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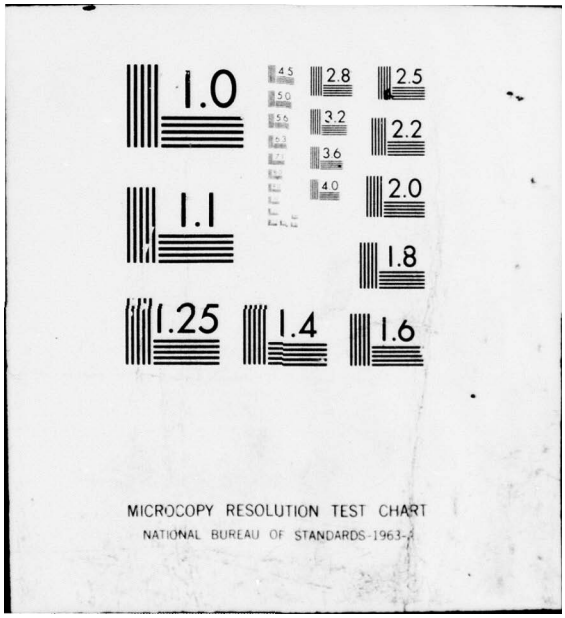
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MATHEMATICAL THEORY OF LAMINAR COMBUSTION IV. STEADY BURNING OF A LINEAR CONDENSATE

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ABSTRACT

We are concerned here with the deflagration of reactants that are produced by gasification at the surface of a solid or liquid. In particular, the influence of pressure on the gasification rate is examined under various conditions. In contrast to earlier treatments, the basic phenomena, including several unsuspected ones, are clearly uncovered by activation-energy asymptotics.

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Key words: Responses, True and Effective Extinction, Solid Pyrolysis, Vaporizing Liquid, Surface and Background Radiation, Distributed Heat Exchange

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SIGNIFICANCE AND EXPLANATION

The burning of a solid actually consists of two processes: gasification, or pyrolysis, of the solid at its surface and reaction of the gases so produced to form a flame. The same two processes are present when a liquid burns, the gasification now being evaporation. Here we are concerned primarily with the effect of pressure on the gasification rate, in particular conditions under which the flame is extinguished (or ignited). Radiation from (and to) the surface is important, as is heat exchange between the gases and their surroundings (by radiation or conduction).

The responsibility for the wording and views expressed in this descriptive summary lies with MRC, and not with the authors of this report.

MATHEMATICAL THEORY OF LAMINAR COMBUSTION

IV. STEADY BURNING OF A LINEAR CONDENSATE

J.D. Buckmaster and G.S.S. Ludford

1. Responses.

In Secs. II.3,4 several methods of supplying a reactant at a station $x = 0$ were considered. In each case four relations between the three surface values (II.24), M and D are prescribed and then the flame eigenvalue determines them. For the switch-on reaction the surface values themselves are prescribed along with D and then the eigenvalue gives M. For the flameholder M, D, T_s and $J_s = 1$ are prescribed and the eigenvalue gives T_∞, i.e. $Y_s + T_s$. (The third example, namely the vaporizing liquid, is discussed at the end of Sec. 7.)

The switch-on reaction provides the simplest example of a response. With the surface values (i.e. the switch-on temperature T_s and the upstream state $Y_{-\infty}, T_{-\infty}$) held fixed, the flame speed (i.e. M) is determined as a function of pressure (i.e. D). The response curve is a parabola $DM^{-2} = \text{const.}$, where the constant is determined by $T_\infty = Y_{-\infty} + T_{-\infty}$ and $J_s = Y_{-\infty}$. Note that, while x_* is fixed, the location of the flame varies along the parabola because M is involved in the length unit.

For the flameholder, where T_s and J_s are fixed, the flame temperature T_∞ becomes a function of both M and D. Such a function can be described by its sections $MT_\infty^{-2}\exp(\theta/2T_\infty) = \sqrt{2D}/\theta = \text{const.}$, which are parabolas flattened along the T_∞-axis near the origin. However, not all of the curve represents the response: T_∞ must lie between T_s and $T_s + 1$ if x_* is to lie in the range $(0,\infty)$. These limits correspond, respectively, to all and none of the heat released at the flame being conducted back to the supply. When $T_\infty = T_s$ the flame has reached the surface and the analysis of Sec. II.5 shows that M may then be decreased indefinitely without changing T_∞. When $T_\infty = T_s + 1$ the flame has become remote and the same section shows that M may then be increased indefinitely. The resulting response is similar to that in Fig. 1 with M,D replaced by T_∞, M. In practice the remote flame signals an effective extinction (cf. Sec. 2).

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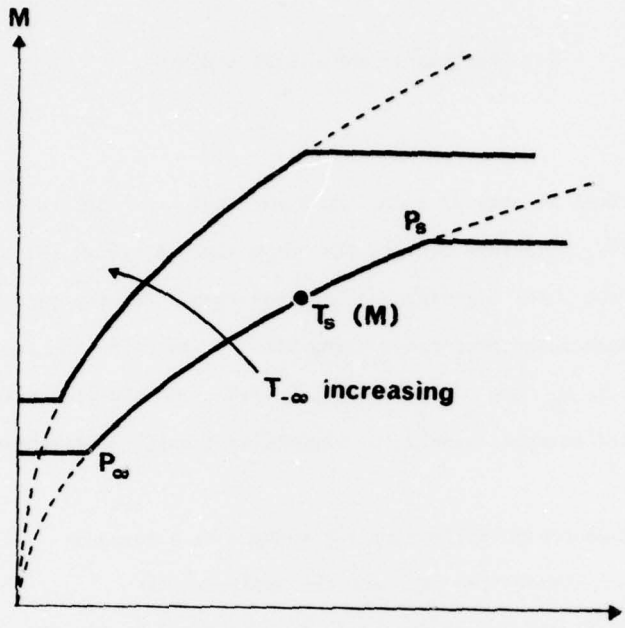


FIG. 1

Solid pyrolysis under adiabatic conditions: ---- basic M,D-curve; ━━ stable response.

A more complicated response, again of M to D, occurs when gasification at the surface of a solid or liquid, lying in $x < 0$, supplies the reactant. We still have $J_s = 1$ and $T_\infty (= Y_s + T_s)$ can be calculated from an overall enthalpy balance. Under adiabatic conditions, T_∞ itself is determined but otherwise it is expressed in terms of T_s and M. A further relation comes from specifying the nature of the gasification: in pyrolysis, the surface temperature T_s determines the production rate M; in vaporization, it determines the partial pressure represented by DY_s. The fourth relation is prescription of D, and then the flame eigenvalue is an equation for M, the T_∞ in it being known (implicitly) as a function of M. Our task is to determine how M varies with D when the remote temperature of the condensate and the background temperature are held fixed.

2. Experimental Results. Extinction.

If a solid or liquid contained in the left half of a long straight uniform tube gasifies into a combustible mixture at its surface then a steady state may be attained in which the surface recedes and is followed at a fixed distance by a flame separating unburnt gas from burnt. An observer moving with the surface sees a constant flux M of unburnt gas towards the flame and an equal flux of burnt gas beyond. The problem of determining the combustion field is of the type which arose in Sec. II.3 while resolving the cold-boundary difficulty, if the combustible mixture can be treated a single reactant; in fact, the vaporizing liquid treated there is one of the two main questions here, and it will have to be reconsidered. The other main question is the pyrolysing solid.

Since the aim is to determine the response of M to D, it might be thought that equation (II.22) has the answer: the response is parabolic. However, the condensate has two important effects. First, it fixes the position of the flame, which must be somewhere between its surface and infinity. The use of the formula (II.22) is thereby restricted and indeed when the flame approaches the surface or recedes to infinity it must be replaced by the appropriate formula from Sec. II.5. Secondly, it can make T_∞ dependent on M or D and hence change completely the response predicted by the original formula. These two effects are the subject of the present chapter.

Experiments which approximate the situation described above have been done for solids which gasify by surface pyrolysis (Johnson & Nachbar, 1962; Nir, 1973). Three basic phenomena are found: (i) the burning rate increases with ambient pressure, but very little beyond a certain pressure; (ii) there is a minimum pressure beyond which gaseous deflagration will not take place (extinction); and (iii) preheating the solid lowers this minimum. All three effects are exhibited by the theory, even when absorption or emission of radiant energy by the surface and heat loss or gain through the wall of the tube are neglected. These departures from adiabatic deflagration will be considered later; here we just note the partial analysis given by Johnson & Nachbar (1962) based on distributed heat loss from the condensed phase.

The analysis follows Buckmaster, Kapila & Ludford (1976) and reveals that extinction, by which is meant the disappearance of gaseous deflagration and not the cessation of pyrolysis,

can be of two kinds. In true extinction, the flame suddenly disappears as the pressure is lowered. However, the pyrolysis continues at a lower temperature, the products passing away unburnt in what is known as flameless combustion. Effective extinction, followed by flameless combustion without sudden drop in surface temperature, occurs when the flame recedes to infinity so that the products of continuing pyrolysis effectively pass away unburnt. The disappearance of a flame is generally taken to be true extinction, although Nir comes close to recognizing effective extinction in his experiments.

We shall find that extinction is always of the effective kind for adiabatic deflagration, and may be so for radiative loss or gain (when a separate phenomenon of ignition is possible). We shall also show that effective extinction is changed to true extinction by heat losses through the tube wall (Kapila & Ludford, 1977).

Apparently no experiments have been reported on vaporizing liquids. A more realistic treatment than that presented in Sec. II.4 reveals the striking effects detailed later, which deserve experimental verification.

3. Solid Pyrolysis Under Adiabatic Conditions.

The gas mixture will be treated as a single reactant with Lewis number 1. The object is to determine the combustion field in general, and M in particular, given the remote temperature $T_{-\infty}$ of the solid and the pressure level in the gas phase, i.e. D. For that purpose (see Sec. II.4) we need only determine (in addition to M) the values Y_s, T_s and $Y_s' = -T_s'$ which the solid in $x < 0$ presents to the gas phase in $x > 0$.

In fact, to determine the eigenvalue $\Lambda = M^{-2}D$ it is only necessary to know the mass flux fraction $J_s = Y_s - Y_s'$ and the flame temperature $T_\infty = T_s + Y_s$. If none of the products of the gaseous reaction is produced or absorbed at the surface of the solid, then $J_s = 1$ and

$$M^{-2}D = \theta^2 \exp(\theta/T_\infty)/2T_\infty^4 , \tag{1}$$

a relation determining M once T_∞ is known. The formula has a mixed character: θ and T_∞ have no dimensions while M and $D^{\frac{1}{2}}$ have those of mass flux. Several such equations will appear in the sequel. Note that the presence of the solid (or whatever else is creating the stream of reactant) is felt solely through T_∞, a fact first recognized by Williams (1973).

$T_\infty = Y_s + T_s$ can be obtained without calculating surface values. In the absence of radiation to or from the surface and of losses elsewhere, the flux of enthalpy at $x = +\infty$ must equal that at $x = -\infty$ (since the kinetic energy is negligible). Reverting to dimensional quantities, we may write

$$(2) \qquad (h^\circ - Q) + c_p(T_\infty - T^\circ) = \hat{h}^\circ + \hat{c}_p(T_{-\infty} - T^\circ),$$

where $h^\circ - Q$ is the heat formation of the product of the deflagration and $\hat{}$ denotes values for the solid. Solving for T_∞ and writing the result in dimensionless form yields

$$(3) \qquad T_\infty = \kappa T_{-\infty} + (1 - \kappa)T^\circ + q + 1,$$

where

$$(4) \qquad \kappa = \hat{c}_p/c_p \quad \text{and} \quad q = (\hat{h}^\circ - h^\circ)/Q.$$

Here q, the heat of pyrolysis, is the difference between the heat of formation of the solid and that of the gaseous reactant, both at the standard temperature T°, expressed in units of the heat of combustion Q. Equation (3) shows that T_∞ (which we shall suppose to be positive) is independent of M and is a linear function of the remote temperature $T_{-\infty}$ of the solid. Fig. 1 sketches the curves (1) for two values of $T_{-\infty}$.

A third condition must be added to $J_s = 1$ and $T_s + Y_s = T_\infty$ in order to determine all the surface values; that takes the form of a pyrolysis law. The rate of gasification is supposed to depend only on the surface temperature and not, for example, the pressure. We shall take

$$(5) \qquad M = kT_s \exp(-\hat{\theta}/T_s),$$

where k and $\hat{\theta}$ are constants. Note that the pyrolysis occurs at any surface temperature, so that the term extinction (or ignition) must refer to the gaseous deflagration, as we have supposed. The law should be viewed as determining the surface temperature T_s which produces the required flux M into the gase phase. Various modifications have been suggested, all of which lead to similar results. The only essential feature is that M should be a steadily increasing function of T_s. Apart from its simplicity, the law adopted here has the advantage of firm theoretical foundations in gas kinetics and reactive solids. Its role in

Fig. 1 is just to make T_s a parameter on the curves.

The gas phase is now completely determined, without reference to the conductivitiy of the solid. Only the enthalpy of the solid enters into the result (1); and the remaining details of the gas phase come from adding the pyrolysis law. The role of the conductivity is to fix the distribution of temperature between $T_{-\infty}$ and T_s so that the total heat flux at each point of the moving solid is constant.

Whatever the value of θ, the surface temperature must lie within certain bounds: $T_\infty = Y_s + T_s$ and $0 < Y_s < 1$ imply

$$T_\infty - 1 < T_s < T_\infty. \tag{6}$$

For finite θ, it is not immediately clear that a solution is then guaranteed; but in the limit $\theta \to \infty$ such is the case. Only the location (II.14) of the flame need be checked. If we note that

$$T_s' = -Y_s' = 1 - Y_s = 1 + T_s - T_\infty, \tag{7}$$

a result expressing heat-flux balance in the gas phase, then

$$x_* = -\mathcal{M}(1 + T_s - T_\infty) \tag{8}$$

and the inequalities (6) ensure $0 < x_* < \infty$, as supposed. It is a characteristic feature of activation-energy asymptotics that such questions can be settled simply.

Fig. 1 shows the corresponding end points P_s and P_∞, so designated because at P_s the flame has moved back to the surface and at P_∞ has receded to infinity. These two possibilities were dealt with before (Sec. II.5), requiring reconsiderations of the structure. It was found that, with conditions at the surface fixed, the remote flame allows D to be decreased to zero while the surface flame allows it to be increased indefinitely, both without change in M; that is just what the pyrolysis law demands. Thus the M,D-curve is completed by horizontal lines, one stretching from P_s to $D = \infty$ and the other from P_∞ to $D = 0$. Of course, if T_∞ is less than 1, the left inequality (6) is ineffective, i.e. P_∞ does not exist and the curve extends to the origin. The following remarks will apply when $T_\infty > 1$ and must be slighly modified otherwise.

The response curve now shows that (i) M increases with D, but not beyond P_s; and that (ii) there is a minimum D, corresponding to P_∞, before which there is effective extinction. The third phenomenon (iii) listed in Sec. 2 concerns the change in D, for $T_s = T_\infty - 1$, as T_∞ increases linearly with $T_{-\infty}$. We find

$$(9) \qquad \frac{dD}{dT_{-\infty}} = -\frac{\theta^3 M^2}{2T_\infty^6} \exp(-\theta/T_\infty) \frac{dT_\infty}{dT_{-\infty}} < 0$$

with relative error $O(\theta^{-1})$, since $dM/dT_\infty = dM/dT_s$ is $O(1)$. The effect (iii) is clearly present and is caused by the exponential factor, which decreases as T_∞ increases irrespective of how M changes.

4. Radiation from the Surface.

It is of interest to see how the picture is modified by radiation between the surface of the solid and the surroundings. Distributed exchange will be treated later. If the background temperature is T_b, there is a heat loss (or gain if negative)

$$(10) \qquad r = \sigma(T_s^4 - T_b^4),$$

where σ is a positive constant which is not always small in practice. Only Spalding (1960) has treated radiative exchange with surroundings at nonzero temperature ($T_b \neq 0$), and then in an approximate fashion which precluded heat gain ($T_b > T_s$). As a consequence he missed the most striking results. Experiments on such loss have been reported by Levy & Friedman (1962).

The loss changes the overall enthalpy balance to

$$(11) \qquad T_\infty = T_\infty^a - r/M,$$

where T_∞^a is the flame temperature under adiabatic conditions, given by the formula (3); but nothing else changes. T_∞ is now a function of M, both directly and through T_s in r; inserted in the response formula (1), it provides a D which is no longer proportional to M^2. Note that the pyrolysis law now affects the shape of the M,D-curve.

Consider first $T_b = 0$. To determine the new response curve it is helpful to sketch the graph of T_∞ versus T_s for fixed $T_{-\infty}$, and that has been done in Fig. 2. There is a maximum at E, corresponding to $T_s = \hat{\theta}/3$, from which the descent is monotonic to $-\infty$ as

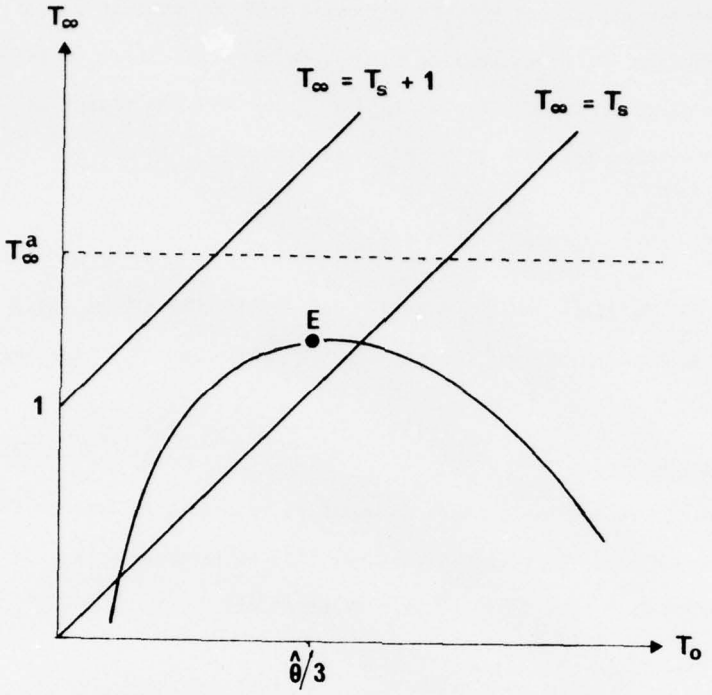


FIG. 2

T_s, T_∞-curves for solid pyrolisis: ---adiabatic;—— radiation with $T_b = 0$.

$T_s \to 0$ or ∞. The shape of the M,D-curve is obtained by rotation through 90° since the asymptotically correct result

(12) $$D^{-1}dD/dM = -(\theta dT_s/T_\infty^2 dM)dT_\infty/dT_s$$

shows that all slopes have their signs changed. Fig. 3 gives sketches of the resulting C-shaped curve, the leftmost point corresponding to E.

As in the absence of radiation, not all of the curve is acceptable. In Fig. 2 only the portions lying between the lines $T_\infty = T_s$ and $T = T_s + 1$ satisfy the inequalities (6), and these depend on $T_{-\infty}$. (An increase in $T_{-\infty}$ merely translates the curve upwards.) If $T_{-\infty}$ is too small, there is no such portions; otherwise five possibilities arise depending on whether the curve intersects one or both of the lines with E between them or not. These lead to the five parts of Fig. 3, where progress is from (a) to (b or b') to (c) to (d) as $T_{-\infty}$ increases. In each case the end points of the portion are marked to correspond with the position of the flame, and horizontal completions are included. The complete responses are shown by unbroken lines.

It is widely believed that if M decreases as D increases the combustion is unstable (Emmons, 1971) and, since there is some analytical evidence to support the idea, we shall adopt it here. (Surface burning corresponding to a horizontal extension from such a point will also be assumed unstable). The whole of Figs. 3a and b' are then discarded, the preheating being too weak for stable combustion. The surviving parts of Figs. 3b, c and d are drawn heavily, as the responses to be expected in an experiment. Clearly they exhibit the phenomena (i) and (ii) mentioned in Sec. 2.

The minimum $T_{-\infty}$ for stable burning can be found by setting $T_\infty = T_s = \hat{\theta}/3$ in (11) and solving for $T_{-\infty}$. As the preheating increases, the true extinction of Figs. 3b and c will occur until $T_{-\infty}$ reaches the value given by (11) for $T_\infty - 1 = T_s = \hat{\theta}/3$. For all larger values of $T_{-\infty}$ the effective extinction of Fig. 3d will occur, as under adiabatic conditions. The extinction value of D is given explicitly by the formula (1), where M and T_∞ are to be calculated from (5) and (11) by setting $T_s = \hat{\theta}/3$ for true extinction and $T_s = T_\infty - 1$ for effective extinction. The third effect, that the extinction value of D decreases as $T_{-\infty}$ increases, then follows from the derivative (9) since T_∞ still increases with $T_{-\infty}$.

5. Background Radiation.

If $T_b \neq 0$ in the radiation term (10) several new responses can occur. These are not associated with T_s large (where the results of Sec. 4 apply) but with T_s small, which not only allows T_b to change the sign of r but also enhances the latter's effect in (11) through the smallness of M. The left-hand side of the curve in Fig. 2 is thereby bent upwards to give Fig. 4. Whether the result is a monotonic curve (Fig. 4a) or one with a minimum E_1 and a maximum E_2 (Fig. 4b) depends on the size of T_b: the polynomial factor $3T_s^5 - \hat{\theta}T_s^4 + T_b^4 T_s + \hat{\theta}T_b^4$ in dT_∞/dT_s has just two positive zeros (both lying between T_b and $\hat{\theta}/3$) if T_b is less than $0.168\hat{\theta}$ ($<\hat{\theta}/3$) and no positive zero otherwise. Since the curve must cross the strip (6) there is always deflagration (albeit unstable) for some range of D, in contrast to Sec. 4 where $T_{-\infty}$ had to be large enough.

The monotonic curve for $T_b > 0.168\hat{\theta}$ leads to a response which is qualitatively the same as for adiabatic conditions (Fig. 1). The strong background radiation tends to compensate for losses from the surface.

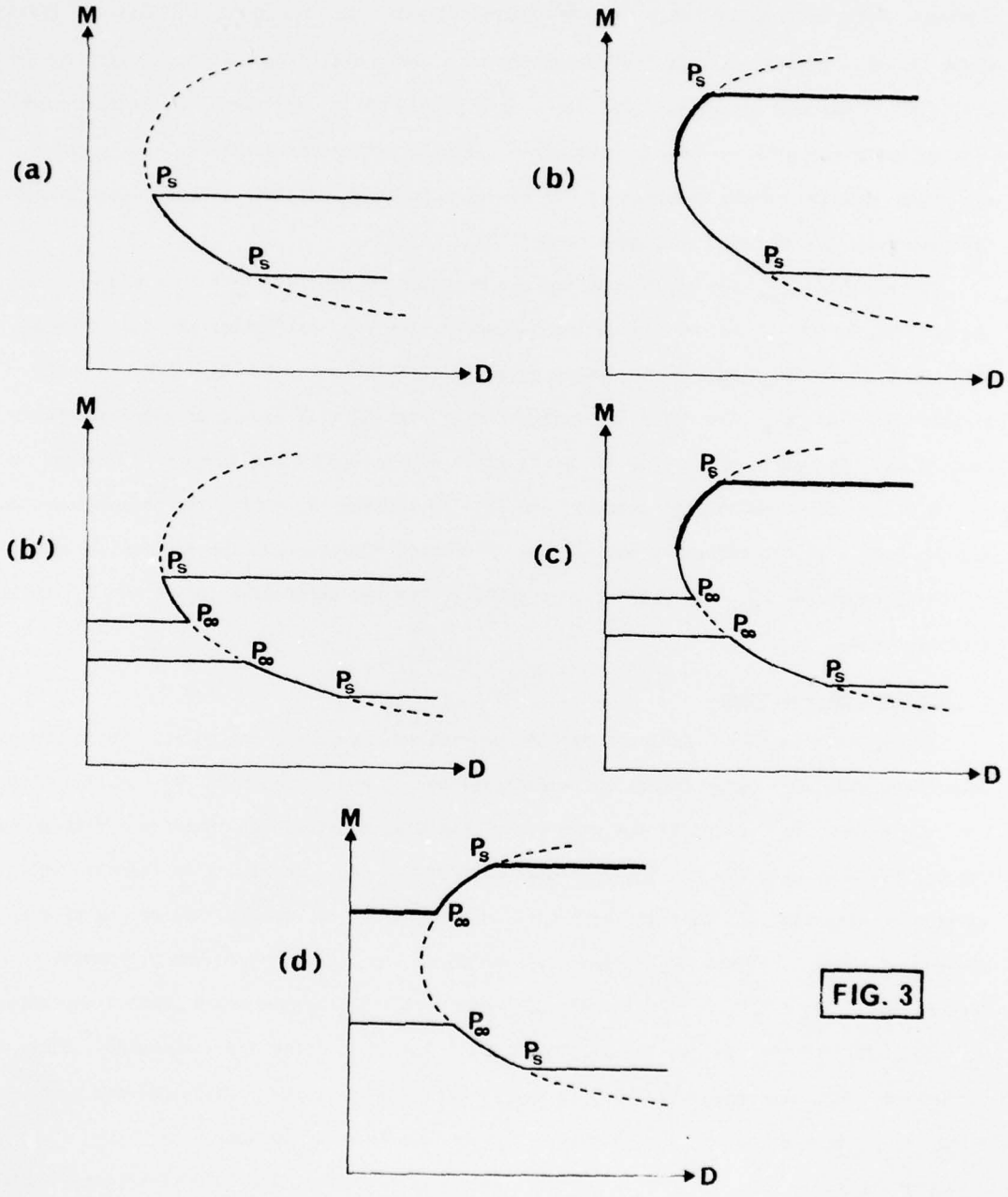


FIG. 3

Solid pyrolysis for radiation with $T_b = 0$:---basic M,D-curve, ——possible response; ▬▬stable response.

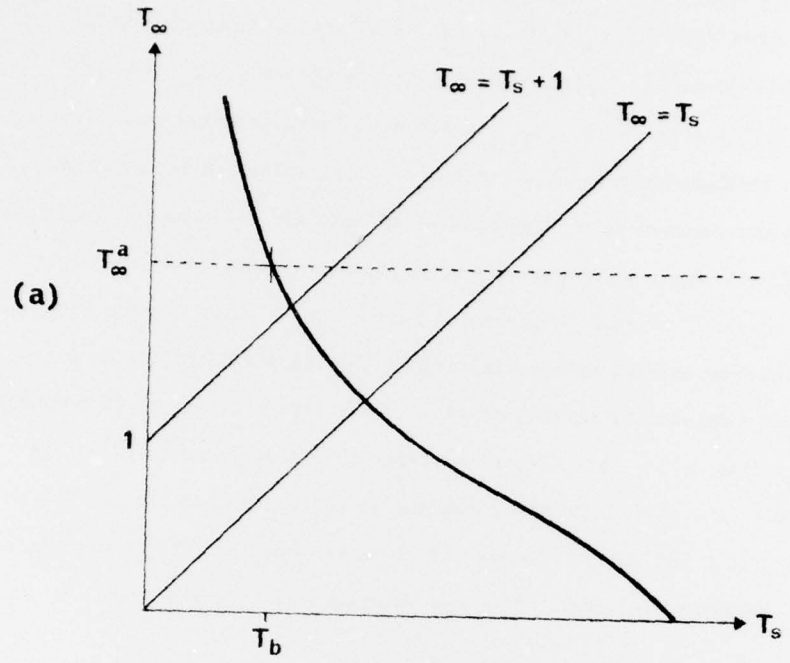
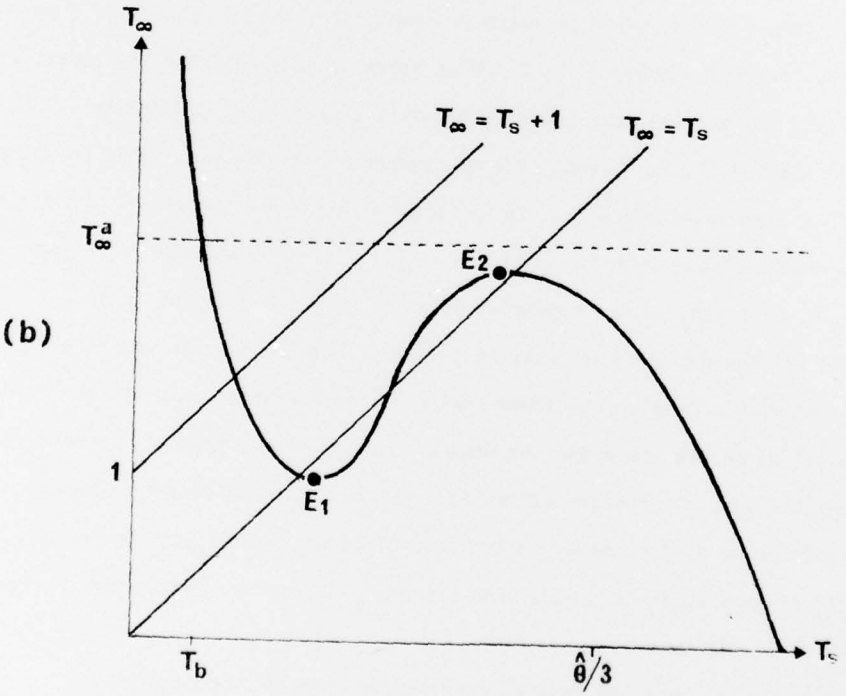


FIG. 4



T_s, T_∞-curves for solid pyrolysis: --- adiabatic; —— radiation with $T_b \neq 0$.
(a) $T_b > 0.168\hat{\theta}$; (b) $T_b < 0.168\hat{\theta}$.

The minimum-maximum curve for $T_b < 0.168\hat{\theta}$ is cut by 45°-lines in at most three points. Such curves present 30 possibilities depending on how the lines $T_\infty = T_s$, $T_s + 1$ are cut(times and order) and on whether E_1, E_2 lie above, between or below them. Three of these can be ruled out because the present curve has only one inflexion point; others lead either to unacceptable responses or to responses which have already appeared for $T_b = 0$. The remainder fall into five groups, according to similarity of response, and one member (the simplest) from each of the five will be presented here. Fig. 5 shows these responses, i.e. the M, D-curves with parts deleted by the limitations (6) and the stability requirement of positive slope but completed by horizontal lines. The first four of these responses have two branches, each ending on the left with either true or effective extinction. In (a) and (b) both branches have a plateau to the right and we shall see that the plateau on the upper branch in each of (c) and (d) is reached for D large enough. The three phenomena in Sec. 2 are therefore exhibited once more. The sole exception is (e), which has no upper branch.

We shall now construct the probable sequence of events first as D increases from 0 to ∞ and then as D decreases from ∞ to 0. When there is only one effective extinction on the left, as in (a), (c) and (e), the lower branch is followed as D increases. The same is true for (b) and (d) if, as we shall assume, weaker burning is preferable to strong when the latter is not already established. In (a) and (b) the lower branch will be followed all the way through surface burning to infinity but in (c) and (d) there will be a jump to the upper branch, i.e. ignition, as the rightmost point is approached on the lower. As D decreases in (c) and (d) the upper branch will be followed, for (d) all the way to effective extinction but for (c) with a jump to the lower branch as true extinction is approached on the upper. In (a) and (b) we invoke the weaker burning assumption to see that the lower branch will be followed all the way to effective extinction. In (e) there is true extinction as D increases and ignition as it decreases. After extinction and before ignition there is no steady burning if we persist in believing that the surface burning which emanates from the unstable branch is itself unstable.

The above description is based on several unproved principles: no part of an M,D-curve with negative slope can be attained physically because the combustion is unstable;

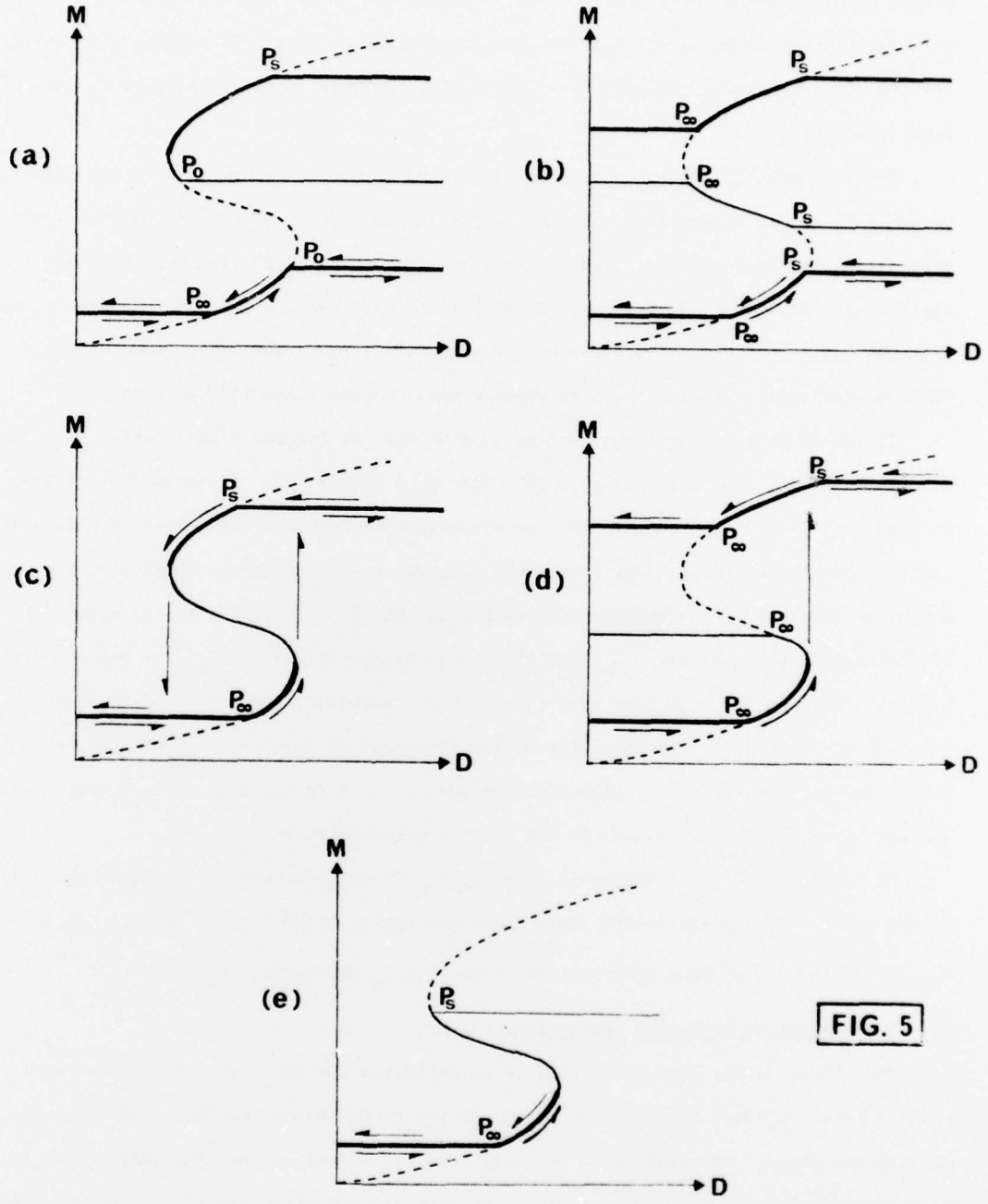


FIG. 5

Solid pyrolysis for radiation with $T_b \neq 0$: --- basic M,D-curve; —— possible response; ▬▬ stable response. Arrows show probable path as D increases from 0 to ∞ and back to 0 again.

a branch will be followed as far as it can be as D increases or decreases; and when a choice remains weaker burning will occur. Whether the other branches in (a) and (b) can ever be attained is an interested open question but, supposing they cannot, (c), (d) and (e) are the only really new responses. Even then, only (e) fails to exhibit the three basic phenomena.

However, data of Johnson & Nachbar (1962) and Guirao & Williams (1971) for ammonium perchlorate can be interpreted as lying on the strong burning branch of Fig. 5(a), see Buckmaster, Kapila & Ludford (1976), suggesting that the weak burning branch is not applicable. That would be the case if pyrolysis ceased below a certain temperature, so that the law (5) only applied above and M was zero below. The whole lower branch could then be eliminated, leaving only the upper branch for the combustion to follow.

It should be noted that the bending back of the M, D-curve from a C-shape into an S occurs for any non-zero $T_b < 0.168\hat{\theta}$. For $T_b > 0.168\hat{\theta}$, the S is pulled cut even further into a monotonic curve. Even weak background radiation can therefore result in quite different responses. Far from being negligible, it can be the dominant effect under suitable conditions. The apparent contradiction as $T_b \to 0$ is due to the nonuniformity of the limit. However small T_b is, there are smaller values of T_s, for which background radiation changes the heat loss into a heat gain. Moreover, the effect of the gain on the enthalpy of the reactant is magnified by the smallness of the mass flux at such surface temperatures. However, it is unlikely that such a limiting behavior could be observed, because of the pyrolysis cut-off at low temperatures mentioned above.

In practice, the most important features of the response are the ignition and extinction values of D. In any particular case, these are easily determined by finding the points E_1, E_2 or the appropriate intersection of the T_s, T_∞-curve with $T_\infty = T_s + 1$.

6. True Nature of Effective Extinction.

The object of the present section is to determine how the previous results are modified when $O(1/\theta)$ heat is lost or gained (by radiation or lateral conduction) throughout the gas phase. For simplicity we shall start by supposing that the solid phase is perfectly insulated. The main conclusion is that all effective extinctions are changed

into true extinctions by heat loss, the explosive regime only being maintainable as the limit for vanishingly small heat gain.

For each point of the relevant response curve determined above, we calculate the new D (due to heat exchange) for the same value of M. The general effect of heat loss can be seen from the formula (1). If the flame temperature is reduced, M can only be maintained by increasing D: in order to maintain the rate of reaction at a lower temperature the concentration of reactant must be increased, i.e. the pressure raised. The pyrolysis law (5) ensures that T_s is unaffected, from which it follows that the temperature distribution in the solid and T_s' are also. Y_s and Y_s' do change, though keeping $Y_s - Y_s'$ equal to 1.

The problem then is to calculate the perturbation of the flame temperature, which Kapila & Ludford (1977) did by straightforward matching. However, we shall follow Sec. III.3 in calculating it directly from the change in enthalpy from the surface up to (and including) the flame sheet. Rather than modifying equation (III.28), we shall derive the result ab initio for the present circumstances.

The governing equations are

$$\mathfrak{L}(Y,1) = -\mathfrak{L}(T,1) + \delta M^{-2}\phi(T) = \Lambda Y \exp(-\theta/T), \tag{13}$$

where ϕ is the function (III.30) with $T_{-\infty}$ replaced by T_b. Integration of the first equality between 0 and $x_* + 0$ immediately yields the flame-temperature perturbation

$$t_\infty = \frac{1}{\delta}\left.\frac{dT}{dx}\right|_{x_*+0} - M^{-2}\int_0^{x_*}\phi(T)dx, \tag{14}$$

since the surface values T_s, T_s' and $Y_s - Y_s'$ are not perturbed. Both terms on the right-hand side are to be evaluated to leading order and, for that purpose, the approximations

$$T = \begin{cases} T_s + T_s'(e^x - 1) & \text{for } 0 < x < x_*, \\ T_\infty + \delta\left[t_\infty + M^{-2}\phi(T_\infty)(x_* - x)\right] & \text{for } x > x_* \end{cases} \tag{15}$$

are used, to obtain

$$t_\infty = -\Phi M^{-2} \quad \text{where } \Phi = \phi(T_\infty) + \int_0^{x_*}\phi(T_s + T_s'(e^x - 1))dx, \tag{16}$$

a result that should be compared with the formula (III.35). The two terms in Φ represent heat exchanges of the unburnt mixture (between the surface and the flame) with the burnt mixture and surroundings, respectively. (The burnt mixture later exchanges the same heat with its surroundings). It follows that

$$D = D_0(M)e^{\Phi M^{-2}} \tag{17}$$

where $D_0(M)$ is given by the eigenvalue (1).

The last three sections have been an investigation of $D_0(M)$, which involves the dependence (11) of T_∞ on M both directly and through the pyrolysis law. The exponent ΦM^{-2} also depends directly and indirectly on M, with the additional involvement of the function ϕ. It is therefore a complicated matter to describe the dependence of D on M in detail, especially when ϕ is left arbitrary. However, if ϕ is not too large, the general shape of the response will be maintained except near P_∞ where $x_* \to \infty$ in Φ. What happens there depends on whether the surface is hotter or cooler than the background.

When, as is usually the case,

$$T_s(M_\infty) > T_b \tag{18}$$

the temperature in the gas phase for M above M_∞ is everywhere higher than T_b, so that ϕ is positive. Consequently Φ is positive and tends to $+\infty$ as $M \to M_\infty$ because x_* does. The response lies to the right of that in Fig. 1, 3 or 5 and bends round as $M \to M_\infty$ to form a C. We conclude that heat loss in the gas phase changes an effective extinction into a true extinction.

In the less likely event that

$$T_s(M_\infty) < T_b, \tag{19}$$

the temperature in the gas phase near the surface is lower than T_b for at least a stretch of values above M_∞. It is easily seen that, as $M \to M_\infty$, the resulting heat gain eventually overwhelms any heat losses further away, so that Φ becomes negative (if it is not already so) and tends to $-\infty$. The response therefore lies ultimately to the left of

that in Fig. 1, 3 or 5 and ends at $D = 0$. Even then the effective extinction may be preceded by a true extinction: if $T_s(M_\infty)$ is sufficiently close to T_b, the function ϕ will only become negative very close to M_∞ and before that will be increasing rapidly (because of x_*), so that an S is formed. For smaller values of $T_s(M_\infty)$ the S straightens out into a monotonic response. Thus the explosive regime, corresponding to the horizontal line through P_∞, is seen to be a limit for vanishingly small heat gain.

Kapila & Ludford (1977) have given details of the above picture for the linear law (III.30a) when the ambient is at the same temperature as the remote solid ($T_b = T_{-\infty}$) and there is no radiative exchange between it and the surface. The conditions (18) and (19) then hold for exothermic and endothermic pyrolysis, respectively. They also consider less than perfect insulation of the solid and find the termination points are unaltered though the curves are somewhat distorted. (T_b is necessarily the same as $T_{-\infty}$ now, since otherwise the solid exchanges an infinite amount of heat.) The reason is that heat exchange in the solid, which adds a term to Φ, is bounded as $M \to M_\infty$ and therefore cannot affect the unboundedness of Φ.

Distributed heat loss from the solid phase alone was considered by Johnson & Nachbar (1962) as a way of modifying the C-shaped responses they obtained analytically when there is radiative loss from the surface. Under their assumptions effective extinction cannot occur.

7. The Vaporizing Liquid Under Adiabatic Conditions.

With one important exception, the analysis follows that in Sec. 3, the superscript $\hat{}$ now referring to the liquid. (It applies equally well to a sublimating solid.) However, since

$$L = -q + (1 - \kappa)(T_s - T^o) \tag{10}$$

is the latent heat of vaporization, which must be increasingly positive at all temperatures T_s of interest, the heat q must be negative and the ratio $\kappa < 1$. We are dealing with a strictly endothermic process in contrast to pyrolysis, which is usually exothermic. The exception just mentioned is the use of the pyrolysis law (5), which must be replaced by the Clausius-Clapeyron relation

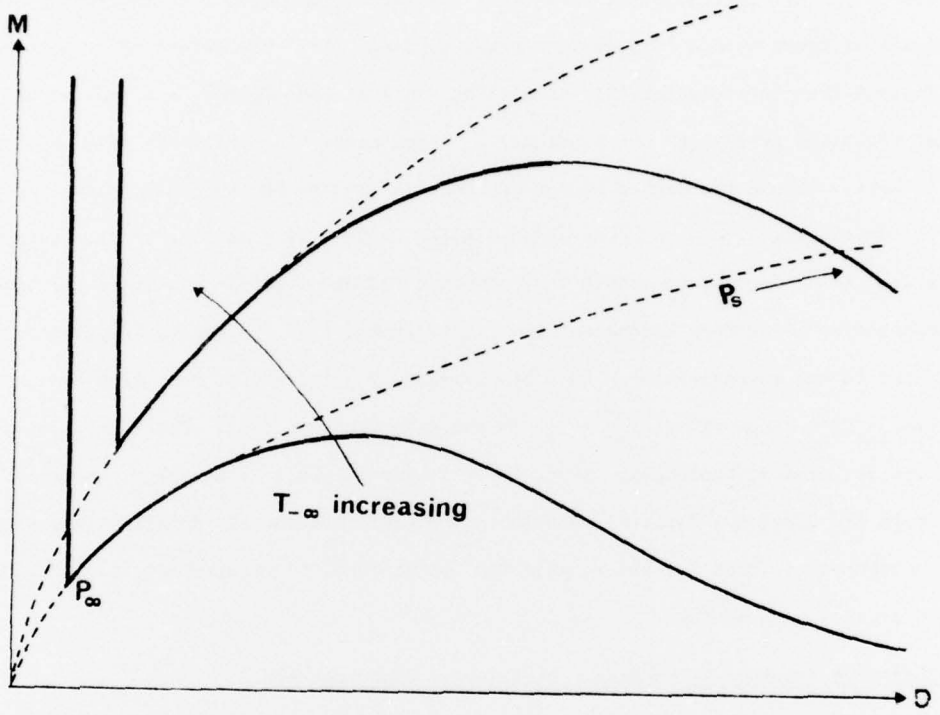
(21) $$Y_s \bar{p}_c = kT_s^{\beta} \exp(-\hat{\theta}/T_s) \qquad (\beta > 0)$$

in calculating boundary values. Here $\beta = \gamma(1-\kappa)/(\gamma-1)$, where κ has the definition (4a) and γ is the ratio of specific heats in the gas. The new law relates the partial pressure of the vapor at the surface to the temperature there and is applicable below the critical point whenever the vaporization is rapid enough for thermodynamic equilibrium to be achieved. The critical pressure is invariably very large so that we shall allow $\bar{p}_c$ to become indefinitely large, as is needed for the Damköhler numbers involved in the asymptotic theory. Equation (21) should be viewed as determining T_s for given D (i.e. $\bar{p}_c$) so that once more the surface temperature is a parameter on the parabola (1), see Fig. 6. For the pyrolyzing solid the surface values depended on M; here they depend on D.

Suppose $T_\infty > 1$ (otherwise the discussion is modified in an obvious way). The point P_∞ corresponding to the left end of the range (6) then exists and is marked in Fig. 6; the point P_s, corresponding to the right end, lies at infinity (according to equation (21)) because Y_s vanishes when $T_s = T_\infty$. So long as T_s is away from the ends of its range the response is identical to that for a pyrolyzing solid. Near the ends, however, the two responses differ markedly, due entirely to the difference between the two laws (5) and (21).

As $T_s \to T_\infty - 1$, the flame sheet recedes to infinity and, since $Y_s \to 1$, the pressure $\bar{p}_c$ (and hence D) tends to a finite non-zero value. The analysis of remote flames, given in Sec. II.5, shows that M can then increase indefinitely, with conditions at the surface fixed, without change in D; and that is just what the Clausius-Clapeyron law demands. The liquid, which is at its saturation temperature for the ambient pressure, must evaporate completely before the pressure can be lowered. Combustion plays no role because heat transfer from the gas phase to the liquid has ceased; the entire heat needed for evaporation is supplied from the remote end of the liquid which, since the evaporation is endothermic ($L > 0$), is now hotter than the surface (cf. equations (3), with $T_\infty = T_s + 1$, and (20)). The process is represented in Fig. 6 by the vertical line through P_∞; before it occurs there will, of course, be effective extinction.

As $T_s \to T_\infty$ the flame moves to the surface and, since Y_s tends to zero like $(T_\infty - T_s)$, the pressure $\bar{p}_c$ (and hence D) tends to infinity like $(T_\infty - T_s)^{-1}$. When the temperature



Vaporizing liquid under adiabatic conditions: --- basic M,D-curve; —— possible response; ▬ stable response.

FIG. 6

difference becomes of order δ the eigenvalue (1) has to be replaced, the surface-flame result (II.27) showing that $M^{-2}D$ now behaves like $(T_\infty - T_s)^{-2}$. Hence M behaves like $(T_\infty - T_s)^{-1}$ or $D^{-\frac{1}{2}}$, and we conclude that the M,D-curve bends down from the parabola to asymptote the D-axis. However, the later portion of the curve does not provide an acceptable response since its slope is negative.

As for the pyrolyzing solid, preheating the liquid (and therefore increasing T_∞) lowers the pressure needed to sustain a given burning rate. The effect of preheating on P_∞ follows from the relation (21) on setting $Y_s = 1$ and $T_s = T_\infty - 1$ and is the opposite of that for solid pyrolysis: the pressure $\bar{p}_c$ (and hence D) increases with T_∞ and hence $T_{-\infty}$. A hotter liquid requires a higher pressure to produce the sudden complete vaporization.

The vaporizing liquid was used as an example in Sec. II.3 and the treatment there can now be seen as an incomplete answer to a somewhat different question. There the temperature was supposed to be uniform throughout the liquid phase, i.e. the remote temperature was maintained at the surface value. As a consequence T_∞, instead of remaining constant, varied with the surface temperature($T_{-\infty} = T_s$ in the determination (3)). The M,D-relation (1), which was not treated thoroughly there, is no longer parabolic since T_∞ now depends on D through the Clausius-Clapeyron relation. (We shall not go into details since they are of limited interest.) Finally, the formula (20) shows that the requirement (6) is simply $0 < L < 1$, as found before.

8. Radiative Exchange at Surface. Distributed Heat Exchange.

In considering radiative exchange at the surface it is convenient, as in Secs. 4 and 5, to sketch the graph of T_∞ versus T_s for fixed $T_{-\infty}$ which now results from eliminating M from the overall heat balance by means of the M,D-relation (1) after having eliminated D from that relation by use of the equilibrium condition (21).

Fig. 7 shows the T_s, T_∞-curve for the three possibilities. (In Figs. 7(a) and (b) we have assumed $T_\infty^a < 1$ but the curves are similar for $T_\infty^a > 1$.) In all cases the curve originates at (T_∞^a, T_∞^a) and asymptotes the T_∞-axis, passing through (T_b, T_∞^a) when that point lies above the line $T_\infty = T_s$. In case (b) there is always an extremum E in the strip (6), but in the other two cases it may lie outside.

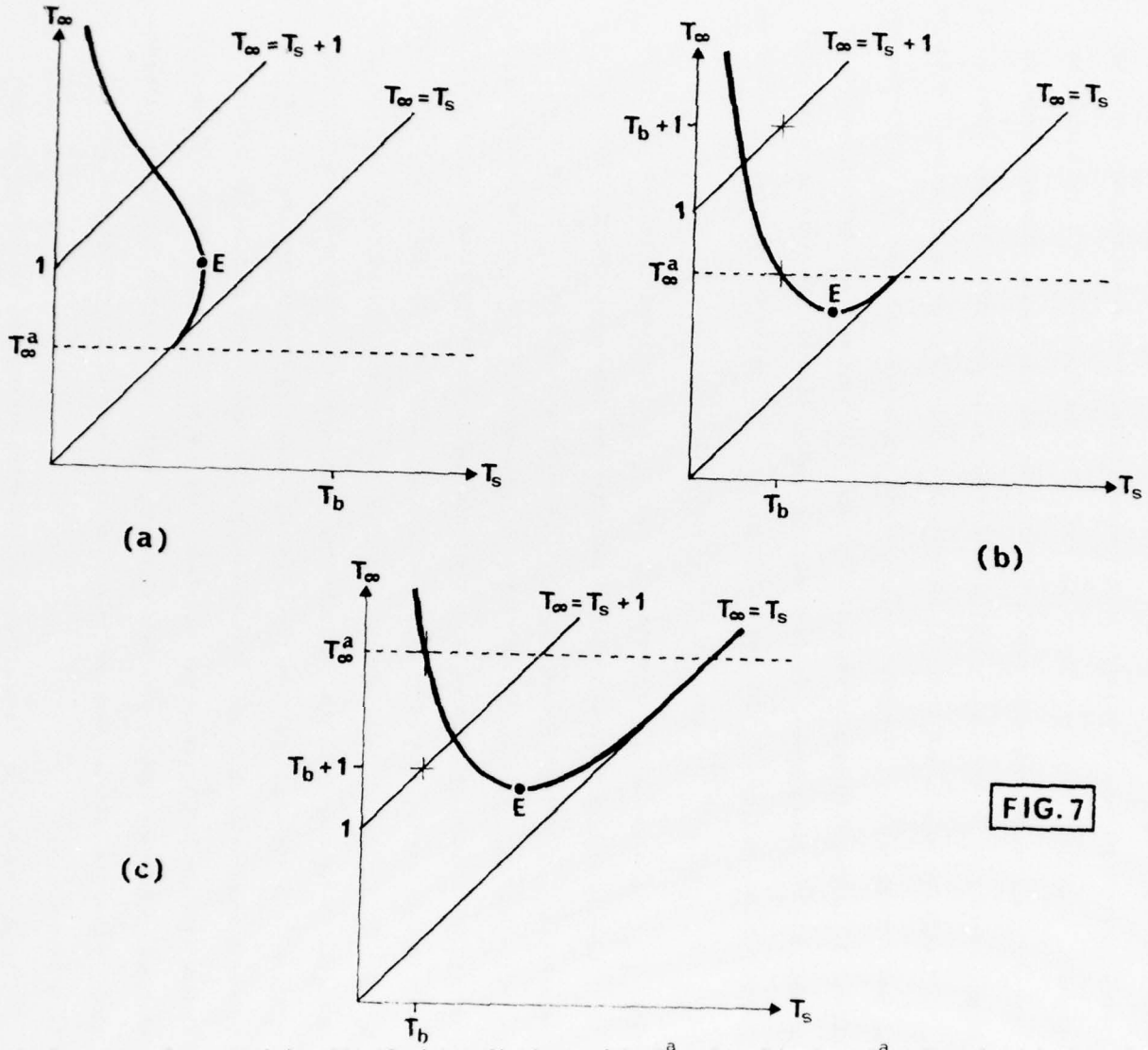


FIG. 7

T_s, T_∞-curves for vaporizing liguid with radiation. (a) $T_\infty^a < T_b$; (b) $T_b < T_\infty^a < T_b + 1$; (c) $T_b + 1 < T_\infty^a$

The asymptotic formula (12) still shows that the sign of the slope is changed on passing to the M,D-plane. All parts of Fig. 7 therefore yield a curve of the general shape of that in Fig. 6 again, the extremum E corresponding to the maximum. As there the portion beyond the crest presumably corresponds to unstable deflagration and therefore is not part of the response. When there is no extremum in the strip (6), the end point P_∞ lies beyond the crest and there is no acceptable response at all. We conclude that no dramatic change in response from that for adiabatic conditions takes place, in contrast to the pyrolyzing solid.

Finally, we come to the effect of distributed heat exchange on the response. The analysis in Sec. 6 makes no use of the pyrolysis law, which only serves to locate T_s on the response curve. It is therefore equally valid for the vaporizing liquid, the Clausius-Clapeyron law serving only the same purpose. In fact complete analogy obtains when there is no radiative exchange at the surface: T_s becomes a function of D alone and the response may be written

$$M = M_0(D)\, e^{-\phi M^{-2}/2} \quad \text{where} \quad M_0 = T_\infty^2 \theta^{-1} \exp(-\theta/2T_\infty)\sqrt{2D} \tag{22}$$

since T_∞ is a constant. (Otherwise T_s and T_∞ are functions of both M and D.)

Arguments similar to those in Sec. 6 determine the shape of the response as $D \to D_\infty$, showing that it depends on whether $T_s(D_\infty)$ is greater or less than T_b. When it is less the curve eventually goes above that in Fig. 6 and asymptotes $D = D_\infty$. The sudden complete evaporation is therefore replaced by an increasing rapid one as the flame recedes to infinity. That was the behavior reported by Kapila and Ludford (1977) who, by taking $T_{-\infty} = T_b$ ensured $T_s(D_\infty) < T_b$ because of the endothermic vaporization. However, for $T_s(D_\infty) > T_b$, the curve continues to dip down until the D-axis is approached when it bends back to the right (because of the M^{-2} in the exponential) to provide a C, exhibiting true extinction. It does not take much imagination to foresee that an oval will be formed, the part beyond the crest closing with the lower part of the C. Such ovals are reported by Spalding (1960) and are sketched by Williams (1965); they were supposedly valid for heat loss by surface radiation alone, whereas we see that they can only occur when there is distributed heat loss (at least when $\theta \to \infty$).

The picture near P_∞ is unaffected by radiative exchange at the surface because, locally, T_∞ in the formula (22) can be replaced by its value at P_∞. Hence the behavior for ϕ small is the same, at least in the neighborhood of effective extinction.

REFERENCES

Buckmaster, J.D., Kapila, A.K. & Ludford, G.S.S. 1976, Linear condensate deflagration for large activation energy, Acta Astronaut. 3, 593-614.

Emmons, H.W. 1971, Fluid mechanics and combustion, Thirteenth International Symposium on Combustion. Pittsburgh: Combustion Institute, pp. 1-18.

Guirao, C. & Williams, F.A. 1971, A model for Ammonium Perchlorate deflagration between 20 and 100 atm., AIAA J. 9, 1345-1356.

Johnson, W.E. & Nachbar, W. 1962, Deflagration limits in the steady linear burning of a monopropellant with application to ammonium perchlorate, Eighth International Symposium on Combustion. Baltimore: Williams & Wilkins, pp. 678-689.

Kapila, A.K. & Ludford, G.S.S. 1977, Deflagration of gasifying condensates with distributed heat loss, Acta Astronaut. 4, 279-289.

Levy, J.B. & Friedman, R. 1962, Further studies of pure ammonium perchlorate deflagration, Eighth International Symposium on Combustion. Baltimore: Williams & Wilkins, pp. 663-672.

Nir, E.C. 1973, An experimental study of the low pressure limit for steady deflagration of Ammonium Perchlorate, Combust. Flame 20, 419-435.

Spalding, D.B. 1960, The theory of burning of solid and liquid propellants, Combust. Flame 4, 59-76.

Williams, F.A. 1973, Quasi-steady gas-phase flame theory in unsteady burning of a homogeneous solid propellant, AIAA J. 11, 1328-1330.

Williams, F.A. 1965, Combustion Theory. Reading, Massachusetts: Addison-Wesley. p. 212.

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We are concerned here with the deflagration of reactants that are produced by gasification at the surface of a solid or liquid. In particular, the influence of pressure on the gasification rate is examined under various conditions. In contrast to earlier treatments, the basic phenomena, including several unsuspected ones, are clearly uncovered by activation-energy asymptotics.

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