

# The structure of the reaction zone in a flame

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The structure of one-dimensional flames is shown to be completely determined by constants such as those of heat conductivity, of diffusion, and of the homogeneous reaction rates. The mathematical problem in the most general case is intractable, but three simple cases are solved fully by a mathematical method of successive approximations. The three cases are those in which diffusion is neglected compared with heat conductivity and in which reaction velocities of the following types are considered: unimolecular, bimolecular, and the quasi-bimolecular form of a unimolecular reaction at low pressures. The method of mathematical approximation is shown to involve errors of the order of only 10% in some actual cases, an error which is negligible compared with other uncertainties of the problem. In these simple cases it is possible to solve all details of the structure such as the variation of composition and temperature through the flame.

## 1. INTRODUCTION

The propagation of flames is an extremely important natural phenomenon, yet the theory of the structure of flames has been very little developed. Here we shall give a contribution to the quantitative calculation of the structure by giving mathematical solutions for some simplified models, which however contain all the essential features of the general problem.

Before proceeding with the detailed calculations it appears worth while to show just what are the difficulties in quantitative theoretical predictions of the structure of any flame. The difficulties are twofold, first, even if we were given all necessary data, the mathematical problem when formulated is a particularly intractable one for either analytic or numerical solutions, and secondly, very little of the necessary data is available for any actual flame. The data necessary are the rates of all the reactions occurring in the flame and their dependences on temperature and concentrations, and also the heat conduction and diffusion constants of all components of the mixture. The necessary data will presumably become more readily available as a result of further experimental measurements and theoretical quantum calculations, but considerable work will have to be done on methods of solution of the mathematical problem. The present calculation provides some progress towards this.

There appears to be no difficulty in the general mathematical theory of the structure and mode of propagation of steadily moving plane flames. The well-known process of reactions evolving heat and new particles, and of heat conduction and diffusion provide a complete explanation of flames which move sufficiently slowly that appreciable pressure waves are not set up. It is to this class that the ordinary designation of flames is usually applied and to which we shall be confining our attention in this paper. If we consider a plane flame in a medium which is moved at such a rate that the flame is stationary all concentrations, etc., will become merely functions of the co-ordinate perpendicular to the flame front, which we shall repre-

sent by  $x$ . If we examine in turn the rate of accumulation of any component or energy in a thin region  $\delta x$  and equate these to zero, since in this steady state there can be no rate of accumulation, we obtain all the differential equations of the structure of the flame.

Let  $y_1$  represent the temperature and  $y_2, y_3, \dots, y_{n+1}$  all the concentrations (as fractions of the total mass) of all the different chemical species. Then the flux of the ( $r$ )th component across any unit cross-section will be a linear combination of all the concentration gradients  $-\sum_s \lambda_{rs} \frac{dy_s}{dx}$ , where  $\lambda_{rs}$  will be given coefficients of heat conduction or diffusion. Hence the rate of accumulation in  $\delta x$  is  $\frac{d}{dx} \sum \lambda_{rs} \frac{dy_s}{dx} \delta x$ . This applies equally whether we are considering the first component, which is the temperature, or one of the concentrations. The amount of the ( $r$ )th component passing across a unit cross-section due to the movement of the medium is  $M y_r$ , where  $M$  is the total flow;  $M$  must be a constant for the whole system, since there cannot be any accumulation of total mass. Hence the accumulation of the ( $r$ )th component in  $x$  must be  $-M \frac{dy_r}{dx} \delta x$  due to the difference of the flux at each side of the thin layer. It must be noted that  $y_1$  is something of an exception in this case, since the energy flux contains terms dependent on the work done by the pressure in this case, and for complete accuracy in the general case we must use a term  $-M \frac{d}{dx} \sum c_s dy_s$  in which the effects of differing specific heats are also allowed for. Lastly, the rates of accumulation due to the generation in the reactions we can write  $\mathcal{R}_r \delta x$  where each of these will be some definite function of all the  $y_s$ . Hence we have the equations

$$\frac{d}{dx} \sum_s \lambda_{1s} \frac{dy_s}{dx} - M \frac{d}{dx} \sum_s c_s y_s + \mathcal{R}_1 = 0,$$

$$\frac{d}{dx} \sum_s \lambda_{rs} \frac{dy_s}{dx} - M \frac{dy_r}{dx} + \mathcal{R}_r = 0. \quad r > 1$$

In addition to this we shall know the values of  $y_r$  at  $x = -\infty$ ; they will be just the concentrations in the unreacted mixture which is provided in the particular experiment. The values at  $x = \infty$  will be calculable from ordinary equilibrium data together with the heat generated in the reactions. Representing these initial and final values as  $y_r^i$  and  $y_r^f$  the mathematical problem is to find solutions for the  $y_r$  as functions of  $x$  which satisfy the differential equations and the boundary conditions, together with the value of  $M$  which makes it possible for all these conditions to be satisfied simultaneously. This is actually an eigenvalue problem for the value of  $M$ , and even when the values of  $\lambda_{rs}$ ,  $C_s$  and  $\mathcal{R}_r$  are all given it is a singularly intractable problem. It might perhaps be stressed that this is the essential nature of the problem and any attempt at solution for simplified models which do not have this essential nature of  $M$  being determined by making the solution of one or more differential equations satisfy the boundary conditions cannot be a valid approximation. Since  $M$  is the mass flux of the medium in the steady state it is the velocity of the flame

expressed by giving the mass of the medium through which unit area of the flame moves per unit time.

There appear to have been only two previous attempts to make predictions of flame velocities on the basis of models of the flame structure from such considerations. An attempt by Zeldowitsch & Frank-Kamenetzki (1938) is on these lines, reducing the system to one differential equation and then making an estimate of a solution by a temporary neglect of one of the terms of the differential equation. It is hard to estimate the significance of this, but it does not give a systematic method of successive approximation to the solution of the differential equation. In the other attempt, by Lewis & von Elbe (1934), a number of *ad hoc* approximations are introduced into the problem and so far as the authors can trace the proper method of determining  $M$  by making the solution fit all the boundary conditions is not used.

The simplified models which we shall treat systematically in this paper are those in which a single reaction occurs, for which we shall consider both unimolecular reactions and bimolecular reactions, and in which diffusion is neglected and only heat conduction considered. The actual circumstances to which such a picture might apply accurately are probably only those of a reaction propagated through a liquid. If an exothermic reaction takes place in the upper layers of a liquid the reaction could be propagated downwards through a metastable liquid in a manner exactly equivalent theoretically to a flame. It is conceivable that such a method might actually be used for the measurement of a particular fast liquid reaction velocity by using one of the formulae of this paper in a reverse sense. However, this was not the aim in performing these calculations. The simple cases were taken because they were possible to solve and would provide formulae for the propagation velocities which were of the correct nature. It was hoped that these could be used as crude approximations for gaseous reactions even though diffusion does occur in these. Actually these formulae did not prove as useful for making predictive estimates for the particular flames in which the authors were interested as had been hoped. Detailed examination indicated that the circumstances were too complicated to be represented by a single reaction. However, the fact that it was possible to carry out the complete analysis for these simple cases appeared to be very helpful in the general understanding of the actual processes in flame, and in estimating what factors were of importance in determining variations of propagation velocities.

We shall now proceed to carry out the mathematical analysis for these simplified models.

## 2. MATHEMATICAL THEORY OF THE PROPAGATION OF A FLAME BY THERMAL REACTION

We shall examine the steady propagation of a plane reaction zone through a homogeneous medium with the following properties:

(i) the medium is capable of a single reaction whose rate at any point in the medium is determined solely by the temperature, pressure, and the stage to which the reaction has already proceeded at the point;

(ii) diffusion is small enough to be neglected in the time concerned;

(iii) the velocity of movement of the reaction zone is sufficiently slow that the pressure is effectively constant through this zone.

The general analysis would apply to a flame in a gas, or the movement of a reaction zone in a solid or liquid provided the above conditions were fulfilled. We shall examine the general case, and then some special cases in which constant specific heats and thermal conductivities, together with activation energy formulae for the reaction rates, are assumed. The general case can always be integrated numerically when the necessary data are available, and in the special cases explicit formulae for the rate of burning can be obtained.

We examine the structure of a steadily moving plane reaction zone. We take an  $x$  axis of reference perpendicular to the plane, so that the condition of the medium is dependent only on  $x$ , and independent of  $y$  and  $z$ . We take an origin moving with the reaction zone, so that relative to our axes of reference the unreacted medium moves from the direction of negative  $x$ , and after passing through the reaction zone the products pass towards  $x = \infty$ . All properties of the system are functions of  $x$ . When  $U$  is the velocity of the medium at any point, the rate at which any property  $X$  of a small given portion of the medium varies with time is given by

$$\frac{dX}{dt} = U \frac{dX}{dx}. \quad (1)$$

$U$  will alter as we pass through the reaction zone.

The quantities whose variation through the reaction zone as required are  $U$  the velocity,  $V$  the volume per unit mass,  $T$  the temperature, and  $\epsilon$  the fraction the reaction has progressed towards completion. We can immediately obtain a relation between  $U$  and  $V$ . If we consider the material moving along a cylinder with walls parallel to the  $x$  axis and of unit cross-section, it is apparent that the same mass is moving across any cross-section of this per unit time, and representing this by  $M$ , we have

$$M = \frac{U}{V}. \quad (2)$$

Since the pressure is constant,  $V$  must be a function of  $T$  and  $\epsilon$  only, known from the equation of state for the medium with a given  $\epsilon$ .

The energy crossing any normal section of the cylinder must be a constant, or energy would accumulate or disappear between two cross-sections. The energy flow is composed of:

- (a) the intrinsic energy  $E$  per unit mass, transported by the mass flow;
- (b) the work done by the material on one side of the section by its pressure on the material on the other side of the section;
- (c) the flow of heat due to thermal conductivity.

The flow by conduction at large distances from the reaction zone will be zero on both sides. Denote the conditions at a large distance before the reaction zone by  $T_0, V_0$ , etc., and at large distances past as  $T_m, V_m$ , etc. Then we have

$$ME + PU - \frac{\lambda dT}{dx} = ME_m + PU_m = ME_0 + PU_0, \quad (3)$$

which gives 
$$\frac{\lambda}{M} \frac{dT}{dx} = E - E_m + P(V - V_m) = H - H_m \quad \text{or} \quad H - H_0, \quad (4)$$

$H$  is the total heat content per unit mass.

We need a further relation, which is supplied by consideration of reaction velocity. The homogeneous rate, expressed as  $d\epsilon/dt$ , will be a function of  $\epsilon$ ,  $V$  and  $T$ , by our initial assumptions. Hence we have

$$U \frac{d\epsilon}{dx} = \frac{d\epsilon}{dt} = \mathcal{R}(\epsilon, V, T). \quad (5)$$

Equations (4) and (5) can be written in terms of  $\epsilon$  and  $T$  alone, since  $H$  will be a known function of  $\epsilon$ ,  $T$  and  $V$ , and the latter can be eliminated by using the equation of state. In this way we can obtain two differential equations in  $\epsilon$ ,  $x$  and  $T$ , which can be simplified by dividing one by the other, giving

$$\frac{d\epsilon}{dT} = \frac{\lambda \mathcal{R}(\epsilon, T)}{M^2 V (H - H_m)}. \quad (6)$$

This is possible only because  $x$  does not appear except as  $dx$ . In more general cases than we are considering in this paper,  $x$  may appear explicitly; this happens when, for example, the phenomena in the flame zone depend on the distance from some solid boundary. In such cases there is no point in forming (6). In our case, however, this step is useful because the problem can be solved from equation (6) alone. If distances in the flame zone are of interest the results can be substituted in (4), giving the relation between  $x$  and  $T$  or  $\epsilon$ .

We require the integral of (6) which is such that  $T = T_0$  when  $\epsilon = 0$ , and  $T = T_m$  when  $\epsilon = 1$ .  $T_0$  is the temperature at a large distance inside the unreacted medium, the initial temperature, which is known in any particular set of experiments.  $T_m$  follows from this by the relation

$$H_m - H_0 = 0,$$

where  $H_m$  is the total heat content for  $\epsilon = 1$ , and  $H_0$  refers to  $\epsilon = 0$ .

$T_m$  is the temperature of burning at constant pressure, easily calculated from thermochemical data.

Equation (6) is a first-order equation, and its solution is determined by the parameters of the equation, together with one pair of corresponding values of  $\epsilon$  and  $T$ . The solution determined by the condition at  $T_0$  will in general not fulfil the condition at the upper limit  $T_m$ . There will be one value of  $M$  for which both conditions are satisfied; this determines the only velocity possible for a steadily moving reaction zone. This value of  $M$  is a function of the other parameters in the equation.

The form of the equations ensures that  $\epsilon$  and  $T$  remain constant beyond the point where  $\epsilon = 1$  and  $T = T_m$ . This has the result that we can restrict our attention to the equation for  $d\epsilon/dT$ , when trying to find the correct value of  $M$ . No matter whether the point  $\epsilon = 1$ ,  $T = T_m$  is at a finite or an infinite distance, we can be sure that everywhere beyond this point the outgoing gases will be at the temperature  $T_m$  and will be completely reacted, which is necessary for a physically satisfactory reaction zone. At distances which are large compared with the effective thickness

of the flame, the gas may be subjected to cooling and consequent changes of composition, but these cannot affect the rate of burning. The only influences which can have any effect on the rate of burning are those which can act in the region where by far the greater part of the reaction takes place.

As the problem is solved by choosing an arbitrary parameter in a differential equation so that it has a solution which satisfies several boundary conditions, the problem is essentially the determination of an eigenvalue. The very general form in which we have left the various functions such as the heat content data, makes no difference to the principles of solution of the problem. We shall of course make much more special assumptions in following sections, but we shall not need to introduce any other general ideas of the reaction zone.

The velocity of the reaction relative to the unburnt medium is  $MV_0$ . The corresponding relation between  $\epsilon$  and  $T$  is the solution of (6) with the proper value of  $M$ ; finally, the  $(x, T)$  relation can be found by substituting in (4). This provides a scale of distances for the variation of  $T$  and  $\epsilon$  through the reaction zone.

### 3. A SOLUTION BY SUCCESSIVE APPROXIMATIONS

We shall now examine three simple cases which can be integrated explicitly by a method of successive approximations. These cases correspond to simple forms of the reaction rate which are frequently found in practice. The method of successive approximations is not necessarily restricted to these cases.

We shall limit our examination to a zone in perfect gases with constant specific heats per unit mass. All these assumptions will be discussed fully in appendices.

If  $Q_m$  is the heat of reaction at constant pressure at the temperature  $T_m$  of the final products, we have

$$H - H_m = (1 - \epsilon) Q_m + (T - T_m) [C_p^1(1 - \epsilon) + \epsilon C_p], \quad (7)$$

where  $C_p^1$  is the specific heat of the reactant and  $C_p$  that of the products, both at constant pressure. It would be possible to integrate this case if the problem required this refinement, but since a simpler case is adequate for our purposes we shall put  $C_p^1 = C_p = C$ . We can also write  $Q$  instead of  $Q_m$ , since now the heat of reaction is independent of the temperature. Thus finally

$$H - H_m = (1 - \epsilon) Q + (T - T_m) C, \quad (8)$$

so that

$$\frac{\lambda}{M} \frac{dT}{dx} = Q(1 - \epsilon) + C(T - T_m), \quad (9)$$

and substituting in (6),

$$\frac{d\epsilon}{dT} = \frac{\lambda \mathcal{R}(\epsilon, T)}{M^2 V \{(1 - \epsilon) Q + (T - T_m) C\}}. \quad (10)$$

In a simple reaction in which molecules of molecular weight  $W$  give molecules of molecular weight  $w$ , the equation of state is

$$PV = \left( \frac{1 - \epsilon}{W} + \frac{\epsilon}{w} \right) RT = (1 + n\epsilon) \frac{RT}{W}, \quad (11)$$

where  $n = \frac{W}{w} - 1$ , and  $R$  is the gas constant per mole.

If the reactant consists of more than one type of molecule with different molecular weights, this equation will have the same form but with a different value of  $n$ .

We shall derive formulae for the rate of burning associated with three types of homogeneous reaction: (I) a first-order rate from a unimolecular mechanism; (II) a second-order rate from a bimolecular reaction; (III) a second-order rate as the low pressure result of a unimolecular breakdown. These are described by the values of  $d\epsilon/dt$  as functions of  $\epsilon$ ,  $V$  and  $T$ .

$$(I) \quad \mathcal{R}(\epsilon, V, T) = \frac{d\epsilon}{dt} = B_1(1-\epsilon) \exp(-A/RT). \quad (12)$$

$$(II) \quad \mathcal{R}(\epsilon, V, T) = \frac{d\epsilon}{dt} = B_2(1-\epsilon)^2 V^{-1} \exp(-A/RT). \quad (13)$$

$$(III) \quad \mathcal{R}(\epsilon, V, T) = \frac{d\epsilon}{dt} = B_3(1-\epsilon)(1+n\epsilon) V^{-1} \exp(-A/RT). \quad (14)$$

The values of the constants will be discussed when the results are applied to particular cases.

Substituting in (10), we have

$$(I) \quad \frac{d\epsilon}{dT} = \frac{\lambda B_1(1-\epsilon) \exp(-A/RT)}{M^2 V \{Q(1-\epsilon) + C(T-T_m)\}}. \quad (15)$$

$$(II) \quad \frac{d\epsilon}{dT} = \frac{\lambda B_2(1-\epsilon)^2 \exp(-A/RT)}{M^2 V^2 \{Q(1-\epsilon) + C(T-T_m)\}}. \quad (16)$$

$$(III) \quad \frac{d\epsilon}{dT} = \frac{\lambda B_3(1-\epsilon)(1+n\epsilon) \exp(-A/RT)}{M^2 V^2 \{Q(1-\epsilon) + C(T-T_m)\}}. \quad (17)$$

The essentials of the method of integration are the same in all cases, but case (III) is simplest in algebraic detail, and we shall consider this first. From (11) and (17), the relation between  $\epsilon$  and  $T$  is

$$\frac{d\epsilon}{dT} = \frac{\lambda B_3 P^2 W^2 (1-\epsilon) \exp(-A/RT)}{M^2 R^2 T^2 (1+n\epsilon) \{Q(1-\epsilon) + C(T-T_m)\}}. \quad (18)$$

This equation cannot be integrated exactly. Near the outer boundary of the reaction zone  $T-T_m$  and  $1-\epsilon$  are small, and these terms determine the behaviour of the solution in this region. All other functions of  $T$  and  $\epsilon$  can be given the values corresponding to  $T=T_m$  and  $\epsilon=1$ . The equation thus simplified has a solution which at large distances, where  $T-T_m$  and  $1-\epsilon$  are sufficiently small, approaches that solution of the original equation satisfying the boundary condition that  $T=T_m$  when  $\epsilon=1$ . This  $(\epsilon, T)$  relation will then be used in the awkward coupling term to make (18) integrable by quadratures. This provides us with a second approximation to the solution of (18). We shall not go beyond this order of approximation, because comparison with step-by-step integration of the differential equation has shown that the accuracy is ample for our purpose; moreover, the next approximation equation would be as difficult to solve analytically as the original equation itself. It is not possible to stop at the extremely simple first approximation, because the error in the rate of burning, as compared with an accurate numerical solution of the equations,

is a factor of about three. The error in the second approximation has not been more than 15 % in those examples which we have tested; these belonged to case (II), and the errors are presumably of the same order of magnitude in cases (I) and (III).

Write  $1 - \epsilon = \xi$  and  $T_m - T = \eta$ .

The first approximation is the solution of the equation

$$\frac{d\xi}{d\eta} = \frac{\lambda B_3 P^2 W^2 \xi \exp(-A/RT_m)}{M^2 R^2 T_m^2 (1+n)(Q\xi - C\eta)} = \frac{D_3 \xi}{Q\xi - C\eta}, \tag{19}$$

where  $D_3$  is defined by this equation. Hence

$$\frac{d\eta}{d\xi} + \frac{C}{D_3} \frac{\eta}{\xi} = \frac{Q}{D_3}. \tag{20}$$

The boundary condition  $T = T_m$  when  $\epsilon = 1$ , is  $\eta = 0$  when  $\xi = 0$ . The solution of (20) which satisfies this condition is

$$\eta = \frac{Q\xi}{C + D_3}. \tag{21}$$

Inserting this in the coupling term of (18), we have as the equation for the second approximation,

$$\frac{d\epsilon}{dT} = \frac{\lambda B_3 P^2 W^2 (C + D_3) \exp(-A/RT)}{M^2 R^2 (1+n\epsilon) Q D_3 T^2},$$

of which the integration is immediate:

$$[\epsilon + \frac{1}{2}n\epsilon^2]_1 = \frac{\lambda B_3 P^2 W^2 (C + D_3) R}{M^2 R^2 Q D_3 A} [\exp(-A/RT)]_{T_m}^T. \tag{22}$$

This contains one parameter which is still arbitrary, namely  $M$ . This we must choose so that the solution satisfies the boundary condition at the beginning of the flame, that  $\epsilon = 0$  when  $T = T_0$ . When  $T$  is small,  $e^{-A/RT_0}$  is effectively zero in comparison with  $e^{-A/RT_m}$ , and so the equation which must be satisfied by  $M$  is

$$1 + \frac{n}{2} = \frac{\lambda B_3 P^2 W^2 (C + D_3)}{M^2 R^2 Q D_3} \left(\frac{R}{A}\right) \exp\left(-\frac{A}{RT_m}\right),$$

and using (19), the definition of  $D_3$ , we find

$$M^2 = \frac{\lambda B_3 P^2 W^2 \exp(-A/RT_m)}{R^2 T_m^2 C(1+n) \left\{ \left(\frac{1 + \frac{1}{2}n}{1+n}\right) \left(\frac{A}{RT_m}\right) \left(\frac{Q}{CT_m}\right) - 1 \right\}}. \tag{23}$$

This gives  $M$ , the mass of the medium which passes through unit cross-section of the reaction zone per unit time.  $V_0$  is the specific volume of the original reactant, and  $MV_0$  is the velocity of movement of the reaction zone relative to the unreacted medium. To obtain the relation between  $\epsilon$  and  $T$  through the flame, the value of  $M$  from (23) would be used in the solution (22). By solving a quadratic the solution can be written as an explicit function  $\epsilon = f(T)$ .



In using this equation and similar ones which we shall obtain later, one point must be noted. The gas constant  $R$  appears from two sources; as it enters from (11), the equation of state of the gas, it has to be in the unit

$$\frac{(\text{unit of pressure}) \times (\text{unit of volume})}{\text{unit of temperature}} \text{ of a mole of gas.}$$

In other words,  $R$  is in the appropriate mechanical units. The activation energy  $A$  is conventionally given in heat units, as calories, so the  $R$  associated with the  $A$  is in heat units, calories per mole per degree. To prevent possible confusion, we have written all the formulae in terms of  $R$  and  $A/R$ , which has the dimensions of temperature.

Case (I) can be treated similarly, and if we make a further small approximation the answer can be written in terms of functions which are as simple as in the case we have just discussed. The accurate relation between  $\epsilon$  and  $T$  is

$$\frac{d\epsilon}{dT} = \frac{\lambda B_1 P W (1 - \epsilon) \exp(-A/RT)}{M^2 R T (1 + n\epsilon) \{Q(1 - \epsilon) + C(T - T_m)\}}, \quad (24)$$

derived from (15) and (11).

For  $T - T_m$  and  $1 - \epsilon$  small the equation takes the form

$$\frac{d\xi}{d\eta} = \frac{D_1 \xi}{Q\xi - C\eta}, \quad (25)$$

where

$$D_1 = \frac{\lambda B_1 P W \exp(-A/RT_m)}{M^2 R T_m (1 + n)}, \quad (26)$$

giving

$$T_m - T = \frac{Q}{C + D_1} (1 - \epsilon), \quad (27)$$

and the equation for the second approximation is

$$\frac{d\epsilon}{dT} = \frac{\lambda B_1 P W T}{M^2 R (1 + n\epsilon)} \left( \frac{C + D_1}{Q D_1} \right) \left( \frac{\exp(-A/RT)}{T^2} \right). \quad (28)$$

This can be integrated exactly, the answer involving the exponential integral, which is a tabulated function. An approximate solution, from which the behaviour is more obvious, can be obtained by replacing  $T$  in the numerator by  $T_m$ . This approximation cannot be a serious source of error, since in any case the representation of the reaction rate as  $B e^{-A/RT}$  is itself an approximation which may not be very close at the temperatures involved. Moreover, the exponential integral of the accurate solution can be expanded in an asymptotic series which shows that the error is of the order of a few per cent for the values of  $A/RT_m$  which we shall consider.

Making this approximation, then, the integration proceeds as before, and the equation for the rate of burning is

$$M^2 = \frac{\lambda B_1 P W \exp(-A/RT_m)}{C R T_m (1 + n) \left\{ \left( \frac{1 + \frac{1}{2}n}{1 + n} \right) \left( \frac{A}{R T_m} \right) \left( \frac{Q}{C T_m} \right) - 1 \right\}}. \quad (29)$$

The presence of a factor  $(1 - \epsilon)^2$  in the case (II) equation makes its treatment more complicated. The method is the same as before. The exact equation is

$$\frac{d\epsilon}{dT} = \frac{\lambda B_2 P^2 W^2 (1 - \epsilon)^2 \exp(-A/RT)}{M^2 R^2 T^2 (1 + n\epsilon)^2 \{Q(1 - \epsilon) + C(T - T_m)\}}, \quad (30)$$

and the equation for the first approximation is

$$\frac{d\xi}{d\eta} = \frac{D_2 \xi^2}{Q\xi - C\eta}, \quad (31)$$

where

$$D_2 = \frac{\lambda B_2 P^2 W^2 \exp(-A/RT_m)}{M^2 R^2 T_m^2 (1 + n)^2}.$$

The equation can be written as

$$\frac{d\eta}{d\xi} + \frac{C\eta}{D_2 \xi^2} = \frac{Q}{D_2 \xi}, \quad (32)$$

of which the solution passing through  $\xi = \eta = 0$  is

$$\eta \exp\left(-\frac{C}{D_2 \xi}\right) = \frac{Q}{D_2} \int_0^\xi \exp\left(-\frac{C}{D_2 \xi}\right) \frac{d\xi}{\xi}. \quad (33)$$

The exponential integral is defined (e.g. Jahnke & Emde, 1933, p. 1) as

$$Ei(-x) = \int_\infty^x e^{-t} dt/t. \quad (34)$$

Let  $\psi = C/D_2$ . Transforming the variable of integration in (33) to  $\psi/\xi$  we see that the solution (33) can be written as

$$T_m - T = -\frac{Q}{D_2} \exp\left(\frac{\psi}{\xi}\right) Ei\left(-\frac{\psi}{\xi}\right). \quad (35)$$

The exponential integral has been tabulated in several places.

Substituting in the  $T - T_m$  term of (30),

$$\frac{d\epsilon}{dT} = \frac{\lambda B_2 P^2 W^2 \exp(-A/RT)}{M^2 R^2 Q (1 + n\epsilon)^2} \frac{\xi^2}{\{\xi + \psi \exp(\psi/\xi) Ei(-\psi/\xi)\}}.$$

Hence 
$$\int_{1-\epsilon}^0 \{\xi + \psi \exp(\psi/\xi) Ei(-\psi/\xi)\} \{(1+n)/\xi - n\}^2 d\xi = \frac{\lambda B_2 P^2 W^2}{M^2 R^2 Q} \left(\frac{R}{A}\right) [\exp(-A/RT) - \exp(-A/RT_m)]. \quad (36)$$

This solution satisfies the boundary condition at  $T_m$ , but not necessarily at the beginning of the flame. Imposing the condition that  $\epsilon = 0$  when  $T = T_0$ , gives as the equation to determine  $M$ ,

$$\int_0^1 (\xi + \psi \exp(\psi/\xi) Ei(-\psi/\xi)) \{(1+n)/\xi - n\}^2 d\xi = \frac{\lambda B_2 P^2 W^2}{M^2 R^2 Q} \left(\frac{R}{A}\right) \exp(-A/RT_m).$$

Write  $\theta = \psi/\xi$ . The result is

$$(1+n)^2 g_1(\psi) - 2n(1+n) g_2(\psi) + n^2 g_3(\psi) = \frac{\psi \lambda B_2 P^2 W^2}{M^2 R^2 Q} \left(\frac{R}{A}\right) \exp(-A/RT_m), \quad (37)$$

where

$$\left. \begin{aligned} g_1(\psi) &= \psi \int_{\psi}^{\infty} \{1/\theta + e^{\theta} Ei(-\theta)\} d\theta, \\ g_2(\psi) &= \psi^2 \int_{\psi}^{\infty} \{1/\theta + e^{\theta} Ei(-\theta)\} d\theta/\theta, \\ g_3(\psi) &= \psi^3 \int_{\psi}^{\infty} \{1/\theta + e^{\theta} Ei(-\theta)\} d\theta/\theta^2. \end{aligned} \right\} \quad (38)$$

Simplifying the right of (37) by using the definitions of  $\psi$  and  $D_2$ , it becomes just  $(CT_m/Q)(RT_m/A)(1+n)^2$ , and (37) becomes

$$g_1(\psi) - \frac{2n}{1+n} g_2(\psi) + \left(\frac{n}{1+n}\right)^2 g_3(\psi) = (CT_m/Q)(RT_m/A). \quad (39)$$

We have tabulated the functions  $g_1$ ,  $g_2$  and  $g_3$  for the whole range of  $\psi$  likely to be used. These are given in table 1.

(39) is an equation to determine  $\psi$ , and when its value for a particular case has been determined the value of  $M$  is found from

$$\psi = C/D_2,$$

giving 
$$M^2 = \lambda B_2 P^2 W^2 \psi \exp(-A/RT_m)/CR^2 T_m^2 (1+n)^2. \quad (40)$$

It should be noted that (39) does not contain  $P$ , so for a given reaction  $\psi$  is independent of the pressure, and  $M$  proportional to the pressure.

The accuracy of the second approximation can be tested by comparison with the results of numerical integration. This has been done only for case (II), but there is no reason to suppose that the results would be any less accurate in other cases; the physical justification for the method of approximation is the same for all. The error seems to depend chiefly on  $A/RT_m$ ; for values near 8, the rate of burning was found to be too low by about 6%, this varying by 2 to 3% from case to case. For  $A/RT_m$  near 5, the rate was too low by an error of 10 to 15%.

For cases (I) and (III) there is an obvious relation between  $\epsilon$  and  $T$  in the second approximation. In case (II) the result is

$$\begin{aligned} (1-\epsilon)g_1(\psi/(1-\epsilon)) - \frac{2n(1-\epsilon)^2}{1+n} g_2\left(\frac{\psi}{1-\epsilon}\right) + \frac{n^2(1-\epsilon)^3}{(1+n)^2} g_3\left(\frac{\psi}{1-\epsilon}\right) \\ = \left(\frac{CT_m}{Q}\right)\left(\frac{RT_m}{A}\right)\left[1 - \exp\left(\frac{A}{RT_m} - \frac{A}{RT}\right)\right] \end{aligned} \quad (41)$$

For any set of values of  $A$ ,  $T_m$ ,  $Q$ ,  $C$ ,  $n$ , equation (39) gives  $\psi$ , which can be used in (41) to find the  $T$  corresponding to any given  $\epsilon$ . The error in the  $(\epsilon, T)$  curve is small; comparison with a numerical integration carried out with the accurate  $M$  showed that  $\epsilon$  was too large by 3% at  $\epsilon = 0.5$ , and the error was everywhere of the same amount except at low temperatures.

This  $(\epsilon, T)$  relation can be used to find a value of  $M$  which is several per cent better than that of the second approximation. For this we choose  $\epsilon_1, \epsilon_2 \simeq 0.4, 0.6$  respectively, and such that  $\psi/(1-\epsilon_1)$  and  $\psi/(1-\epsilon_2)$  occur in table 1. (41) gives the corresponding  $T_1, T_2$  and hence  $d\epsilon/dT$  at  $\frac{1}{2}(T_1 + T_2)$ . Substitution in the accurate equation of the zone gives  $M$ .

TABLE I. FUNCTIONS FOR THE SOLUTION OF THE CASE (II) EQUATION

$\psi$	$g_1$	$g_2$	$g_3$
4.5	0.840	0.397	0.258
3.9	0.822	0.386	0.250
3.3	0.800	0.372	0.240
2.7	0.771	0.355	0.228
2.1	0.731	0.332	0.211
1.5	0.672	0.298	0.188
1.4	0.660	0.291	0.183
1.3	0.646	0.283	0.178
1.2	0.631	0.274	0.172
1.1	0.615	0.265	0.165
1.0	0.596	0.255	0.159
0.95	0.586	0.249	0.155
0.9	0.576	0.244	0.151
0.85	0.565	0.238	0.147
0.8	0.553	0.231	0.143
0.75	0.541	0.224	0.138
0.7	0.527	0.217	0.133
0.65	0.512	0.210	0.128
0.6	0.497	0.202	0.123
0.55	0.480	0.193	0.117
0.5	0.461	0.183	0.111
0.45	0.442	0.173	0.104
0.4	0.419	0.162	0.097
0.38	0.410	0.158	0.094
0.36	0.400	0.153	0.091
0.34	0.389	0.148	0.088
0.32	0.378	0.142	0.085
0.30	0.367	0.137	0.081
0.28	0.355	0.131	0.077
0.26	0.342	0.125	0.074
0.24	0.328	0.119	0.070
0.22	0.314	0.112	0.066
0.20	0.299	0.106	0.061
0.18	0.282	0.098	0.057
0.16	0.265	0.091	0.052
0.14	0.245	0.082	0.047
0.12	0.224	0.074	0.042
0.10	0.201	0.064	0.036
0.08	0.176	0.054	0.030
0.06	0.146	0.043	0.024

When the  $(\epsilon, T)$  relation has been found, it can be used in the equation for the heat-conduction (9), to find the values of  $x$  corresponding to various  $T$ . We have imposed the condition, necessary for a physically possible reaction zone, that  $T = T_m$  and  $\epsilon = 1$  together. It is immaterial whether this point has a finite or an infinite value of  $x$ , though usually the latter is the case. The flame is then theoretically infinite, though most of the reaction takes place within a very small distance of the surface. If  $\epsilon = 1$  and  $T = T_m$  at a finite value of  $x$ , the form of the equations ensures that  $\epsilon$  and  $T$  remain constant for all larger values of  $x$ . At distances from the surface which are large compared with the effective thickness of the flame, the gas may be

subjected to cooling and subsequent change of composition, but these cannot affect the rate of burning, no matter whether the flame thickness is finite or not. The only influences which can have any effect on the rate of burning are those which can act in the region where all but a small fraction of the chemical change takes place.

First approximations to the  $(x, T)$  relation can be found from the first approximation to the  $(\epsilon, T)$  law.

*Cases (I) and (III).* The first approximation is (21) or (27), and using this in (9)

$$\frac{\lambda}{M} \frac{dT}{dx} = D(T_m - T),$$

with  $D = D_1$  or  $D_3$  in the two cases.

Hence  $T_m - T$  and  $1 - \epsilon$  behave at large distances like multiples of  $\exp(-MDx/\lambda)$ . The thickness of the reaction zone is, strictly speaking, infinite.

*Case (II).* From (31) and (9),

$$d\xi/dx = -MD_2\xi^2/\lambda,$$

with the solution  $(1 - \epsilon)^{-1} = \xi^{-1} = MD_2x/\lambda + \text{constant}$ ,

and an infinite flame thickness.

To get a second approximation in these cases, it is easiest to tabulate  $\epsilon$  as a function of  $T$ , given by the appropriate second approximation, and then carry out a numerical integration of

$$x = \int_{T_1}^T \frac{\lambda dT}{M\{Q(1 - \epsilon) + C(T - T_m)\}},$$

where  $T_1$  is the temperature at the arbitrarily chosen origin of  $x$ .

In all these cases the 'thickness of the flame' is in the first approximation proportional to  $\lambda/MD$ .

$$\text{In case (II), } \frac{\lambda}{MD_2} = RT_m(1+n)[\lambda\psi/CB_2 \exp(-A/RT_m)]^{1/2}/PW. \quad (42)$$

Using (23) and (19) for case (III),

$$\lambda/MD_3 = (RT_m/PW) \left[ \lambda(1+n)/CB_3 \exp(-A/RT_m) \left\{ \left( \frac{1+\frac{1}{2}n}{1+n} \right) \left( \frac{A}{RT_m} \right) \left( \frac{Q}{CT_m} \right) - 1 \right\} \right]^{1/2}.$$

In case (I),

$$\lambda/MD_1 = \left[ \lambda RT_m(1+n)/B_1 PW \exp(-A/RT_m) \left\{ \left( \frac{1+\frac{1}{2}n}{1+n} \right) \left( \frac{A}{RT_m} \right) \left( \frac{Q}{RT_m} \right) - 1 \right\} \right]^{1/2}.$$

#### 4. SEPARATION OF CERTAIN PARAMETERS

It is possible to obtain explicit formulae for the effect of certain of the parameters of the problem by a method which is simple and exact. We take the equations of case (I) as an example:

$$\frac{d\epsilon}{dx} = B_1(1 - \epsilon) PW \exp(-A/RT)/MRT(1 + n\epsilon), \quad (43)$$

$$\frac{dT}{dx} = M\{Q(1 - \epsilon) + C(T - T_m)\}/\lambda, \quad (44)$$

which can be written as

$$(\lambda/B_1PW)^{\frac{1}{2}} \frac{d\epsilon}{dx} = (\lambda B_1PW/M^2)^{\frac{1}{2}} f(\epsilon, T, A, n), \tag{45}$$

$$(\lambda/B_1PW)^{\frac{1}{2}} \frac{dT}{dx} = (\lambda B_1PW/M^2)^{-\frac{1}{2}} g(\epsilon, T, A, n), \tag{46}$$

where  $f$  and  $g$  are functions of their arguments which are obvious from (43) and (44), and whose precise form will not be needed hereafter. This pair of equations connects  $\epsilon$  and  $T$  with  $x(B_1PW/\lambda)^{\frac{1}{2}}$  and the only parameter left in them is  $(M^2/\lambda B_1PW)^{\frac{1}{2}}$ . The boundary conditions fix the values of  $\epsilon$  and  $T$  at two points, where  $x(B_1PW/\lambda)^{\frac{1}{2}}$  has fixed values (0 and  $\infty$ ).

The values of  $\epsilon$  and  $T$  at these points are independent of  $B_1, P, W$ , and  $\lambda$ ; it follows that the solution of (45) and (46) which satisfies such boundary conditions has

$$\frac{M}{(\lambda B_1PW)^{\frac{1}{2}}} = \text{function of } (A, n, Q, C, T_m), \tag{47}$$

and any particular value of  $T$  or  $\epsilon$  occurs at a value of  $x(B_1PW/\lambda)^{\frac{1}{2}}$  which depends only on  $A, n, Q, C, T_m$ .

In other words, the rate of burning  $M = (\lambda B_1PW)^{\frac{1}{2}} \times \text{function of } (A, n, Q, C, T_m)$ , and any dimension (of the reaction zone) which is defined by values of  $\epsilon$  and  $T$ , will be proportional to

$$\left(\frac{\lambda}{B_1PW}\right)^{\frac{1}{2}} \times \text{function of } (A, n, Q, C, T_m). \tag{48}$$

The thickness of the complete zone of burning is infinite, but it is convenient to speak of a 'flame thickness', which in this case is proportional to the quantity (48). In particular, the pressure variation of the rate of burning is

$$M \propto P^{\frac{1}{2}}. \tag{49}$$

The same process can be applied to cases (II) and (III), and the results are

$$M = PW(\lambda B)^{\frac{1}{2}} \times \text{function of } (A, n, Q, C, T_m), \tag{50}$$

$$\text{'flame thickness'} = \frac{1}{PW} (\lambda/B)^{\frac{1}{2}} \times \text{function of } (A, n, Q, C, T_m), \tag{51}$$

with  $B = B_2$  or  $B_3$ .

It will be noticed that the rate of burning is proportional to  $\lambda^{\frac{1}{2}}$  for all three chemical mechanisms. This suggests that the result may be true under more general assumptions. We shall now show that our fundamental equations, without any assumption other than that the conductivity is constant, lead to the results that the rate of burning and the 'flame thickness' are both proportional to  $\lambda^{\frac{1}{2}}$ .

Equation (4) is 
$$\frac{\lambda}{M} \frac{dT}{dx} = H - H_m, \tag{52}$$

and (5) is 
$$VM \frac{d}{dx} = \mathcal{R}(\epsilon, V, T), \tag{53}$$

which can be written as

$$\lambda^{\frac{1}{2}} \frac{dT}{dx} = \frac{M}{\lambda^{\frac{1}{2}}} (H - H_m), \quad \lambda^{\frac{1}{2}} \frac{d\epsilon}{dx} = \frac{\lambda^{\frac{1}{2}} \mathcal{R}(\epsilon, V, T)}{M V},$$

and it follows that the rate of burning and flame thickness are proportional to  $\lambda^{\frac{1}{2}}$ .

### 5. THE METHOD OF NUMERICAL INTEGRATION

In § 3 we gave approximate solutions for the equations of the reaction zone. These solutions are easily handled, but the method would fail if the equations were substantially more complicated, as, for example, if the thermal conductivity were a function of the temperature. In such a case it would be necessary to solve the equations numerically.

The reaction zone equation is very easily integrated numerically. Consider, for example, case (II), whose equation is (30) of § 2:

$$\frac{d\epsilon}{dT} = \frac{\lambda B_2 P^2 W^2 (1 - \epsilon)^2 \exp(-A/RT)}{M^2 R^2 T^2 (1 + n\epsilon)^2 \{Q(1 - \epsilon) + C(T - T_m)\}}.$$

This can be integrated by a step-by-step process, for any assumed value of  $M$ . Starting from one of the boundary conditions, the solution can be carried sufficiently near to the other extreme temperature of the reaction zone, to see whether the solution satisfies the other boundary condition. For example, suppose that the integration has been started at the cool side of the flame, where  $\epsilon$  is practically zero and  $T = T_0$ . If  $M$  is less than a certain critical value,  $dT/dx$  becomes negative after a certain value of  $T$  has been reached in the integration.  $d\epsilon/dx$  is still positive, so that beyond the point where  $dT/dx = 0$ ,  $\epsilon$  continues to increase but  $T$  decreases and never attains  $T_m$ . This is not a physically satisfactory form for the reaction zone, for it does not have the essential feature of the actual zone, that the temperature rises to the value corresponding to complete reaction. For large  $M$  the solution has the property that  $d\epsilon/dT$  is so small that when the solution has reached  $T = T_m$ ,  $\epsilon$  has not attained the limit value 1. This solution, too, is not physically satisfactory. There is one value of  $M$  for which the corresponding solution  $\epsilon = 1$  at  $T = T_m$ . This solution is the true reaction zone which would be set up in steady burning (if our equations were exact descriptions of the phenomena).

Steps of 100° C have been found convenient for the integration of the differential equation. If the solution is started from the hot side of the flame, the first approximation is used until a stage has been reached at which it is possible to use the differential equation. There are points in favour of each end as the commencement of integration, but for case (II), for which our numerical computations were carried out, it has been found better to start at the low temperature side.

The advantage of numerical integration, finding  $M$  by trial and error, is that it can be used whatever the form of  $d\epsilon/dT$ . The only practical point to be mentioned is that it is essential to work the calculation with  $T$  as the independent variable; if  $\epsilon$  were used as the independent variable slight errors in guessing  $T$  for the  $n$  arc would lead to large errors in  $dT/d\epsilon$  (because of the presence of  $e^{-A/RT}$ ), and the arc would have to be reworked a large number of times.

## 6. CHOICE OF THERMAL CONDUCTIVITY

In the theory of § 2,  $\lambda$  has been taken as a constant. In numerical integrations on the burning of nitrate esters it has been found that a simple mean value gives practically the same rate of burning as the actual conductivity which varies through the reaction zone.

The thermal conductivity is a function of  $\epsilon$  and  $T$ . For low pressures it is independent of the pressure. It is usual to represent the temperature dependence by

$$\lambda(T)/\lambda(273^\circ \text{K}) = \frac{(273 + C')(T)^{\frac{1}{2}}}{(T + C')(273)}, \quad (54)$$

where  $C'$  depends only on the nature of the gas, and for nitrogen and gases of similar molecular weight is about 100. The agreement with the observations is better at high temperatures than at low. Tests with a  $\lambda$  depending on temperature in this manner ( $C' = 100$ ) showed that this was equivalent to a constant conductivity whose value was that appropriate to a temperature somewhat above the middle of the temperature range encountered in the flame zone.

The conductivity at any point depends on the composition of the gas at that point, that is, on  $\epsilon$ . The reactant has a higher molecular weight than the final products, and its conductivity is less. For organic vapours such as benzene,  $\lambda$  at  $0^\circ \text{C}$  is about  $2.5 \times 10^{-5}$  cal./sq.cm./sec. per ( $^\circ \text{C}/\text{cm.}$ ), which is about half that of the final products at the same temperature. Assuming  $C' = 100$  this would make their  $\lambda$  (at  $2000^\circ \text{K}$ ) =  $0.92 \times 10^{-4}$ . Numerical solutions have shown that it is sufficiently accurate to take an average of the initial and final conductivities, when calculating rates of burning by using a theory with constant  $\lambda$ . Of course the  $(\epsilon, T, x)$  relations are not reproduced by a constant conductivity, but this is usually not of any great importance, and the error is not large.

## 7. DISCUSSION

The chief result of the foregoing analysis is that we have obtained formulae which give the flame velocities in terms of the reaction velocity constants, the specific heat and heat conductivity for the three simple cases considered. These cases were: a unimolecular reaction with velocity given by equation (29), a bimolecular reaction given by equation (40), and a quasi-bimolecular reaction given by equation (23), the effect of diffusion being neglected compared with that of heat conductivity in all cases. The actual formulae are only approximations, but the approximation is one in which higher order terms are neglected in a purely mathematical method of solving the accurate physical equations. The error due to this approximation in some actual cases solved exactly by numerical integration has been found to be from 5 to 15 %. This is negligible compared with the degree of uncertainty in any initial data at the present stage.

The analysis also provides the dependence of the composition and temperature on the co-ordinate perpendicular to the flame front, to a corresponding degree of accuracy. This would give any conventional measure of the flame thickness which it



is desired to make. 'Flame thickness' always depends on an arbitrary convention, since theoretically the variations of composition and temperature extend an infinite distance. The analysis shows that all particulars of the flame structure can be found to about the above degree of accuracy. If the same models are considered but with more detailed knowledge of certain properties the problem could still be solved by direct numerical integration coupled with a trial and error process for the velocity. Hence for such simple reaction systems there are no uncertainties in the theory, only detailed difficulties in the numerical work.

The qualitative aspect of the results can be summed up by stating that the mass flame velocity is proportional to the product of the square roots of the heat conductivity, the density, the reciprocal of the specific heat, and the reaction velocity near the final temperature. Hence if the homogeneous reaction velocity varies as (pressure)<sup>n</sup> the mass flame velocity will vary as (pressure)<sup>½(n+1)</sup>, giving  $p^{\frac{1}{2}}$  for a unimolecular reaction or  $p$  for a bimolecular reaction.

In conclusion we may restate our general view that there are no real subtleties in the quantitative theory of flames but there are very great mathematical complexities.

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#### APPENDIX

##### *Validity of the 'local temperature' in the reaction zone*

We assume that the molecules are activated by collisions with other molecules, and that the rate of activation at any point depends on the temperature *at that point only*, just as if the gas were in a large container at that uniform temperature. In other words, we assume that the mean free path of the molecules is much smaller than the thickness of the effective reaction zone. The Maxwell mean free path is

$$\bar{l} = \frac{1}{\pi 2^{\frac{1}{2}} (\text{diameter of molecule})^2 (\text{no. of molecules per cm.}^3)}$$

The diameter of the molecule is of order 2 to 3 Å. Let  $P$  atmospheres be the pressure. Taking 2000° K as the temperature in the most important zone of a typical flame, we find that  $\bar{l}$  is of the order  $10^{-4}/P$  cm. Hence, for our assumption to be valid, the effective breadth of the reaction zone must be greater than  $10^{-3}/P$  cm.

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