# NEAR-EQUILIBRIUM DECOMPOSITIONAL BURNING OF MONOPROPELLANT DROPLETS IN A STAGNANT ATMOSPHERE

## FRANCIS FENDELL

Member of the Technical Staff, Aerosciences Laboratory (R4/2050) TRW Systems, One Space Park, Redondo Beach, California, U.S.A.

#### (Received 26 February 1968 and in revised form 24 June 1968)

Abstract—The conventional formulation of quasi-steady radially symmetric burning of a pure spherical monopropellant droplet is re-examined for Lewis-Semenov number unity. The droplet undergoes adiabatic vaporization and exothermic direct one-step irreversible first-order decompositional burning. The singular near-equilibrium limit is examined by asymptotic analysis, and the dependence of the vaporization rate on the first Damköhler number as that number becomes indefinitely large, is sought. In the near-equilibrium limit the flame is confined to a narrow spherical shell contiguous to the droplet. As the first Damköhler number becomes large without bound, some experimental and theoretical work has reported that the vaporization rate is proportional to the droplet radius squared, while other work has suggested that the vaporization rate is linearly proportional to the droplet radius. While such nonuniqueness does not exist for a plane one-dimensional formulation of decomposition burning, the three-dimensional droplet problem seems to permit nonunique solution. Necessary conditions for realizing each of the dependencies of the vaporization rate on droplet radius are developed. Both dependencies predict that the maximum vaporization rate does not occur at chemical equilibrium (in contrast to bipropellant droplets). Further, in contradiction to previous work, the current analysis indicates that for vaporization rate to be proportional to the droplet radius squared, the ratio of specific heat of vaporization to specific heat of combustion must be less than unity. Furthermore, it is this ratio which is important, not the nondimensionalized droplet or ambient-state enthalpies.

#### NOMENCLATURE

- a\*. droplet radius;
- **B**. product gas;
- b. stoichiometric coefficient of fuel;
- frequency factor, pre-exponential B\*, factor of specific rate constant;
- heat capacity at constant pressure;  $c_{p}^{*}, D^{*}.$
- mass transfer coefficient of Fick's first law:
- first Damköhler number,  $a^{*2}B_f^*/D^*$ ;  $D_1$ ,
- $\overline{D}_1$ ,  $D_1 \exp\left(-\frac{\theta^*}{T_a^*}\right);$
- stoichiometric coefficient of product: *d*. F. fuel:
- h#, h#, heat of formation of fuel and product at some reference condition;
- k\*, specific rate constant,  $B_{f}^{*} \exp(-\theta^{*}/T^{*});$

- Ľ\*. specific heat of vaporization of fuel;
- $L^{*}(h_{R}^{*} h_{R}^{*});$ L,
- *m*\*. net mass transfer rate;
- ṁ.  $\dot{m}^{*}/4\pi\rho_{a}^{*}a^{*}D^{*};$
- **p\***, pressure;
- р, **r\***,  $p^*/(\rho_a^*D^{*2}/a^{*2});$ 
  - spherical radial coordinate;

- r, T\*, temperature;
- $T^*/[(h_F^* h_B^*)/c_P^*];$
- droplet temperature (just below boiling temperature):
- $T_a^*$ , representative temperature;
- v\*. spherical radial velocity;
- $v^{*}/(D^{*}/a^{*});$ v,

$$\varepsilon, \qquad (\overline{D}_1)^{-1};$$

ρ**\***, gas density;  $\begin{array}{ll} \rho, & \text{scaled radial coordinate, } (r-1)/\varepsilon^{\frac{1}{2}}; \\ \theta^*, & \text{activation temperature}; \\ \theta, & \theta^*/\lceil (h_F^* - h_B^*)/c_p^* \rceil. \end{array}$ 

Superscript

\*、

dimensional quantity.

## 1. INTRODUCTION

FOR MONOPROPELLANT droplets burning under quasi-steady conditions in a stagnant unbounded atmosphere [1] there is agreement between theory and experiment for small first Damköhler number conditions that the vaporization rate  $\dot{m}^*$  is linearly proportional to the droplet radius  $a^*$  [2–6]. The first Damköhler similarity parameter  $\bar{D}_1$  is the ratio of the rate of chemical reaction (including appropriate characterization of the Arrhenius factor) to the rate of diffusional mass transport. Small  $\bar{D}_1$  implies that decompositional burning occurs a distance of order  $a^*\bar{D}_1^{-1}(D_1 \ll 1)$  from the droplet surface for a first-order reaction [4].

In contrast, large  $\overline{D}_1$  implies that decompositional burning occurs entirely within a small distance of order  $a^*\overline{D}_1^{-\frac{1}{2}}(D_1 \gg 1)$  from the droplet surface for a first-order reaction [4]. For this case experimental results conflict since, for example, Berrère and Moutet [1] found  $\dot{m}^* \sim a^*$  for ethyl nitrate, while Rosser [1, 7] found  $\dot{m}^* \sim a^{*2}$ . Theoretical results conflict also, since Spalding and Jain [2] and Tarifa, del Notario and Moreno [6] by an approximate analysis, Rosser and Peskin [7] by WKB analysis, and Williams [3] by numerical analysis reported  $\dot{m}^* \sim a^{*2}$  while Fendell [4] by asymptotic analysis suggested  $\dot{m}^* \sim a^*$ . This paper will attempt to consider a resolution to the theoretical controversy in the large  $\overline{D}_1$ limit and to decide whether such a resolution explains the experimental discrepancies as well.

The singular limit of indefinitely fast, irreversible burning has not been elucidated as clearly for a monopropellant droplet as Burke and Schumann [8] elucidated the analogous limit for bipropellant systems with initially unmixed reactants. Understanding of this limit for monopropellants under simplified kinetics may also provide a guide for the difficult task of numerical integration under complex kinetics for nearequilibrium ("stiff") conditions.

# 2. MATHEMATICAL DESCRIPTION

A radially symmetric model of the quasisteady adiabatic vaporization and homogeneous decomposition of a pure spherical monopropellant droplet is now formulated. The simplest physically reasonable case is examined to permit closed-form solution [9]. The droplet is immersed in an unbounded expanse of its product gas. An incompressible, constantproperty flow with a direct first-order one-step irreversible reaction is adopted :

$$bF \xrightarrow{\Lambda_f} dB \qquad k_f^* = B_f^* \exp\left(-\frac{\theta^*}{T^*}\right).$$
 (1)

While this form for  $k_f^*$  will be retained as long as possible, ultimately only the case  $k_f^* = \text{const.}$ will be treated in detail. Mass, momentum, and energy are diffused according to the laws of Fick, Newton, and Fourier, respectively. The Lewis-Semenov number is taken as unity; the droplet is uniformly at a temperature  $T_s^*$ , just below the boiling temperature at ambient pressure  $P_{\infty}^*$  (on the order of a few atmospheres); mechanical dissipation is negligible.

The governing boundary-value problem for the so-called eigenvalue  $\dot{m}$  (the mass transfer rate or Sherwood number) is described by the following ordinary differential equations and two-point boundary conditions [10]:

$$\rho_g^* = \text{const.}$$
 (equation of state) (2)  
 $v = \frac{\dot{m}}{r^2}$  (continuity equation) (3)

1.\*

$$P = P_{\infty} - \left(\frac{\dot{m}}{r^2}\right)^2 \qquad (\text{conservation of momentum}) \quad (4)$$

$$\frac{\dot{m}}{r^2} \frac{\mathrm{d}Y_F}{\mathrm{d}r} - \frac{1}{r^2} \frac{\mathrm{d}}{\mathrm{d}r} \left(r^2 \frac{\mathrm{d}Y_F}{\mathrm{d}r}\right) = -D_1 Y_F \exp\left(-\theta/T\right) \quad (\text{conservation of fuel}) \quad (5)$$

$$\frac{\dot{m}}{r^2} \frac{\mathrm{d}T}{\mathrm{d}r} - \frac{1}{r^2} \frac{\mathrm{d}}{\mathrm{d}r} \left(r^2 \frac{\mathrm{d}T}{\mathrm{d}r}\right) = D_1 Y_F \exp\left(-\theta/T\right) \quad (\text{conservation of energy}) \quad (6)$$

$$At r \to \infty; \quad T \to T, \quad Y_T \to 0 \quad (7)$$

$$At r = 1: T = T_s$$
(8)

$$\frac{\mathrm{d}T}{\mathrm{d}r} = \dot{m}L \qquad (\text{adiabatic vaporization})$$

$$\frac{\mathrm{d}Y_F}{\mathrm{d}r} = \dot{m}(Y_F - 1) \qquad (\text{pure fuel condition}). \tag{10}$$

An identical formulation would hold for a compressible gas if one invoked isobaric flow and linear variation of the mass-transfer co-efficient with temperature.

A Shvab–Zeldovich integral of the governing set is given by adding equations (5) and (6), integrating and using (7)–(10):

$$Y_F + T = \alpha + \beta \exp(-\dot{m}/r) \qquad (11)$$

 $\alpha = T_s + 1 - L, \quad \beta = T_{\infty} - T_s - L - 1.$  (12)

By introducing equation (11) in equation (6) and by invoking equations (7)-(9), one may form a boundary-value problem for the temperature alone. Johnson and Nachbar [11, 12] have demonstrated that for a given value of  $T_{s}$ , the analogous one-dimensional boundary-value problem has a solution and the eigenvalue is uniquely specified. Because nonuniqueness is important to the subsequent development in this paper, the differences from the J-N problem are now discussed. First, as  $D_1 \rightarrow \infty$  the reaction rate expression is undefined and additional physical information must be provided to obtain a well-formulated problem in this singular limit. The information adopted here is either  $\dot{m}^* \sim a^*$  or  $\dot{m}^* \sim a^{*2}$ , both of which seem worthy of study. Second, for any  $D_1$  the Johnson-Nachbar proof of uniqueness is based crucially on the plane one-dimensional nature of their formulation; for example, their system permits no heat loss to the environment. For a threedimensional formulation, even with radial symmetry, the J-N formulation does not in general apply. The more complicated nature of the Shvab-Zeldovich integral for three-dimensional problems [ $\beta$  in equation (11) is effectively zero in a plane one-dimensional problem] acknowledges that there may occur heat loss to the ambient gas. When such heat loss occurs, the solution may be nonunique.

## 3. APPROXIMATE SOLUTION

The boundary-value problem in general requires numerical solution owing to the transcendental nonlinearity of the Arrhenius factor. For analytic treatment the problem will be linearized by approximating the Arrhenius factor  $\exp(-\theta/T_a)$  where  $T_a$  is a chosen constant. Perhaps the most representative choice for  $T_a$ is the maximum gas temperature expected anywhere in the flow field. Such modelling ought to give a qualitatively correct answer for a gross property like the vaporization rate  $\dot{m}$ . Extensive numerical treatment of the exact equation may not be warranted in view of the crude state of knowledge of the chemical

(9)

kinetics of most monopropellants in general and activation temperatures in particular, and also in view of the fact that the almost universally adopted one-step kinetics does not really describe the actual multistep reaction. An effective Damköhler number  $\overline{D}_1$  is now defined :

$$\bar{D}_1 = D_1 \exp\left(-\theta/T_a\right)$$

The case of interest here is  $\overline{D}_1 \ge 1$ ; this situation arises when  $\theta/T_a$  is not too large and  $D_1 \ge 1$ . Clearly a low-activation-energy mono-propellant in conjunction with a hot environmental temperature is under consideration.

Despite the resulting linearity of equation (5), now approximated in the form

$$\left(r^2 \frac{d^2}{dr^2} + (2r - \dot{m})\frac{d}{dr} - \bar{D}_1 r^2\right) Y_F = 0, \quad (13)$$

a tractable series solution is not readily carried out [4]. Here asymptotic solution for  $\overline{D}_1 \ge 1$ will be sought by invoking boundary-layer theory. On the basis of experimental results [6], qualitative examination of equation (13) [4], or or previous theories [1] it may be anticipated that the burning zone is a narrow region contiguous to the droplet surface. In this region both reaction and diffusion must be present; boundary-layer theory suggests reformulation in terms of a scaled independent variable:

$$\rho = \frac{r-1}{\varepsilon^{\frac{1}{2}}} \qquad \varepsilon = (\overline{D}_1)^{-1}. \tag{14}$$

Hence, equations (13), (7), and (10) yield:

$$\left( 1 + \varepsilon^{\frac{1}{2}} \rho \right)^{2} \frac{\mathrm{d}^{2} Y_{F}}{\mathrm{d}\rho^{2}} + \left[ 2 - \dot{m} + 2\varepsilon^{\frac{1}{2}} \rho \right]$$

$$\times \varepsilon^{\frac{1}{2}} \frac{\mathrm{d} Y_{F}}{\mathrm{d}\rho} - (1 + \varepsilon^{\frac{1}{2}} \rho)^{2} Y_{F} = 0$$
 (15)

$$Y_F(\rho \to \infty) \to 0, \frac{\mathrm{d}Y_F(0)}{\mathrm{d}\rho} = \varepsilon^{\frac{1}{2}} \dot{m} [Y_F(0) - 1]. \quad (16)$$

The somewhat planar nature of a flame zone near the surface (to lowest order) is revealed by this independent-variable transformation. The thickness of the reaction zone has been characterized as  $O(\overline{D}_1^{-\frac{1}{2}})$ , and thus inversely proportional to the droplet radius. As  $\overline{D}_1 \to \infty$ , the flame zone collapses to a spherical shell coincident with the droplet surface.

If  $\dot{m}^* \sim a^*$  to lowest order,  $\dot{m} = O(1)$  to lowest order. Such a choice would treat convective transport [the first-derivative terms in equation (15)] as a higher-order effect. Such a model recalls the treatment of bipropellant droplet burning adopted by physicochemical hydrodynamicists under the dilute diffusionflame conditions. It also recalls, perhaps more relevantly, the lowest approximation to the flame zone in near-equilibrium, near-irreversible burning of bipropellant droplets according to singular perturbation theory [13]. On the other hand, if  $\dot{m}^* \sim a^{*2}$  to lowest order,  $\dot{m} = O(\bar{D}_1^{\frac{1}{2}})$ . Under this much greater rate of evaporative mass transfer, convective mass transport is just as important as both diffusive mass transport and chemical reaction. The next task is to determine whether equations (15) and (16) admit physically reasonable asymptotic expansions of either or both of these models. While of course such nonexistence cannot be established, no plausible asymptotic expansion has been found for the case  $\dot{m}^* \sim a^{*c}$ , 1 < c < 2as  $\varepsilon \to 0$ .

### 4. ASYMPTOTIC SOLUTIONS

For the  $\dot{m}^* \sim a^*$  solution one adopts [4]

$$Y_F(r,\varepsilon) = \varepsilon^{\frac{1}{2}} Y_{F_0}(\rho) + \varepsilon Y_{F_1}(\rho) + \varepsilon^{\frac{3}{2}} Y_{F_2}(\rho) + \dots (17)$$

$$\dot{m}(\varepsilon) = \dot{m}_0 + \varepsilon^{\frac{1}{2}} \dot{m}_1 + \varepsilon^{\frac{3}{2}} \dot{m}_2 + \dots \qquad (18)$$

Substitution of equations (17) and (18) into equations (15) and (16) leads to a sequence of problems, the first two of which are:

$$\frac{d^{2} Y_{F_{0}}}{d\rho^{2}} - Y_{F_{0}} = 0, 
Y_{F_{0}}(\rho \to \infty) \to 0, 
\frac{d Y_{F_{0}}(0)}{d\rho} = -\dot{m}_{0}$$
(19)

or

$$Y_{F_0} = \dot{m}_0 \,\mathrm{e}^{-\rho} \tag{20}$$

and

$$\frac{d^{2} Y_{F_{1}}}{d\rho^{2}} - Y_{F_{1}} = (2 - \dot{m}_{0}) \dot{m}_{0} e^{-\rho}, 
Y_{F_{1}}(\rho \to \infty) \to 0, 
\frac{d Y_{F_{1}}(0)}{d\rho} = \dot{m}_{0} Y_{F_{0}}(0) - \dot{m}_{1}$$
(21)

or

$$Y_{F_1} = \left[ \left( \dot{m}_1 - \dot{m}_0 - \frac{\dot{m}_0^2}{2} \right) - \frac{\dot{m}_0}{2} (2 - \dot{m}_0) \rho \right] e^{-\rho}.$$
 (22)

Equations (20), (22), and (9)-(12) yield

$$\dot{m}_0 = \ln \left[ \beta / (L-1) \right], \dot{m}_1 = -\frac{\dot{m}_0}{L-1}.$$
 (23)

A physical interpretation of these results is now given. For the usual case of specific heat of combustion exceeding the specific heat of vaporization (L < 1), the ambient temperature  $T_{\infty}$  must be less than the droplet temperature  $T_s$  for a quasi-steady solution to exist. As  $T_s \uparrow T_{\infty}$  the mass-transfer rate vanishes. The reason for this restriction is that the current model demands that an intense exothermic reaction be occurring near the droplet surface, but that the rate of vaporization be fixed in magnitude at no more than order unity. Such a model can only be achieved in the quasi-steady state if the chemically released heat is permitted to flow into a sink at infinity. The requirement  $\beta < 0$  (i.e.,  $T_{\infty} < T_s$  for L < 1) insures that heat is lost to the environment. If  $T_s \uparrow T_{\infty}$  there is no tendency for heat to flow outward, and no solution can exist. For the rare case L > 1,  $T_{\infty} > T_s$  is required for a steady state; since the reaction does not yield sufficient heat, the ambient environment must maintain the required heat flux to sustain vaporization.

For L < 1, reducing  $\overline{D}_1$  (increasing  $\varepsilon$ ) increases

 $\dot{m}$ ; thus, unlike the analogous limit in bipropellant droplets with initially unmixed reactants [13], in monopropellants the maximum vaporization rate does not always occur for the limit of equilibrium irreversible kinetics. It is of course quite possible for  $\dot{m}$  for intermediate  $\bar{D}_1$  not to lie within the vaporization rate bounds set by the frozen  $(\overline{D}_1 \to 0)$  and equilibrium  $(\overline{D}_1 \to \infty)$ limits. It is emphasized that the increase of  $\dot{m}$ with  $\varepsilon$  for L < 1 holds only vanishingly small (though finite)  $\varepsilon$ ; in fact, it has been explicitly shown for large  $\varepsilon$  that  $\dot{m}$  decreases with increasing  $\varepsilon$  in [4]. The reason for the anomalous increase seems to be that in the limit  $\varepsilon \to 0$  an exponentially small amount of fuel is convected and diffused through the very thin reaction zone fast enough to be unreacted. As the reaction rate is very slightly decreased, the reaction zone remains of  $\varepsilon^{\frac{1}{2}}$  thickness in order of magnitude, but is slightly increased in width (cf. Equations (20) and (22)). The increase is just enough to react some of the fuel that to lowest order escaped combustion at a given radial position. Of course, thickening the reaction zone for other than very small  $\varepsilon$  would have a detrimental effect on the vaporization rate. For L > 1, decreasing the reaction rate is harmful to the vaporization rate;  $\dot{m}$  is found by equation (23) to decrease as  $\varepsilon$  increases.

Finally, it is noted that adopting  $\dot{m}^* \sim a^*$ implies for a first-order reaction that the gasphase mass fraction  $Y_F$  vanishes as  $\overline{D}_1^{-\frac{1}{2}}$  as  $\overline{D}_1 \rightarrow \infty$ —this is indicative of singular behavior.† For the  $\dot{m}^* \sim a^{*2}$  solution one adopts

$$Y_F(r,\varepsilon) = Y_{F_0}(\rho) + \varepsilon^{\frac{1}{2}}Y_{F_1}(\rho) + o(\varepsilon^{\frac{1}{2}}) \qquad (24)$$

$$\dot{m}(\varepsilon) = \varepsilon^{-\frac{1}{2}} \dot{m}_0 + \dot{m}_1 + o(1)$$
(25)

Dimensionally equation (25) states that  $\dot{m}^* \sim a^{*2} (k_t^*)^{\frac{1}{2}}$ ; this relation, found by Williams [3] after extensive approximations, is here an

<sup>†</sup> If  $T_a^*$  is set equal to  $T_s^*$ , the results for  $\dot{m}_0$  and  $Y_{F_0}$ hold for the transcendentally nonlinear Arrhenius kinetics as well. However, while  $Y_{F_1}$  and  $\dot{m}_1$  could also be found in such a case, the expressions would be far more complex than those given in equations (22) and (23).

immediate result of simple dimensional arguments. In contrast to equations (17) and (18)the vaporization rate now becomes large without bonds as equilibrium, irreversible conditions are approached. This is indicative of singular behavior in this alternative expansion. Furthermore, the mass fraction abruptly changes from an order-unity quantity to an exponentially small one as the flame zone (of thickness  $O(\varepsilon^{\frac{1}{2}})$  as  $\varepsilon \to 0$  collapses. In the limit the flame zone is analogous to the vortex sheet to which a viscous boundary layer collapses as the Reynolds number becomes unboundedly large. Whereas the tangential velocity discontinuously jumps to zero across the vortex sheet, across the flame sheet in the  $\varepsilon \rightarrow 0$  limit the fuel mass fraction discontinuously jumps to zero.

Substitution of equations (24) and (25) in equations (15) and (16) yields with the aid of equations (9)–(12) the following problem to lowest order (identical to the analogous one-dimensional problem):

$$\frac{d^2 Y_{F_0}}{d\rho^2} - \dot{m}_0 \frac{d Y_{F_0}}{d\rho} - Y_{F_0} = 0$$
 (26)

subject to

$$Y_{F_0}(0) = 1 - L, \frac{dY_{F_0}(0)}{d\rho}$$
  
=  $\dot{m}_0 [Y_{F_0}(0) - 1], Y_{F_0}(\rho \to \infty) \to 0.$  (27)

From this formulation it is clear that L < 1 [so  $Y_{F_0}(0) > 0$ ], or no solution of the type postulated can exist. Physically, unless the heat of vaporization is less than the heat of combustion, no intense vaporization can be expected. Since  $T_{\infty}$  and  $T_s$  do not enter the formulation (except to characterize the magnitude of  $\overline{D}_1$ ), the vaporization rate becomes relatively independent of these quantities;  $\dot{m}$  is a function of L only. The dependence on L and independence of  $T_{\infty}$  and  $T_s$  is in direct contrast to the model of Spalding and Jain, as interpreted by Williams [1]. In cases of intense vaporization the roles of impressed thermal gradients of moderate magnitude have negligible effect (according to the current model)

compared with the heat generation by reaction and absorbed by vaporization. From equations (26) and (27)

$$Y_{F_0}(\rho) = (1 - L) \exp\left\{\frac{\dot{m}_0}{2} \left[1 - (1 + 4/\dot{m}_0^2)^{\frac{1}{2}}\right]\rho\right\}$$
(28)

where

$$\dot{m}_0 = \frac{1-L}{L^{\frac{1}{2}}}.$$
 (29†)

For  $\dot{m}_0 > 0$ , 0 < L < 1—the specific heat of combustion must be greater than the heat of vaporization. It has formally been shown that the case  $\dot{m}^* \sim a^{*2}$  implies that the temperature rises to the adiabatic flame temperatures in a distance roughly  $\varepsilon^{\pm}$  off the droplet, and maintains the adiabatic flame temperature until distances  $O(\varepsilon^{-\frac{1}{2}})$ .

The first perturbation to equations (28) and (29) is governed by

$$\frac{d^2 Y_{F_1}}{d\rho^2} - \dot{m}_0 \frac{d Y_{F_1}}{d\rho} - Y_{F_1} = \frac{d Y_{F_0}}{d\rho} \\ \times \left[ \dot{m}_1 - 2(1 + \dot{m}_0 \rho) \right]$$
(30)

where

$$\frac{dY_{F_1}(0)}{d\rho} = -L\dot{m}_1, Y_{F_1}(0) = 0,$$
$$Y_{F_1}(\rho \to \infty) \to 0.$$
(31)

Consideration of this boundary-value problem reveals that  $\dot{m}_1 > 0$ —thus again it is found that the vaporization rate for indefinitely fast, irreversible kinetics is not the maximum rate possible. Substitution of equation (28) in equation (30) gives in view of (31)

$$Y_{F_1} = (H\rho + J\rho^2) \\ \exp\left\{\frac{\dot{m}_0}{2} \left[1 - (1 + 4/\dot{m}_0^2)^{\frac{1}{2}}\right]\rho\right\}$$
(32)

<sup>†</sup> If the Arrhenius factor had been retained, even the lowest-order solution would have been intractable because of the nonlinearities. However, one can show that while  $m_0$  might depend on  $T_s$  in such a case,  $m_0$  remains independent of  $T_{\infty}$ .

where

$$-J = \frac{(1-L)^2 L^{\frac{1}{2}}}{1+L}$$
(33)

$$H = L\left(\frac{1-L}{1+L}\right)\left(\dot{m}_1 - \frac{4}{1+L}\right) \quad (34)$$

$$\dot{\boldsymbol{m}}_1 = 2\left(\frac{1-L}{1+L}\right). \tag{35}$$

Thus as  $\varepsilon \to 0$  either  $\dot{m}^* \sim a^*$  or  $\dot{m}^* \sim a^{*2}$ seems to be compatible with an asymptotic expansion that is both physically plausible and capable of extension to higher order. The only satisfactory stability analysis would be to ascertain what physically realizable initial conditions (if any) would lead to each of the two quasi-steady configurations; this quite difficult unsteady analysis will not be undertaken here.

## 5. COMPARISON WITH EXPERIMENTS AND SUGGESTED EXTENSIONS

For the first-order reaction examined in this paper one may conclude the following.

(1) A quasi-steady solution theoretically exists for  $\overline{D}_1 \to \infty$  in which  $\dot{m}^* \sim a^*$  provided  $T_s^* > T_\infty^*$  when L < 1. Barrère and Moutel [1] are the only experimentalists to report  $\dot{m}^* \sim a^*$ for other than  $\overline{D}_1 \to 0$ , but their results have been challenged on several grounds [5]. Most experimentalists find it necessary to introduce an oxidant into the environment to sustain the quasi-steady monopropellant burning [14]. The oxidant is chemically active with the products of the decompositional burning so a bipropellant flame [15] exists outside the monopropellant flame. Naturally the current theory for an inert atmosphere cannot be rigorously applied to such an experiment. Naturally, also, the hot bipropellant flame violates the condition  $T_s^* > T_{\infty}^*$ . Since spherical droplets can be achieved to only a certain size, physical realization of the  $\overline{D}_1 \gg 1$  condition would require a very large porous sphere with baffles to inhibit internal circulation currents; the gaseous atmosphere would have to be held at a high pressure.

Perhaps the  $\dot{m}^* \sim a^*$  result, which has never been experimentally observed in the nearequilibrium limit, might then be noted.

(2) A quasi-steady solution theoretically exists for  $\overline{D}_1 \to \infty$  in which  $\dot{m}^* \sim a^{*2}$  provided L < 1. This solution for  $\dot{m}$  (equations (25), (29), and (35)) indicates  $\dot{m}$  depends more on L than on  $T_{\infty}$  and  $T_s$ . Many experimentalists report  $\dot{m}^* \sim a^{*2}$  for  $\bar{D}_1$  of order unity or larger. Some caution is warranted when applying the current theory to these experiments. Again, these experimentalists often resort to oxidant-containing ambient environments. Furthermore, often they use simple ("eveball") judgements as to when a quasi-steady state was established [7]. It should be noted that in the experiments of Faeth, Karhan and Yanyecic [5] with actual droplets the quasi-steady state took longer and longer to achieve as  $\overline{D}_1$  was increased. During the short time it was achieved for large  $\overline{D}_1$ ,  $\dot{m} \sim a^{*2}$ was observed. Sometimes it appears virtually no quasi-steady combustion was realized before burnout. Failure to attain in all cases a quasisteady burning is confirmed by Lawver [14], who also used droplets.

(3) If one wishes to maximize  $\dot{m}$ , there is sometimes little incentive for as large a forward rate as possible (while suppressing the reverse reaction) for quasi-steady burning of monopropellants, because  $\dot{m}$  is not necessarily a maximum for  $\overline{D}_1 \rightarrow \infty$ .

(4) The monopropellant flames for  $\overline{D}_1 \to \infty$ lies contiguous to the droplet and is of thickness  $O(\overline{D}_1^{-\frac{1}{2}})$ . There seems just as great a need as ever for a theory of sequential monopropellant and bipropellant flames—a need previously emphasized by Williams [1] in discussing decompositional burning in the presence of species chemically active with the product gases.

Finally it is conjectured that the difficulty of establishing quasi-steady purely decompositional flame in constant-diameter porous-sphere experiments at any finite Damköhler number may be owing to a failure to preheat the liquid fuel to its boiling temperature. Provision for preheating is not quoted in the apparatus diagram of [7]; such an omission would render the experiment completely unsuited for the quasi-steady theory with adiabatic vaporization which the authors of [7] themselves present. If the liquid were preheated before introduction into the porous sphere, the present conjecture is that a decompositional flame would be sustained for some finite Damköhler numbers.

### ACKNOWLEDGEMENTS

The author is indebted to Dr. R. L. Chapkis of TRW Systems, Professor P. R. Choudhury of the University of Southern California and Dynamic Science Corp., and Professor F. A. Williams of the University of California at San Diego for their sustained interest and helpful discussions. This work was supported under Contract DAHC04 67 C 0015 with the U.S. Army Research Office (Durham, North Carolina).

#### REFERENCES

- 1. F. A. WILLIAMS, Combustion Theory, Chaps. 3 and 10. Addison-Wesley, Palo Alto (1965).
- D. B. SPALDING and V. K. JAIN, Theory of the burning of monopropellant droplets, *Aeronautical Research Council Rep.* No. 20-176, Current Paper 447, Ministry of Supply, London, England (1959).
- F. A. WILLIAMS, Theory of the burning of monopropellant droplets, *Combust. Flame*, 3, 529-544 (1959).
- 4. F. E. FENDELL, Finite-rate burning of a monopropellant droplet in a stagnant atmosphere, *Astronautica Acta* 11, 418-421 (1965).
- 5. G. M. FAETH, B. L. KARHAN, and G. A. YANYECIC,

Ignition and combustion of monopropellant droplets, *AIAA Paper* No. 67-480, presented at the AIAA Third Propulsion Joint Specialist Conference, Washington, D.C. (1967).

- C. S. TARIFA, P. P. DEL NOTARIO, and F. G. MORENO, Combustion of liquid monopropellants and bipropellants in droplets, 8th (International) Symposium on Combustion, pp. 1035–1056. Williams and Wilkins, Baltimore (1962).
- W. A. ROSSER, JR. and R. L. PESKIN, A study of decomposition burning, *Combust. Flame* 10, 152–160 (1966).
- S. P. BURKE and T. E. W. SCHUMANN, Diffusion flames, Ind. Engng Chem. 20, 998-1004 (1928).
- F. A. WILLIAMS, On the assumptions underlying droplet vaporization and combustion theories, J. Chem. Phys. 33, 133-144 (1960).
- J. LORRELL and H. WISE, Steady-state burning of a liquid droplet. I. Monopropellant flame, J. Chem. Phys. 23, 1928-1932 (1955).
- 11. W. E. JOHNSON and W. NACHBAR, Laminar flame theory and the steady linear burning of a monopropellant, *Archs. Ration. Mech. Analysis* 12, 58–92 (1963).
- 12. W. E. JOHNSON and W. NACHBAR, Deflagration limits in the steady linear burning of a monopropellant with application to ammonium perchlorate, 8th (International) Symposium on Combustion, pp. 678–689. Williams and Wilkins, Baltimore (1962).
- F. E. FENDELL, Ignition and extinction in combustion of initially unmixed reactants, J. Fluid Mech. 21, 281-303 (1965).
- B. R. LAWVER, Some observations on the combustion of N<sub>2</sub>H<sub>4</sub> droplets, AIAA Jl 4, 659–662 (1966).
- F. E. FENDELL, Flame structure in initially unmixed reactants under one-step kinetics, *Chem. Engng Sci.* 22, 1829–1837 (1967).

Résumé—La formulation classique de la combustion quasi-stationnaire à symétrie radiale d'une gouttelette sphérique de monergol pur est réexaminée pour un nombre de Lewis-Semenov égal à l'unité. La gouttelette subit une vaporisation adiabatique et une combustion de décomposition du premier ordre irréversible, en une étape, directe et exothermique. La limite singulière près de l'équilibre est examinée par l'analyse asymptotique et l'on a cherché la dépendance de la vitesse de vaporisation sur le premier nombre de Damköhler lorsque ce nombre croît indéfiniment. Dans la limite près de l'équilibre, la flamme est confinée dans une enveloppe sphérique voisine de la gouttelette. Lorsque le nombre de Damköhler croît sans limite, un certain travail expérimental et théoretique a signalé que la vitesse de vaporisation est proportionnelle au carré du rayon de la gouttelette, tandis qu'un autre a suggéré que la vitesse de vaporisation est proportionnelle au rayon de la gouttelette. Alors qu'une telle non-unicité n'existe pas pour une formulation unidimensionnelle plane de la combustion par décomposition, le problème tridimensionnel de la goutte permet une solution non unique. Les conditions nécessaires pour réaliser chacune des dépendances de la vitesse de vaporisation en fonction du rayon de la gouttelette sont exposées. Ces deux dépendances prédisent que le maximum de la vitesse de vaporisation ne se produit pas à l'équilibre chimique (en contraste avec les gouttelettes de diergol). En outre, en contradiction avec un travail prédédent, l'analyse actuelle indique que pour une vitesse de vaporisation proportionnelle au carré du rayon de la gouttelette, le rapport de la chaleur spécifique de vaporisation à la chaleur spécifique de combustion est important, mais non les enthalpies mises sans dimensions de la gouttelette ou de l'ambiance. La stabilité de chaque dépendance du rayon de la gouttelette est examinée en pensant à un appareil à sphère poreuse de diamètre constant, et

les résultats semblent être compatibles avec toutes les observations expérimentales publiées.

Zusammenfassung-Der konventionelle Ansatz fär quasi-stationäre radialsymmetrische Verbrennung eines reinen kugelförmigen Tröpfchens eines Einkomponententreibstoffs wurde für eine Lewis-Semenov-Zahl 1 von neuem untersucht. Das Tröpfchen erfährt eine adiabate Verdampfung und eine exotherme direkte, in einem Schritt erfolgende, irreversible Abbrandreaktion erster Ordnung. Der besondere Grenzbereich in der Nähe des Gleichgewichts wurde mit einer asymptotischen Theorie untersucht, und es wurde die Abhängigkeit der Verdampfungsrate von der ersten Damköhler-Zahl gesucht, wenn diese Zahl unendlich gross wird. Im Grenzbereich in der Nähe des Gleichgewichts ist die Flamme auf eine schmale Kugelschale, die an das Tröpfchen angrenzt, beschränkt. Für den Fall, dass die erste Damköhler-Zahl unbegrenzt gross wird, wurde einerseits in einer experimentellen und theoretischen Arbeit berichtet, dass die Verdampfungsrate proportional dem Quadrat des Tropfenradius ist, wogegen in einer anderen Arbeit angenommen war, dass die Verdampfungsrate direkt proportional dem Tropfenradius ist. Während für den ebenen eindimensionalen Ansatz der Abbrandreaktion derartige Widersprüche nicht auftreten, lässt das Problem des dreidimensionalen Tröpfchens eine nicht eindeutige Lösung zu. Es sind die notwendigen Bedingungen für die Verwirklichung jedes der beiden Gesetze für die Abhängigkeit der Verdampfungsrate vom Tropfeuradius dargestellt. Beide Abhängigkeitsgesetze sagen voraus, dass die maximale Verdampfungsrate nicht beim chemischen Gleichgewicht auftritt (im Gegensatz zu den Tröpfchen eines Zweikomponententreibstoffs). Weiterhin zeigt -im Gegensatz zu früheren Arbeiten- die gebräuchliche Analyse, dass dann, wenn die Verdampfungsrate proportional dem Quadrat des Radius ist, das Verhältnis von spezifischer Verdampfungswärme zur spezifischen Verbrennungswärme von Bedeutung ist, und nicht die dimensionslos gemachten Tropfen, oder Umgebungsenthalpien. Die Stabilität der beiden Abhängigkeitsgesetze vom Tropfenradius wurde mit einem konstanten Durchmesser mit Berücksichtigung des Mechanismus einer porösen Kugel überprüft und die Ergebnisse erscheinen mit allen dargelegten experimentellen Beobachtungen verträglich.

Аннотация-Рассматривается обычная формулировка установившегося радиальносимметричного горения чисто сферической однокомпонентной капли для числа Льюиса-Семенова, равного единице. Капля подвергается адиабатическому испарению и непосредственному экзотермическому одноступенчатому необратимому горению. Квазиравновесный процесс исследуется с помощью асимптотических методов. Найдена зависимость интенсивности испарения от числа Дамкёлера, когда оно становится бесконечно большим. В квази-равновесном процессе пламя ограничивается узкой сферической оболочкой, прилегающей к капле. Согласно экспериментальным и теоретическим данным при больших числах Дамкёлера скорость испарения пропорциональна квадрату радиуса капли. Однако, в других работах предполагается, что скорость испарения линейно пропорциональна радиусу капли. Если нет такой неоднозначности для плоского одномерного горения в условиях разложения, то трехмерную задачу для капли можно решить неоднозначно. В работе анализируются зависимости скорости испарения от радиуса капли. Обе зависимости предсказывают, что максимальная скорость испарения не наблюдается при химическом равновесии (в противоположность случаю двухкомпонентных капель). Настоящий анализ показывает, что для скорости испарения, пропорциональной квадрату радиуса капли, важным фактором является отношение удельной теплоты испарения к удельной теплоте горения, а не безразмерная энтальния капли или состояние окружающей среды. Эксперименты проводились с каплями одинакового диаметра при прочих равных условиях. Результаты исследования согласуются с опубликованными экспериментальными данными.