$$\frac{k_1}{k_5} = \frac{B_1}{B_5}\,e^{-\theta_1/\theta}\,. \qquad (18)$$

Equation (15) now becomes

$$\frac{dX_1}{d\theta} = \left[\frac{\lambda_f\bar{W}}{m^2\bar{c}_p}\left(\frac{B_1}{B_5}\right)^{1/2} B_2\left(\frac{p}{RT_f}\right)^{3/2}\theta^{-1/2}\,e^{-\theta_2'/\theta}\right] \times \qquad (19)$$

$$\left\{\frac{(2a-X_1)\left(1-a-\frac{X_1}{2}\right)^{3/2}}{\left[(1-a)-\left(\frac{1}{2}-\frac{k_4}{k_3}\right)X_1\right]\left[(\theta-1)+(1-\theta_o)\left(1-\frac{X_1}{X_{1,f}}\right)\right]}\right\}\,,$$

where

$$\theta_2' = \theta_2 + \frac{1}{2}\,\theta_1\,. \qquad (20)$$

It is now convenient to introduce the parameter Λ through the relation

$$\Lambda = \frac{\lambda_f\bar{W}}{m^2\bar{c}_p}\,B_2\left(\frac{B_1}{B_5}\right)^{1/2}\left(\frac{p}{RT_f}\right)^{3/2} \qquad (21)$$

whence Eq. (19) becomes

$$\frac{dX_1}{d\theta} = \frac{\Lambda \theta^{-1/2} e^{-\theta'_2/\theta}}{(\theta-1)+(1-\theta_o)(1-\frac{X_1}{X_{1,f}})} \frac{(2a-X_1)(1-a-\frac{X_1}{2})^{3/2}}{\left[(1-a)-(\frac{1}{2} - k_4/k_3)X_1\right]} \quad . \qquad (22)$$

The boundary conditions are:

$$\theta = \theta_i \qquad \text{when} \qquad X_1 = 0 \qquad (23)$$

and

$$\theta = 1 \qquad \text{when} \qquad \left\{ \begin{array}{ll} X_{1,f} = 2a & \text{for } a < 1/2 \\ X_{1,f} = 2a & \text{for } a = 1/2 \\ X_{1,f} = 2(1-a) & \text{for } a > 1/2 \end{array} \right\} . \qquad (24)$$

The solution of the boundary value problems is discussed in the following Sections III, IV, and V for a < 1/2, a = 1/2, and a > 1/2 respectively.

III. BROMINE-RICH FLAMES

For the bromine-rich flames, solution of the boundary-value problem can be effected conveniently by use of the von Kármán-Millán technique.(8) The boundary conditions are

$$\left.\begin{array}{ll} \theta = \theta_i & \text{when } X_1 = 0 \\ & \\ \theta = 1 & \text{when } X_1 = 2a \end{array}\right\} . \tag{24}$$

and

From Eq. (22)

$$\frac{dX_1}{d\theta} = \frac{\Lambda\, \theta^{-\frac{1}{2}}\, e^{-\theta_2'/\theta}}{(\theta-1)+(1-\theta_o)(1-\frac{X_1}{2a})}\; \frac{(2a-X_1)(1-a-\frac{X_1}{2})^{3/2}}{(1-a-0.381X_1)} \tag{25}$$

where the appropriate numerical value of k_4/k_3 has been introduced (see Section VI C for details).

Rearranging Eq. (25), we get

$$\Lambda\theta^{-\frac{1}{2}}\, e^{-\theta_2'/\theta}\, \frac{d\theta}{dX_1} = \frac{(1-a-0.381X_1)}{(1-a-\frac{1}{2}X_1)^{3/2}} \left[\frac{(\theta-1)+(1-\theta_o)(1-\frac{X_1}{2a})}{2a-X_1}\right] , \tag{26}$$

from which it follows that

$$\Lambda e^{-\theta_2'} \lim_{\theta \to 1} (\frac{d\theta}{dX_1}) = \frac{(1-1.762a)}{(1-2a)^{3/2}}\; \frac{\left[\lim\limits_{\theta \to 1} (\frac{d\theta}{dX_1}) - (\frac{1-\theta_o}{2a})\right]}{-1} , \tag{27}$$

or

$$\lim_{\theta \to 1} (\frac{d\theta}{dX_1}) \left[\Lambda e^{-\theta_2'} + \frac{(1-1.762a)}{(1-2a)^{3/2}}\right] = \frac{(1-\theta_o)}{2a}\, \frac{(1-1.762a)}{(1-2a)^{3/2}} . \tag{28}$$

Defining

$$\delta\,(a) = \frac{1-1.762a}{(1-2a)^{3/2}} \tag{29}$$

and

$$b'(a,\theta_o) = \frac{1-\theta_o}{2a}\ , \tag{30}$$

then Eq. (28) becomes

$$\lim_{\theta\to 1}\left(\frac{d\theta}{dX_1}\right) = \frac{\delta(a)\, b'(a,\theta_o)}{\Lambda e^{-\theta'_2} + \delta(a)}\ . \tag{31}$$

Introduction of Eq. (31) on the left hand side of Eq. (26) for $\theta \sim 1$, $X_1 \sim 2a$, leads to the following relation:

$$\Lambda e^{-\theta'_2}\ \frac{b'(a,\theta_o)}{\Lambda e^{-\theta'_2} + \delta(a)} = \frac{(\theta-1)+(1-\theta_o)(1-\frac{X_1}{2a})}{2a-X_1}$$

or, using Eq. (30),

$$1-\theta = b'(a,\theta_o)(2a-X_1)\left[1-\frac{\Lambda e^{-\theta'_2}}{\Lambda e^{-\theta'_2} + \delta(a)}\right]$$

or

$$1-\theta = b'(a,\theta_o)(2a-X_1)\left[\frac{\delta(a)}{\Lambda e^{-\theta'_2} + \delta(a)}\right]. \tag{32}$$

Introduction of Eq. (32) on the right-hand side of Eq. (26) yields

$$\Lambda \theta^{-\frac{1}{2}} e^{-\theta'_2/\theta}\frac{d\theta}{dX_1} = \frac{(1-a-0.381X_1)}{(1-a-\frac{1}{2}X_1)^{3/2}}\ b'(a,\theta_o)\left[1-\frac{\delta(a)}{\Lambda e^{-\theta'_2} + \delta(a)}\right]; \tag{33}$$

integration of this last relation between θ_t, X_t and $\theta = 1$, $X_1 = 2a$, leads to the result

$$\int_{\theta_t}^{1} \theta^{-\frac{1}{2}} e^{-\theta'_2/\theta}\, d\theta = \frac{b'(a,\theta_o)\, e^{-\theta'_2}}{\Lambda e^{-\theta'_2} + \delta(a)} \int_{X_t}^{2a} \frac{(1-a-0.381X_1)}{(1-a-\frac{1}{2}X_1)^{3/2}}\, dX_1\ . \tag{34}$$

For $\theta \sim \theta_i$, $X_1 \sim 0$, we get from Eq. (26)

$$\Lambda \theta^{-\frac{1}{2}} e^{-\theta_2'/\theta} \frac{d\theta}{dX_1} = \left[\frac{(\theta-1)+(1-\theta_o)}{2a}\right] \frac{(1-a-0.381\,X_1)}{(1-a-\frac{1}{2}\,X_1)^{3/2}} \;; \tag{35}$$

the integral of Eq. (35) from $\theta_i, 0$ to θ_t, X_t is

$$\int_{\theta_i}^{\theta_t} \frac{\theta^{-\frac{1}{2}} e^{-\theta_2'/\theta}}{(\theta-1)+(1-\theta_o)}\, d\theta = \frac{1}{2a\Lambda} \int_0^{X_t} \frac{(1-a-0.381X_1)}{(1-a-\frac{1}{2}X_1)^{3/2}}\, dX_1 \;. \tag{36}$$

But$^{(8)}$

$$\int_{\theta_i}^{\theta_t} \frac{\theta^{-\frac{1}{2}} e^{-\theta_2'/\theta}}{(\theta-1)+(1-\theta_o)}\, d\theta \simeq \frac{1}{(\theta_t-1)+(1-\theta_o)} \int_{\theta_i}^{\theta_t} \theta^{-\frac{1}{2}} e^{-\theta_2'/\theta}\, d\theta$$

whence

$$\int_{\theta_i}^{\theta_t} \theta^{-\frac{1}{2}} e^{-\theta_2'/\theta}\, d\theta \simeq \frac{(\theta_t-1)+(1-\theta_o)}{2a\Lambda} \int_0^{X_t} \frac{(1-a-0.381X_1)}{(1-a-\frac{1}{2}X_1)^{3/2}}\, dX_1 . \tag{37}$$

Since $\frac{d\theta}{dX_1}$ is to be continuous at θ_t, X_t it follows from Eqs. (35) and (33) that

$$\frac{(\theta_t-1)+(1-\theta_o)}{2a} \; \frac{1}{\Lambda\theta_t^{-\frac{1}{2}} e^{-\theta_2'/\theta_t}} \; \frac{(1-a-0.381X_1)}{(1-a-\frac{1}{2}X_1)^{3/2}} =$$

$$\frac{1-a-0.381X_1}{(1-a-\frac{1}{2}X_1)^{3/2}} \; \frac{1}{\Lambda\theta_t^{-\frac{1}{2}} e^{-\theta_2'/\theta_t}} \; b'(a,\theta_o) \left[1 - \frac{\delta(a)}{\Lambda e^{-\theta_2'} + \delta(a)}\right]$$

whence

$$\frac{(\theta_t-1)+(1-\theta_o)}{2a\Lambda} = \frac{b'(a,\theta_o)\, e^{-\theta_2'}}{\Lambda e^{-\theta_2'} + \delta(a)} \;. \tag{38}$$

In view of Eq. (38), Eqs. (34) and (37) can be added to yield the result

$$\int_{\theta_i}^{1} \theta^{-\frac{1}{2}} e^{-\theta_2'/\theta} d\theta = \frac{b'(a,\theta_o)\, e^{-\theta_2'}}{\Lambda e^{-\theta_2'}+\delta(a)} \int_0^{2a} \frac{(1-a-0.381X_1)}{(1-a-\frac{1}{2}X_1)^{3/2}}\, dX_1 \,. \qquad (39)$$

In order to evaluate the integral

$$\int_{\theta_i}^{1} \theta^{-\frac{1}{2}} e^{-\theta_2'/\theta} d\theta$$

we set

$$\frac{1}{\sqrt{\theta}} = y, \quad \frac{1}{\theta} = y^2, \quad \frac{1}{\theta^2} = y^4 \quad \text{and } d\theta = -\frac{2}{y^3}\, dy.$$

Substitution of these relations yields

$$\int_{\theta_i}^{1} \theta^{-\frac{1}{2}} e^{-\theta_2'/\theta} d\theta = -2 \int_{\frac{1}{\sqrt{\theta_i}}}^{1} y\, e^{-\theta_2' y^2} \frac{1}{y^3}\, dy = 2 \int_1^{\frac{1}{\sqrt{\theta_i}}} \frac{e^{-\theta_2' y^2}}{y^2}\, dy.$$

But

$$\int_1^{\frac{1}{\sqrt{\theta_i}}} e^{-\theta_2' y^2} dy = \int_1^{\frac{1}{\sqrt{\theta_i}}} -2\theta_2'\, y e^{-\theta_2' y^2} \frac{dy}{-2y\theta_2'}$$

or

$$= -\frac{1}{2y\theta_2'}\, e^{-\theta_2' y^2} \Bigg]_1^{\frac{1}{\sqrt{\theta_i}}} - \frac{1}{2\theta_2'} \int_1^{\frac{1}{\sqrt{\theta_i}}} \frac{1}{y^2}\, e^{-\theta_2' y^2} dy.$$

Comparison of the two preceding relations leads to the result

$$\int_{\theta_i}^{1} \theta^{-\frac{1}{2}} e^{-\theta_2'/\theta}\, d\theta = -4\theta_2' \left\{ \int_{1}^{\frac{1}{\sqrt{\theta_i}}} e^{-\theta_2' y^2} dy + \left[\frac{1}{2\theta_2' y} e^{-\theta_2' y^2} \right]_{1}^{\frac{1}{\sqrt{\theta_i}}} \right\}$$

$$= 4\theta_2' \left(\int_{0}^{1} e^{-\theta_2' y^2} dy - \int_{0}^{\frac{1}{\sqrt{\theta_i}}} e^{-\theta_2' y^2} dy \right) + 2e^{-\theta_2'} - 2\sqrt{\theta_i}\, e^{-\theta_2'/\theta_i}$$

$$= \left(2e^{-\theta_2'} - 2\sqrt{\theta_i}\, e^{-\theta_2'/\theta_i} \right) + 4\sqrt{\theta_2'} \left(\int_{0}^{\sqrt{\theta_2'}} e^{-t^2} dt - \int_{0}^{\sqrt{\frac{\theta_2'}{\theta_i}}} e^{-t^2} dt \right) .$$

For sufficiently large values$^{(8)}$ of θ_2'/θ_i we obtain*

$$\int_{\theta_i}^{1} \theta^{-\frac{1}{2}} e^{-\theta_2'/\theta}\, d\theta = \left(2e^{-\theta_2'} - 2\sqrt{\theta_i}\, e^{-\theta_2'/\theta_i} \right) - 2\sqrt{\theta_2'} \left(2\int_{0}^{\infty} e^{-t^2} dt - 2\int_{0}^{\sqrt{\theta_2'}} e^{-t^2} dt \right)$$

$$= \left(2e^{-\theta_2'} - 2\sqrt{\theta_i}\, e^{-\theta_2'/\theta_i} \right) - 2\sqrt{\pi\theta_2'} \left[1 - E_2 (\sqrt{\theta_2'}) \right]$$

where

$$(\tfrac{1}{2})!\, E_2(\sqrt{\theta_2'}) = \frac{\sqrt{\pi}}{2}\, E_2(\sqrt{\theta_2'}) = \int_{0}^{\sqrt{\theta_2'}} e^{-t^2}\, dt.$$

But

$$(\tfrac{1}{2})! \left[1 - E_2 (\sqrt{\theta_2'}) \right] \sim \frac{e^{-\theta_2'}}{2\sqrt{\theta_2'}} \left[1 - \frac{1}{2\theta_2'} + \frac{1.3}{(2\theta_2')^2} - \frac{1.3.5}{(2\theta_2')^3} + \dots \right]$$

---

*In the practical applications considered here, θ_2'/θ_i is sufficiently large to justify the approximations made here.

whence, finally,

$$\int_{\theta_i}^{1} \theta^{-\frac{1}{2}} e^{-\theta_2'/\theta} \, d\theta \simeq 2e^{-\theta_2'} - 2e^{-\theta_2'} \left[1 - \frac{1}{2\theta_2'} + \frac{1\cdot 3}{(2\theta_2')^2} - \frac{1\cdot 3\cdot 5}{(2\theta_2')^3} + \dots \right]$$

or

$$\int_{\theta_i}^{1} \theta^{-\frac{1}{2}} e^{-\theta_2'/\theta} \, d\theta \simeq \frac{e^{-\theta_2'}}{\theta_2'} \left[1 - \frac{1\cdot 3}{(2\theta_2')} + \frac{1\cdot 3\cdot 5}{(2\theta_2')^2} - \dots \quad . \right] \tag{40}$$

Equation (39) can now be solved for $\mathcal{A} e^{-\theta_2'}$ with the result

$$\mathcal{A} e^{-\theta_2'} = \frac{(1-\theta_o)e^{-\theta_2'} \int_0^{2a} \frac{(1-a-0.381X_1)\,dX_1}{(1-a-\frac{1}{2}X_1)^{3/2}}}{2a \frac{e^{-\theta_2'}}{\theta_2'} \left[1 - \frac{1\cdot 3}{(2\theta_2')} + \frac{1\cdot 3\cdot 5}{(2\theta_2')^2} - \dots \right]} - \frac{1-1.762a}{(1-2a)^{3/2}}$$

or

$$\mathcal{A} e^{-\theta_2'} = \frac{(1-\theta_o)\theta_2' \int_0^{2a} \frac{(1-a-0.381\,X_1)}{(1-a-1/2\,X_1)^{3/2}} dX_1}{2a \left[1 - \frac{1\cdot 3}{(2\theta_2')} + \frac{1\cdot 3\cdot 5}{(2\theta_2')^2} - \dots \right]} - \frac{(1-1.762a)}{(1-2a)^{3/2}} \tag{41}$$

where δ (a) and b'(a, θ_o) have been replaced according to Eqs. (29) and (30) respectively. It is now necessary to evaluate the integral

$$\int_0^{2a} \frac{(1-a-0.381X_1)}{(1-a-\frac{1}{2}X_1)^{3/2}} dX_1 = \int_0^{2a} \frac{(1-a)}{(1-a-\frac{1}{2}X_1)^{3/2}} dX_1 - 0.381 \int_0^{2a} \frac{X_1\,dX_1}{(1-a-\frac{1}{2}X_1)^{3/2}} \, .$$

Evidently

$$\int_0^{2a} \frac{(1-a)dX_1}{(1-a-\frac{1}{2}X_1)^{3/2}} = 4(1-a)\left(\frac{1}{\sqrt{1-2a}} - \frac{1}{\sqrt{1-a}}\right)$$

and

$$0.381 \int_0^{2a} \frac{X_1 dX_1}{(1-a-\frac{1}{2}X_1)^{3/2}} = 0.381 \left[\frac{8a}{\sqrt{1-2a}} + 16\left(\sqrt{1-2a} - \sqrt{1-a}\right)\right] .$$

Therefore

$$\int_0^{2a} \frac{(1-a-0.381X_1)}{(1-a-\frac{1}{2}X_1)^{3/2}} \, dX_1 = \frac{1}{\sqrt{1-2a}} \left[4(1-a)-3.05a-6.10+12.20a\right]$$

$$- \frac{1}{\sqrt{1-a}} \left[4(1-a)-6.10(1-a)\right]$$

$$= \frac{5.15a-2.10}{\sqrt{1-2a}} + \frac{2.10(1-a)}{\sqrt{1-a}} \equiv f(a). \qquad (42)$$

The final result for bromine-rich flames becomes

$$\Lambda e^{-\theta_2'} = \frac{(1-\theta_o)\theta_2' f(a)}{2a\left[1 - \frac{1\cdot 3}{(2\theta_2')} + \frac{1\cdot 3\cdot 5}{(2\theta_2')^2} - \dots\right]} - \frac{(1-1.762a)}{(1-2a)^{3/2}} \qquad (43)$$

from which the eigenvalue Λ can be obtained for bromine-rich mixtures. The mass burning rate m is then determined through Eq. (21).

IV. THE STOICHIOMETRIC MIXTURE

For the case $a = \frac{1}{2}$ and $X_{1,f} = 1$ the basic differential equation, Eq. (22), becomes

$$\frac{dX_1}{d\theta} = \frac{\Lambda / \sqrt{2}\ \theta^{-\frac{1}{2}} e^{-\theta'_2/\theta}}{(\theta-1)+(1-\theta_o)(1-X_1)} \quad \frac{(1-X_1)^{5/2}}{(1-0.761\, X_1)}$$

or

$$\frac{\Lambda}{\sqrt{2}}\ \theta^{-\frac{1}{2}} e^{-\theta'_2/\theta} \ \frac{(1-X_1)^{5/2}}{(1-0.761 X_1)} \ \frac{d\theta}{dX_1} = (\theta-1)+(1-\theta_o)(1-X_1) \ . \tag{44}$$

In order to integrate Eq. (44) we apply an ingenious, as yet unpublished, method invented by Dr. Theodore von Kármán. We replace the singular point ($\theta = 1$, $X_1 = 1$) by ($\theta = 1$, $X_1 = X'_1 < 1$); then Eq. (44) becomes, for ($\theta - 1$) small compared to $(1-\theta_o)(1-X_1)$,

$$\frac{\Lambda}{\sqrt{2}} \ \frac{\theta^{-\frac{1}{2}} e^{-\theta'_2/\theta}}{1-0.761\, X_1} \ \frac{d\theta}{dX_1} = \frac{1-\theta_o}{(1-X_1)^{3/2}} \ . \tag{45}$$

Integrating Eq. (45) from (θ^*, X_1^*) to $(1, X'_1)$ leads to the result

$$\frac{\Lambda}{\sqrt{2}} \int_{\theta^*}^{1} \frac{e^{-\theta'_2/\theta}}{\sqrt{\theta}} \, d\theta = (1-\theta_o) \int_{X_1^*}^{X'_1} \frac{(1-0.761\, X_1)}{(1-X_1)^{3/2}} \, dX_1 \ . \tag{46}$$

For $\theta^* \sim 1$, the preceding expression becomes

$$\frac{\Lambda}{\sqrt{2}} \, e^{-\theta'_2} (1-\theta^*) \simeq (1-\theta_o) \int_{X_1^*}^{X'_1} \frac{(1-0.761\, X_1)}{(1-X_1)^{3/2}} \, dX_1 \ . \tag{46a}$$

If Eq. (45) holds, as a first approximation, from $(\theta_i, 0)$ to $(1, X'_1)$, then

$$\frac{\Lambda}{\sqrt{2}}\int_{\theta_i}^{1}\frac{e^{-\theta_2'/\theta}}{\sqrt{\theta}}\,d\theta = (1-\theta_o)\int_{0}^{X_1'}\frac{(1-0.761X_1)}{(1-X_1)^{3/2}}\,dX_1 \tag{47}$$

or, utilizing the result obtained previously for the integral appearing on the left side of Eq. (47),

$$\frac{\Lambda}{\sqrt{2}}\,\frac{e^{-\theta_2'}}{\theta_2'}\left[1-\frac{1\cdot 3}{(2\theta_2')}+\frac{1\cdot 3\cdot 5}{(2\theta_2')^2}-\ldots\right] \simeq (1-\theta_o)\int_{0}^{X_1'}\frac{(1-0.761X_1)dX_1}{(1-X_1)^{3/2}}\,. \tag{48}$$

From the original differential equation it is apparent that the limiting slope at the hot boundary is

$$\frac{d\theta}{dX_1} = (1-\theta_o)$$

to which we join the curve of Eq. (46a) at (θ^*, X_1^*). Therefore, at (θ^*, X_1^*),

$$(1-\theta^*) = (1-\theta_o)\,(1-X_1^*) \quad . \tag{49}$$

From Eqs. (46a) and (49)

$$\frac{\Lambda}{\sqrt{2}}\,e^{-\theta_2'}\,(1-X_1^*) = \int_{X_1^*}^{X_1'}\frac{(1-0.761X_1)}{(1-X_1)^{3/2}}\,dX_1\,. \tag{50}$$

With $\frac{d\theta}{dX} = (1-\theta_o)$, Eq. (45) becomes at (θ^*, X_1^*):

$$\frac{\Lambda}{\sqrt{2}}\,\frac{e^{-\theta_2'}}{(1-0.761X_1^*)}\,(1-X_1^*)^{3/2} = 1. \tag{51}$$

We next integrate Eq. (50) noting that X_1^* and X_1' are very close together so that we may approximate $(1 - 0.761X_1)$ in the interval X^*_1 to X'_1 by $(1 - 0.761X^*_1)$. Hence Eq. (50) becomes

$$\frac{\Lambda}{\sqrt{2}}\, e^{-\theta'_2}(1-X^*_1) = (1-0.761X^*_1)\int_{X^*_1}^{X'_1}\frac{dX_1}{(1-X_1)^{3/2}} = 2(1-0.761X^*_1)\left[\frac{\sqrt{1-X^*_1}-\sqrt{1-X'_1}}{\sqrt{(1-X'_1)(1-X^*_1)}}\right]$$

or

$$\frac{\Lambda}{\sqrt{2}}\,\frac{e^{-\theta'_2}(1-X^*_1)^{3/2}}{(1-0.761X^*_1)} = 2\,\frac{\sqrt{1-X^*_1}-\sqrt{1-X'_1}}{\sqrt{1-X'_1}} \quad . \qquad (52)$$

From Eqs. (51) and (52) we now see that

$$2\sqrt{\frac{1-X^*_1}{1-X'_1}} - 2 = 1$$

or

$$\sqrt{\frac{1-X^*_1}{1-X'_1}} = \frac{3}{2}$$

whence

$$X^*_1 = \frac{9}{4}X'_1 - \frac{5}{4} \quad . \qquad (53)$$

The next step is to obtain an explicit expression for X'_1 from Eqs. (48) and (50). Equation (50) may be written in the form

$$\frac{\Lambda}{\sqrt{2}}\,\frac{e^{-\theta'_2}}{\theta'_2} = \frac{1}{\theta'_2(1-X^*_1)}\int_{X^*_1}^{X'_1}\frac{(1-0.761\,X_1)dX_1}{(1-X_1)^{3/2}} \qquad (54)$$

or, using Eq. (48),

$$\frac{(1-\theta_o)\displaystyle\int_0^{X'_1}\frac{(1-0.761X_1)dX_1}{(1-X_1)^{3/2}}}{\left[1-\dfrac{1\cdot 3}{(2\theta'_2)}+\dfrac{1\cdot 3\cdot 5}{(2\theta'_2)^2}-\dots\right]} = \frac{1}{\theta'_2(1-X^*_1)}\int_{X^*_1}^{X'_1}\frac{(1-0.761X_1)dX_1}{(1-X_1)^{3/2}} \quad .$$

Replacing X_1^* in terms of X_1' according to Eq. (53) in the preceding expression leads to the following explicit relation for X_1':

$$\frac{\left[1-\frac{1\cdot 3}{2\theta_2'}+\frac{1\cdot 3\cdot 5}{(2\theta_2')^2}-\ldots\right]}{\frac{9}{4}(1-X_1')\,\theta_2'}\int_{\frac{9}{4}X_1'-\frac{5}{4}}^{X_1'}\frac{(1-0.761X_1)}{(1-X_1)^{3/2}}\,dX_1=(1-\theta_o)\int_0^{X_1'}\frac{(1-0.761X_1)}{(1-X_1)^{3/2}}\,dX_1\,. \tag{55}$$

Integration of Eq. (55) leads to the following first approximation for X_1':

$$X_1' = 1-\frac{\left[1-\frac{1\cdot 3}{(2\theta_2')}+\frac{1\cdot 3\cdot 5}{(2\theta_2')^2}-\ldots\right]}{\frac{27}{4}\,\theta_2'\,(1-\theta_o)}\,. \tag{56}$$

Hence, from Eq. (53),

$$X_1^* \simeq 1-\frac{\left[1-\frac{1\cdot 3}{(2\theta_2')}+\frac{1\cdot 3\cdot 5}{(2\theta_2')^2}-\ldots\right]}{3\theta_2'\,(1-\theta_o)}\,, \tag{57}$$

and, from Eq. (49),

$$\theta^* \simeq 1-\frac{\left[1-\frac{1\cdot 3}{(2\theta_2')}+\frac{1\cdot 3\cdot 5}{(2\theta_2')^2}-\ldots\right]}{3\theta_2'} \tag{58}$$

Comparison of Eqs. (56) and (57) shows that X_1' and X_1^* are indeed so close together as to justify the approximation made in the derivation of Eq. (52).

In order to obtain a first approximation to $\Lambda e^{-\theta_2'}$ we proceed from Eq. (54) as follows:

$$\frac{\Lambda}{\sqrt{2}}\,e^{-\theta_2'}\simeq\frac{2(1-0.761X_1^*)}{1-X_1^*}\left[\frac{1}{\sqrt{1-X_1'}}-\frac{1}{\sqrt{1-X_1^*}}\right]$$

$$=\frac{1-0.761X_1^*}{(1-X_1^*)^{3/2}}=\frac{1-0.761(\frac{9}{4}X_1'-\frac{5}{4})}{\left[1-(\frac{9}{4}X_1'-\frac{5}{4})\right]^{3/2}}\;;$$

after replacing X_1' according to Eq. (56) it is found that

$$\frac{\Lambda}{\sqrt{2}}\, e^{-\theta_2'} = \frac{0.239+0.761\left[\dfrac{1-\dfrac{1\cdot 3}{(2\theta_2')}+\dfrac{1\cdot 3\cdot 5}{(2\theta_2')^2}-\dots}{3\theta_2'\,(1-\theta_o)}\right]}{\left\{\dfrac{\left[1-\dfrac{1\cdot 3}{(2\theta_2')}+\dfrac{1\cdot 3\cdot 5}{(2\theta_2')^2}-\dots\right]}{3\theta_2'\,(1-\theta_o)}\right\}^{3/2}} \,. \qquad (59)$$

Therefore, for the range of values of θ_2' actually encountered,

$$\Lambda e^{-\theta_2'} \simeq \sqrt{6}\;\sqrt{\theta_2'(1-\theta_o)}\;\left[0.761 + 0.717\;\theta_2'(1-\theta_o)\right] \qquad (59a)$$

from which the eigenvalue Λ for the stoichiometric mixture ratio can be calculated.

V. HYDROGEN-RICH MIXTURES

The mathematical technique which we have employed for stoichiometric mixtures can be used also to solve the boundary-value problem for hydrogen-rich mixtures. However, since the calculation is somewhat laborious, we follow another suggestion by Dr. von Kármán, according to which we test a more highly approximate procedure for mixtures containing 43.3°/o Br_2, for which the solutions become particularly simple. The success of the simplified procedure for mixtures containing 43.3°/o Br_2 gives us confidence in the results obtained for hydrogen-rich mixtures, in general, for which we utilize a method of calculation in which the limiting slope of the θ vs. X_1 curve does not have the correct value at the hot boundary.

A. The Mixture Containing 43.3°/o of Bromine

For mixtures containing 43.3°/o of Br_2 a considerable simplification is noted in the basic differential equation. For these mixtures $X_{1,f} = 2(1-a)$ and it is seen that

$$2a = \frac{1-a}{0.381}\ , \qquad 1-a = 0.433;$$

Equation (22) becomes, for $(\theta - 1)$ small compared to $(1-\theta_o)(1-X_1)$,

$$\frac{\left(1-a-\frac{X_1}{2}\right)^{3/2}}{0.381}\,\Lambda\theta^{-1/2}\,e^{-\theta_2'/\theta}\,\frac{d\theta}{dX_1} \simeq \frac{(1-\theta_o)\left(1-a-\frac{X_1}{2}\right)}{(1-a)}\ . \tag{60}$$

(1) Direct Integration of Eq. (60)

Without regard to the limiting slope at the hot boundary, we can integrate Eq. (60) directly with the result

$$\Lambda \int_{\theta_i}^{1} \frac{e^{-\theta_2'/\theta}}{\theta^{1/2}}\, d\theta = \frac{0.381(1-\theta_o)}{0.433} \int_{0}^{2(1-a)} \frac{dX_1}{\left(1-a-\frac{X_1}{2}\right)^{1/2}} \qquad (61)$$

since 1-a = 0.433. Hence

$$\frac{\Lambda e^{-\theta_2'}}{\theta_2'} \left[1 - \frac{1\cdot 3}{(2\theta_2')} + \frac{1\cdot 3\cdot 5}{(2\theta_2')^2} - \dots \right] = \frac{0.381(1-\theta_o)(-4)}{0.433} \sqrt{1-a-\frac{X_1}{2}}\,\Bigg]_{0}^{2(1-a)}$$

$$= 2.318(1-\theta_o)$$

and

$$\Lambda e^{-\theta_2'} = \frac{2.318(1-\theta_o)\,\theta_2'}{\left[1-\frac{1\cdot 3}{(2\theta_2')} + \frac{1\cdot 3\cdot 5}{(2\theta_2')^2} - \dots\right]} \;. \qquad (62)$$

The fact that Eq. (62) yields a fair approximation to the solution of the boundary-value problem will now be established by a more careful integration in which $d\theta/dX_1$ has its correct limiting value at the hot boundary. On the basis of this result, we shall integrate the flame equation for all hydrogen-rich mixtures directly in Section VB.

(2) Integration of Eq. (60) With the Correct Limiting Slope at the Hot Boundary

Integration of Eq. (60) from (θ^*, X_1^*) to (1, X_1') leads to the relation:

$$\Lambda \int_{\theta^*}^{1} \frac{e^{-\theta_2'/\theta}}{\theta^{1/2}}\, d\theta = (1-\theta_o)\left(\frac{0.381}{0.433}\right) \int_{X_1^*}^{X_1'} \frac{dX_1}{\left(1-a-\frac{X_1}{2}\right)^{1/2}} \quad . \tag{63}$$

For $\theta^* \simeq 1$

$$\Lambda e^{-\theta_2'}(1-\theta^*) = 0.880(1-\theta_o) \int_{X_1^*}^{X_1'} \frac{dX_1}{\left(1-a-\frac{X_1}{2}\right)^{1/2}} \quad . \tag{64}$$

If Eq. (63) holds from $(\theta_i, 0)$ to $(1, X_1')$, then

$$\Lambda \int_{\theta_i}^{1} \frac{e^{-\theta_2'}}{\theta^{1/2}}\, d\theta = 0.880\,(1-\theta_o) \int_{0}^{X_1'} \frac{dX_1}{\left(1-a-\frac{X_1}{2}\right)^{1/2}}$$

or

$$\frac{\Lambda e^{-\theta_2'}}{\theta_2'}\left[1-\frac{1\cdot 3}{(2\theta_2')}+\frac{1\cdot 3\cdot 5}{(2\theta_2')^2}-\dots\right] \simeq 0.880(1-\theta_o)\int_{0}^{X_1'} \frac{dX_1}{\left(1-a-\frac{X_1}{2}\right)^{1/2}} \quad . \tag{65}$$

We now join Eq. (64) to

$$\frac{d\theta}{dX_1} = \frac{1-\theta_o}{2(1-a)} \qquad \text{at} \quad (\theta_1^*, X_1^*) \ ,$$

since $d\theta/dX_1 = (1-\theta_o)/2(1-a)$ is the correct limiting slope obtained from Eq. (22). At $\theta = \theta^*$, $X_1 = X_1^*$:

$$\frac{1-\theta^*}{2(1-a)-X_1^*} = \frac{1-\theta_o}{2(1-a)} \tag{66}$$

and, from Eqs. (64) and (65),

$$\mathcal{A} e^{-\theta_2'} \frac{\left(1-a-\frac{X_1}{2}\right)}{(1-a)} = 0.880 \int_{X_1^*}^{X_1'} \frac{dX_1}{\left[(1-a)-\frac{X_1}{2}\right]^{1/2}} \quad . \qquad (67)$$

With

$$\frac{d\theta}{dX_1} \simeq \frac{(1-\theta_o)}{2(1-a)}$$

Eq. (60) becomes at (θ^*, X_1^*) for $\theta^* \simeq 1$:

$$\mathcal{A} e^{-\theta_2'} \frac{\left(1-a-\frac{X_1^*}{2}\right)^{1/2}}{2(1-a)} = 0.880 \quad . \qquad (68)$$

From Eq. (67)

$$\mathcal{A} e^{-\theta_2'} \frac{\left[2(1-a)-X^*\right]}{2(1-a)} = -3.520 \left\{ \left[(1-a)-\frac{X_1'}{2}\right]^{1/2} - \left[(1-a)-\frac{X_1^*}{2}\right]^{1/2} \right\} . \qquad (69)$$

But, from Eqs. (68) and (69):

$$\sqrt{2} \times 0.880 \left[2(1-a)-X_1^*\right]^{1/2} = 3.520 \left\{ \left[(1-a)-\frac{X_1^*}{2}\right]^{1/2} - \left[(1-a)-\frac{X_1'}{2}\right]^{1/2} \right\}$$

or

$$\left[(1-a)-\frac{X_1^*}{2}\right]^{1/2} - \left[(1-a)-\frac{X_1'}{2}\right]^{1/2} = \frac{1}{2}\left[(1-a) - \frac{X_1^*}{2}\right]^{1/2}$$

whence

$$\left(1-a-\frac{X_1'}{2}\right) = \frac{1}{4}\left(1-a-\frac{X_1^*}{2}\right) \quad . \qquad (70)$$

From Eq. (67):

$$\frac{\mathcal{A}\, e^{-\theta_2'}}{\theta_2'} = \frac{2(1-a)0.880}{\theta_2'[2(1-a)-X_1^*]} \int_{X_1^*}^{X_1'} \frac{dX_1}{\left[(1-a)-\frac{X_1}{2}\right]^{1/2}}$$

and, using Eq. (65),

$$\frac{0.880\,(1-\theta_o)}{\left[1-\frac{1\cdot 3}{(2\theta_2')}+\frac{1\cdot 3\cdot 5}{(2\theta_2')^2}-\cdots\right]} \int_0^{X_1'} \frac{dX_1}{\left[(1-a)-\frac{X_1}{2}\right]^{1/2}} = \frac{0.880(1-a)}{\theta_2'\left[1-a-\frac{X_1^*}{2}\right]} \int_{X_1^*}^{X_1'} \frac{dX_1}{\left[(1-a)-\frac{X_1}{2}\right]^{1/2}} \cdot$$

Thus

$$\frac{(1-a)\left[1-\frac{1\cdot 3}{(2\theta_2')}+\frac{1\cdot 3\cdot 5}{(2\theta_2')^2}-\cdots\right]}{(1-\theta_o)\,\theta_2'\left[(1-a)-\frac{X_1^*}{2}\right]} \left[\left(1-a-\frac{X_1^*}{2}\right)^{1/2}-\left(1-a-\frac{X_1'}{2}\right)^{1/2}\right] = \left[(1-a)^{1/2}-\left(1-a-\frac{X_1'}{2}\right)^{1/2}\right].$$

Using Eq. (70) to eliminate X_1', the preceding expression becomes

$$\frac{\frac{1}{2}(1-a)\left[1-\frac{1\cdot 3}{(2\theta_2')}+\frac{1\cdot 3\cdot 5}{(2\theta_2')^2}-\cdots\right]}{(1-\theta_o)\,\theta_2'\left[(1-a)-\frac{X_1^*}{2}\right]^{1/2}} = (1-a)^{1/2}-\frac{1}{2}\left(1-a-\frac{X_1^*}{2}\right)^{1/2}$$

which yields

$$\left(1-a-\frac{X_1^*}{2}\right)^{1/2} = (1-a)^{1/2}\left\{1-\left\{1-\frac{1}{(1-\theta_o)\theta_2'}\left[1-\frac{1\cdot 3}{(2\theta_2')}+\frac{1\cdot 3\cdot 5}{(2\theta_2')^2}\right]\right\}^{1/2}\right\} \cdot \tag{71}$$

Combining Eqs. (68) and (71), and noting that (1-a) = 0.433, we get

$$\mathcal{A} e^{-\theta_2'} = \frac{1.16}{1-\left\{1-\frac{1}{(1-\theta_o)\theta_2'}\left[1-\frac{1\cdot 3}{(2\theta_2')}+\frac{1\cdot 3\cdot 5}{(2\theta_2')^2}-\cdots\right]\right\}^{1/2}} \cdot \tag{72}$$

The fact that Eqs. (62) and (72) yield similar results can be seen by expanding the denominator of Eq. (72) for large values of $(1-\theta_o)\,\theta_2'$. In this manner it is found that

$$\Lambda e^{-\theta_2'} \simeq 2.32(1-\theta_o)\theta_2' \tag{72a}$$

which is seen to be practically identical with Eq. (62) for large values of θ_2'. On the basis of this result we are encouraged to integrate the basic differential equation for hydrogen-rich mixtures directly between $\theta_i, 0$ and $1, 2(1-a)$ after neglecting the term in $(\theta-1)$. Details concerning this work are described in the following Section VB.

V.B. Hydrogen-Rich Flames with Arbitrary Concentrations of Bromine

The result for the general case of hydrogen-rich flames is obtained most conveniently by using direct integration of the differential equation with the term in $(\theta-1)$ neglected. For hydrogen-rich flames $a > \frac{1}{2}$ and $X_{1,f} = 2(1-a)$. Equation (25) becomes

$$\Lambda \int_0^1 \frac{e^{-\theta_2'/\theta}}{\theta^{1/2}}\, d\theta = 0.381\sqrt{2}\,\frac{(1-\theta_o)}{1-a}\int_0^{2(1-a)} \frac{\left[\frac{1-a}{0.381} - X_1\right] dX_1}{(2a-X_1)\left[2(1-a)-X_1\right]^{1/2}}. \tag{73}$$

But

$$\int_0^{2(1-a)} \frac{\left[\frac{1-a}{0.381} - X_1\right] dX_1}{(2a-X_1)\left[2(1-a)-X_1\right]^{1/2}} = \int_{4a-2}^{2a} \frac{\left[\frac{1-1.762a}{0.381} + y\right] dy}{y\sqrt{y-(4a-2)}}$$

$$= \frac{1.1762a}{0.381}\int_{4a-2}^{2a}\frac{dy}{y\sqrt{y-(4a-2)}} + \int_{4a-2}^{2a}\frac{dy}{\sqrt{y-(4a-2)}}$$

or

$$\int_0^{2(1-a)} \frac{\left[\frac{1-a}{0.381} - X_1\right] dX_1}{(2a-X_1)\left[2(1-a)-X_1\right]^{1/2}} = \left[\frac{1-1.762a}{0.381}\right]\frac{2}{\sqrt{4a-2}}\left[\cos^{-1}\left(\sqrt{\frac{2a-1}{a}}\right)\right] + 2\sqrt{2-2a}$$

and Eq. (73) becomes

$$\Lambda\int_0^1 \frac{e^{-\theta_2'/\theta}}{\sqrt{\theta}}\, d\theta = \left[\sqrt{2}\times 0.381\,\frac{(1-\theta_o)}{(1-a)}\right] \times$$

$$\left[\frac{1-1.762a}{0.381}\,\frac{2}{\sqrt{4a-2}}\,\cos^{-1}\left(\frac{\sqrt{2a-1}}{a}\right) + 2\sqrt{2-2a}\right]. \quad (74)$$

Since θ_o is not a sensitive function of a we shall treat it as a constant. Then

$$\Lambda\int_0^1 \frac{e^{-\theta_2'/\theta}}{\sqrt{\theta}}\, d\theta = 0.539(1-\theta_o)\, g(a) \qquad (74a)$$

where g(a) is defined as

$$g(a) \equiv \frac{1}{1-a}\left[\frac{1-1.762a}{0.381}\,\frac{2}{\sqrt{4a-2}}\,\cos^{-1}\left(\sqrt{\frac{2a-1}{a}}\right) + 2\sqrt{2-2a}\right]. \qquad (75)$$

Finally, integration of Eq. (74a) yields the result

$$\Lambda e^{-\theta_2'} \simeq \frac{0.539\,(1-\theta_0)\,\theta_2'\,g(a)}{\left[1-\frac{1\cdot 3}{(2\theta_2')}+\frac{1\cdot 3\cdot 5}{(2\theta_2')^2}-\ldots\right]} \qquad (76)$$

from which the eigenvalue Λ for hydrogen-rich mixtures can be calculated. For $(1-a) = 0.433$, $1.762a = 1$, and Eqs. (75) and (76) reduce, of course, to Eq. (62).

We have now obtained analytic expressions for $\Lambda e^{-\theta_2'}$ for all possible hydrogen-bromine mixtures. Before summarizing the basic expressions for the laminar burning velocity, we proceed to consider the relevant physico-chemical parameters which must be used in order to obtain numerical results.

VI. PHYSICO-CHEMICAL PARAMETERS

A. Equilibrium Constant for the Reaction $Br_2 \rightleftarrows 2Br$

The value of the equilibrium constant K_p (i.e., of the equilibrium constant expressed in terms of partial pressure ratios) for the bromine molecule-bromine atom system have been taken from the Bureau of Standards compilation(13) which covers the temperature range between 298°K and 1500°K. Equilibrium constants at 1600°K and 1700°K were obtained by extrapolation of the Bureau of Standards data. Equilibrium constants as a function of temperature are summarized in Table I.

The data given in Table I have been fitted to an expression of the form

$$K_p = BTe^{-A/RT}$$

by plotting $\log(K_p/T)$ vs. $(1/T)$. The plot is shown in Fig. 1. Appropriate numerical values derived from Fig. 1 are

$$A = 45,210 \text{ cal./mole} \qquad \text{and } B = 230.5 \text{ atmos./}^{\circ}\text{K}.$$

The equilibrium constant K_c, expressed in terms of concentration ratios, for the reaction

$$Br_2 \rightleftarrows 2Br,$$

is related to K_p through the expression $K_c = K_p/RT$. Hence it follows that

$$K_c = \frac{230.5T}{82.07T} e^{-45,210/RT}$$

$$= 2.808\, e^{-45,210/RT} \text{ moles/cm}^3$$

if concentrations are expressed in moles/cm^3. But

$$K_c = k_1/k_5$$

where k_1 and k_5 are the specific reaction rate constants for the processes described in Eqs. (1) and (5), respectively.

In terms of the parameters needed for the calculation of laminar burning velocities we find, therefore, that

$$B_1/B_5 = 2.808 \text{ moles}/\text{cm}^3 \qquad (77)$$

and

$$\theta_1 = 45,210/RT_f. \qquad (78)$$

B. The Specific Reaction-Rate Constant for the Reaction Between Br and H_2

The specific reaction-rate constant for the process

$$Br + H_2 \xrightarrow{k_2} HBr + H$$

is based on careful experimental studies carried out by Bodenstein and Lind.$^{(14)}$ The experimental results have been re-evaluated by Pease$^{(12)}$ who finds that

$$k_2 = 4.56 \times 10^{12}\sqrt{T}\, e^{-18,780/RT} \text{ cm}^3/(\text{mole-sec}), \qquad (79)$$

whence

$$B_2 = 4.56 \times 10^{12} \sqrt{T_f} \quad \text{cm}^3/(\text{mole-sec}).$$

We shall utilize Eq. (79) for the specific reaction-rate constant k_2 in preference to slightly different forms proposed by other investigators.$^{(6,7)}$ However, it is important to note that alternate correlations of the available experimental data lead to greatly different predicted values for k_2 at elevated temperatures. Thus Hirschfelder and his collaborators$^{(6)}$ recommend the relation

$$k_2 = 3.45 \times 10^{10}\, T\, e^{-16,640/RT} \text{cm}^3/(\text{mole-sec}). \qquad (79a)$$

A comparison of the calculated values of k_2 determined from Eqs. (79) and (79a) is shown in Table II for the temperature range which is of interest in connection with calculations of laminar burning velocities for H_2-Br_2 mixtures. Reference to Table II shows, for example, that the values of k_2 calculated from Eq. (79) at 1500°K could be too large by roughly a factor of 1.7. Hence the laminar burning velocities, which vary as the square root of k_2, could be too large by perhaps a factor of 1.3.

C. Ratio of the Reaction Rates k_4/k_3 for the Removal of Hydrogen Atoms

The ratio of the reaction rates k_4/k_3 for the removal of H-atoms according to the processes

$$H+Br_2 \xrightarrow{k_3} HBr + Br$$

and

$$H+HBr \xrightarrow{k_4} H_2 + Br$$

is again based on the experimental work of Bodenstein and Lind$^{(14)}$ and Bodenstein and Jung.$^{(15)}$ The value

$$k_4/k_3 = 1/8.4 \tag{80}$$

does not vary with temperature over the relatively narrow temperature range for which experimental measurements are made. We assume that this result can be extrapolated from about 600°K to temperatures as high as 1700°K. Since the activation energies for the reactions (3) and (4) are probably very small, this extrapolation should not introduce a large error even if the activation energies for reactions (3) and (4) are not identical.

D. The Adiabatic Flame Temperatures and Equilibrium Compositions for H_2-Br_2 Mixtures

Adiabatic flame temperatures and equilibrium compositions have been determined by the use of standard procedures.(16) The results for T_f as a function of composition of the gas mixture are plotted in Fig. 2.; the equilibrium mole fractions of HBr, H_2, Br_2, and Br as a function of composition are shown in Fig. 3. Relevant numerical values are summarized in Table III.

E. Thermal Conductivities in H_2-Br_2 Mixtures

Values of λ_f as a function of composition for H_2-Br_2 mixtures have been calculated by Cooley and Anderson(5) on the basis of the elementary kinetic theory of gases, which does not include proper allowance for the influence on thermal conductivity of energy transfer between internal and translational degrees of freedom. The results of Cooley and Anderson, which represent lower limits for the thermal conductivities, are summarized in Fig. 4, where we have plotted λ_f as a function of composition. Reference to Fig. 4 shows that λ_f increases slightly with T_f and more rapidly with the concentration of H_2 in the gas mixture.

Actually the problem of estimating appropriate thermal conduction coefficients is greatly complicated for flames by the inevitable composition changes occurring during reaction. Campbell and Hirschfelder(6) propose a relation of the form

$$\lambda = \lambda' + \lambda'' T, \tag{81}$$

where both λ' and λ'' are parameters which must be determined separately for each gas mixture. Our formulation of the problem of flame propagation does not permit the use of this two-parameter expression for λ without a complete recalculation of the results, because of the change in the assumed temperature dependence of λ. In view of the crudeness of the approximations for λ , we do not feel that the additional labor is warranted. For this reason we have used the following relation$^{(16)}$ for the thermal conductivity of a mixture of species i and j:

$$\lambda_f = \lambda_{\mathrm{mixture}}(T_f) = \frac{1}{2}\left[\lambda_i X_i + \lambda_j X_j + \frac{\lambda_i \lambda_j}{(X_i\sqrt{\lambda_j} + X_j\sqrt{\lambda_i})^2}\right] . \qquad (82)$$

Equation (82) yields reasonable results for binary mixtures in which the pure components have greatly different thermal conductivities. Thus Eq. (82) is particularly well suited for making estimates of λ_f in hydrogen-rich flames. In order to calculate the thermal conductivities of the pure components, we utilize the following relations proposed by Campbell and Hirschfelder,$^{(6)}$ and neglect again the contributions of Br and H at T_f to the thermal conductivity:

$$\lambda H_2(T_f) = 5.13 \times 10^{-4}\sqrt{\frac{T_f}{373}} , \qquad (83)$$

$$\lambda Br_2(T_f) = 1.20 \times 10^{-5}\sqrt{\frac{T_f}{373}} , \qquad (84)$$

$$\lambda HBr(T_f) = \frac{6.08 \times 10^{-6}\sqrt{T_f}}{1 + \frac{1.275 \times 10^3}{T_f}} \qquad (85)$$

where λ_f is expressed in cal/(cm sec ^{o}K).

Numerical values for λ_f as a function of mixture ratio are given in Table IV and are plotted in Fig. 4 as a function of composition.

It should be noted that our method for calculating λ_f

emphasizes the numerical values at temperatures close to T_f. This procedure receives partial support through the well-known result that most of the chemical reactions in a flame occur at temperatures close to T_f.

F. The Average Specific Heat

A more exact expression for the average specific heat than was used in the derivation of Eq. (14) can be obtained from Eq. (13), viz.,

$$\overline{c}_p = \frac{-1}{T_f(1-\theta_o)}\left[\frac{W_1}{\overline{W}}X_{1,f}h_1^o + \frac{W_2}{\overline{W}}(X_{2,f}-X_{2,o})h_2^o + \frac{W_4}{\overline{W}}X_{4,f}h_4^o + \frac{W_5}{\overline{W}}X_{5,f}h_5^o\right] \qquad (85)$$

since $X_{1,o} = X_{4,o} = X_{5,o} = 0$ and $h_3^o = 0$ if the subscripts 4 and 5 identify, respectively, the species H and Br. Although the contributions of H and Br are small, they have been included in Eq. (85). Average specific heats as a function of composition have been calculated both with and without allowance for dissociation into hydrogen and bromine atoms. The results are listed in Table V. Reference to the data given in Table V shows that the influence of the atomic species on the average specific heat is negligibly small except for near-stoichiometric mixtures.

If dissociation into atoms is neglected, then simple explicit relations can be obtained for the average specific heats. After introduction of appropriate numerical values* the following relations are obtained:

for $X_{1,f} = 2a$, $X_{2,f} - X_{2,o} = (1-2a)-(1-a) = -a$, i.e., for $a \lesssim \frac{1}{2}$,

$$\overline{c}_p = \frac{2.466 \times 10^4 a}{(159.8-157.8a)T_f(1-\theta_o)} ; \qquad (86)$$

---

*Appropriate numerical values are

$$W_1\, h_1^o = -8660 \text{ cal/mole and } W_2\, h_2^o = 7340 \text{ cal/mole}^{(13)}$$

for $X_{1,f} = 2(1-a)$, $X_{2,f} - X_{2,o} = -(1-a)$, i.e., for $a \geqslant \frac{1}{2}$,

$$\bar{c}_p = \frac{2.466 \times 10^4 (1-a)}{(159.8 - 157.8a)T_f(1-\theta_o)} \quad , \tag{87}$$

since

$$\overline{W} = 2.016a + 159.8(1-a) = 159.8 - 157.8a.$$

The values of $\bar{c}_p$ calculated from Eqs. (86) and (87) are plotted in Fig. 5.

VII. COMPARISON OF CALCULATED AND OBSERVED BURNING VELOCITIES

In order to calculate the laminar burning velocity as a function of mixture ratio, it is convenient to summarize first the relevant theoretical relations.

The laminar burning velocity $\underline{u}_o$ is given in terms of the parameter Λ through the basic relation expressed in Eq. (21), viz.,

$$u_o = \frac{m}{\rho_o} = \frac{RT_o}{p} \sqrt{\frac{\lambda_f}{\Lambda(\bar{c}_p \overline{W})} B_2 \left(\frac{B_1}{B_5}\right)^{1/2} \left(\frac{p}{RT_f}\right)^{3/2}} \quad . \tag{88}$$

Introduction of appropriate numerical values for B_2, B_1/B_5, and R for p = 1 atmos. leads to the relation

$$u_o = 8.31 \times 10^6 \sqrt{\frac{\lambda_f T_o}{\bar{c}_p \overline{W}}} \, \theta_o \quad \text{cm/sec} \tag{89}$$

if $\overline{W}$ is expressed in g/mole, λ_f in cal/cm sec °K, T_o in °K, $\bar{c}_p$ in cal/g °K, and T_f in °K.

For the eigenvalue $\Lambda e^{-\theta'_2}$ we have obtained in Sections III, IV, and V the relations listed below.

<u>Bromine-Rich Mixtures ($a < \frac{1}{2}$, $X_{1,f} = 2a$):</u>

$$\Lambda e^{-\theta'_2} \simeq \frac{(1-\theta_o)\theta'_2 \left[\frac{5.15a-2.10}{\sqrt{1-2a}} + \frac{2.10(1-a)}{\sqrt{1-a}}\right]}{2a\left[1 - \frac{1 \cdot 3}{(2\theta'_2)} + \frac{1 \cdot 3 \cdot 5}{(2\theta'_2)^2} - \cdots\right]} - \frac{(1-1.762a)}{(1-2a)^{3/2}} \quad . \tag{43}$$

<u>Stoichiometric Mixtures ($a = \frac{1}{2}$, $X_{1,f} = 1$):</u>

$$\Lambda e^{-\theta'_2} \simeq \sqrt{2}\, \frac{\left\{0.239 + 0.761\, \frac{\left[1 - \frac{1.3}{(2\theta'_2)} + \frac{1 \cdot 3 \cdot 5}{(2\theta'_2)^2} - \cdots\right]}{3\theta'_2(1-\theta_o)}\right\}}{\left\{\frac{\left[1 - \frac{1.3}{(2\theta'_2)} + \frac{1 \cdot 3 \cdot 5}{(2\theta'_2)^2} - \cdots\right]}{3\theta'_2(1-\theta_o)}\right\}^{3/2}} \tag{59}$$

$$\simeq \sqrt{6\,\theta_2'(1-\theta_o)}\left[0.761 + 0.717\theta_2'(1-\theta_o)\right] . \tag{59a}$$

Hydrogen-Rich Mixtures for $2a = 1-a/0.381$, $X_{1,f} = 2(1-a)$:

$$\Lambda e^{-\theta_2'} \simeq \frac{2.32\,(1-\theta_o)\theta_2'}{\left[1 - \frac{1\cdot 3}{(2\theta_2')} + \frac{1\cdot 3\cdot 5}{(2\theta_2')^2} - \dots\right]} \tag{62}$$

or, in somewhat better approximation,

$$\Lambda e^{-\theta_2'} = \frac{1.16}{1 - \left\{1 - \frac{1}{(1-\theta_o)\theta_2'}\left[1 - \frac{1\cdot 3}{(2\theta_2')} + \frac{1\cdot 3\cdot 5}{(2\theta_2')^2} - \dots\right]\right\}^{1/2}} \tag{72}$$

Hydrogen-Rich Mixtures ($a > \frac{1}{2}$, $X_{1,f} = 2-2a$):

$$\Lambda e^{-\theta_2'} = \frac{0.539\,\frac{\theta_2'(1-\theta_o)}{(1-a)}}{\left[1 - \frac{1\cdot 3}{(2\theta_2')} + \frac{1\cdot 3\cdot 5}{(2\theta_2')^2} - \dots\right]}\left[\frac{1-1.762a}{0.381(a-\frac{1}{2})^{1/2}}\cos^{-1}\left(\sqrt{\frac{2a-1}{a}}\right) + 2\sqrt{2-2a}\right] . \tag{76}$$

Explicit relations for $\underline{u}_o$ can be obtained readily by combining Eq. (89) with Eqs. (43), (59), (72) and (76).

Laminar burning velocities as a function of mixture composition, computed by use of the preceding relations, are plotted in Fig. 6 and recorded in Table VI. The data shown in Fig. 6 and Table VI correspond to the two extreme sets of values of thermal conductivity discussed in Section VI. E. Also plotted in Fig. 6 are the experimentally determined values for the laminar burning velocity reported by Anderson and his collaborators.

Reference to Fig. 6 shows that the calculated values for the burning velocity are appreciably larger than the observed results. Although laminar burning velocities determined from Bunsen burner experiments are notably unreliable, it appears likely that the major source of the discrepancy between theory and experiment is the result of uncertainties in the chemical kinetics data and in the thermal conductivities used in our calculations. For example, on the basis of the ratios of rate constants listed in Table II, it is not unreasonable to reduce the largest calculated values of the burning velocities by as much as a factor of 1.3, thereby producing much better agreement between theory and experiment than is indicated in Fig. 6. Furthermore, our calculations are based on the steady-state approximation for hydrogen and bromine atoms. We neglect, therefore, the influence of diffusion. It is well-known that the effect of diffusion on burning velocity is to decrease the burning velocity.(9) Finally, it has been demonstrated that the steady-state approximation for bromine atoms cannot apply exactly at elevated temperatures for the bromine-rich and near-stoichiometric mixture compositions. Details concerning the corrections required because of failure of the steady-state approximation for Br- atoms have been worked out by von Kármán and Millán and will not be given here.

In spite of the discrepancies noted for the absolute values of calculated and observed burning velocities, it is evident that the calculated burning velocities have the correct functional dependence on composition. This result gives us confidence that, except for the questionable approximation concerning the steady-state approximation for Br- atoms, we have a valid first approximation to the physico-chemical processes occurring in a hydrogen-bromine flame.

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Table I. Logarithm of the equilibrium constants K_p, for the reaction $Br_2 \rightleftharpoons 2Br$, as a function of temperature, taken from reference 13

$T(^{o}K)$	$-\log K_p$ (p in atmos.)
298.16	28.318
300	28.110
400	19.7096
500	14.6528
600	11.2754
700	8.8570
800	7.0392
900	5.6220
1000	4.4858
1100	3.5536
1200	2.7746
1300	2.1136
1400	1.5454
1500	1.0512
1600	.5730
1700	.0175

Table II. The ratio of reaction rates, k_2, calculated from Eqs. (79) and (79a) as a function of temperature

T (^{o}K)	k2 from Eq. (79)/k2 from Eq. (79a)
500	.69
600	.91
1000	1.42
1500	1.67
1700	1.72

Table III. Adiabatic flame temperatures and equilibrium mole fractions as a function of composition (p = 1 atmos. T_o = 323 °K, a = initial mole fraction of H_2)

1-a	T_f(°K)	$X_{HBr,f}$	$X_{H_{2},f}$	$X_{Br_{2},f}$	$X_{H,f}$	$X_{Br,f}$
.1	675	.20	.80	----	----	----
.2	1014	.40	.60	8.0×10^{-5}	----	----
.3	1324	.60	.40	----	----	----
.4	1585	.79	.21	1.6×10^{-4}	2.5×10^{-5}	7.3×10^{-3}
.5	1683	.95	2.7×10^{-2}	2.9×10^{-3}	2.2×10^{-5}	4.9×10^{-2}
.57	1475	.86	3.5×10^{-4}	.085	3.3×10^{-7}	7.9×10^{-2}
.6	1395	.80	7.6×10^{-5}	.162	4.3×10^{-8}	6.0×10^{-2}
.7	1182	.60	7.1×10^{-6}	.378	1.2×10^{-9}	3.4×10^{-2}
.8	923	.40	----	.60	----	----
.9	725	.20	----	.80	----	----

Table IV. Thermal conductivities λ_f as a function of composition, calculated from the empirical relation given in Eq. (82) and based on the data of Campbell and Hirschfelder (6)

1-a	$\lambda_f \times 10^{+5}$ (cal/cm sec °K)
0.1	43.2
0.2	39.6
0.3	33.1
0.4	25.0
0.5	14.1
0.6	8.8
0.7	6.0
0.8	3.6
0.9	2.3

Table V. Average specific heat $\bar{c}_p$ as a function of composition for the H_2-Br_2 flames

1-a	$\bar{c}_p$(cal/g °K)(dissociation neglected)*	$\bar{c}_p$(cal/g °K)**
0.1	0.394	.394
0.2	0.213	.213
0.3	0.151	.151
0.4	0.119	.116
0.433	0.116	.114
0.5	0.112	.098
0.6	0.095	.076
0.7	0.071	.065
0.8	0.064	.064
0.9	0.043	.043

*Calculated from Eqs. (86) and (87)

**Calculated from Eq. (85)

Table VI. Calculated laminar burning velocities, u_o, for H_2-Br_2 flames as a function of mixture composition

1-a	u_o(cm/sec)*	u_o(cm/sec)**
0.1	0.13	0.27
0.2	3.18	6.9
0.3	22.7	52.0
0.4	57.5	121
0.433	61.0	122
0.5	45.5	70.2
0.6	23.9	31.9
0.7	9.75	12.2
0.8	0.48	0.56
0.9	0.020	0.027

*Based on the thermal conductivity data of Cooley and Anderson.(5)

**Based on thermal conductivities calculated from Eq. (82) and the data of Campbell and Hirschfelder.(6)

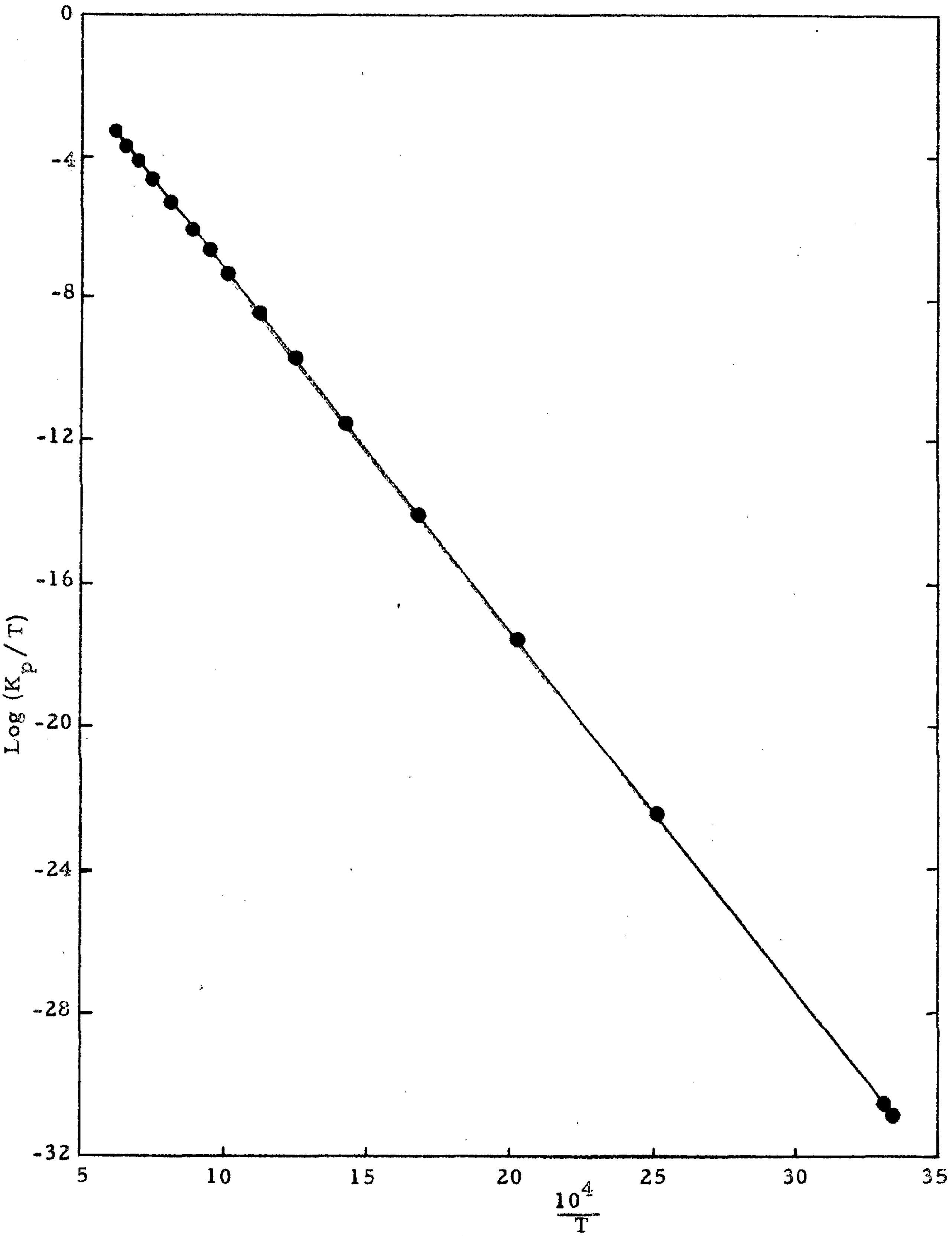

Fig. 1 Plot of log (K_p/T) vs. $10^4/T$ for the reaction $Br_2 \rightleftarrows 2Br$, where K_p is expressed in atmos.; data taken from Bureau of Standards.(13)

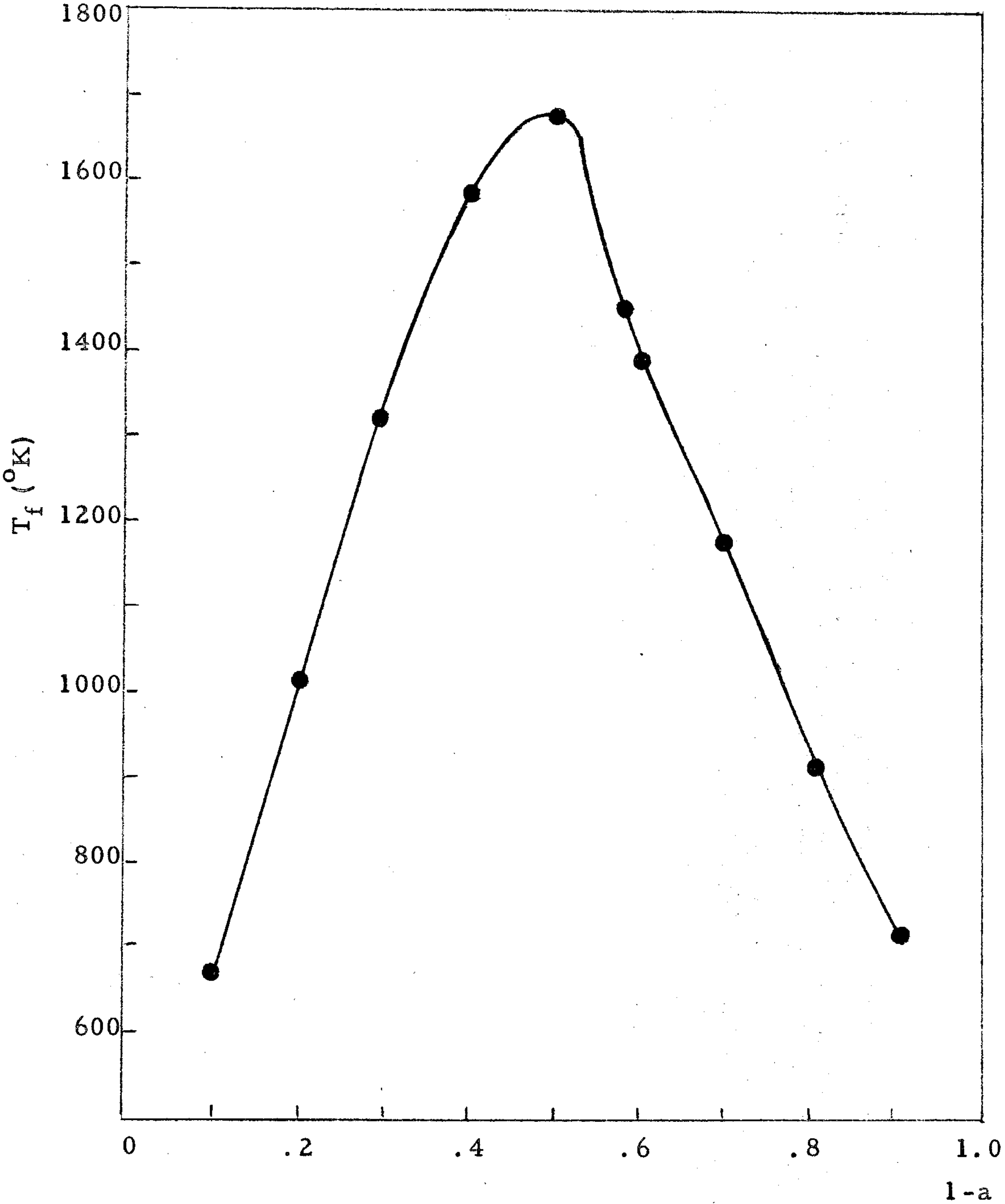

Fig. 2 Adiabatic flame temperature T_f as a function of composition for H_2-Br_2 mixtures (p = 1 atmos., T_o = 323°K)

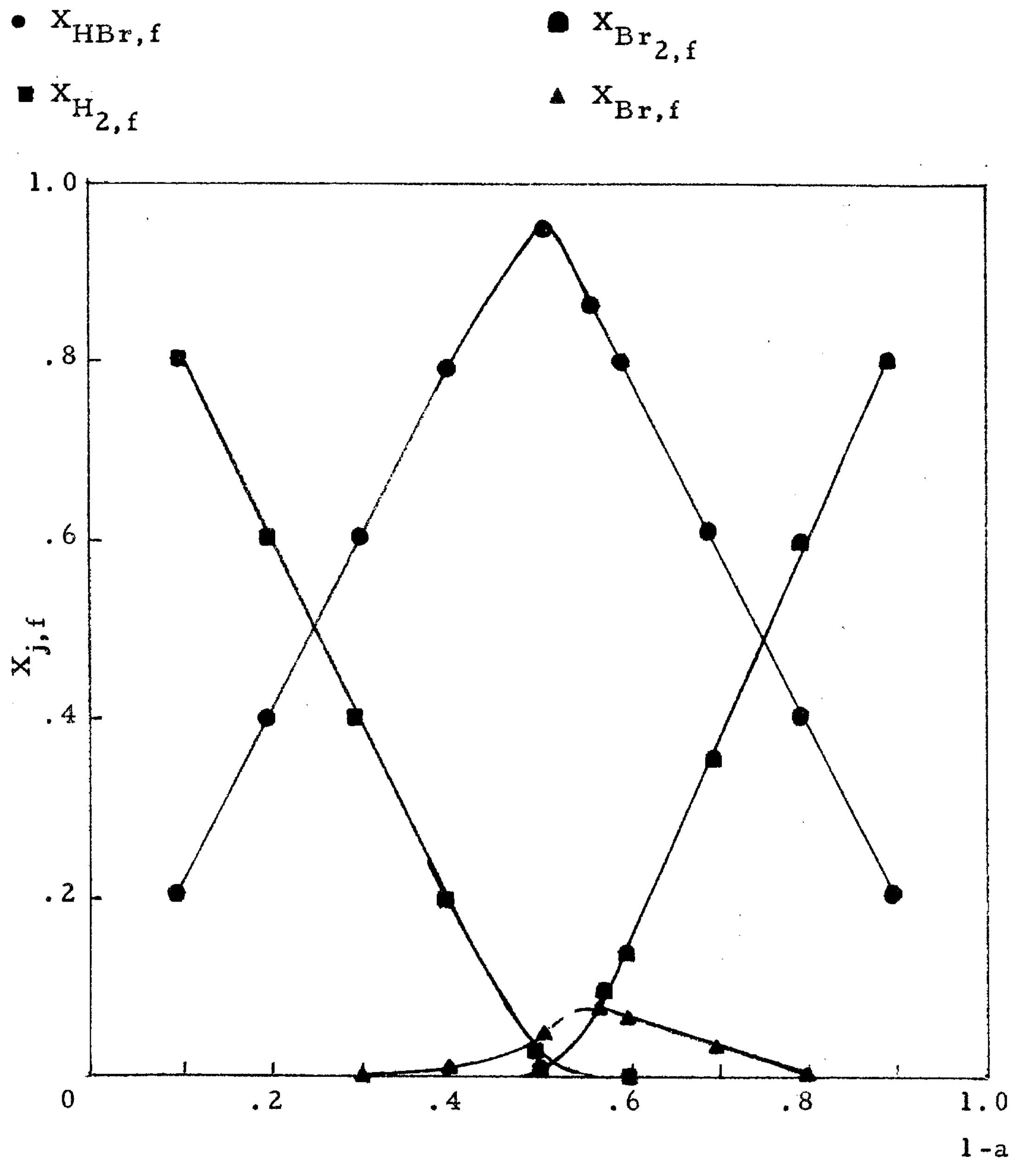

Fig. 3 Equilibrium mole fractions as a function of gas composition for H_2-Br_2 mixtures (p = 1 atmos., T_o = 323°K). The values of $X_{H,f}$ are so small that they cannot be shown on this plot (see Table III for data on $X_{H,f}$).

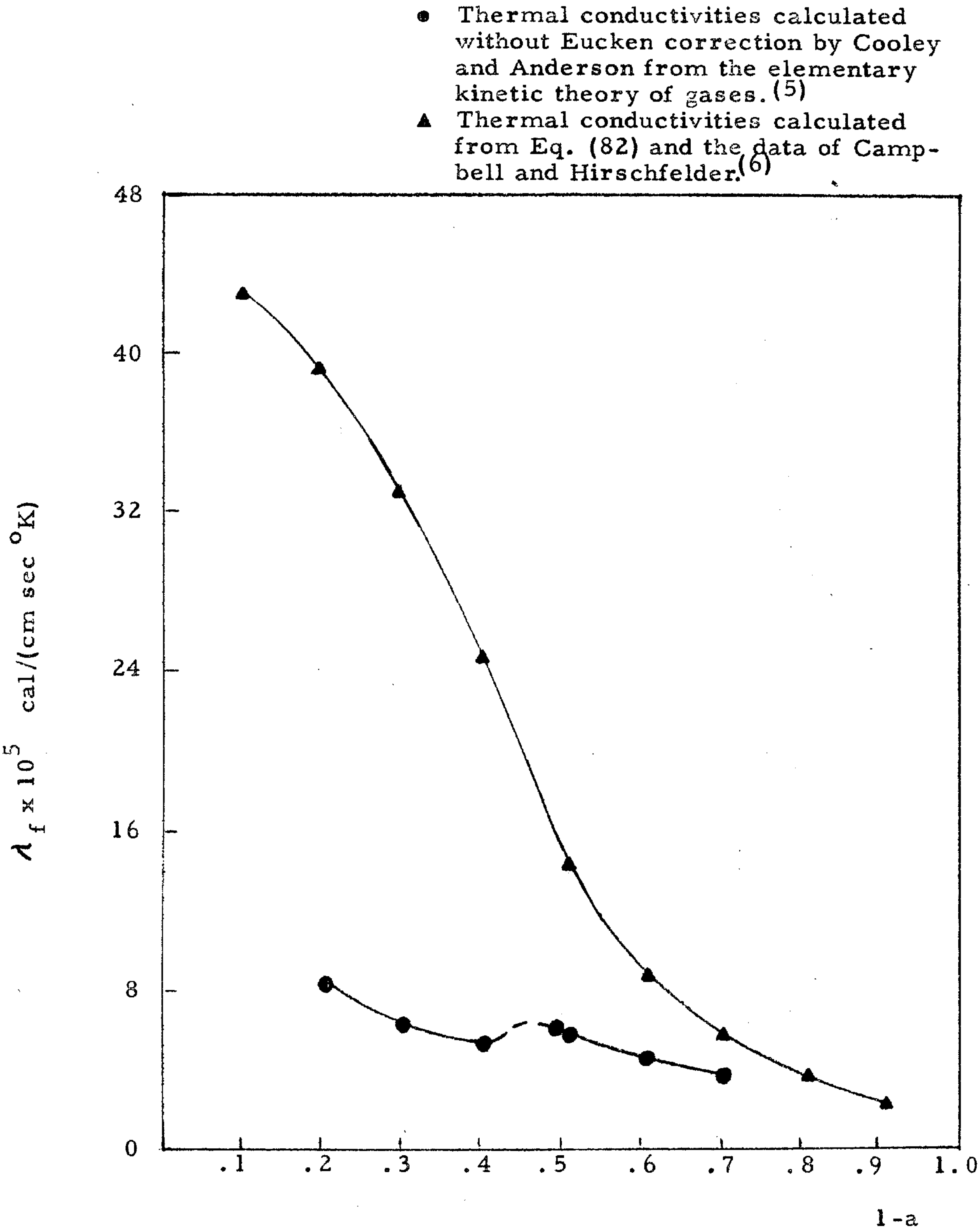

Fig. 4 The thermal conductivity λ_f as a function of mixture composition for H_2-Br_2 flames.

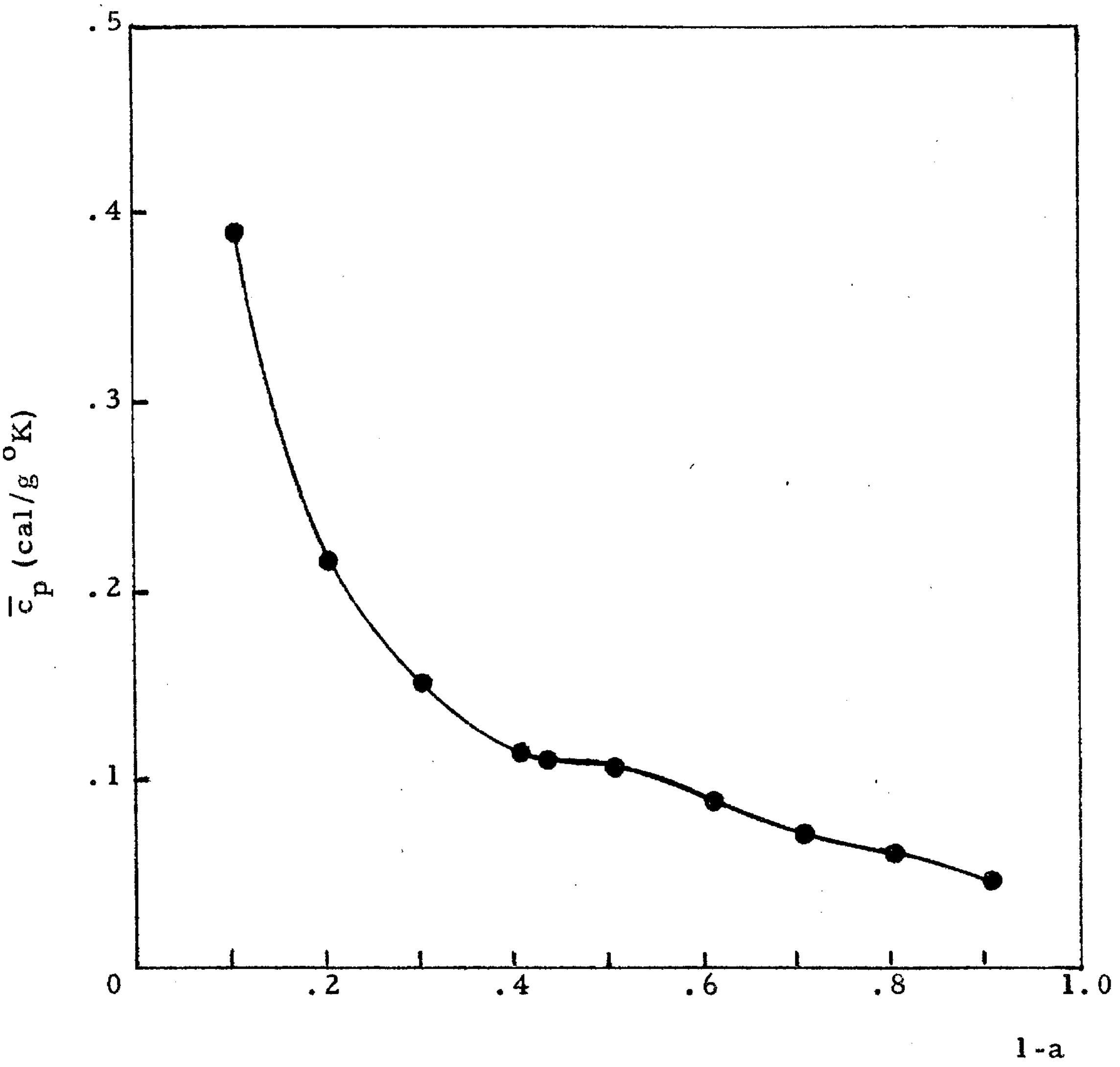

Fig. 5 Average specified heat $\overline{c}_p$ as a function of composition for the H_2-Br_2 flame (p = 1 atmos., T_o = 323 °K). The effect of dissociation on $\overline{c}_p$ has been neglected.

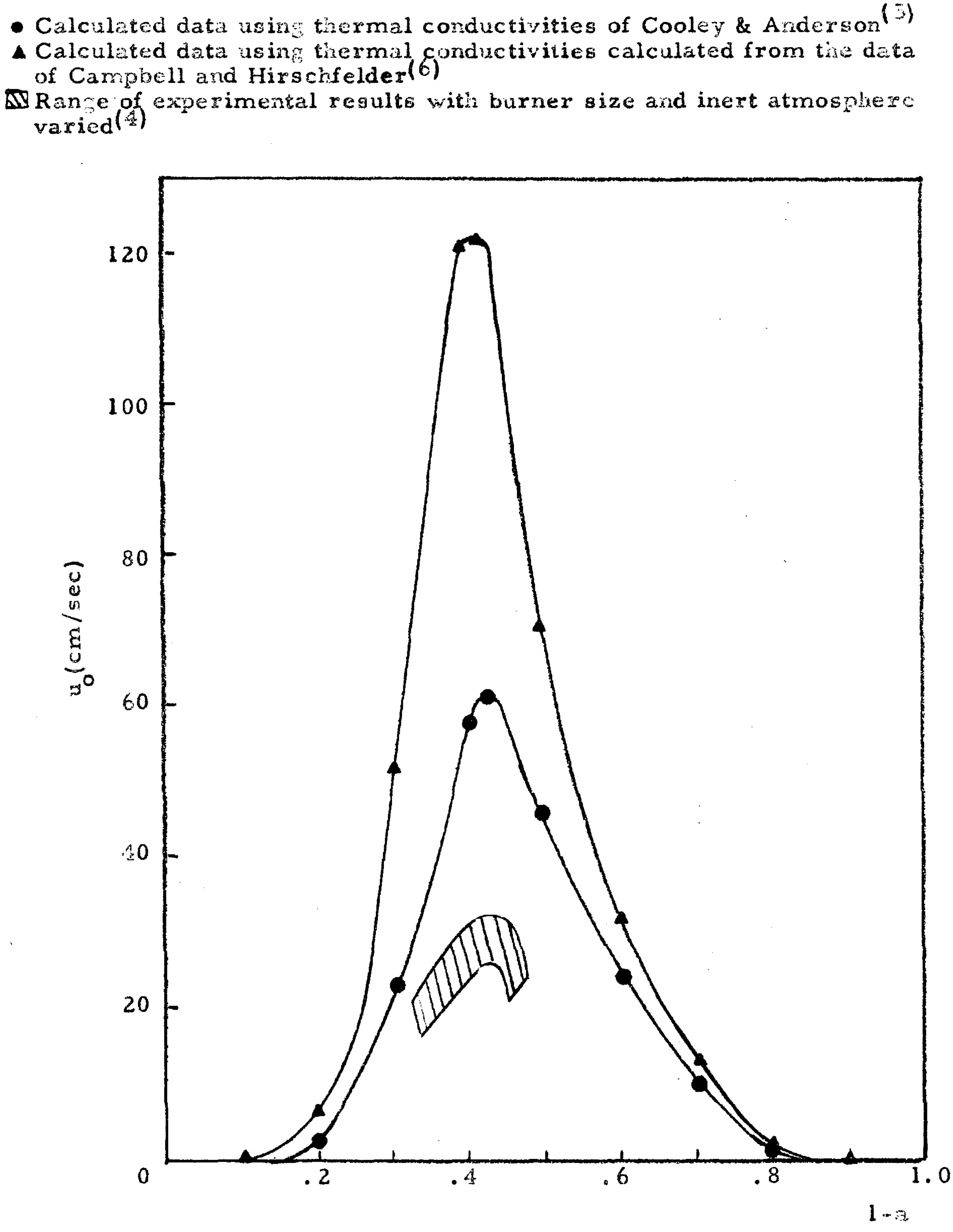

Fig. 6 Comparison of observed and calculated values for the laminar burning velocity in H_2-Br_2 mixtures.