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A Model for Ammonium Perchlorate Deflagration between 20 and 100 atm

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It is argued that exothermic condensed-phase reactions occurring in a liquid layer at the surface of ammonium perchlorate, coupled with exothermic gas-phase reactions, are responsible for the steady deflagration of the monopropellant in the pressure range from 20 to 100 atms. 70% of the heat release is found to occur in the liquid layer, thereby making the over-all gasification process exothermic by roughly 100 cal/g. Isothermal kinetic calculations for a gas-phase chain reaction mechanism yield an over-all reaction rate (with an activation energy of about 15 kcal/mole) which is used along with the assumption of equilibrium dissociative vaporization, to calculate upper and lower bounds for the burning velocity. It is concluded that, when the surface temperature drops below the melting piont, the condensed-phase reaction rates decrease greatly and thereby cause the extinction identified as the low-pressure deflagration limit. A matched asymptotic expansion method yields an overall activation energy of about 60 kcal/mole for the condensed-phase reactions, which we believe to be initiated by thermal breakdown of perchlorate ions.

Nomenclature

A_g = temperature-independent rate factor for the over-all gas-phase reaction, cm³/mole-sec-°K
A_j = chemical symbol for species j
$A(T_s)$ = function defined in Eq. (39)
a_j = stoichiometric coefficient for species j in gasification process
B = frequency factor of over-all condensed-phase reaction, sec^{-1}
b = steady, linear regression (or burning) rate, cm/sec
C_j = molar concentration of species j, moles/cm³
c = mean isobaric specific heat, cal/g-°K
D = binary diffusion coefficient of all pairs of species, cm/sec
E = activation energy of over-all condensed-phase reaction, kcal/mole
E_g = activation energy of over-all gas-phase reaction, kcal/mole
G = dilution coefficient
g = constant defined in Eq. (33)
$\bar{K}$ = constant defined by Eq. (26)
k = over-all reaction rate constant for the chain reaction, cm³/mole-sec
k_p = specific reaction rate constant for reaction p
p = pressure, atm
p_{DL} = low-pressure deflagration limit, atm
$p_d(T_s)$ = AP dissociation vapor pressure at temperature T_s, atm
R = nondimensional regression rate
$R°$ = universal gas constant
T = temperature, °K
T^* = temperature characterizing gas-phase heat release, °K
t = time, sec
v = velocity of gaseous mixture, cm/sec
$\bar{W}$ = mean molecular weight of gaseous mixture, g/mole
W_j = molecular weight of species j, g/mole
x = space coordinate, cm
x_f = reaction zone thickness, cm
Y = concentration variable given by Eq. (22)
Y_j = mass fraction of species j
Y_j^* = stoichiometric mass fraction of species j
ΔH = standard heat of reaction at 298.16°K, kcal/mole
Δh_g = heat absorbed in over-all gas-phase reaction per gram of product formed, cal/g
Δh_s = heat absorbed in liquid-phase reaction per gram of product formed, cal/g
Δh_t = sum of heat absorbed per unit mass in melting (Δh_m) and in phase transition (Δh_{tr}), cal/g
ϵ_s = total hemispherical emissivity of condensed-phase surface
Λ = eigenvalue of laminar-flame mnopropellant problem
λ = coefficient of thermal conductivity, cal/cm-sec-°K
ν_j = stoichiometric coefficient for product j in gas-phase reaction
$\varphi(Y)$ = dimensionless chemical source function
ρ = density, g/cm³
τ_g = residence time of gaseous mixture, sec
τ_r = reaction time for gas-phase reaction, sec
θ_s = $\Delta h_s/c_l T_s$
θ_∞ = T_∞/T_s

Subscripts

f = flame
fa = adiabatic flame conditions
g = gas phase
I = products of condensed-phase reaction
i = initiation
j = any species present in gas phase
l = liquid phase
m = melting of AP (solid-liquid interface)
0 = conditions at $x = -\infty$ in the solid
P = products of gas-phase reaction
s = interface between gaseous and condensed phases
tr = orthorhombic-to-cubic transition
π = condensed phase
$\pi 1$ = orthorhombic phase
$\pi 2$ = cubic phase
∞ = effective conditions at $x = -\infty$ in the liquid

1. Motivation

MANY composite solid propellants use ammonium perchlorate (NH_4ClO_4, denoted herein as AP) as the primary oxidizer. But AP, as a monopropellant, can sustain its own steady deflagration at atmospheric pressure if its initial temperature exceeds 270°C (Refs. 1 and 2) and at room tem-

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perature, for pressures above roughly 20 atm.[3] Clearly, a thorough understanding of AP deflagration would aid in analyzing composite propellant combustion. The theoretical studies presented herein are intended to contribute to this understanding.

2. Background

At room temperature, the experimental burning rate-pressure curve for AP obeys the power law $b \sim p^n$ with $n \approx 0.77$ in the pressure range 20–50 atm.[3,4] In the pressure range 50–150 atm, the slope db/dp gradually decreases with increasing pressure, but remains positive.[3–5] At pressures above 150 atm, AP crystal and pressed-pellet burning rates decrease drastically with increasing pressure up to 300 atm, then increase again up to roughly 700 atm, the limit of the reported experiments.[4,5] On the other hand, burning rates of asbestos-wrapped pressed pellets retain a non-negative db/dp up to 350 atm, the limit of one experiment,[3] and at about 400 atm exhibit an increase in db/dp, to a slope exceeding unity, which is maintained up to 1500 atm, the highest pressure achieved in burning-rate experiments.[6] The primary deflagration products are H_2O, O_2, HCl, N_2, NO, N_2O, and Cl_2 (Refs. 2 and 3); they differ from the adiabatic equilibrium composition which is H_2O, O_2, HCl, N_2, and very small amounts of Cl_2 (Ref. 7). Many additional quantitative facts concerning AP deflagration have been established experimentally,[7] such as flame temperatures and surface temperatures, but space prevents us from discussing them here. Since any complete theoretical description must be consistent with all of these observations, we shall return to consider many of them after completing our theoretical development.

The energy necessary to sustain a steady deflagration may be liberated by condensed-phase reactions, gas-phase reactions, interface reactions, or any combination of these, and the endothermic part of the surface gasification process may be an equilibrium process, a rate-controlled process or of intermediate character. Johnson and Nachbar[8] have developed a gas-phase reaction model assuming a rate-controlled surface process. Their model predicts a low-pressure deflagration limit p_{DL} due to heat loss, but agreement with the experimental value was obtained by assuming an unjustifiable large heat loss in the solid. A gas-phase model with a reversible non-equilibrium gasification process has been developed by Nachbar.[9] The theoretically predicted p_{DL} is again roughly an order of magnitude below the observed value when physically reasonable heat-loss parameters are employed. In addition, to fit the observed deflagration rate the gas-phase theory requires a flame thickness of the order of ten molecular mean free paths,[10] a result which is not necessarily impossible for a fast chain reaction but which motivates one to look more closely at the gas-phase kinetics and at the possibility of interface or condensed-phase reactions. Although a condensed-phase reaction model has been developed[11] for AP-based composite propellants, we are unaware of any detailed condensed-phase or interface reaction models for deflagration of pure AP.

Recent observations, mostly by Boggs, of quenched samples using a scanning electron microscope and of burning samples using high-speed motion-picture photography[4,12,13] have revealed many aspects of the deflagration process that can aid in the development of theories. A thin liquid layer (2–5 μ estimated thickness, depending on the pressure) entrapping gas bubbles, at the surface of deflagrating AP was inferred to exist in the pressure range 20–50 atm. From 50 to 150 atm, the surface was observed to be covered by a pattern of ridges and valleys with sites of increased activity at the bottoms of the valleys. Reference 13 concludes that exothermic reactions occurring in a "pseudo-condensed" phase, coupled with gas-phase reactions, are responsible for the heat transfer to the deflagrating crystal between 20 and 150 atm. At higher pressures, up to 700 atm, the surface consists of closely packed solid AP "needles," typically 100 μ long, apparently extending uniformly to the line of orthorhombic-to-cubic phase transition; under these conditions only gas-phase reactions were inferred to feed back energy to the surface.[13]

3. Model

An inescapable conclusion of these microscopic observation is that the deflagration process does not seem one-dimensional.[13] Yet, we shall employ a one-dimensional model. We do so with the knowledge that the model will not explain the detailed structures observed (bubbles, ridges, active sites, needles) and with the hope that by implicitly averaging over these structures we will still explain properly the average temperature field, chemical compositions, chemical kinetics, heat flux and regression rate.

It has been reasoned[14] that in deflagration, because of the high temperatures and high pressures encountered, the gas-solid interface condition for AP is likely to be equilibrium dissociative sublimation into NH_3(g) and $HClO_4$(g). These same arguments suggest equilibrium dissociative vaporization if the condensed phase is a liquid layer. Since the known low-temperature interface decomposition processes are too slow to be important during deflagration,[14] we postulate herein in an exothermic condensed-phase gas-producing reaction in a liquid layer[13] which covers the surface completely, and equilibrium dissociative vaporization followed by gas-phase combustion for AP not consumed in the liquid-phase reaction. The major portion of the present paper is devoted to a thorough exposition of this model, which we believe represents the most reasonable AP deflagration mechanism for pressures up to 100 atm.

Since the liquid-phase activation energy turns out to be large, our model can equally well be interpreted as an interface reaction model. We choose not to do this because a reasonable condensed-phase reaction mechanism can be suggested, because sufficiently rapid interface reactions have not been proposed, and because a logical explanation of the deflagration limit stems from the condensed-phase interpretation. In unpublished work, Price has suggested that p_{DL} corresponds to disappearance of the liquid layer as a result of the surface temperature falling below the melting point. Since the rates for the condensed-phase reactions that we postulate typically are two orders of magnitude less in the solid than in the liquid,[15] we subscribe to this melting-point interpretation of p_{DL}.

4. Outline

In the following section we develop a chain mechanism for the gas-phase combustion reaction. By calculating concentration histories, based on this mechanism, for a few isothermal, isobaric systems, we infer in Sec. 6 an over-all reaction rate and activation energy for the gas-phase reaction. Since the chain mechanism, while containing some new attributes, seems reasonable, and since the over-all rate constants are relatively insensitive to reasonable variations in the elementary steps, it appears that the resulting description of the over-all gas-phase combustion can be accepted with relative confidence. This has the important effect of removing all gas-phase parameters from the list of arbitrary adjustable constants; degrees of freedom-of-fit, that were present in earlier models, are now eliminated.

In Secs. 7 and 8, we develop a mathematical model for calculating the deflagration rate when a specified fraction G of the AP reacts in the gas phase and the rest forms final reaction products instantaneously at the condensed interface. This particular application of the method of upper and lower bounds employs a surface equilibrium boundary condition. The only adjustable parameter in the theory is G, which is taken to be 0.3 to fit the experimental deflagration-rate curve. Results of the calculation are presented and discussed in Secs. 9 and 10.

In Sects. 11–13, these results are used to discuss the character of the liquid-phase reaction. The probable reaction mechanism is considered, and the over-all activation energy, frequency factor, thickness of the liquid layer and thickness of the liquid-phase reaction zone are deduced from a singular perturbation analysis

The theory is criticized in Sec. 14, and the high pressure regime is considered in Sec. 15.

5. Chain Reaction Mechanism

The chain reaction mechanism that we employed in our kinetic calculations for the gas-phase reaction is

$$HClO_4 + NH_3 \rightarrow ClO_3 + NH_2 + \mathbf{H_2O}, \quad \Delta H = 31.5\ \text{kcal/mole} \tag{1}$$

$$ClO_3 \rightarrow ClO + \mathbf{O_2}, \quad \Delta H = -12.8\ \text{kcal/mole} \tag{2}$$

$$NH_3 + ClO \rightarrow NH_2 + ClOH, \quad \Delta H = 5.1\ \text{kcal/mole} \tag{3}$$

$$NH_2 + \mathbf{O_2} \rightarrow HNO + OH, \quad \Delta H = -6.2\ \text{kcal/mole} \tag{4}$$

$$HClO_4 + HNO \rightarrow ClO_3 + \mathbf{NO} + \mathbf{H_2O}, \quad \Delta H = -11.79\ \text{kcal/mole} \tag{5}$$

$$ClOH + OH \rightarrow ClO + \mathbf{H_2O}, \quad \Delta H = -21.6\ \text{kcal/mole} \tag{6}$$

$$ClO + ClO \rightarrow 2Cl + \mathbf{O_2}, \quad \Delta H = 9.72\ \text{kcal/mole} \tag{7}$$

$$Cl + ClOH \rightarrow \mathbf{HCl} + ClO, \quad \Delta H = -4.8\ \text{kcal/mole} \tag{8}$$

$$Cl + Cl + M \rightarrow \mathbf{Cl_2} + M, \quad \Delta H = -58.0\ \text{kcal/mole} \tag{9}$$

$$ClO + OH \rightarrow \mathbf{HCl} + \mathbf{O_2}, \quad \Delta H = -55.7\ \text{kcal/mole} \tag{10}$$

Boldface species are observed reaction products. Reaction (1) is the initiation step, (2–8) are chain carrying steps, and (9) and (10) are termination steps. Discussion of our reasons for selecting this mechanism is in order.

Because AP vaporizes by proton transfer and desorption, into NH_3(g) and $HClO_4$(g),[14,17] the chain reaction may be initiated by decomposition of $HCLO_4$; above 315°C, $HClO_4$ decomposition is a homogeneous, first-order reaction with rate constant (Ref. 16) $k = 5.8 \times 10^{13} \exp(-45, 100/R°T)$ and with steps $HClO_4 \rightarrow ClO_3 + OH$, $ClO_3 \rightarrow ClO + O_2$. Pearson and Jacobs[18] have developed a chain reaction mechanism, initiated by $HClO_4$ decomposition alone, which yields the observed deflagration product concentrations for a preheated pellet.[2] However, it has been suggested that in AP deflagration a direct reaction between NH_3 and $HClO_4$ may occur,[19] and we have chosen reaction (1), which requires one bond to be broken in each colliding molecule; a reaction path may exist for which the activation energy is well below the sum of the two broken bond energies. We note that for the rate constants that will be assigned to reaction (1), the reaction rate is roughly the same as that for $HClO_4$ decomposition in the range of temperature and composition prevailing in deflagration, and the activation energy is somewhat less. Moreover, the species needed to initiate our chain can be produced equally well by the acid decomposition. Therefore, the acid decomposition must be as important as Eq. (1), and our neglect of it constitutes a simplifying approximation. Without verification by detailed numerical calculation, we estimate that replacement of Eq. (1) by the acid decomposition will increase the over-all activation energy for our gas-phase reaction, perhaps to 25 kcal/mole, without appreciably changing either the over-all gas-phase reaction rate under deflagration conditions or any of our other deflagration results. Thus, our results do not rule out the possibility that $HClO_4$ decomposition is the only initiation step.

Except for reaction (5), all of the other reactions given above are among those proposed and discussed in Ref. 18. Reaction (2) rapidly produces the principal chain carrier ClO, which oxidizes NH_3 by reaction (3). The radical NH_2 can produce HNO by reaction (4). The principal new aspect of our proposed mechanism is the postulate that nitroxyl acts as a chain carrier through reaction (5), which seems quite feasible because of its low exothermicity and sterically favorable conformality. Reaction (5) is essential to our gas-phase kinetic scheme, in the sense that the over-all reaction rate would be much lower without this step. Although neither NH_2 nor HNO have been observed in AP decomposition or deflagration experiments, it is difficult to conceive of a reasonable gas-phase combustion scheme that does not involve these two species.

Equations (1–10) comprise fewer steps than previously proposed mechanisms for AP deflagration. The only nitrogenous product that they form is nitric oxide. Nitrogen and nitrous oxide can be presumed to be formed later on in the flame, where they do not affect the over-all reaction rate, through the air-chemistry reactions

$$NO + NO \rightarrow \mathbf{N_2O} + O, \quad \Delta H = 35.5\ \text{kcal/mole} \tag{11}$$

$$NO + O \rightarrow N + \mathbf{O_2}, \quad \Delta H = 32.0\ \text{kcal/mole} \tag{12}$$

$$NO + N \rightarrow \mathbf{N_2} + O, \quad \Delta H = -75.2\ \text{kcal/mole} \tag{13}$$

$$O + O + M \rightarrow \mathbf{O_2} + M, \quad \Delta H = -118.3\ \text{kcal/mole} \tag{14}$$

whose rate constants are known.[20] The end products from this simplified gas-phase reaction scheme then become the observed AP deflagration products. For simplicity in performing kinetic calculations (Sec. 6) we shall not include Eqs. (11–14), and therefore all nitrogen will appear as NO. We have not undertaken the kinetic calculations needed for ascertaining whether the rates of reactions (11–14) are appropriate for producing the observed final compositions of nitrogenous products.

Table 1 gives a set of multiplying factors for the relative extents of the reactions, that produces the stoichiometry observed at 75 atm,[3] viz.,

$$NH_4ClO_4 \rightarrow 1.62H_2O + 1.015O_2 + 0.76HCl + 0.265N_2 + 0.23NO + 0.12Cl_2 + 0.12N_2O \tag{15}$$

To achieve stoichiometry in this calculation, we converted all of the nitrogen in Eq. (15) to NO by reaction with O_2, chose multiplying factors in Eqs. (2–10) to give the new stoichiometry, then adjusted the multiplying factors in Eqs. (11–14) to give stoichiometry shown in Eq. (15).

Although it seems quite plausible to us that aside from the initiation step the mechanism just outlined contains the dominant reactions, there certainly must be numerous other subsidiary reactions that occur. A definitive determination of the mechanism is impossible today. The mechanism that

Table 1 Stoichiometry and rates for AP deflagration

Reaction p	ΔH_p (kcal/mole)	Frequency factor[a] A_p	Multiplying factors
(1)	31.5	$1.4 \times 10^{13}T^{1/2}$	$<10^{-3}$
(2)	−12.8	$1.71 \times 10^{12}T^{1/2}$	$\lesssim 1$
(3)	5.1	$4.24 \times 10^{13}T^{1/2}$	$\lesssim 1$
(4)	−6.2	$3.98 \times 10^{13}T^{1/2}$	$\lesssim 1$
(5)	−11.79	$1.11 \times 10^{14}T^{1/2}$	$\lesssim 1$
(6)	−21.6	$3.32 \times 10^{13}T^{1/2}$	0.62
(7)	9.72	$2.67 \times 10^{13}T^{1/2}$	0.31
(8)	−4.8	$3.22 \times 10^{13}T^{1/2}$	0.38
(9)	−58.0	$3 \times 10^{14}T^{1/2}$	0.12
(10)	−55.7	$3.1 \times 10^{13}T^{1/2}$	0.38
(11)	35.5	$2.5 \times 10^{13}T$	0.12
(12)	32.0	$3.2 \times 10^{9}T$	0.265
(13)	−75.2	1.5×10^{13}	0.265
(14)	−118.3	8×10^{16}	0.06

[a] Concentration unit = mole/cm^3.

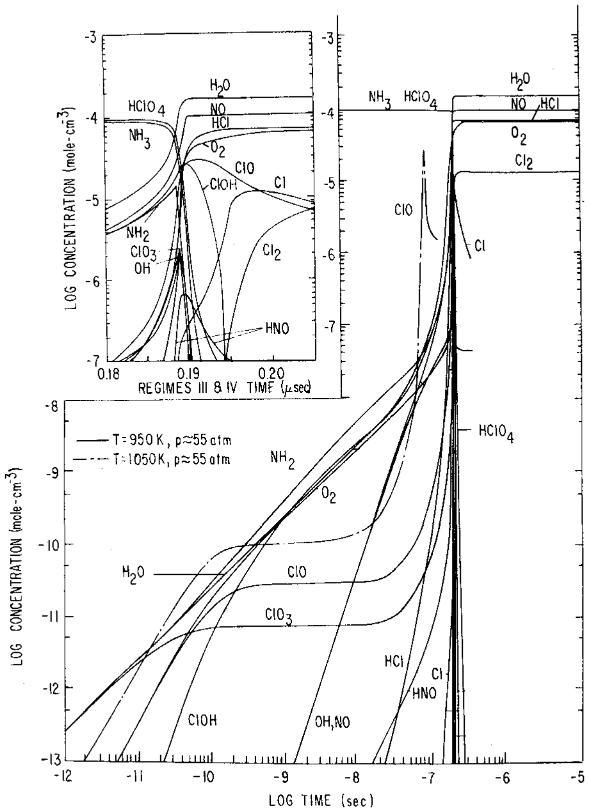

Fig. 1 Species concentration profiles for the gas-phase reaction.

we have proposed is simple enough for us to perform rate calculations, provided that the rates of the elementary steps are known. Unfortunately, of reactions (1–10), rate data are available only for reaction (9).[21] To obtain rates for the other reactions, we have used activation energies of zero for exothermic steps and of ΔH for endothermic steps, and we have employed collision reaction rate theory,[22] with steric factors of unity and with collision diameters of 4 Å, 3.5 Å, 4 Å, and 10 Å, respectively, for ClO_3, ClO, HNO, and $HClO_4$ (Ref. 14). We believe that the resulting frequency factors, listed in Table 1, should be correct within an order of magnitude for the rapid chain-carrying steps.

6. Gas-Phase Kinetic Calculations

It is not feasible to carry out kinetic calculations, for a mechanism as complex as that given in Eqs. (1–10), in the context of a deflagration eigenvalue problem with diffusion and heat conduction. Therefore, we have performed kinetic calculations only for isothermal, isobaric systems. We have done this at a variety of temperatures, pressures and compositions, with the aim of extracting over-all reaction orders, an over-all activation energy, and an over-all pre-exponential rate constant, in the range of pressure, temperature and composition expected in the gas-phase AP flame. These over-all rate parameters are to be used in the one-step reaction model for the deflagration, discussed in the following section. In the present section, we describe the character of the gas-phase reaction, as inferred from the calculations of isothermal, isobaric kinetics.

The kinetic equations are given in Table 2, where the subscript for each rate constant $k_p (p = 1, \ldots, 10)$ corresponds to the reaction number listed in Table 1. This system of fourteen nonlinear first-order differential equations was solved by the Runge-Kutta method. Reverse reactions were neglected on the grounds that their rates are small. The forward rate A (all positive terms) and backward rate $-B$ (all negative terms) were monitored for each species concentration C_j, and whenever $[dC_j/dt]/A$ or $[dC_j/dt]/B$ was less than $10^{-n} (3 \leq n \leq 6)$, the steady-state approximation was introduced for species j. Various step sizes were employed and atom balances were monitored as checks on the accuracy of the results.

Typical results are shown in Fig. 1. The concentration histories with the most character are ClO_3 and ClO. These exhibit five different regimes: regime I corresponds to the growth of radical concentrations during initiation. The numerical calculations show the initiation time to be independent of the temperature and pressure at which the reaction takes place, as can be justified heuristically. Regime II represents the steady-state of ClO_3 and ClO concentrations, obtained primarily through reactions (1–3). In this regime, dC_j/dt was set equal to zero in the numerical calculations for ClO_3. None of the other intermediates reach a steady-state in this regime. Regime III exhibits a rapid but nearly steady-state increase in ClO_3 and ClO concentrations and is characterized by HNO reaching a steady-state. The increased rate of production of chlorine oxides is traceable primarily to the increase in the rate of the reaction given in Eq. (5), which in turn stems from the increasing HNO concentration. In regime IV all radical concentrations reach their maximum values and H_2O and NO achieve their stoichiometric values. Regime V corresponds to the decay of radical and reactant concentrations and O_2, HCl, and Cl_2 reaching their stoichiometric concentrations.

Figure 1 shows that the reactant concentrations remain practically constant at their initial values during the first three regimes, since initiation and buildup of chain carriers require a very small amount of reactants to be consumed. In regime IV, the reactant concentrations decrease drastically in a very short time. The reaction time τ_r is therefore defined very precisely as the time of the peak in the concentration-time curves for radicals.

Table 2 Kinetic equations for gas-phase reaction mechanism

$$(d/dt)[HClO_4] = -k_1[HClO_4][NH_3] - k_5[HClO_4][HNO] \qquad (1)$$

$$(d/dt)[NH_3] = -k_1[HClO_4][NH_3] - k_3[NH_3][ClO] \qquad (2)$$

$$(d/dt)[H_2O] = k_1[HClO_4][NH_3] + k_5[HClO_4][HNO] + k_6[ClOH][OH] \qquad (3)$$

$$(d/dt)[O_2] = k_2[ClO_3][M] + k_7[ClO]^2 + k_{10}[ClO][OH] - k_4[NH_2][O_2] \qquad (4$$

$$(d/dt)[NO] = k_5[HClO_4][HNO] \qquad (5)$$

$$(d/dt)[HCl] = k_8[ClOH][Cl] + k_{10}[ClO][OH] \qquad (6)$$

$$(d/dt)[Cl_2] = k_6[Cl]^2[M] \qquad (7)$$

$$(d/dt)[ClO_3] = k_1[HClO_4][NH_3] + k_5[HClO_4][HNO] - k_2[ClO_3][M] \qquad (8)$$

$$(d/dt)[ClO] = k_2[ClO_3][M] + k_8[ClOH][Cl] + k_6[ClOH][OH] - k_3[NH_3][ClO] - 2k_7[ClO]^2 - k_{10}[ClO][OH] \qquad (9)$$

$$(d/dt)[NH_2] = k_1[HClO_4][NH_3] + k_3[NH_3][ClO] - k_4[NH_2][O_2] \qquad (10)$$

$$(d/dt)[OH] = k_4[NH_2][O_2] - k_6[ClOH][OH] - k_{10}[ClO][OH] \qquad (11)$$

$$(d/dt)[HNO] = k_4[NH_2][O_2] - k_5[HClO_4][HNO] \qquad (12)$$

$$(d/dt)[ClOH] = k_3[NH_3][ClO] - k_8[ClOH][Cl] - k_6[ClOH][OH] \qquad (13)$$

$$(d/dt)[Cl] = 2k_7[ClO]^2 - k_8[ClOH][OH] - 2k_9[Cl]^2[M] \qquad (14)$$

An overall reaction-rate constant k is deduced by assuming a one-step, second-order reaction $NH_3 + HClO_4 \rightarrow$ products, with a rate proportional to the product of the concentrations of NH_3 and $HClO_4$. The validity of this assumption was checked by performing calculations with various initial concentrations of NH_3 and $HClO_4$ (10^{-4} and 10^{-6} moles/cm^3), pressurized by inerts (to 55 atm), but always with $[HClO_4] = [NH_3]$ initially, a requirement of stoichiometry. The over-all kinetic equation

$$d[HClO_4]/dt = -k[HClO_4][NH_3] \tag{16}$$

implies

$$k \approx 1/\{\tau_r[HClO_4]_{t=0}\} \tag{17}$$

which is shown on an Arrhenius plot in Fig. 2. This figure yields

$$k = A_g T \exp(-E_g/R^\circ T) \tag{18a}$$

$$A_g = 2.03 \times 10^{11} \text{ (cm}^3\text{/mole-sec-°K)} \tag{18b}$$

$$E_g = 15.47 \text{(kcal/mole)} \tag{18c}$$

where $A_g T$ is the frequency factor and E_g the over-all activation energy for the chain mechanism approximated as a one-step reaction. The activation energy given in Eq. (18) is in good agreement with the estimations of Ref. 23, and extrapolation of the rate constant to 367°C yields good agreement with an experimentally measured rate of the homogeneous reaction between NH_3 and $HClO_4$, reported in Ref. 19. Rough heuristic and computational observations suggest that changing the rates of the chain-carrying steps by as much as an order of magnitude will not greatly affect the result given in Eq. (18), while increasing the rate of the initiation step increases A_g nearly proportionally.

7. Gas-Phase Deflagration Theory

To analyze the gas-phase deflagration process on the basis of a one-dimensional model, we assume that the condensed phase, of initial density ρ_π and initial temperature T_0 at $x = -\infty$, moves with the constant linear speed b (at $x = -\infty$) into the stationary plane $x = 0$ (the surface of the condensed phase). At the surface, the condensed phase (subscript π) gasifies according to the reaction

$$A_\pi(c) \rightarrow \sum_{j=1}^{n} a_j A_j(g) \tag{19}$$

where the A's are the chemical symbols for the species present in the reaction and the a's, the corresponding stoichiometric coefficients. We let $A_1(g) = NH_3(g)$ and $A_2(g) = HClO_4(g)$, so that $a_1 = a_2$. The remaining species ($j = 3,\ldots,n$) are presumed to be final reaction products, present in the same relative proportions as in the final mixture; they are produced by exothermic reactions occurring in a liquid layer at the surface temperature T_s. These products are assumed to have identical diffusion coefficients so that in the gas phase they behave as a single inert. In fact, a Lewis number of unity will be introduced as an approximation for every gas-phase species. The sublimation products further react in the gas phase through the chain reaction mechanism described in Sec. 5, which can be approximated by an overall one-step, second-order reaction which yields the observed deflagration products,

$$A_1(g) + A_2(g) \rightarrow \sum_{j=3}^{n} \nu_j A_j(g) \tag{20}$$

where the ν's are the stoichiometric coefficients for reaction products $[\nu_j = a_j/(1 - a_1)]$.

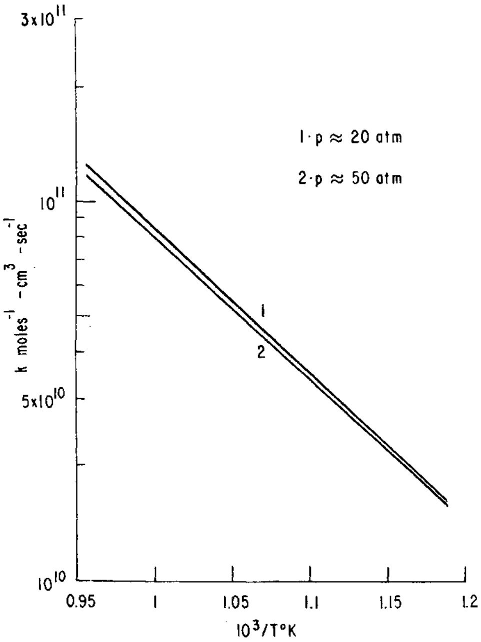

Fig. 2 Arrhenius plot for the over-all rate of the chain reaction.

Johnson and Nachbar[24] have developed a method for calculating laminar flame velocities which accounts for the presence of an inert I with mass fraction $1 - G$ in the propellant. The gas-phase part of their analysis can be applied directly to our present problem if we define their dilution coefficient to be

$$G \equiv 1 - \sum_{j=3}^{n} a_j W_j / W_\pi \tag{21}$$

Therefore we refer the reader to Ref. 24 for the relevant conservation equations and for the detailed mathematical analysis; only those formulas needed for communication with Ref. 24 will be given herein. The gas-phase mass fraction of inerts Y_I, appearing in the equations of Ref. 24, turns out to be $Y_I = 1 - G$. It has been shown[24] that all other gas-phase mass fractions can be expressed in terms of a single function $Y \equiv (Y_1 + Y_2)/G$, according to

$$Y_j = Y_j^*[a_j - G(1 - Y)],\ j = 1,2 \tag{22a}$$

$$Y_j = Y_j^* G(1 - Y),\ j = 3,\ldots,n \tag{22b}$$

where $Y_j^* \equiv W_j/W_\pi (j = 1,2)$ and $Y_j^* \equiv \nu_j W_j/W_\pi$ $(j = 3,\ldots,n)$. Here for $j = 3,\ldots,n, Y_j$ represents the mass fraction of only those products produced in the gas-phase reaction, so that

$$\sum_{j=1}^{n} Y_j + Y_I = 1$$

The temperature is also expressible in terms of Y, according to

$$Y = (T_f - T)/(GT^*) \tag{23}$$

where $T^* \equiv -\Delta h_g/c_g$. Since evaluation of Eq. (23) at $x = 0$ yields $T_f = T_s + GT^*Y_s$, an over-all energy balance for the system requires that

$$\rho_\pi b c_g(T_{fa} - T_s - GT^*Y_s) = \rho_\pi b c_g(T_{fa} - T_f) = 1.36\epsilon_s(T_s/1000)^4 \text{(cal/cm}^2\text{sec)} \tag{24}$$

where we have neglected nonradiative heat losses, intending to compare our results with experiments performed on samples of sufficiently large cross-sectional areas.

Reference 24 shows that the burning rate b, the pressure p and Y_s, the function Y evaluated at $x = 0$, are connected by the definition of the eigenvalue Λ,

$$(\bar{K}p/b)^2 = \Lambda \tag{25}$$

where $\bar{K}$ is a constant involving transport and kinetic

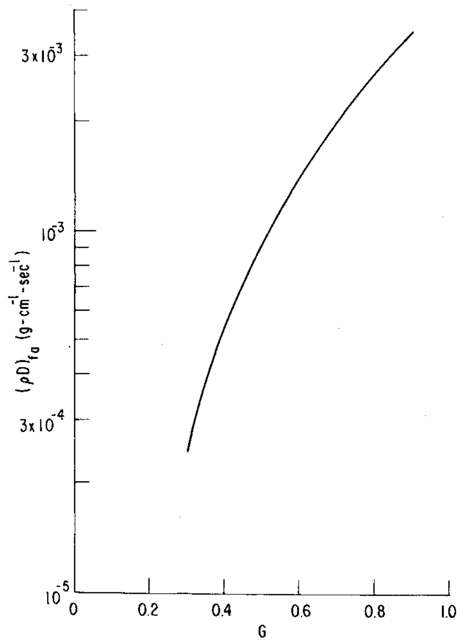

Fig. 3 Dependence of $(\rho D)_{fa}$ on dilution coefficient G.

parameters, as defined in Eq. (1.34e) of Ref. 24, viz.,

$$\bar{K} \equiv [(\rho D)_{fa} A_g G / T_{fa} W_\pi]^{1/2} \overline{W}_P / \rho_\pi R^\circ \tag{26}$$

In the present calculation it has been assumed that the gas-phase reaction is of second order (see Sec. 6) and that the frequency factor $A_g T$ and the product $\rho_g D$ are each proportional to the temperature. Strict upper and lower bound formulas for Λ are[24]

$$\Lambda^\pm = \left\{2 \int_0^{Y_s} \frac{\varphi(Y)}{(1-Y)^j}\, dY\right\}^{-1} \tag{27}$$

where $j = 1$ for Λ^+, $j = 2$ for Λ^-, and $\Lambda^- < \Lambda < \Lambda^+$. Here

$$\varphi(Y) = Y^2[\overline{W}(Y)/\overline{W}(0)]^2 \exp[-E_g/R^\circ T(Y)] \tag{28}$$

and

$$\overline{W}(Y) \equiv \left\{\sum_{j=1}^{n} \left(\frac{Y_j}{W_j}\right) + \left(\frac{Y_I}{W_I}\right)\right\}^{-1} \tag{29}$$

Since Eq. (24) expresses T_f and T_s in terms of b and Y_s, it is seen that substitution of Eqs. (22, 23, 28, and 29) into Eq. (27) provides upper and lower bounds on Λ as functions of the two variables Y_s and b. Use of these bounds in Eq. (25), therefore, provides bounds for one relationship between the three variables Y_s, b, and p. One more relationship is, therefore, needed for obtaining upper and lower bounds for a curve of burning rate vs pressure. The missing relationship is a surface boundary condition that enables us to express Y_s in terms of b and p.

8. Interface Condition and Method of Computation

Reference 14 gives support to an equilibrium dissociative sublimation at the surface of AP. Through introduction of such a hypothesis herein, the present analysis will differ from that of Ref. 24. The surface equilibrium condition at the surface temperature T_s is given by

$$\prod_{j=1}^{2} p_j(T_s) = \left[\frac{p_d(T_s)}{2}\right]^2 \tag{30}$$

where the p_j's are the partial pressures of NH_3(g) and $HClO_4$(g), and where $p_d(T_s)$ is the equilibrium dissociation pressure of AP.[17] By relating partial pressures to mass fractions, it can be shown from Eq. (30) that

$$p_d(T_s) = 2p\overline{W}_s G Y_s / W_\pi \tag{31}$$

where the mean molecular weight at the surface is given by

$$\overline{W}_s = \{2[1 + g(1 - GY_s)]/W_\pi\}^{-1} \tag{32}$$

in which

$$g \equiv \left(\frac{W_\pi}{2\overline{W}_P}\right) - 1, \quad \overline{W}_P \equiv \left[\sum_{j=3}^{n} \frac{Y_j^*}{W_j}\right]^{-1} = W_I \tag{33}$$

Substitution of Eq. (32) into Eq. (31) yields the final surface condition,

$$p_d(T_s) = pGY_s[1 + g(1 - GY_s)]^{-1} \tag{34}$$

which becomes a relationship between Y_s, b, and p when Eq. (24) is used to eliminate T_s.

A step-by-step iteration method, described fully in Ref. 54, was used to solve the system of nonlinear algebraic equations [Eqs. (24, 25, 27, and 34)]. The dilution coefficient G is taken to be constant, and in principle its value is adjusted to fit an experimental point (b°, p°) of the burning rate-pressure curve. In actual calculations, since G enters in a number of places but $\bar{K}$ only in one, the value of G was selected in advance and the value of $\bar{K}$ needed to fit the point (b°, p°) was computed. Since the theoretical analysis yields only bounds Λ^+ and Λ^-, the mean eigenvalue Λ, defined by $2(\Lambda)^{1/2} = (\Lambda^+)^{1/2} + (\Lambda^-)^{1/2}$, was used in making the $\bar{K}$ calculation (viz., $\bar{K} = (b^\circ/p^\circ)[\Lambda(b^\circ, p^\circ)]^{1/2}$). The calculation of $\Lambda(b^\circ, p^\circ)$ involves selection of a value of T_s, calculation of Y_s from Eq. (24), then calculation of p from Eq. (34); the resulting value of p generally differs from p°, and so an iteration on T_s is performed by the modified false position method[51] until convergence to $p = p^\circ$ is obtained. After convergence, Y_s° and T_f° are calculated from Eq. (24), so that the integrals in Eq. (27) can be evaluated to obtain $\Lambda(b^\circ, p^\circ)$. Since $\bar{K}$ depends on the gas-phase diffusivity $(\rho D)_{fa} = (\lambda/c_g)_{fa}$, by employing the kinetic constants given in Eq. (18), we obtain from the fit a different value of diffusivity for each choice of G. The dependence of diffusivity on G is shown in Fig. 3, for $b^\circ = 1$ cm/sec, $p^\circ = 100$ atm.

Having employed the known value of $\bar{K}$ to select G from Fig. 3, we generate upper-bound and lower-bound curves of burning rate, flame temperature and surface temperature, as

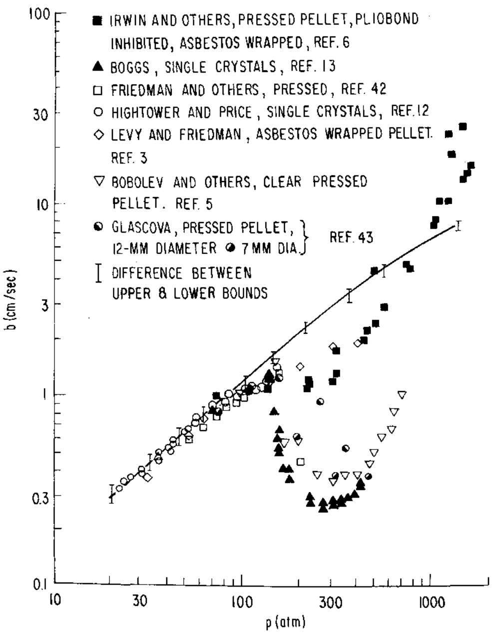

Fig. 4 Pressure dependence of AP deflagration rate.

functions of pressure, by solving the nonlinear algebraic system in a stepwise fashion.[54]

9. Results of Gas-Phase Deflagration Theory

A typical value for λ_{fa} is 10^{-4} cal/cm-sec-°K at 1200°K. Assuming $c_g = 0.3$ cal/g-°K, Fig. 3 yields approximately $G = 0.3$, i.e., 70% of AP decomposes at the surface through condensed-phase reactions, and 30% vaporizes into $NH_3(g)$ and $HClO_4(g)$. This result implies that the over-all gasification process is exothermic by approximately 100 cal/g, a result which is in good agreement with inferences from models of composite propellant combustion[25,26] and with deductions from temperature profile measurements.[27] It is seen from Fig. 3 that $(\rho D)_{fa}$ is a very sensitive function of G, so that a reasonable best-fit value of G is not likely to be less than 0.25 or to exceed 0.4.

Figure 4 shows the variation of burning rate with pressure. The solution is defined as $b = (b^+ + b^-)/2$, where b^+ and b^- are the upper and the lower bounds, obtained by using Λ^- and Λ^+, respectively, for $\bar{K} = 5.01$ cm/sec atm (viz., $G = 0.3$). A very good agreement with the experimental data is obtained in the pressure range 20 to 100 atm.

The calculated dependence of flame temperature on surface temperature is shown in Fig. 5, from which it is seen that the flame temperature is practically constant ($T_f \gtrsim T_{fa}$) in this pressure range. The variation of surface temperature with pressure, shown in Fig. 6, reveals that the surface temperature is not a constant over the whole pressure range, contrary to the results reported in Refs. 27 and 28. Thermocouple measurements,[27] giving surface temperatures that lie in the vicinity of 400°C and that decrease somewhat with increasing pressure, are exceedingly difficult to perform accurately since the temperature gradients are very high. We believe that the procedure of Beckstead and Hightower[28] yields the melting point of AP, $T_m = (560 \pm 20)$°C (Refs. 28 and 29), rather than the true surface temperature. The possibility of this interpretation has been indicated in Ref. 28, where it is stated that the true surface temperature of the interface between the gaseous and condensed phases should then be 50–200°C higher than that of the solid surface for the pressures under consideration. Our values of T_s, which vary from 564°C to roughly 630°C, are in agreement with this inference.

At 20 atm, the observed low-pressure deflagration limit, Fig. 6 shows that T_s is just about equal to the melting point T_m of AP, as just quoted. The numerical calculations with

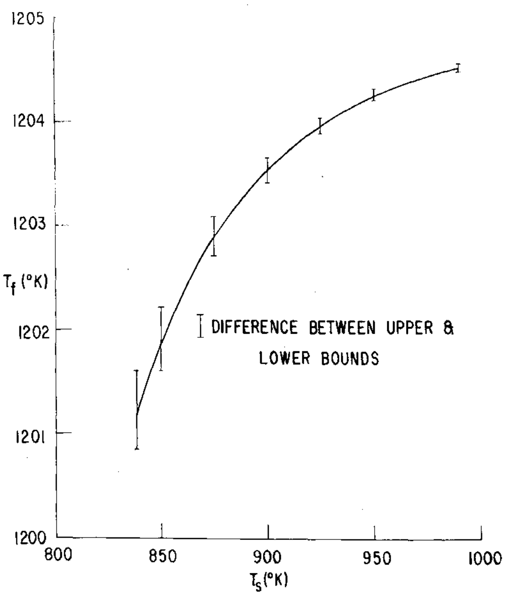

Fig. 5 **Dependence of flame temperature on surface temperature.**

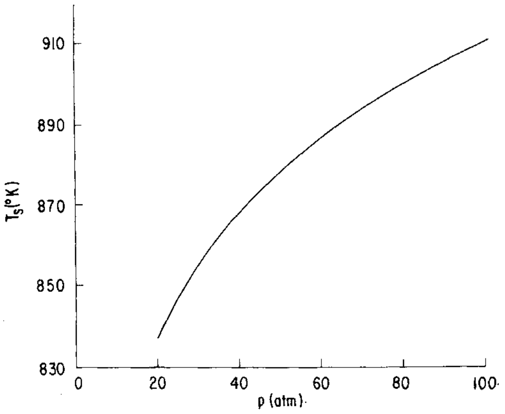

Fig. 6 **Dependence of surface temperature on pressure.**

$G = 0.3$ can be extended well below 20 atm and continue to yield a solution which is nearly a straight line in Fig. 4. However, for all points along this low-pressure part of the curve, $T_s < T_m$. It therefore, seems reasonable to assume, as discussed in Sec. 3, that the present calculations are inapplicable for $T_s < T_m$, because the great reduction in condensed-phase reaction rates upon solidification requires that essentially $G = 1$. Changing G to unity for the theoretical calculation in this pressure range produces a burning rate that is lower by about an order of magnitude and that soon exhibits extinction due to radiative heat losses. Thus, although experimental surface temperatures are under dispute, in that estimates have ranged from 400°C (Refs. 27 and 30) to 816°C (Ref. 31), the identification of the deflagration limit with $T_s = T_m \approx 560$°C seems reasonable. It is remarkable that by an empirical adjustment of only one constant G, both the burning rate curve and the deflagration limit are fitted with reasonable accuracy.

10. Gas-Phase Flame Thickness and Residence Time

Figures 7 and 8 compare the gas-phase flame thickness with the molecular mean-free path and the gas-phase residence time with the reaction time, showing that in the present model the residence time is clearly long enough for the gas-phase reaction to occur. The mean free path is more than two orders of magnitude below a lower bound for the reaction-zone thickness, and the reaction time is comparable with the residence time, as must be true for the analysis to be consistent. The analysis leading to Figs. 7 and 8 is given in Ref. 54.

11. Condensed-Phase Reaction Analysis

In the preceding analysis, the condensed-phase reaction was assumed to occur instantaneously at the liquid-gas interface. To see whether this approximation is consistent with our assumption of a distributed liquid-phase reaction, it is necessary to analyze the processes that occur in the liquid phase. We shall treat the liquid-phase reaction as a one-step, Arrhenius process and employ the theory of Lengelle,[32] which was developed for predicting linear regression rates of polymers. Although this theory considered only endothermic condensed-phase reactions, it is equally applicable for exothermic reactions, provided that the exothermicity is not too large. For sufficiently large condensed-phase exothermicity, the condensed-phase process becomes self-propagating at a flame speed of its own, which exceeds the gas-phase deflagration rate and which is independent of gas-phase processes; under this condition the analysis of Ref. 32 becomes inapplicable. By showing that the results of Ref. 32 can indeed be employed here, we shall have demonstrated that both the gas-

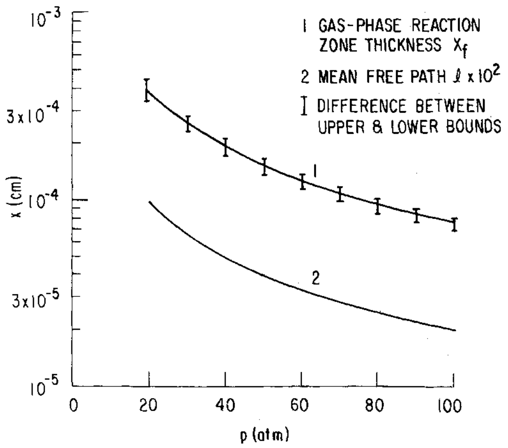

Fig. 7 Dependence of flame thickness and mean free path on pressure.

phase and the liquid-phase reactions are essential to the deflagration process.

The technique of Ref. 32 employs matched asymptotic expansions, with the large parameter being the nondimensional activation energy for the condensed-phase reaction, $E' \equiv E/R^\circ T_s$. A thin reaction zone exists at the surface of the liquid and a heat conduction zone in the interior of the liquid. With a nondimensional regression rate R, defined (for reaction order of unity) by

$$b^2 \equiv R^2 E'^{-1} B e^{-E'} (\lambda_l / c_l \rho_l) \tag{35}$$

Reference 32 shows that if E' is large enough, then an asymptotic expansion of the differential equations for conservation of mass and energy can be performed, with suitable matching of the inner and the outer solutions yielding

$$R^2 = [-(\theta_s + 1 - \theta_\infty) \ln G - \theta_s(1 - G)]^{-1} \tag{36}$$

Analogous results were obtained for reaction order less than unity.[32] The previously defined dilution coefficient is precisely the same as the surface mass fraction of reactant defined in Ref. 32. We note that since θ_s is negative for an exothermic condensed-phase reaction, the right-hand side of Eq. (36) can become negative if $-\Delta h_s$ is sufficiently large; in particular, if the exothermicity is large enough for $(\theta_s + 1 - \theta_\infty)$ to be negative, which is in fact true for AP deflagration, then there always will exist a critical value of G below which the R^2 given by Eq. (36) is negative. This corresponds to the condition for the breakdown of the theory of Ref. 32 and for the development of a self-propagating condensed-phase flame.

Although the analysis of Ref. 32 is restricted to constant thermophysical properties for the condensed phase, the results should be applicable, within a reasonable degree of approximation, even in the presence of phase transition and melting, provided that there is an appreciable temperature change in the liquid layer, and provided that the thermochemical effects of the melting and phase transition are considered properly. We account for these by letting Δh_t denote the sum of the enthalpy change per unit mass in melting and phase transition and by employing the over-all energy conservation condition

$$c_l(T_s - T_\infty) + \Delta h_s + c_g(T_{fa} - T_s) = 0 \tag{37}$$

with

$$c_l(T_s - T_\infty) = c_{\pi 1}(T_{tr} - T_0) + c_{\pi 2}(T_m - T_{tr}) + c_l(T_s - T_m) + \Delta h_t \tag{38}$$

Equation (37) is the energy balance for the hypothetical system whose condensed phase is purely liquid, and the combination of Eqs. (37) and (38) is the true energy balance for AP deflagration. Equation (38) can be used to calculate the effective temperature T_∞ of the liquid at $x = -\infty$. Equation (37) can then be used to calculate Δh_s. Suitable estimates for c_l and Δh_t are required (Table 3). We find from these results that $\theta_\infty \simeq 0$ and that θ_s varies from -1.4 at 20 atm to -1.3 at 100 atm. For $G = 0.3$, the corresponding range of R^2, obtained from Eq. (36), is 2.00 to 1.86. Thus, the condensed-phase reaction is not self-sustaining.

12. Deductions from Condensed-Phase Theory

If we define

$$A(T_s) \equiv (b/R)^2 (c_l \rho_l / \lambda_l)(R^\circ T_s)^{-1} \tag{39}$$

so that Eq. (35) becomes

$$A(T_s) = BE^{-1}e^{-E'} \tag{40}$$

then by taking the logarithm of both sides of Eq. (40), we see that a plot of $\ln[A(T_s)]$vs T_s^{-1} should yield a straight line with slope $-E/R^\circ$. From the ordinate at infinite surface temperature, the frequency factor B can be obtained. This plot can be constructed from preceding results and is shown in Fig. 9; $A(T_s)$ is calculated by using the burning rates and surface temperatures shown in Figs. 4 and 6 for a dilution coefficient of 0.3. It is seen from Fig. 9 that a straight line is obtained, and calculations show that the activation energy is 58.38 kcal/mole. A parallel development for a zero-order liquid-phase reaction yields an activation energy of 58.22 kcal/mole, thereby demonstrating that the activation energy is not strongly dependent on the choice of reaction order. The high activation energy gives $E' \geq 32$, thereby justifying the underlying hypothesis of the singular perturbation analysis. For a first-order reaction, the calculated frequency factor is $B = 2.46 \times 10^{18}(\text{sec}^{-1})$, the corresponding value being $2.39 \times 10^{18}(\text{sec}^{-1})$ for a zero-order reaction. The value of B increases with decreasing liquid-phase thermal conductivity.

The theory of Ref. 32 also enables us to calculate the thickness of the liquid layer and the thickness of the liquid-phase reaction zone at the surface of the liquid, as indicated in Ref. 54. These results are shown in Fig. 10. In good agreement with the measurements of Ref. 13, it is seen that the liquid layer is never more than 2 μ thick; its thickness approaches zero at the deflagration limit and tends to approach zero asymptotically as the pressure goes to infinity. The liquid phase reaction region is very thin, particularly at the higher pressures, for the high calculated activation energy. As the

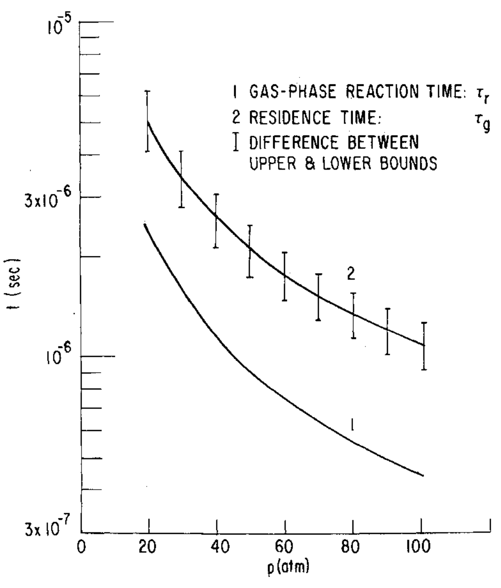

Fig. 8 Dependence of gas-phase reaction time and residence time of gaseous mixture on pressure.

pressure decreases and approaches the low-pressure deflagration limit, the reaction-zone thickness becomes comparable with that of the liquid layer, and at pressures below 30 atm, the former exceeds the latter so that the extent of condensed-phase reaction occurring in the liquid layer begins to decrease. Under this condition, our application of the analysis of Ref. 32 is no longer valid for the present problem. A proper analysis would require a discontinuity (melting) inside the inner (reaction) zone, with a zero reaction rate on the low-temperature side of the discontinuity. The outer region of Ref. 32 would become the cubic phase.

It would not be difficult to write down an appropriate theory. But this hardly seems justified because the qualitative behavior of the solution is already clear on physical grounds. The residence time in the liquid layer will become too small for the liquid-phase reaction to proceed to $G = 0.3$. Hence G will begin to increase toward unity, and the burning rate will begin to decrease below the theoretical curve shown in Fig. 4. A precise determination of the deflagration limit would then require gas-phase flame-theory calculations with variable G and probably a closer look at heat losses. There seems little doubt that it would be possible to fit the data, which is all that the present study is intended to show.

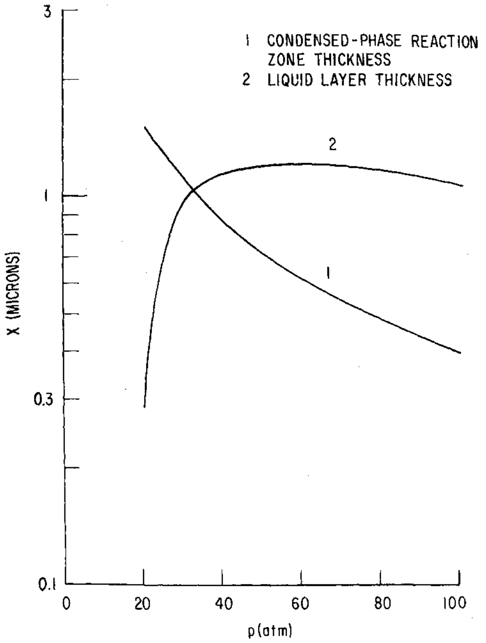

Fig. 10 Dependence of condensed-phase reaction zone thickness and liquid layer thickness on pressure.

13. Condensed-Phase Reaction Chemistry

It is of interest to ask whether the activation energy and frequency factor that we have calculated for the liquid-phase reaction are consistent with known perchlorate kinetics. It is well known that the low-temperature decomposition of AP, the high-temperature decomposition and the sublimation process are all initiated by proton transfer from NH_4^+ to ClO_4^-, the corresponding activation energy lying on the range 27–34 kcal/mole, close to half the heat of dissociation of AP (Ref. 33). Comparison with our condensed-phase activation energies would suggest that the same mechanism can be the rate-determining process in condensed-phase or surface reactions occurring in deflagration. However, rate extrapolations suggest that proton transfer will maintain equilibrium and that subsequent decompositions may be too slow. The presumed presence of a liquid layer on the surface of deflagrating AP suggests comparison with perchlorates which melt rather than sublime.

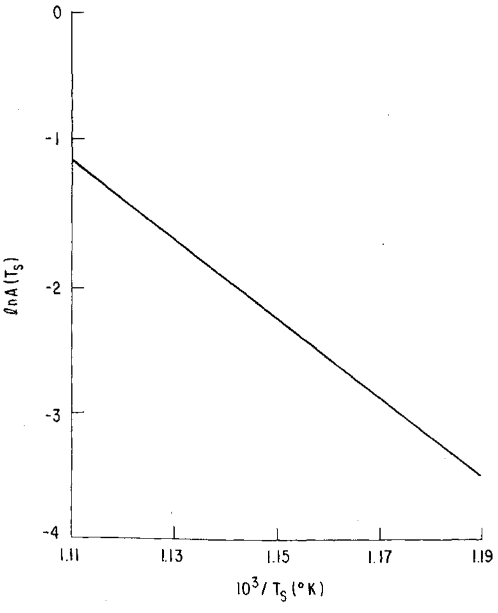

Fig. 9 Arrhenius plot for over-all rate of condensed-phase reaction.

The thermal decomposition of $KClO_4$ has an activation energy in the range 60–70 kcal/mole; $KClO_4$ melts between 525 and 620°C (Ref. 15). Experiments always show the presence of a liquid phase, and the rate-determining step for the thermal decomposition is ascribed to the breaking of the Cl—O bond in the ClO_4^- ion[34,35] since the calculated bond dissociation energy[36] is 64.3 kcal/mole, in good agreement with the observed activation energy. The same mechanism also seems responsible for $Mg(ClO_4)_2$ decomposition[37] although in anhydrous form this perchlorate does not melt below 600°C. In vacuo, acceleratory and deceleratory periods were identified, and the rate constants for both periods obeyed an Arrhenius law, with corresponding activation energies of $E_1 = 58.1 \pm 4.4$ kcal/mole and $E_2 = 66.7 \pm 3.6$ kcal/mole. The results suggested that a similar process is operative in both steps, viz., the thermal breakage of a Cl—O bond,

$$ClO_4^- \xrightarrow{E_1} ClO_3^- \xrightarrow{E_2} ClO^-$$

each activation energy being interpreted as the dissociation energy of the relevant Cl—O bond.[37]

In analyzing their observations on the decomposition of mixtures of magnesium perchlorate and ammonium perchlorate, Acheson and Jacobs[37] argue convincingly that their observed acceleration of AP decomposition by addition of small amounts of magnesium perchlorate is due to the formation of a melt in which perchlorate ions decompose at an enhanced rate. Since it does not seem that the metal ion must participate directly in this decomposition, it appears that if AP melts, then it may decompose very rapidly by a mechanism initiated by breaking of a Cl—O bond in ClO_4^-. Our results are consistent with such an interpretation. Our activation energy (58.38 kcal/mole) is right, and our frequency factor (2.46×10^{18} sec^{-1}) lies in the range[15] (10^{14} to 10^{19} sec^{-1}) of observed frequency factors for liquid-phase decomposition of metallic perchlorate salts, such as $KClO_4$, which are believed to decompose in this way.

It, therefore, seems reasonable to assume that the condensed-phase reactions in deflagration of pure AP begin with[37,38]

$$ClO_4^- \rightarrow ClO_3^- + O \qquad (41a)$$

$$ClO_3^- \rightarrow ClO_2^- + O \qquad (41b)$$

$$ClO_2^- \rightarrow ClO^- + O \qquad (41c)$$

$$O + O + M \rightarrow O_2 + M \qquad (41d)$$

$$2ClO^- \rightarrow O^{2-} + Cl_2 + O \qquad (41e)$$

Table 3 Table of physical constants

Isobaric specific heat of AP orthorhombic phase $c_{\pi 1}$	0.309 cal/g-°K[7]
Isobaric specific heat of AP cubic phase $c_{\pi 2}$	0.365 cal/g-°K[7]
Isobaric specific heat of AP liquid phase c_l	0.328 cal/g-°K[a]
Mean isobaric specific heat of gaseous mixture c_g	0.3 cal/g-°K
Heat of phase transition Δh_{tr}	2.5 kcal/mole[b]
Heat of fusion Δh_m	7 kcal/mole[c]
Heat of vaporization	58 ± 2 kcal/mole[17]
Heat absorbed by gas-phase reactions Δh_g	−772 cal/g[3]
Melting point temperature T_m	560 ± 20°C (Refs. 28, 29)
Transition temperature T_{tr}	240°C (Ref. 47)
Effective liquid temperature at $x = -\infty$, T_∞	0°K
Dissociation pressure of AP	$\log_{10} p_d(\text{torr}) = 10.56 + 6283.7/T_s$ (Ref. 17)
Molecular weight of AP W_π	117.5 g/mole
Orthorhombic phase density ρ_π	1.95 g/cm³ (Refs. 48, 49)
Liquid phase density ρ_l	1.71 g/cm³[d]
Thermal conductivity of the gaseous mixture λ_{fa}	10^{-4} cal/cm-sec-°K
Thermal conductivity of the liquid phase λ_l	9×10^{-4} cal/cm-sec-°K[e]
Total hemispherical emissivity of the condensed-phase surface ϵ_s	1
Adiabatic flame temperature	1205°K[3]
Mean molecular weight of gaseous products $\bar{W}_P$	28.4 g/mole

[a] Assumed to be the same as the isobaric specific heat of $LiClO_4(l)$ (Ref. 44).
[b] Arithmetic mean of the values reported in Refs. 45 and 46.
[c] Assumed to be the same as the heat of fusion of $LiClO_4$ (Ref. 44).
[d] Assumed to be the same as the density of the cubic phase of AP.[50]
[e] Assumed to be the same as the extrapolated thermal conductivity of the cubic phase from orthorhombic data[28] at the melting point T_m.

Electron transfer from ClO^- may further facilitate these reactions.[39] Equation (41) can be followed by proton transfer from NH_4^+ to the oxide ions O^{2-} and OH^-

$$O^{2-} + NH_4^+ \rightarrow OH^- + NH_3 \tag{42a}$$

$$OH^- + NH_4^+ \rightarrow H_2O + NH_3 \tag{42b}$$

and oxidation of NH_3 by oxygen atoms according to the mechanism described in Ref. 33 yields NO, H_2O and H atoms which can react with chlorine molecules to form HCl.[40,41] Chlorine atoms so produced will recombine through three-body collisions. It thus appears that condensed-phase reactions can indeed yield the major products observed in AP deflagration. This observation further supports the previous hypothesis that between 20 and 100 atm, coupling of condensed-phase reactions with gas-phase reactions is responsible for AP deflagration.

14. Critique

We have performed a few peripheral calculations that bear on the validity and on the accuracy of the present results. The analysis of Sec. 8 was repeated for $G = 0.3$ with an added constant heat loss of 5 cal/cm²sec, which was chosen from rough estimates of conductive and convective heat losses to represent an upper bound (perhaps an order of magnitude too high) for these effects in typical experiments. The resulting burning rate curve differed little from that in Fig. 4; thus heat losses are not significant within the context of the present model.

From exploratory calculations we have estimated the theoretical effect of AP temperature on the deflagration limit. In agreement with experimental observations,[52,53] an increase in T_0 (and in T_{fa}) by 40°C was found to reduce p_{DL} (the pressure at which $T_s = 560°C$) by approximately 3 atm.

We also calculated the burning rate at 1 atm and 270°C, by arbitrarily increasing both T_0 and T_{fa} by 250°C. The resulting burning rate is in reasonable agreement with that reported in Refs. 1 and 2, although the agreement should be viewed with some reservation for two reasons. First the flame temperatures reported in Refs. 1 and 2 were appreciably lower than our adopted T_{fa}. Second, extrapolation of the vapor pressure data of Ref. 17 to 560°C, our assumed melting point, which should be very near the temperature of the triple point, reveals that the vapor pressure at the triple point of AP is approximately 1.3 atm. If the pressure of dissociation products lies below the triple-point vapor pressure in the experiments of Refs. 1 and 2, as seems almost certain from this result, then the liquid phase cannot exist, and our analysis cannot be applied. In this respect, our results should be viewed with caution for application to AP propellants (or to AP in any other system) at pressures below a few atmospheres.

A related observation bears on the accuracy of our results; in applying the surface-equilibrium boundary condition, we merely extrapolated the data of Ref. 17 to our surface temperatures, without accounting for the change in the slope of the vapor-pressure curve upon melting. Since the estimated heat of fusion (Table 3) is small, the ensuing error will not be large. However, uncertainties in our quoted activation energies are at least ±2 kcal/mole. Our objective has been to demonstrate plausibility of the model, not to make accurate rate-parameter calculations.

A primary objection that should be raised against the ideas advanced herein is that the single empirical dilution constant G is not likely to be so fundamental a parameter as the empirical constants (e.g., activation energies, frequency factors) introduced in other theories. Of course, we could choose to interpret G as a fundamental physical constant, by claiming that the basic structure of cold AP is such that only 70% of it can decompose in the liquid phase. However, it seems more likely that the value of G is determined by processes that occur during deflagration and that we have not considered. From this viewpoint, there is no fundamental reason to presume that G is independent of pressure. Probably the processes determining G merely conspire to keep its value practically constant for pressures between 20 and 100 atm.

The experimental decrease in burning rate at pressures above 150 atm suggests a possible physical mechanism that may determine G. The decreased burning rate must be associated with a decrease in the condensed-phase reaction rate, since this is the main contributor to the deflagration rate (the gas-phase reactions being capable of sustaining a deflagration rate at most approximately one tenth of the observed value). However, since the calculated surface temperature is continuously increasing with increasing pressure, the condensed-phase reaction rate should continue to increase, unless it is inhibited in some way. Inhibition may conceivably be traceable to absorption of dissociated vapor in the liquid phase. Calculations show that the equilibrium vapor pressures of NH_3 and $HClO_4$ become quite high at the surface temperatures computed at pressures above 100 atmospheres. Since equilibrium mole fractions of gases absorbed generally increase with increasing gas partial pressure, and since gas partial pressures of dissociation products at the liquid surface equal equilibrium vapor pressures in the present model, increased quantities of gas absorption within the liquid layer are expected to arise with increasing pressure. If absorbed gas were to inhibit ClO_4^- breakdown, then the rate of the condensed-phase reaction could decrease with increasing pressure. This, in turn, might lead to a decreasing surface temperature, eventual disappearance of the liquid layer, and a high-pressure extinction.

Such a mechanism would imply that G increases as p increases at pressures above 100 atm. To develop a theory for calculating the consequent p dependence of G would be difficult. The task would be simpler had we chosen to consider surface decomposition instead of liquid-phase decomposition, since extensions of the type of reasoning in Ref. 14 could then be employed; however, liquid-phase decomposition seems more plausible. Under the assumption of equilibrium absorption, reasonable estimates of solubilities might be used to calculate equilibrium amounts of gases absorbed. Quantitative estimates of the dependence of the condensed-phase reaction rate on absorbed gas concentration would require a postulated inhibition mechanism, which may range from simple obstruction between two essential reactants to absorbed-gas participation in a kinetic mechanism. The empirical requirement that $G \approx 0.3$ for $p \lesssim 100$ atm may serve to rule out many of the possibilities. We shall not try to develop a theory here for calculating G, although this seems to us to be the logical next step in the theoretical development.

15. Behavior at Higher Pressures

Inhibition by gas absorption may also help to explain the diversity of experimental burning rates at pressures above 150 atm. In this range of near-extinction, it is clear that many effects that are small in magnitude, such as conductive heat losses, can exert large influences on the deflagration rate and account for differences as large as those between the data of Boggs and Glaskova. It would, however, be surprising if, by its thermal insulating properties alone, asbestos wrapping could raise the burning rate nearly to our theoretical constant-G value (see Fig. 4) in the presence of absorbed-gas inhibition. Perhaps asbestos absorbs the inhibiting gas, thereby preventing equilibrium liquid-phase absorption from occurring, and consequently extending the presence of the liquid phase and its fast reactions to higher pressures.

The deflagration mechanism, observed microscopically,[13] at pressures above 300 atm, is qualitatively quite different from the mechanism analyzed herein. In fact, it seems that if a second mechanism did not come into play, then there would always be a high-pressure deflagration limit. Discussion of the character of this high-pressure mechanism is purely speculative. We do, however, wish to offer a few remarks. The thick ($\gtrsim 100\mu$) layer of "needles" would seem to us to prevent the observable gas-phase reactions above the sample surface from influencing the regression rate. Processes occurring above the surface and within the needle forest (e.g., burning rates of needles) should govern the depth of the needle layer without appreciably influencing the regression rate. The regression rate probably is determined by hidden processes occurring at the base of the needle layer, the surface of the virgin AP. It seems unlikely that this surface can be hot enough to support a sustained condensed-phase deflagration. Development of a finite-rate orthorhombic-to-cubic phase transformation, driven by heat from gas-phase reactions occurring at the base of the needle layer, may control the regression rate. In addition, the previously discussed process[6] of crack propagation, although lacking in completeness, seems increasingly attractive as an element in the regression mechanism.

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