Structure and Propagation of Laminar Flames

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THE PRESENT STATUS OF THE THEORY OF LAMINAR FLAME PROPAGATION

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1. Formulation of the Problem

There seems to be general agreement between the scientific workers engaged in the theory of laminar flame propagation that the theory shall be based on the application of the equations of conservation of mass, momentum and energy to a one-dimensional flow of a mixture which is unburned at the "cold boundary" and approaches an equilibrium state at the "hot boundary." It is assumed that the flow can be considered as that of a continuous gas, that chemical kinetics furnishes the necessary expressions for the quantities entering into the conservation equations due to chemical changes, and finally that the transfer phenomena are determined by full knowledge of the heat transfer coefficient and the laws of diffusion.

We have to satisfy the equations for the conservation of matter and energy. The law of conservation of momentum is taken care of by the assumption that pressure variations can be neglected.

The conservation of total mass requires for a one-dimensional flow that

$$\rho v = m \tag{1}$$

where m is the constant mass flow per unit cross-sectional area.

The continuity equation for the species, j, requires that

$$m \frac{d\epsilon_j}{dx} = w_j \tag{2}$$

where w_j is the mass rate of production per unit volume of the species, j.

The rate of production can be expressed in terms of the specific reaction rates, k_r, of the individual reactions in which the species j participates, and in terms of the stoichiometric co-

efficients ν'_{jr} and ν''_{jr} for the forward and backward reactions, respectively, in the following way:

$$w_j = M_j \sum_r (\nu''_{jr} - \nu'_{jr}) k_r \left(\frac{p}{RT}\right)^{n_r} \prod_{i=1}^{s} (X_i)^{\nu'_r} \tag{3}$$

where the exponent $n_r = \sum_{i=1}^{s} \nu'_{ir}$. The preceding formula follows from the law of mass action.

For the specific rate of reaction, we write the semitheoretical equation:

$$k_r = B_r \left(\frac{T}{T_f}\right)^{\alpha_r} \exp\left(-\frac{A_r}{RT}\right) \tag{4}$$

The quantity A_r is called the activation energy, the factor $B_r \left(\frac{T}{T_f}\right)^{\alpha_r}$ the frequency factor.

The diffusion equations express the relation between the fractional mass flow rate ϵ_j and the weight ratio Y_j of the species j in the form

$$\epsilon_j = Y_j \left(1 + \frac{V_j}{v}\right) \tag{5}$$

Following Curtiss and Hirschfelder,[1] we use the expression for the diffusion stream in terms of the binary diffusion coefficients, D_{jk}, viz.,

$$\frac{dX_j}{dx} = \frac{m}{c_t} \sum_k \frac{1}{D_{jk}} \left(X_j \frac{\epsilon_k}{M_k} - X_k \frac{\epsilon_j}{M_j}\right) \tag{6}$$

Finally, the equation for the conservation of energy reads:

$$\frac{\lambda}{m_h \overline{C}_p} \frac{dT}{dx} = T - T_f + \sum_j (\epsilon_j - \epsilon_{jf}) \frac{h_j^0}{\overline{C}_p} \tag{7}$$

where ϵ_{jf} is the final value of the mass flow ratio ϵ_j.

It is seen that the last equation enables us to eliminate the space coordinate, x, and for a reaction scheme involving s species, one has to deter-

mine $2(s - 1)$ dependent variables ϵ_j and x_j as functions of the independent variable, T. The remaining variables, ϵ_s and X_s, are determined by the conditions that the algebraic sum of the ϵ_j and X_j must be equal to unity.

However, we have to satisfy $2(s\text{-}1)$ boundary conditions for the ϵ_j and X_j at $T = T_0$ and $T = T_f$. The values of the ϵ_j and X_j for $T = T_0$ are given by the initial state of the unburned gas and the values for $T = T_f$ by the chemical equilibrium between the products. Therefore, it is seen that the boundary conditions cannot be satisfied for arbitrary values of the parameter m, and the problem of laminar flame propagation culminates in the determination of an eigenvalue of the mass flow, m, for which all boundary conditions can be satisfied.

The system of differential equations can be written, after introduction of a dimensionless variable $\theta = \dfrac{T}{T_f}$ and the corresponding notations $\theta_0 = \dfrac{T_0}{T_f}$ and $\theta_a = \dfrac{A_r}{RT_f}$, in the following form:

$$\frac{d\epsilon_i}{d\theta} = \frac{\lambda}{m^2 \overline{C_p}} \; \frac{w_i}{(\theta - 1) + \sum (\epsilon_j - \epsilon_{jf})\left(\dfrac{h_j^0}{\overline{C_p} T_f}\right)} \quad (8a)$$

$$\frac{dX_i}{d\theta} = \frac{\lambda}{\overline{C_p}} \left(\frac{RT}{p}\right)$$

$$\frac{\sum_k \dfrac{1}{D_{ik}} \left(X_i \dfrac{\epsilon_k}{M_k} - X_k \dfrac{\epsilon_i}{M_i}\right)}{(\theta - 1) + \sum_j (\epsilon_j - \epsilon_{jf})\left(\dfrac{h_i^0}{\overline{C_p} T_f}\right)} \quad (8b)$$

2. Methods of Solution. The Problem of the Cold Boundary

One easily recognizes by computing a simple example that the problem stated in the foregoing paragraph, strictly speaking, has no solution. It appears necessary to assume that the chemical changes do not start at the initial temperature, T_0, but at a higher temperature, T_i, which is called the ignition temperature. Computing a simple example, such as the case of a one-step unimolecular reaction, Millán and I found[2] that the value of the mass flow, m, becomes infinite if the ignition temperature coincides with the initial temperature, and becomes zero if the ignition temperature is equal to the final temperature, T_f. However, the eigenvalue considered as a function of T_i remains practically constant over a large interval of T_i, at least in the case that the

activation energy is large in comparison with the quantity, RT_f.

We concluded that in most cases it must be possible to determine a value of the velocity of the propagation of the laminar flame, which is practically independent of the ignition process.

Hirschfelder, Curtiss and Campbell[3] proposed to eliminate the difficulty arising from the boundary condition at the cold boundary by means of the assumption of a flameholder which is represented mathematically by a heat sink of small intensity. This means that the temperature as a function of the coordinate x starts at $x = 0$ with a small but finite value of the gradient dT/dx. The intensity of the heat sink is given by $(-\lambda(dt/dx))_{x=0}$. Then it can be shown—as was first pointed out by Emmons[4] for the case of the simple thermal theory—that the eigenvalue which satisfies the condition at the hot end and the new condition at the cold boundary is insensitive to the assumed intensity of the heat sink. To be sure, when the heat loss at the flame holder converges to zero, the computed flame velocity increases to infinity.

The result obtained by Millán and myself holds for both the pure thermal theory of flame propagation and the complete theory which takes into account the diffusion. For this second case, Hirschfelder, Curtiss and Campbell,[3, 5] propose that, in addition to the heat sink, the existence of a filter be assumed which prevents the diffusion of the burned gas products into the unburned gas upstream of the heat sink. This assumption, however, has the disadvantage that the composition of the gas at $x = 0$ is a priori unknown and, therefore, it is difficult to start the integration of the system of differential equations at the cold boundary. The procedure applied by Hirschfelder and his school until 1954 consisted of calculating by numeric integration a sequence of temperature vs. mass ratio curves which satisfy the boundary conditions at the hot boundary. These curves correspond to a sequence of chosen values of the flame velocity or the mass flow. Then one tries to interpolate a curve which satisfies approximately the conditions at the cold boundary and obtains by this interpolation the eigenvalue sought for. It appears that by replacing the method of point by point integration of the differential equations by an integral method, the difficulty created by the boundary conditions at the cold boundary disappears at least for reactions with not too small activation energies. The method is applicable both to the thermal

and the complete theory, i.e., the theory taking into account both heat conduction and diffusion.

In our joint publications (with Millán and Penner[2, 6, 7]) in the years 1952–1953, we tried to develop such a method, which is relatively simple and sufficiently accurate for the computation of the flame velocity. Since 1954, after the British mathematician Klein joined the Wisconsin group, this group also uses, in addition to the numerical point by point integration procedure, an integral equation method, which by iteration furnishes the solution of the flame equations and the value of the flame velocity.[8] The first step of this method is very similar to the procedure proposed previously by our group.

Fundamentally, our procedure is similar to the methods proposed by Zeldovich, Frank-Kamenetski, and Semenow,[9] and by Boyr and Corner.[10] We believe, however, that our method is somewhat more systematic and leads to fair accuracy already for the first step of the calculation.

Before I try to describe our method and compare it with the methods of the authors quoted, I want to note that a group of other authors published so-called pure diffusional theories of laminar flame propagation. The common fundamental idea of these latter theories is the concept that the presence of "active centers" in the reaction zone determines the flame velocity. Tanford and Pease[11] analyzed various mechanisms producing atom and radical concentrations, such as equilibrium production in the burned gas and diffusion from the hot boundary. They arrived at the conclusion that in most cases the diffusion of atoms or radicals from the burned gases into the reaction zone is the governing mechanism. Van Tiggelen[12] calculates for chain reactions the probability of chain branching and chain breaking for active centers which move from the burned gas into the reaction zone. He obtains from the analysis of such a mechanism a simple expression for the progression of the flame into the unburned gas. The theory of Gaydon and Wolfhard[13] is also based on the picture that the diffusion of atoms or radicals from the burned gas into the unburned gas determines the propagation velocity of the flame.

I will not say that the formulae developed by these authors are not useful for comparative studies of certain reactions; for example, for a quick determination of the dependence of the flame velocity on the initial concentrations of the reaction partners. Nevertheless, I believe that the good accordance with experiments is some-

times more a matter of good luck in the choice of the numerical parameters than a proof for the correct description of the phenomena. In my belief, all these diffusional theories tend toward oversimplification of the problem of laminar flame propagation.

3. The Proposed Integral Method for Computation of the Flame Velocity

The method proposed and actually used in our calculations can be described in the following way:

The main assumption is that the behavior of the functions ϵ_j and X_j near the hot boundary, $\theta = 1$, has an overwhelming influence on the value of the flame velocity. Therefore, for the first approximation, approximate expressions for these functions are used which correspond to their behavior near $\theta = 1$.

Concerning the diffusion process, it is known from the pioneering work of Lewis and von Elbe[14] and Semenow[15] that, in the special case of two species for which the Lewis number $\left(\text{ratio between the binary diffusion coefficient, } D, \text{ and the thermal diffusivity, } \dfrac{\lambda}{C_p \rho} \right)$ is equal to one, the weight ratio of each component is a linear function of the temperature.[7] This corresponds to the rule—correct for this special case—that the sum of the thermal and chemical enthalpies of the gas mixture remains constant through the flame zone. Correspondingly, in the general case, we assume that Y_j and X_j behave as linear functions near $\theta = 1$.

The behavior of ϵ_j near $\theta = 1$ is evaluated from the Equation (8a) and depends largely on the order of the reactions considered.

The first approximation for the burning velocity is obtained by integration of the Equation (8b) between the limits $\theta = \theta_0$ and $\theta = 1$ and substituting for the functions ϵ_j and X_j the approximate expressions established as indicated above.

Jointly with Millán[16] we have compared, for a simple case, the results obtained by our method with those obtained from the so-called Semenow formula and by the method of Boys and Corner. The comparison was made for an idealized reaction of first order. We consider only two components in the mixture, reactants and products. We assume for the sake of simplicity that both the molecular weight and the specific heat of the mixture are constant; furthermore, that the

thermal conductivity is independent of the composition and varies proportionally with the temperature of the mixture. Finally, we assume that the diffusion coefficient between the two components is equal to the thermal diffusivity of the mixture.

Because of the last assumption, the mass ratio of the products, Y, can be assumed to be a linear function of the temperature in the form

$$Y = \frac{\theta - \theta_0}{1 - \theta_0} \qquad (9)$$

The differential equation for the fractional mass flow ratio, ϵ, of the products can be written in the form

$$\frac{d\epsilon}{d\theta} = \frac{\lambda}{m^2 \bar{C}_p} \frac{w}{(\theta - 1) + (1 - \theta_0)(1 - \epsilon)} \qquad (10)$$

For the rate of production of the products, we write

$$w = k \frac{1 - Y}{\theta} \exp\left(-\frac{\theta_a}{\theta}\right) \qquad (11)$$

where k is a constant. The factor $(1 - Y)/\theta$ corresponds to the assumption that the reaction is of the first order.

Thus, after substituting for Y the expression $(\theta - \theta_0)/(1 - \theta_0)$ and writing $\lambda = \lambda_f \theta$, we obtain from Equation (10)

$$\frac{d\epsilon}{d\theta} = \Lambda \frac{(1 - \theta) \exp\left(-\theta_a \frac{1 - \theta}{\theta}\right)}{(\theta - 1) + (1 - \theta_0)(1 - \epsilon)} \qquad (12)$$

where the parameter Λ is defined by

$$\Lambda = \frac{\lambda_f k \exp(-\theta_0)}{m^2 \bar{C}_p (1 - \theta_0)} \qquad (13)$$

The factor $e^{-\theta_a}$ is included for convenience in the definition of Λ; otherwise Λ would be a very large number.

The problem of the burning velocity is reduced to the determination of the value for the parameter Λ which allows that the boundary conditions $\epsilon = 0$ for $\theta = \theta_0$ and $\epsilon = 1$ for $\theta = 1$ be satisfied.

The consideration that the behavior of ϵ near $\theta \equiv 1$ has an overwhelming influence on the correct value of Λ allows us to obtain a simple approximate formula which I would consider a zero-order approximation. We neglect in the denominator the quantity $(\theta - 1)$ in comparison with $(1 - \theta_0)(1 - \epsilon)$. This corresponds to neg-

lecting in the energy balance the change of the heat content of the mixture in comparison with the heat transfer by conduction and the heat production by chemical reaction.

Then we readily obtain the equation

$$(1 - \epsilon)\, d\epsilon = \Lambda \frac{d\theta}{1 - \theta_0} (1 - \theta) \\ \exp\left(-\theta_a \frac{1 - \theta}{\theta}\right) \qquad (14)$$

in which the variables appear separated. Integrating this equation between the limits $\theta = \theta_0$ and $\theta = 1$, we obtain the zero-order approximation for the quantity $1/\sqrt{\Lambda}$ which is proportional to the burning velocity, S_b, i.e.,

$$\frac{1}{\sqrt{\Lambda}} = \sqrt{\frac{2I}{1 - \theta_0}} \qquad (15)$$

where I denotes the integral

$$I = \int_{\theta_0}^{1} (1 - \theta) \exp\left(-\theta_a \frac{1 - \theta}{\theta}\right) d\theta \qquad (16)$$

which can be easily evaluated.

If we want a better, say a first-order approximation, we approximate the quantity $(\theta - 1)$ which we neglected above, by an expression valid near $\theta = 1$. Setting

$$1 - \theta = \alpha(1 - \epsilon) \qquad (17)$$

we evidently obtain from Equation (12) the relation

$$\frac{1}{\alpha} = \Lambda \frac{1}{-1 + \frac{1}{\alpha}(1 - \theta_0)} \qquad (18)$$

Using this value for α, we find after integration

$$\frac{1}{\sqrt{\Lambda}} = \sqrt{\frac{2I}{1 - \theta_0 - \sqrt{2I}}} \qquad (19)$$

In most cases this first-order approximation is satisfactory. A further improvement of the approximation can be obtained by computing the correction term $(\theta - 1)$ from numerical integration of Equation (12).

Comparing now our result first with the well-known Semenow formula, it is interesting to find that Semenow, Zeldovich and Frank-Kamenetski obtained an approximation for the value of S_b which corresponds exactly to our zero-order approximation. However, they proceeded to evaluate the integral I by means of a semiconvergent expansion in powers of $1/\theta_a$. In our notation

this leads to the expression

$$\frac{1}{\sqrt{\Lambda}} = \frac{1}{\theta_a} \sqrt{\frac{2}{1 - \theta_0}} \qquad (20)$$

This formula, as will be clarified in the discussion of Figure 1, is greatly inferior to our first-order approximation.

The procedure of Boys and Corner has the following common feature with our method: they use the linear relation between $(1 - \epsilon)$ and $(1 - \theta)$ which is expressed by Equation (17). But they substitute the expression for $(1 - \epsilon)$ in the denominator of Equation (12). I believe this procedure is fundamentally wrong because one retains in the denominator the small quantity $(1 - \theta)$ and approximates the relatively large quantity $(1 - \epsilon)$ in terms of $(1 - \theta)$. The consequence is a large error in the first-order approximation and a slow convergence of the iteration process which is, in general, quite laborious.

In Figure 1 we represent the error in the evaluation of S_b for the three methods in the special case $\theta_0 = 0.125$. The ratio between the approximate values of $1/\sqrt{\Lambda}$ and the exact value obtained by careful numerical integration is plotted as a function of θ_a. It is seen that our zero-order approximation is better than the result obtained from the Zeldovich-Semenow formula and from the first-order approximation of Boys and Corner. The figure also includes the results of our first-order approximation corresponding to Equation (19) as well as the results derived from the Boys-Corner procedure by a further iteration. It is seen that both of our approximations involve a smaller error than the values obtained from the rather laborious iteration of Boys and Corner.

Similar comparative calculations have been made for the case of a second-order reaction and for values of the Lewis-Semenow number different from unity. These calculations led to the same general conclusions as were discussed above.

In the case of chain reactions (reactions in which atoms or free radicals play a role), the assumption that the mass or mole ratios can be approximated by linear functions of $(1 - \theta)$ is restricted to the main reactants and reaction products, i.e., to the stable species. The concentrations of the radicals are approximated by functions whose forms are determined by the chain-initiating, chain-branching and chain-breaking reactions. The procedure followed for chain reactions will be clear from the examples treated in the following Section 4. Particularly, I want

to show the application of the steady-state assumption to the computation of the flame velocity in the case of simple chain reactions.

4. Application of the Steady-State Assumption

The application of the steady-state assumption to the problem of the computation of the flame velocity in the case of chain reactions was proposed in 1953 by the present writer and Penner
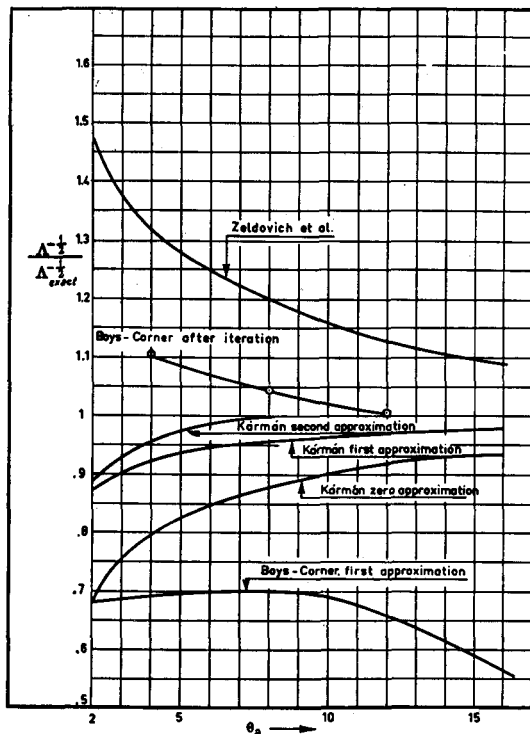

FIG. 1. Comparison between various semi-analytical methods for computation of the flame velocity.

in connection with the theory of the ozone decomposition flame.[7]

The principle involved in the steady-state approximation is the following: one assumes that the production and removal of every species of radicals compensate each other in every cross-sectional element of the flow. If we apply these conditions to all species of radicals, we obtain definite expressions for the radical concentrations as functions of the temperature and the mole fractions of the main reactants. Therefore, the system of reactions is reduced to a scheme in which only the main reactants enter. Then the computation of the flame velocity can be pursued

by means of any of the methods mentioned and explained in the foregoing Section 3.

It is noted that the assumption of the steady-state condition for the concentrations of radicals is based on a physical picture diametrically opposite to that underlying the so-called diffusional theories. The diffusion of the radicals from the burned gas into the flame zone—the most important process from the viewpoint of the diffusion theories—is neglected in our theory. The distribution of the radicals throughout the
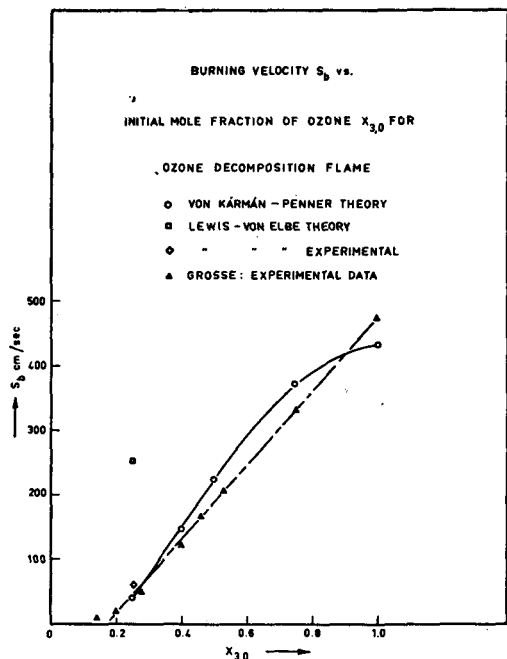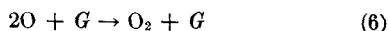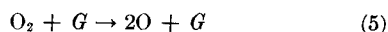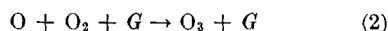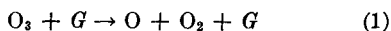

FIG. 2. The ozone dissociation; comparison between compiled and measured values of the burning velocity.

flame zone is computed from the balance between their production and disappearance by chemical reactions.

I want to present the results of calculation for three typical chain reactions for which the chemical kinetics data are sufficiently well known and experimental data are available so that a judgment on the validity and value of the steady-state assumption can be formed.

A. OZONE DECOMPOSITION

The scheme of reactions involved in the ozone decomposition flame is assumed to be the following:

$$O_3 + G \rightarrow O + O_2 + G \qquad (1)$$

$$O + O_2 + G \rightarrow O_3 + G \qquad (2)$$

$$O + O_3 \rightarrow 2O_2 \qquad (3)$$

$$2O_2 \rightarrow O + O_3 \qquad (4)$$

$$O_2 + G \rightarrow 2O + G \qquad (5)$$

$$2O + G \rightarrow O_2 + G \qquad (6)$$
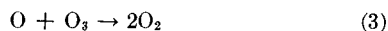
Here G represents any of the three species O, O_2, or O_3.

The examination of available chemical kinetics data (Ref. 17) shows that the reactions (4) and (5) have extremely high activation energies in comparison with the other reactions; for reactions (2) and (6) the frequency factor is of a very small order of magnitude. One concludes that the rate governing reactions are reactions (1) and (3).

The condition that the production of O atoms according to the reaction (1) is balanced by their removal by means of reaction (3) leads to the following formula for the mole fraction X_1 of the oxygen atoms

$$X_1 = 1.48 \exp(-7.30/\theta) \qquad (21)$$

The problem of the ozone decomposition flame has now been reduced to the solution of the following two equations:

$$\frac{d\epsilon_3}{d\theta} = -\Lambda \frac{\left(\dfrac{X_3}{\theta}\right)\exp\left(-\dfrac{9.719}{\theta}\right)}{\theta - 1 + \left(\dfrac{h_3^0}{\overline{C}_p T_f}\right)\epsilon_3} \qquad (22a)$$

$$\frac{dX_3}{d\theta} = \frac{\lambda_f}{\overline{C}_p}\left(\frac{RT_f}{p}\right)\frac{1}{D_{2,3}}\frac{\dfrac{9}{10}X_3 - \dfrac{3}{5}\epsilon_3 - \dfrac{3}{10}X_3\epsilon_3}{\theta - 1 + \left(\dfrac{h_3^0}{\overline{C}_p T_f}\right)\epsilon_3} \qquad (22b)$$

where

$$\Lambda = 2\lambda_f M_3\left(\frac{p}{RT_f}\right)^2 B_1/m^2\overline{C}_p$$

[B_1 denotes the frequency factor for reaction (1)]. The laminar flame velocity S_b is obtained, as usual, from the relation

$$S_b = \frac{m}{\rho_0} \qquad (23)$$

In Figure 2 we have plotted the following data: (1) The computed values of S_b according to the steady-state approximation for the following values of the initial ratio X_{30} (mole fraction of ozone): 0.25, 0.40, 0.50, 0.75 and 1.00. (2) The experimentally measured values of S_b. The

value for $X_3 = 0.25$ is taken from the publication of Lewis and von Elbe.[18] All other values were obtained by Grosse.[19]

It is seen that the general trends of the experimental and the computed values are in fair accordance; the maximum deviation is of the order of 15 to 20 per cent. The value of S_b for $X_{30} = 0.25$ was computed by Hirschfelder and his group by numerical integration of the system of equations without using the steady-state assumption.[17] Near the final adiabatic flame temperature, temperature intervals as small as one-tenth of a degree had to be used in the numerical integration. Nevertheless, the deviation between his and our results for the value of $X_{30} = 0.25$ is no more than 10 per cent.

However, if one assumes—as Lewis and von Elbe did[18]—that the atom concentration X_1 is determined by the equilibrium condition between O_3, O, and O_2, i.e., by the balance between the reactions (1) and (2), then one obtains a value for S_b which is more than five times larger than the measured value for $X_{30} = 0.25$. We have also calculated the burning velocity according to the assumption used by Lewis and von Elbe for other values of the initial concentration, namely, for $X_{30} = 0.50$, 0.75 and 1.00. We have found that, using the hypothesis of Lewis and von Elbe,[18] the computed value agrees for $X_{30} = 0.65$; for $X_{30} = 1.00$ the computed value becomes 40 per cent smaller than the measured value. As a matter of fact, the computed values are relatively insensitive to the initial concentration of O_3 and to the flame temperature, whereas the measured values, for the same range of initial concentrations, change in a ratio of about 1:10. In this connection, it is worthwhile to mention that the early measurements of S_b by Lewis and von Elbe are in good accord with the more extensive study of Grosse.[19]
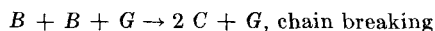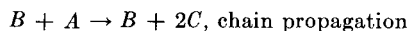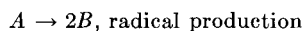
B. HYDRAZINE DECOMPOSITION FLAME

In the matter of the hydrazine decomposition, a small accident occurred in the past both to the Wisconsin group[20] and to our group.[7] We all considered the first order reaction

$$N_2H_4 \rightarrow 2NH_2$$
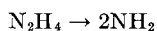
as the rate-governing step. We all used a numerical value for the heat conduction coefficient which was given in a paper of Murray and Hall[21] as ten times larger than the actual value because of a common misprint. We obtained perfect agreement between the numerical integration of the Wisconsin group and our semianalytical method but too high numerical values for the burning velocity compared with the measurements.

Spalding[22] took up the problem again in 1955 and introduced a chain reaction scheme proposed by Adams,[23] as follows:

$A \rightarrow 2B$, radical production

$B + A \rightarrow B + 2C$, chain propagation

$B + B + G \rightarrow 2\ C + G$, chain breaking

In this scheme no difference is made between the radicals NH_2, H or other radicals which may be present. A denotes hydrazine and C end products. Spalding used for the computation of the radical concentration and for the burning velocity a numerical integration method which starts from an arbitrary temperature profile through the flame zone and tries to follow the transient process which converges to the stationary state. He uses the assumption that the sum of the thermal and chemical enthalpies remains constant throughout the flame zone so that the mass fraction of the hydrazine is a linear function of the temperature.

Using the same assumption and the same chemical data, Millán and Sanz[24] recalculated Spalding's result using our way of computation, then they computed the burning velocity using the steady-state assumption. The first calculation is more laborious because, if one uses the steady-state condition, the mass fraction of the radicals is explicitly given as a function of the mass fraction of the hydrazine and the temperature; thus, one has to deal only with one differential equation for the fractional mass flow ratio of the hydrazine. If the steady-state assumption is not used, one has a system of simultaneous differential equations for the fractional mass flow ratio of the hydrazine and both the mass fraction and fractional mass flow ratios of the radicals.

Figure 3 shows the result of these calculations including comparison with the available experimental values. The burning velocity is plotted as a function of the flame temperature. Spalding gave two theoretical values of the burning velocity corresponding to one hot and one cool flame. These values were in good agreement with the observations. The recalculation according to our semianalytical method agreed with Spalding's results. The figure shows in addition three other theoretical values for intermediate temperatures. The general trend of the calculated burning velocities is in fair agreement with the experimen-
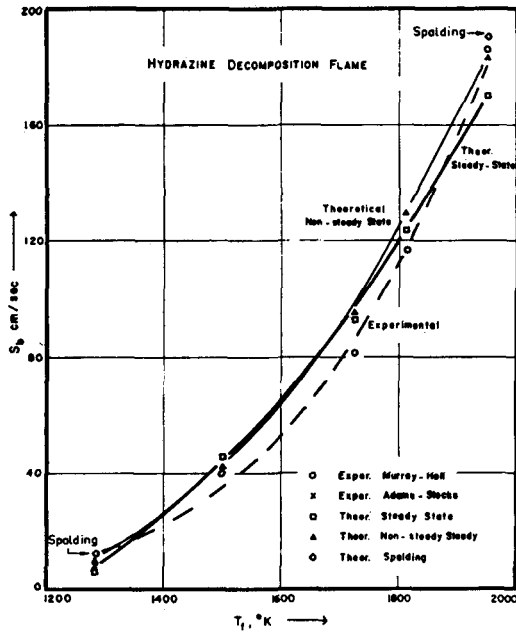
FIG. 3. Hydrazine decomposition flame; comparison between compiled and measured values of the burning velocity.
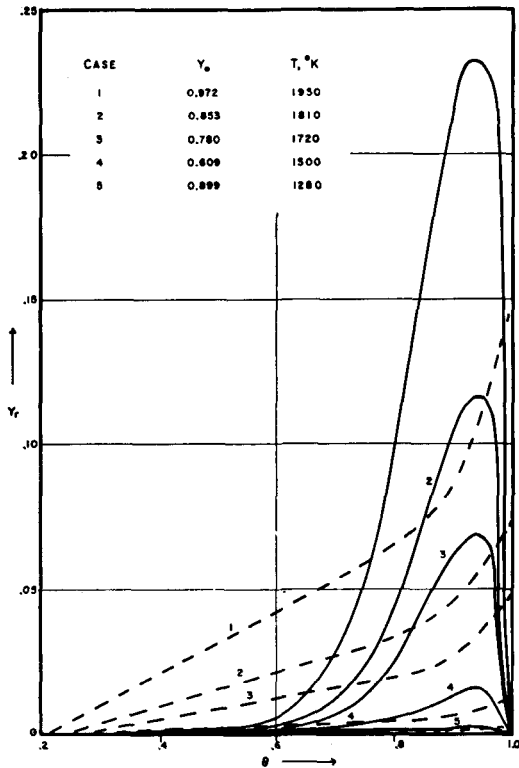

FIG. 4. Radical concentration vs temperature; computed with and without the use of the steady-state assumption for the case of hydrazine decomposition.

tal curve. Finally, the burning velocity has been computed for the same cases using the steady-state assumption. These values are also shown in Figure 3.

It is rather remarkable how little the theoretical values based on the steady-state assumption differ from the values calculated without the use of this assumption.

In order to find out the reason for this rather surprising state of affairs, Millán and Sanz compared the radical concentrations computed with and without the steady-state assumption. The
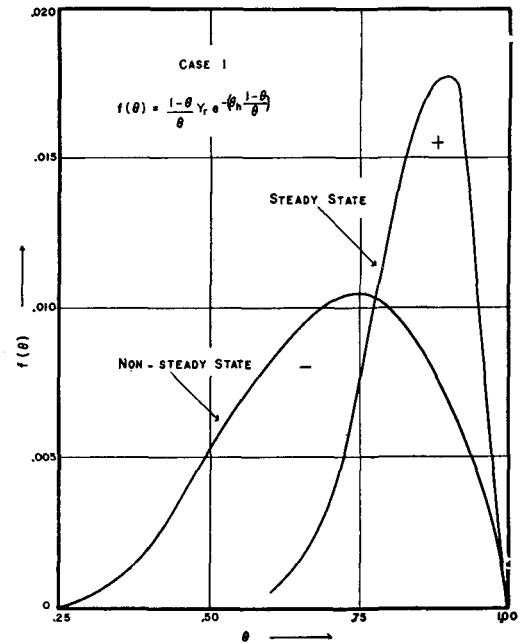

FIG. 5. The integrand used in the computation of the burning velocity in the case of the hydrazine dissociation with and without use of the steady-state assumption.

results of this investigation are shown in Figures 4 and 5. It appears from Figure 4 that the steady-state assumption (full lines) has the effect of exaggerating the radical concentration near the hot boundary. This was also found by Spalding, although the effect is much smaller than indicated in his paper. Spalding concluded that because of this effect the steady-state assumption overestimates the burning velocity. This conclusion seems to be false because, for example, in the case of the hot flame, as shown in Figure 3, the theoretical value calculated with the use of the steady-state assumption is considerably lower than Spalding's value. The explanation of this apparent contradiction is given in Figure 5

In Section 3 of this paper we have shown that the first-order approximation to the burning velocity is obtained in terms of a definite integral, I, over a given function of the nondimensional temperature, θ. Figure 5 shows the corresponding function which enters as the integrand in the analogous computation in the case of the hydrazine flame. One sees that the steady-state assumption overestimates the integrand near the hot boundary because it overestimates the radical concentration. However, this effect is compensated by the fact that the same assumption underestimates the radical concentration and the magnitude of the integrand in the lower temperature range since it neglects the diffusion of the radicals. This is clearly shown also in Figure 4.

The conclusion is that, at least in the case of the hydrazine flame, the steady-state assumption leads to a fair estimate of the magnitude of the burning velocity and its dependence on the flame-temperature but does not necessarily give a correct picture of the actual radical concentration.

C. THE HYDROGEN BROMINE FLAME

The reaction between hydrogen and bromine, forming hydrogen bromide, is of great interest because it is a rare example of a chain reaction whose reaction mechanism and rate constants are well defined and have been determined experimentally.[25] As a matter of fact, this reaction played an important part in the history of the knowledge of chain reactions.[26]

The reaction scheme is the following:

(1) $Br_2 + G \rightarrow 2\ Br + G$ radical production

(2) $Br + H_2 \rightarrow HBr + H$ chain propagation

(3) $H + Br_2 \rightarrow HBr + Br$ chain propagation

(4) $HBr + H \rightarrow H_2 + Br$ chain propagation

(5) $2Br + G \rightarrow Br_2 + G$ chain breaking

where G denotes any of the chemical species present.

The steady-state assumption requires that the number of H atoms produced by reaction (2) be equal to the sum of the number of H atoms removed by the reactions (3) and (4). Furthermore, the total number of Br atoms produced by reactions (1), (3) and (4) has to be equal to the number removed by reactions (2) and (5). These conditions lead to the following equation for the production of HBr molecules in unit time:

$$\frac{d(HBr)}{dt} = (\text{const}) \frac{(H_2)(Br_2)^{3/2}}{(Br_2) + (\text{const})(HBr)} \quad (24)$$

It is seen that this Equation (24) contains only the main or stable reactants, H_2 and Br_2, and the product, HBr. The proportionality factors are a known function of the temperature.

The present author, jointly with Penner,[27] applied this equation to the computation of the burning velocity with the additional assumption that the mass fraction of the radicals, H and Br, are small in comparison with the mass fractions of the stable reaction partners; in other words, that in the expressions for the conservation of the numbers of Br and H atoms through the flame zone, i.e., $2(Br_2) + (HBr) + (Br) = 2(Br_2)_0$ and $2(H_2) + (H) + (HBr) = 2(H_2)_0$ the quantities (Br) and (H) can be neglected. As a matter of fact, the H concentration is always small; however, as was first pointed out by
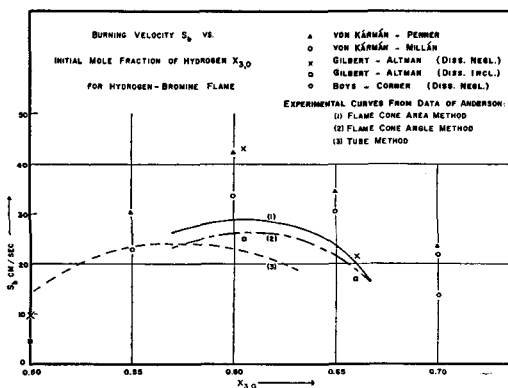

FIG. 6. The hydrogen bromine flame; computed and measured values of the burning velocity for hydrogen-rich mixtures.

Gilbert and Altman[28] the concentration of Br is not negligible. This is especially true for the hydrogen-rich mixtures.

Figure 6 represents the experimental curves for the burning velocity, S_b, plotted as a function of the initial mole ratio of H_2 in the interval between the stoichiometric mole ratio $X_{2,0} = X_{3,0} = 0.5$ and the mole ratio $X_{3,0} = 0.67$.

The observations were made by Anderson.[29] Curves (1) and (2) were obtained by observations of the flame cone, measuring the flame cone area and the cone angle respectively. Curve (3) was obtained from observations of flame propagation in a tube.

The first calculations of the author and Penner, as shown in the same figure, led to values of the flame speed which are definitely too high. Then Millán introduced a correction, which takes into

account the presence of Br atoms due to the dissociation of Br_2.

Instead of the relation $2(Br_2) + (HBr) = 2(Br_2)_0$ the complete equation $2(Br_2) + (Br) + (HBr) = 2(Br_2)_0$ is used and the quantity Br is determined from the steady-state condition $d(Br)/dt = 0$. According to this condition (Br) is proportional to $\sqrt{(Br_2)}$. Therefore, for hydrogen-rich mixtures, $(Br_2) \to 0$ at the hot boundary and the Br concentration becomes even larger than the Br_2 concentration and reduces the latter very considerably. The reduction of (Br_2) means —according to Equation (24)—a reduction of the over-all reaction rate and of the burning velocity.

As I mentioned before, Gilbert and Altman pointed out previously the importance of this correction for dissociation.[28] However, they carried out the computation of the correction only for the pure thermal theory. Then they computed the burning velocity including the effect of diffusion but neglecting the influence of the presence of (Br) atoms due to dissociation. In order to include the effect of dissociation they simply applied the same percentage reduction which they had obtained from the thermal theory. This assumption is rather arbitrary and overestimates the influence of dissociation which is, in general, less for a reaction with diffusion than for a pure thermal process. In addition, Gilbert and Altman followed the procedure of Boys and Corner and the apparent coincidence between the computed and measured values is essentially due to the fact that the first approximation of Boys and Corner furnishes too low values for the burning velocity, as we have shown in Figure 1. For example, Millán calculated for $X_{3,0} = 0.7$ the burning velocity using first our method without and with dissociation and then the Boys-Corner approximation without dissociation. These results are also shown in Figure 6. It is seen that the value computed by the Boys-Corner approximation, without taking into account dissociation, lies even below our value corrected for dissociation.

If we apply the same equations to the case of bromine-rich mixtures, we obtain values for the burning velocity which decrease rather rapidly with the increasing initial bromine concentration but are finite for arbitrary bromine-hydrogen ratios. The experimental evidence shows that it is not possible to obtain a stable flame if the bromine-hydrogen ratio is larger than the stoichiometric ratio. It is possible that this apparent instability is a consequence of the environment, for example, of heat removal from the

flame. In fact it can be shown—as suggested by Spalding[30]—that, if the external cooling of the mixture is taken into account, below and above certain well-defined initial mixture ratios there is no real eigenvalue at all.

Summary

Summarizing our considerations concerning the present status of the theory of laminar flame propagation, I wish to state:

(1) That it appears in cases in which the reaction-scheme and the corresponding chemical kinetics are well-defined, a semianalytical method, as presented in this paper, makes a relatively easy determination of the flame velocity possible. There is no necessity for radical simplifying assumptions such as are introduced, for example, in the pure diffusion theories.

(2) There is no necessity to take recourse to laborious numerical integration of the differential equations, although the use of digital computers may facilitate such methods.

(3) It appears that in the cases dealt with until now, the steady-state assumption facilitates a rather quick determination of the flame velocity of a chain reaction, even in those cases where it does not furnish an exact picture for the distribution of the radicals through the flame zone.

(4) It is believed that in order to make further progress in the theory, the most urgent need is a better knowledge of the reaction schemes and the chemical kinetics of the important chain reactions. Especially more exact data are necessary concerning the presence and distribution of the radicals involved.

A paper by K. A. Wilde [J. Chem. Phys. 22, 1788 (1954)] has recently come to our attention. The procedure used by this author for the integration of the simple one-step flame reaction is the same as that used in our first approximation except that ϵ is assumed to vary as $[(\theta = \theta_0)/(1 - \theta_0)]^{n+1}$. Here the exponent n is determined by equating the limiting slope of $[(\theta - \theta_0)/(1 - \theta_0)]^n$ to the limiting slope of $\{\exp[-\theta_a(1 - \theta)/\theta]\}$. This procedure leads to the relation

$$\frac{1}{\sqrt{\Lambda}} = \sqrt{\frac{2I}{1 - \theta_0}\left[1 + \frac{2}{\theta_a(1 - \theta_0)}\right]} \quad (A\text{-}1)$$

which is similar to our Equation (19). For sufficiently large values of θ_a, i.e., small values of I, Equations (A-1) and (19) become evidently equivalent. We have evaluated $1/\sqrt{\Lambda}$ according to Equation (A-1) and find the results to be less accurate than our second approximation for

$\theta_a \geqslant 5$ but to be better at smaller values of θ_a. Equation (A-1) gives results which are superior to those determined from Equation (19) for $\theta_a < 8$ but are roughly comparable [with $\sqrt{\Lambda}$ about as much too small according to Equation (A-1) as it is too large according to Equation (19)] for larger values of θ_a.

Nomenclature

ϵ_j fractional mass flow rate of the species j
Y_j weight fraction of the species j
X_j mole fraction of the species j
$\bar{C}_p$ average specific heat
h_j^0 standard specific formation enthalpy of the species j
C_t total concentration, i.e., number of moles of mixture in unit volume
T_0 initial temperature of mixture
T_f final temperature of mixture
M_j molecular weight of the species j
λ heat conduction coefficient of the mixture
ρ density of the mixture
v mean mass velocity of the mixture
V_j diffusion velocity of the species j

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