

# Model and Chemistry of HMX Combustion

Norman S. Cohen,\* George A. Lo,† and Joseph C. Crowley‡  
*Lockheed Missiles & Space Company, Palo Alto, California*

This paper presents an analytical model for the combustion of HMX that is based upon the work of Ben Reuven and Caveny. Two alternative schemes for the combustion chemistry are proposed. Simplifying assumptions are made to achieve a closed-form solution for the condensed phase and three model versions differing in complexity for the gas phase. The paper emphasizes one of the chemistries in the calculated results presented. It is concluded that the combustion is controlled by vapor phase decomposition and that it would be difficult to achieve large burning rate increases by catalysis. For this particular problem, it is permissible to neglect mass diffusion in the conservation equations in the interests of computational convenience, but energy diffusion cannot be neglected except for limited purposes.

## Nomenclature

- $A_a$  = kinetics prefactor for vapor phase decomposition (simple model:  $2.8 \times 10^{10} \text{ s}^{-1}$ ; intermediate model:  $2.6 \times 10^9 \text{ s}^{-1}$ )  
 $A_c$  = for liquid phase decomposition,  $= 5 \times 10^{20} \text{ s}^{-1}$   
 $A_d$  = for  $\text{CH}_2\text{O} + \text{N}_2\text{O}$  reaction ( $3.2 \times 10^7 \text{ cm}^3/\text{mole-s}$ ); for  $\text{CH}_2\text{O} + \text{NO}_2 = 10^9 \text{ cm}^3/\text{mole-s}$ ; for  $\text{CH}_2\text{O} + \text{NO} = 3 \times 10^7 \text{ cm}^3/\text{mole-s}$   
 $A_v$  = for vaporization law,  $1.1 \times 10^{11} \text{ atm}$   
 $B$  =  $\alpha_s A_c / r^2$   
 $C$  =  $BH_c \exp[-E_c/(RT_s)]$   
 $c_g$  = specific heat of the gas,  $= 0.45 \text{ cal/g-K}$   
 $c_s$  = specific heat of the condensed phase,  $= 0.43 \text{ cal/g-K}$   
 $D$  =  $E_c(T_s - T_0)/(RT_s^2)$   
 $E_a$  = activation energy for vapor phase decomposition,  $= 20,000 \text{ cal/mole}$   
 $E_c$  = for liquid phase decomposition,  $= 52,700 \text{ cal/mole}$   
 $E_d$  = for  $\text{CH}_2\text{O} + \text{N}_2\text{O}$  reaction,  $= 16,000 \text{ cal/mole}$ ; for  $\text{CH}_2\text{O} + \text{NO}_2 = 19,000 \text{ cal/mole}$ ; for  $\text{CH}_2\text{O} + \text{NO} = 50,000 \text{ cal/mole}$   
 $H$  =  $Q/[C_s(T_s - T_0)]$   
 $K$  =  $C/D$   
 $K_g$  = thermal conductivity of the gas,  $= 0.0006 \text{ cal/cm-s-K}$   
 $K_s$  = thermal conductivity of the condensed phase,  $= 0.0009 \text{ cal/cm-s-K}$   
 $M_g$  = molecular weight of the gas (subscript 1 = HMX; 2 =  $\text{CH}_2\text{O}$ ; 5 =  $\text{N}_2\text{O}$ )  
 $P$  = pressure  
 $Q_a$  = heat release of vapor phase decomposition,  $= 133,830 \text{ cal/mole}$   
 $Q_c$  = of liquid phase decomposition,  $= 171.4 \text{ cal/g}$   
 $Q_d$  = of the  $\text{CH}_2\text{O} + \text{N}_2\text{O}$  reaction,  $= 304,040 \text{ cal/mole}$ ; for  $\text{CH}_2\text{O} + \text{NO}_2 = 61,580 \text{ cal/mole}$ ; for  $\text{CH}_2\text{O} + \text{NO} = 101,350 \text{ cal/mole}$   
 $Q_f$  = sum of HMX heats of crystal phase change and fusion,  $= -46.3 \text{ cal/g}$   
 $Q_s$  = portion of  $Q_c$  released in the liquid layer  
 $Q_v$  = heat of vaporization,  $= -94.3 \text{ cal/g}$   
 $r$  = burning rate

- $R$  = universal gas constant,  $= 1.987 \text{ cal/mole-K}$   
 $T$  = temperature (subscript 0 = initial value;  $m$  = melting point,  $551 \text{ K}$ ;  $s$  = surface)  
 $W_a$  = reaction rate for vapor phase decomposition  
 $W_d$  = reaction rate for  $\text{CH}_2\text{O} + \text{N}_2\text{O}$  reaction  
 $X$  = distance from the surface  
 $Y$  = species mass fraction  
 $\alpha_s$  = thermal diffusivity of the condensed phase,  $= 0.0011 \text{ cm}^2/\text{s}$   
 $\beta$  = fraction of HMX that vaporizes directly  
 $\rho_s$  = density of HMX,  $= 1.91 \text{ g/cm}^3$   
 $\tau$  =  $(T - T_0)/(T_s - T_0)$

## Introduction

Propellants containing cyclotetramethylene tetranitramine (HMX) are of considerable interest for solid rocket propulsion, but are limited by an inability to tailor their burning rates beyond a fairly narrow range. Trial and error approaches have not been successful, therefore, it is necessary to acquire a better understanding of the combustion process. One approach to the problem has been to study the combustion of HMX itself, as a monopropellant. This could afford bases for combustion tailoring through modifications of the combustion of HMX, or through the relationship of HMX combustion to the burning of the aggregate propellant.

Several models of HMX combustion have been published.<sup>1-3</sup> The most comprehensive is the model of Ben Reuven and Caveny.<sup>3</sup> The unique features of that model are its incorporation of combustion chemistry into the analytical framework and rigorous expression of the mass and energy conservation equations. It is considered important to incorporate the chemistry in order to provide foundations for the kinetics and energetics used in the model and more rational bases for approaches to modification.

This paper builds upon the work of Ben Reuven and Caveny in the following respects. First, it updates the combustion chemistry in accordance with more recent information and ideas which have been expressed.<sup>4-14</sup> It carries the reaction scheme to completion, and provides for an alternative scheme based upon the formation of  $\text{H}_2\text{CN}$  and  $\text{NO}_2$  as well as the more conventional scheme in which  $\text{CH}_2\text{O}$  and  $\text{N}_2\text{O}$  are formed. The precise nature of the chemistry has not been established, therefore, it is important to consider the various possibilities which have been discussed. Second, several simplifications are made in the interests of tractability. Solving the complete problem required a cumbersome, expensive computer program operation, and numerical convergence problems were encountered when attempting to use such a program in a flexible way. The original code did not

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\*Contractor, Cohen Professional Services, Inc., Redlands, Calif. Member AIAA.

†Senior Staff Scientist, Palo Alto Research Laboratory. Member AIAA.

‡Senior Scientist, Palo Alto Research Laboratory. Member AIAA.

calculate burning rates, but used measured burning rates as input to calculate other features of the combustion process. Reasonable approximations permit a closed-form solution for the condensed phase. Neglecting the mass diffusion terms in the equations for the conservation of mass is found to simplify the numerical integration in the gas phase without losing any of the essential mechanistic features of the problem. However, it is not permissible to neglect the energy diffusion term in the energy equation except for limited purposes. These assertions are supported by the computations we have made. Third, this model is applied to evaluate limiting conditions of interest and possible combustion modifications that might be considered.

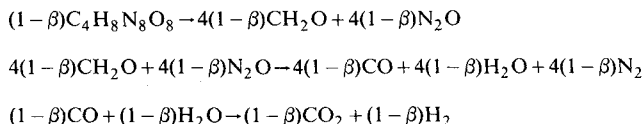
### Combustion Chemistry

The approach follows other models<sup>2,3</sup> in that it provides for a portion of HMX decomposition to occur in the liquid layer adjacent to the surface, vaporization by the fraction of HMX that does not undergo liquid phase decomposition, vapor phase decomposition by that fraction, and reactions between decomposition products. Although the precise nature of the chemistry has not been ascertained, there are presently two schools of thought: one based upon the formation of  $\text{CH}_2\text{O}$ , and one based upon the formation of  $\text{H}_2\text{CN}$  or  $\text{HCN}$ . Perhaps both occur to some extent, calling for a more complicated combined scheme to be developed, but at present they are treated separately for liquid phase and vapor phase decomposition.

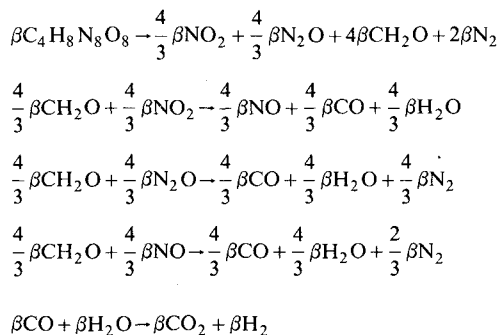
The first scheme, which may involve C-N bond rupture in the liquid phase and N-N bond rupture in the vapor phase, is presented in Table 1. The reactions are shown as sequences of global steps, with  $\beta$  being the fraction of HMX that vaporizes. The reactions following liquid phase decomposition follow in a straightforward manner, with the assumption that the water-gas reaction is the mechanism by which final products are achieved at the end of the combustion zone. The final product distribution was established by thermochemical calculations. The sequence following vapor phase decomposition is based on the premise that the reaction with  $\text{NO}_2$  is relatively rapid and that the reaction with  $\text{NO}$  (high activation energy) occurs at higher temperatures further out in the combustion zone. Again, the formation of  $\text{CO}_2$  and  $\text{H}_2$  present at thermochemical equilibrium is derived from the water-gas reaction.

Table 1 HMX combustion chemistry:  $\text{CH}_2\text{O}$  scheme

From liquid phase decomposition:



From vapor phase decomposition:



N.B.: In the above equations the factors  $(1-\beta)$  and  $\beta$  are included to show explicitly the amount of material reacted in each phase, for the convenience and understanding of the reader.

The alternative scheme, which may involve a molecular rearrangement, depolymerization, or N-N bond rupture, is presented in Table 2. This scheme is more difficult to establish, and is shown to be more complicated. The first step in liquid phase decomposition is a more global representation of the initial formation of  $\text{H}_2\text{CN}$  and  $\text{NO}_2$ , a rapid decomposition to  $\text{HCN}$ , and reaction of  $\text{H}_2$ . The subsequent steps follow the same reasoning as above. The first step in vapor phase decomposition is also a more global representation of a process that includes  $\text{H}_2\text{CN}$  formation, but the mechanism produces  $\text{CH}_2\text{O}$  as well. The remaining steps in part follow the above reasoning, but in part result from speculation.

### Mathematical Models

#### Condensed Phase

The energy equation in the liquid layer provides for decomposition in the form of an Arrhenius law.

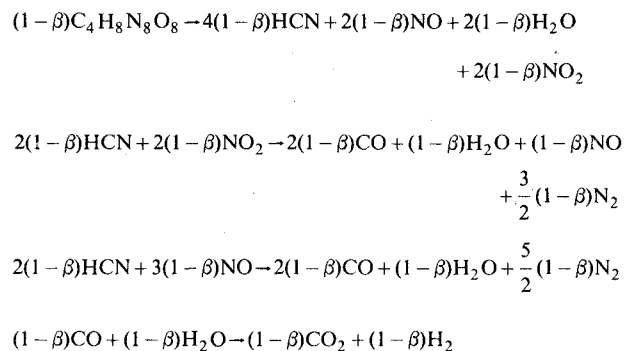
$$K_s \frac{d^2 T}{dx^2} - \rho_s c_s r \frac{dT}{dx} + \rho_s Q_c A_c \exp\left(-\frac{E_c}{RT}\right) = 0 \quad (1)$$

The analysis assumes constant thermal properties. Other models<sup>2,3</sup> have used variable thermal properties, but the data and extrapolations to temperatures of interest were not considered reliable.<sup>2</sup> The analysis also neglects the bubbles in the liquid layer that were considered by Ben Reuven and Caveny.<sup>3</sup> These simplifications help to achieve a closed-form solution for the liquid layer.

Boundary conditions are applied to the solid/liquid and liquid/gas (surface) interfaces. Combined with the first integral of Eq. (1) through the solid (no reactions) and the

Table 2 HMX combustion chemistry: HCN scheme

From liquid phase decomposition:



From vapor phase decomposition:

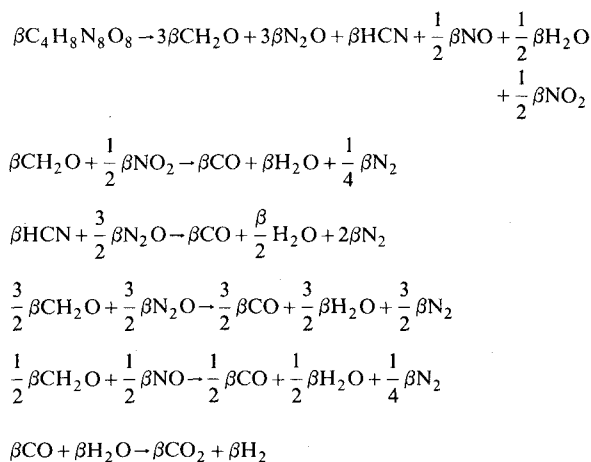


Table 3 Energy balance in the gas phase at 2 MPa

Distance from surface, $\mu\text{m}$	Energy balance components ( $\text{cal}/\text{cm}^3\text{-s}$ )		
	Diffusive term	Convective term	Source term
0	129,568	142,526	12,958
1	119,257	150,624	31,367
3	685	161,218	160,533
	Changing sign	Maximum value	
5	-210,647	150,356	361,003
7	-358,300	109,630	467,930
	Maximum negative value		Maximum value
10	-209,589	53,132	262,721
20	-18,888	6,916	25,804
30	-3,330	1,477	4,807
50	-7	277	284
	Changing sign	Minimum value	
60	281	375	94
70	566	622	56
80	1,123	1,170	47
		Secondary reactions becoming important	
100	3,870	3,918	48
120	13,432	13,493	61

liquid, the boundary conditions may be expressed as

$$K_s \frac{dT}{dx}(\ell) = \rho_s r [c_s (T_m - T_0) - Q_\ell] \quad (2)$$

$$K_g \frac{dT}{dx}(0) = \rho_s r [c_s (T_s - T_0) - (Q_s + Q_\ell + \beta Q_v)] \quad (3)$$

where

$$Q_s = (1 - \beta) Q_c \quad (4)$$

The problem is to solve for  $Q_s$ , or the fraction of HMX that decomposes in the liquid layer. The solution is obtained in closed form by assuming that the melting or liquefaction point is not far below the surface temperature. This assumption facilitates a transformation of variables that enables the integration of Eq. (1). The technique has been published previously in a different context,<sup>15</sup> and is valid over the temperature range encountered. The integration yields

$$H_s = (1 - H_\ell) - \{ (1 - H_\ell)^2 - 2K [1 - \exp(D\tau_m - D)] \}^{1/2} \quad (5)$$

The quantity  $\beta$  is then calculated from Eq. (4) given a specified value of  $T_s$  (see later).

It is of interest to examine the limiting condition  $\beta = 0$ , or  $H_s = H_c$ , which corresponds to full decomposition in the liquid layer. For a given set of values for the constants, the surface temperature that needs to be reached depends upon the dimensionless quantity  $B$ . The quantity  $B$  is a ratio of time constants defined in the Nomenclature. A plot of this relationship for the constants used is shown in Fig. 1. Also shown is the result for solutions attained, which corresponds to a computed value of  $\beta$  of about 0.95. A value of  $\beta$  close to 1 means that there is little liquid phase decomposition, which is the result of calculations made in this study (see later discussion). The horizontal line corresponds to the special case where an exothermic decomposition would itself sustain combustion; this is determined from a zero value of the square root argument in Eq. (5), or from Eq. (3) with zero  $\beta$  and zero gradient.

$$T_s = T_0 + (Q_c + Q_\ell) / c_s \quad (6)$$

The limiting temperature given by Eq. (6) corresponds to a limiting flameless combustion burning rate that is independent of pressure. For the constants used, associated with exothermic decomposition (and given in Table 1), the limiting

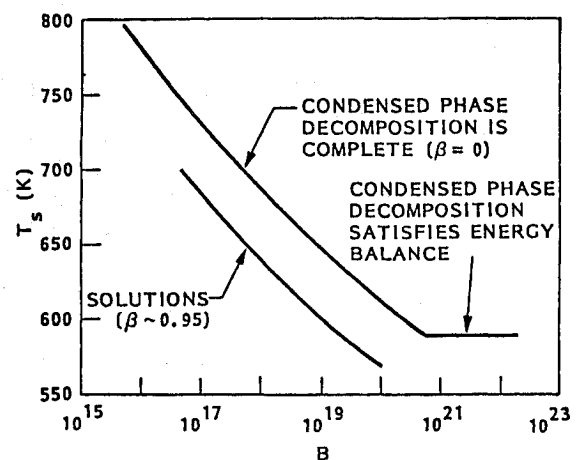


Fig. 1 Surface temperature solutions and limiting conditions.

burn rate is 0.03 cm/s. It may be of interest to examine the effect of  $Q_c$  on this limiting burning rate. With the present Table 1 mechanism, the heat release from liquid phase decomposition is only about 15% of the available HMX heat release. What if the chemistry could be altered to increase this percentage, maintaining a sufficiently rapid reaction rate to maintain this limiting condition? The main effect of increasing  $Q_c$  is to raise the horizontal branch from the  $\beta = 0$  curve; the curve itself moves only slightly to the left. The upward movement of the horizontal branch also creates a leftward movement of the branch point, such that there can be orders of magnitude increases in the square of the burning rate. This movement is sensitive to  $Q_c$ . A plot of the factor increase in the limiting ( $\beta = 0$ ) burn rate vs  $Q_c$  is shown in Fig. 2. It is observed that a rather modest increase in  $Q_c$  can raise the limiting burn rate by nearly two orders of magnitude. Although the result is interesting, it may not be a practical approach because combustion that is controlled by a highly exothermic condensed phase is very sensitive to the input parameters and is a less stable form of combustion. For  $\beta = 0.95$ , the same increase in  $Q_c$  would increase the burn rate by only 15%.

The solution surface temperatures are prescribed by a vaporization law

$$T_s = \frac{M_l Q_v}{R \ln(P/A_v)} \quad (7)$$

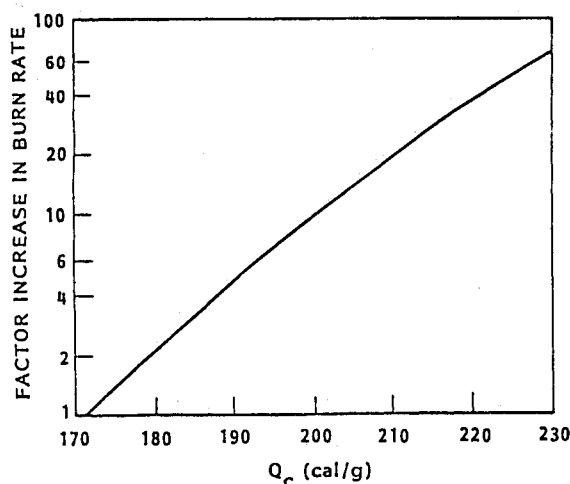


Fig. 2 Effect of condensed phase heat release on burn rate when combustion is controlled by condensed phase decomposition.

The ability to prescribe the surface temperature in this manner and to solve the liquid layer in closed-form, provides significant simplifications to the computation procedure and better insight into the role of the condensed phase.

#### Gas Phase

The complete representation of the gas phase follows the essentials of the Ben Reuven and Caveny model,<sup>3</sup> so it need not be reproduced here. There are two simplifications relative to that model: constant thermal properties are used here, and it is assumed that the Lewis number = 1 for the species (mass) equations. The only other difference is in the chemistry employed. Detailed outputs from the Ben Reuven and Caveny code<sup>16</sup> were used to guide the solution method. For example, similarity properties between the mass and energy equations were used to establish initial trials, and the appearance of a distinct near-field (near the surface) region—something akin to the fizz and dark zones of double-base propellants—was used to allow the depletion of HMX vapor to help set convergence criteria.

An approximate model was developed for the purpose of simplifying and speeding up the numerical iterations. This version neglects the diffusion (second derivative) term in the species equations, but retains the analogous term in the energy equation. It is referred to as the intermediate model, and will be compared to the complete model in the results section.

A major simplification is possible if the diffusion term is neglected in the energy as well as species equations. Unfortunately, it turns out that this is not a good assumption for HMX combustion, but it is useful because it provides a closed-form solution to the problem and focuses the controlling feature of the combustion. The result is referred to as the simple model. With this simplification, the left-hand side of Eq. (3) is immediately evaluated from the energy equation in the gas phase, for Table 1 chemistry, as

$$K_g \frac{dT}{dx}(0) = \frac{K_g (W_a Q_a + W_d Q_d)_0}{\rho_s r C_g} \quad (8)$$

with

$$W_a(0) = \frac{PM_g Y_1 A_a}{RT_s M_1} \exp\left[-\frac{E_a}{RT_s}\right] \quad (9)$$

$$W_d(0) = \left[\frac{PM_g}{RT_s}\right]^2 \left(\frac{Y_2}{M_2}\right) \left(\frac{Y_5}{M_5}\right) A_d \exp\left[-\frac{E_d}{RT_s}\right] \quad (10)$$

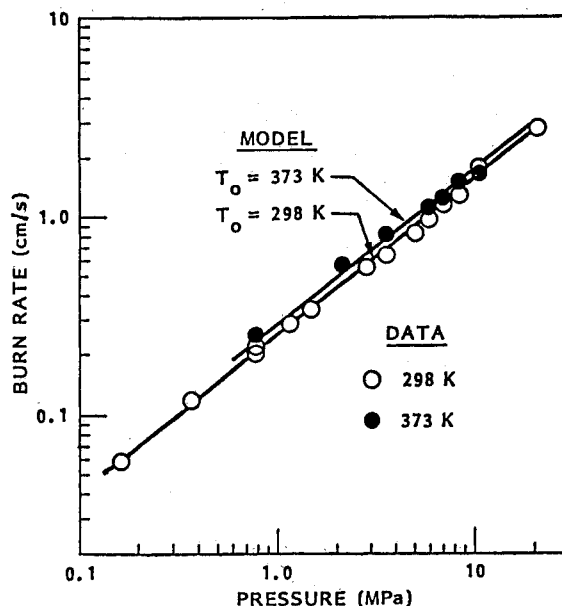


Fig. 3 Comparison of calculated and experimental burning rates.

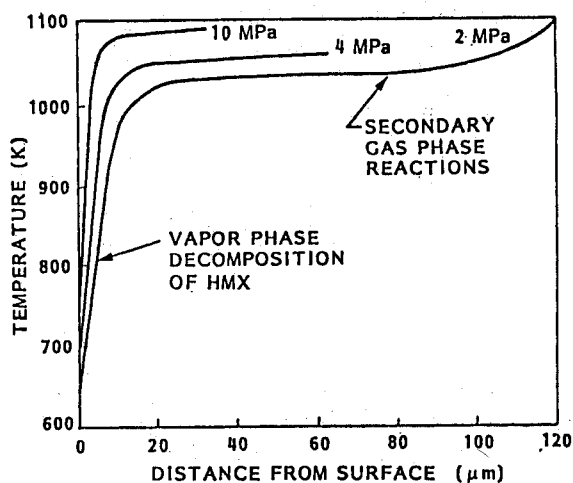


Fig. 4 Temperature profiles in the gas at various pressures.

$$Y_1(0) = \beta; \quad Y_2(0) = 4(1-\beta)M_2/M_1; \quad (11)$$

$$Y_5(0) = 4(1-\beta)M_5/M_1$$

$$M_g = \beta M_1 + (1-\beta)(M_2^2 + M_5^2)/(M_2 + M_5) \quad (12)$$

so it is now possible to calculate  $r$  by iteration. It is of interest to examine the special case of  $\beta=1$ , or no liquid phase decomposition. Combining Eqs. (3), (8), (9), and (11) for  $\beta=1$ , the simple closed-form result is

$$r^2 = \frac{K_g}{\rho_s c_g} \frac{PQ_a}{RT_s} \frac{A_a \exp[-E_a/(RT_s)]}{\rho_s [c_s(T_s - T_0) - (Q_f + Q_v)]} \quad (13)$$

and it is clear that the combustion is controlled by exothermic vapor phase decomposition. About one third of the available heat release is provided by this step. The remainder is provided by subsequent gas phase reactions between the vapor phase decomposition products. If it were possible to modify the chemistry to increase  $Q_a$ , and/or if  $A_a$  could be increased, there would be meaningful increases in the burning rate. For

Table 4 Key species in the gas phase at 2 MPa

Distance from surface, $\mu\text{m}$	Species mass fractions, $Y_i$					
	HMX	$\text{CH}_2\text{O}$	$\text{N}_2\text{O}$	$\text{NO}_2$	NO	$\text{N}_2$
0	0.9520	0.0195	0.0285	0	0	0
1	0.9466	0.0217	0.0296	0.0011	$10^{-10}$	0.0010
3	0.9028	0.0394	0.0383	0.0102	$10^{-8}$	0.0093
5	0.7890	0.0855	0.0609	0.0333	$10^{-7}$	0.0308
7	0.5582	0.1791	0.1066	0.0816	$10^{-6}$	0.0745
10	0.2739	0.2943	0.1630	0.1405	$2 \times 10^{-5}$	0.1283
20	0.0378	0.3900	0.2097	0.1893	$5 \times 10^{-5}$	0.1730
30	0.0078	0.4022	0.2157	0.1955	$7 \times 10^{-5}$	0.1786
50	0.0004	0.4051	0.2171	0.1970	0.0001	0.1800
60	$8 \times 10^{-5}$	0.4053	0.2172	Maximum value 0.1970	0.0001	0.1801
70	$2 \times 10^{-5}$	Maximum value 0.4053	0.2172	0.1970	0.0001	0.1801
80	$4 \times 10^{-6}$	0.4053	Maximum value 0.2172	0.1970	0.0002	0.1801
100	$2 \times 10^{-7}$	0.4052	0.2172	0.1969	0.0002	0.1801
120	$4 \times 10^{-9}$	0.4052	0.2172	0.1969	0.0002	0.1801

the limiting condition of  $\beta = 0$ , the result is

$$r^2 = \frac{K_g}{\rho_s c_g} \left[ \frac{P}{RT_s} \left( \frac{M_2^2 + M_5^2}{M_2 + M_5} \right) \right]^2 \frac{Q_d A_d \exp[-E_d/RT_s]}{\rho_s [c_s(T_s - T_0) - (Q_t + Q_c)]} \quad (14)$$

Here, the combustion is controlled in part by the liquid phase decomposition and in part by the gas phase reaction between decomposition products. The benefit of catalyzing gas phase reactions is better illustrated by the intermediate model.

## Results

### Simple Model

Calculated burning rates are shown together with experimental data<sup>2</sup> in Fig. 3. These calculations were based upon Table 1 chemistry. It is observed that the burning rates, pressure exponent, and temperature sensitivity are predicted quite well by this model. Values of surface temperatures calculated ranged from 569 K at 0.2 MPa to 698 K at 20 MPa. Values of  $\beta$  ranged from 0.92 to 0.98— $\beta$  decreasing with increasing pressure because of the relatively high activation energy (high sensitivity to temperature) of liquid phase decomposition. Values of  $\beta$  close to 1 indicate that the major portion of HMX decomposition occurs in the vapor phase, and that the combustion is controlled by vapor phase decomposition. The  $\text{CH}_2\text{O}$ - $\text{N}_2\text{O}$  reaction is not a factor because too little of these species are formed in the liquid layer and the reaction rate is too slow at calculated surface temperatures. The good agreement with data was achieved by adjusting the kinetics of the vapor phase decomposition, which are not known. Even though this step is first order with respect to pressure, the calculated pressure exponent is about 0.9 because of the increase in surface temperature with pressure in accordance with the vaporization law.

Calculations incorporating Table 2 chemistry were able to produce the same results as Fig. 3. Since the same kinetics were used for liquid phase decomposition, the essential result that  $\beta$  is close to 1 was obtained, and the fact that the decomposition is now endothermic rather than exothermic made a negligible difference to the energetics of the liquid layer. However, the heat release of the Table 2 vapor phase decomposition is much less than that of Table 1, therefore, it was necessary to increase its rate constant in order to reproduce the burning rates. In other words, the reaction rate had to be made higher in order to compensate for the reduced energy available near the surface. Reactions between liquid

phase decomposition products at the surface continue to be negligible. Therefore, meaningful differences in the chemistries will not show up until further out in the gas phase, and that requires use of the numerical models to evaluate them. To date, such calculations have been limited to the Table 1 chemistry.

### Intermediate Model

While the simple model was sufficient to point out the relative importance of the vapor phase decomposition, it lacks one other potentially important mechanism. This is illustrated first by Table 3, which presents the calculated components of the energy equation in the gas phase as a function of distance from the surface for one case. It is clear that the diffusive term is not negligible, contrary to a key assumption of the simple model. Thus, the fact that the convective term (proportional to the temperature gradient) remains fairly constant close to the surface is misleading.

The behavior of the temperature gradient (convective term) and the chemical heat release (source term) roughly follow one another. Maxima are reached fairly close to the surface. In this region, the contributions of the secondary reactions to the source term are negligible. These terms decline as the HMX vapor becomes depleted further away from the surface. At a distance of 50  $\mu\text{m}$ , the terms have declined by three orders of magnitude from the maxima. At this point, the HMX vapor is nearly gone. At a distance of about 100  $\mu\text{m}$ , the secondary reactions start to become important so that the source term once again increases and the temperature gradient increases more sharply.

The behavior of the source term may be compared with the behavior of the concentrations of the key species, as shown in Table 4.  $\text{CH}_2\text{O}$ ,  $\text{N}_2\text{O}$ , and  $\text{NO}_2$  are key species because they are products of HMX decomposition and reactants for the secondary reactions. NO is in a different category because it is not a product of HMX decomposition, but is both a product and a reactant in the secondary reaction scheme.  $\text{N}_2$  is a final product formed as a result of both HMX decomposition and the secondary reactions. Omitted are the products CO,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$ ; these are products of secondary reactions which are in negligible amounts out to the distance of 120  $\mu\text{m}$ . It is observed that the depletion of HMX, and the attendant formation of  $\text{CH}_2\text{O}$ ,  $\text{NO}_2$ , and  $\text{N}_2\text{O}$ , are responsible for the heat release near the surface. Maximum heat release coincides with the maximum concentration gradients associated with the HMX decomposition. Negligible values for NO are indicative of the slight occurrence of the secondary reactions. Thus the  $\text{N}_2$  being formed is, essentially, all due to HMX

decomposition. The secondary reactions do not show themselves until the distance exceeds 50  $\mu\text{m}$ . At this point, the concentration gradients of the secondary reactants start to become negative, but note that the changes are relatively small. The secondary reactions, at the temperatures in the region, are much slower than HMX decomposition.

Temperature profiles in the gas phase at three pressures are shown in Fig. 4. The dominance of HMX decomposition close to the surface is clearly evident in these profiles. The temperature levels off at the conclusion of the decomposition, then rises again due to the secondary reactions at a greater distance. It is for this reason that the combustion can be said to be a two-stage process analogous to the combustion of double-base propellants. Note that the leveling temperatures are about one-third of the equilibrium flame temperature. As expected, increasing the pressure increases the temperature gradients and thins the combustion zone. The reason is that the kinetics of all of the gas phase reactions are pressure-dependent. The increase in the leveling temperature with pressure is a very interesting effect of the heat feedback mechanism not accounted for by the simple method. In fact, it was necessary to reduce the value of  $A_d$  by an order of magnitude, relative to the simple model, in order to match the experimental burning rate and achieve these results. Otherwise, the diffusivity term operates to collapse the combustion zone and raise the burning rate considerably.

The effect of catalyzing the liquid phase decomposition reaction was examined with this model. There has been a school of thought which believes that the burning rate of HMX can be increased in this manner. The results were very interesting and are summarized in Table 5.

It is observed that the first 2000 factor increase in the rate constant (first three rows) increases the burn rate by only 20%. The next substantial increase in the rate constant causes the burn rate to decrease. Calculations were made with the simple model to help explain this effect. The result was that an order of magnitude increase in the rate constant caused the burn rate to decrease substantially. The explanation is as follows.

Accelerating the rate of liquid phase decomposition does not necessarily mean that the surface will regress faster. It simply means that more decomposition will take place within the liquid layer by the time the surface temperature is reached. In the limit, with  $\beta=0$ , the surface temperature will be prescribed by full decomposition and not by the vaporization law. It does not necessarily follow, however, that the burning rate will increase. Basically, what is happening here is an energy redistribution or tradeoff. In the framework of this model, the more decomposition that occurs in the liquid phase, the less that will occur in the vapor phase. The tradeoff, in terms of the energy balance at the surface, is an increase in  $Q_s$  and an increase in the amount of  $\text{CH}_2\text{O}$  and  $\text{N}_2\text{O}$  formed at the surface (to increase burn rate) vs a decrease in the amount of HMX vapor (to decrease burn rate). In the simple model, the loss of HMX vapor with its greater rate of heat release is the dominant effect. The intermediate model, which includes the effect of diffusion, gives more weight to the increased presence of liquid phase decomposition products in the vapor phase decomposition region; but, eventually, the loss of HMX vapor wins out. Therefore, it is predicted that increasing the rate of liquid phase decomposition would not be effective to increase the burn rate.

The model was also used to explore the effects of catalyzing the gas phase reactions between decomposition products. Results are summarized in Table 6. The first reaction is nominally faster, but the second is more energetic and gets a bit of a head start because  $\text{N}_2\text{O}$  is a product of liquid phase decomposition. As further evidence that these reactions are not important under baseline conditions, reducing the rate constants had no effect on burn rate. Increasing the rate constants two orders of magnitude produced small increases

in burn rate, a bit more with the first reaction. Increasing the first rate constant by three orders of magnitude provided a significant burn rate increase, but still not large in the sense of what can be achieved with ammonium perchlorate propellants. These effects could not be predicted without accounting for the energy diffusivity term. Finally, accelerating the  $\text{CH}_2\text{O}-\text{NO}$  reaction by three orders of magnitude had no effect on the burn rate.

It would seem that the most effective step to catalyze is vapor phase decomposition. This would be difficult to accomplish because most of its heat release is already occurring within 10  $\mu\text{m}$  of the surface. Therefore, changes in the chemistry to increase the proximate heat release would appear to be more productive than catalysis of the present chemistry.

### Complete Model

Strictly speaking, it is not a good approximation to neglect the diffusive term in the conservation of mass equations. However, the effect of doing so is not as serious as for the energy equation. In going from the simple model to the intermediate model, the ratio of the convective term to the source term in the energy equation at the surface increases from 1 to the order of 10. This could be accommodated by a change in  $A_d$  to calculate burning rates with the simple model, but an essential heat feedback mechanism was lost so that other features of the combustion could not be explored with the simple model. It turns out that in going from the intermediate model to the complete model, the ratio of the convective term to the source term increases by another factor of 10; the effect is to further collapse the combustion zone. But since the energy transport terms are already an order of magnitude larger than the source term in the intermediate model, making them two orders of magnitude larger has no substantial qualitative effect. Figure 5 compares the temperature gradient profiles calculated from the two models. They are qualitatively the same. Plots of the  $d^2T/dx^2$  and heat generation profiles are also qualitatively the same. In order to bring the complete model into line with the intermediate model and calculate the correct burning rate, it is necessary to reduce  $A_d$  by only a factor of about 2. This compares favorably with the factor 11 reduction needed in going from the simple model to the intermediate model. The mass equations are significant to the problem only insofar as

Table 5 Effect of kinetics of liquid phase decomposition on burn rate

Rate constant	Burn rate
baseline value	baseline value
$10^{-3}$	0.89
0.2	0.92
2	1.08
$10^2$	0.70
10 (simple model)	0.22

Table 6 Effect of gas phase reaction kinetics on burn rate

Rate constant	Burn rate
baseline value	baseline value
$\text{CH}_2\text{O} + \text{NO}_2$ reaction	
0.4	1.00
$10^2$	1.13
$10^3$	1.57
$\text{CH}_2\text{O} + \text{N}_2\text{O}$ reaction	
0.4	1.00
$10^2$	1.09

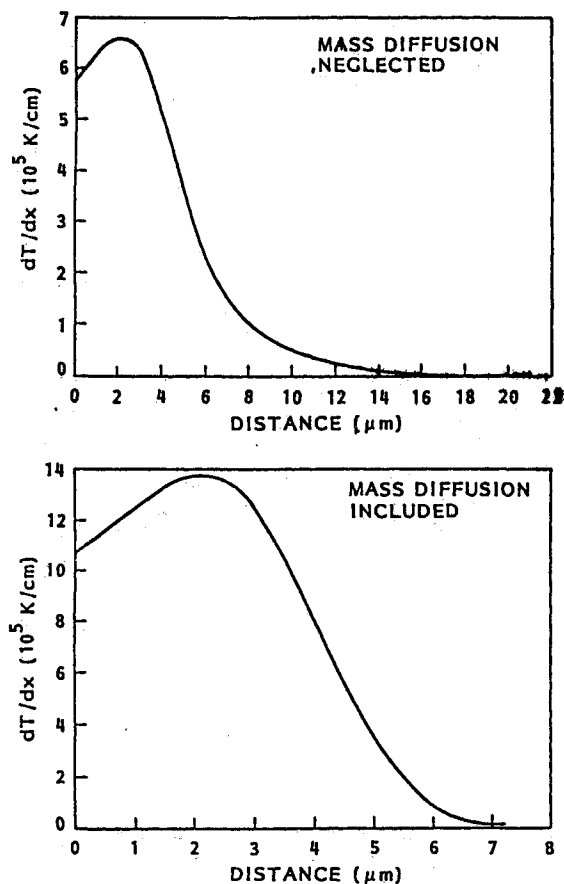


Fig. 5 Temperature gradients in the gas phase.

they affect the terms in the energy equation. Since neglect of mass diffusion can be compensated for without impairing essential mechanisms, the intermediate model is acceptable for this particular problem in the interests of convenience.

### Conclusions

A more flexible adaptation of the Ben Reuven and Caveny model has been developed which incorporates modified combustion chemistries, useful simplifications, and enables the burning rate to be calculated. It is concluded that HMX combustion is controlled by exothermic vapor phase decomposition in accordance with the Ben Reuven and Caveny result. This paper more clearly establishes the basis and nature of that control. It is also concluded that it will be difficult to achieve large burn rate increases by catalysis because the controlling step already takes place very close to the surface, other gas phase reactions are nominally too slow, and liquid phase decomposition has a competing effect on

vapor phase decomposition. It would be more productive to change the chemistry to increase the amount of heat released near the surface. Finally, in the mathematical analysis of this particular problem, it is permissible to neglect mass diffusion for computational convenience, but it is not permissible to neglect energy diffusion except for limited purposes.

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