

Fig. 1 Effects of $\rho c \Omega$ variations on the temperature field of an x_1 monoclinic alternately laminated slab.

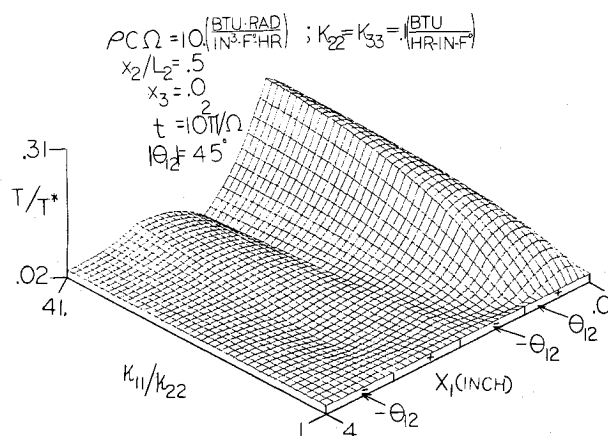


Fig. 2 Effects of conductivity variations (k_{11}/k_{22}) on the temperature field of an x_3 monoclinic alternately laminated slab.

obtained to any degree of accuracy required; 2) the series can be used to obtain either an "entire" history or more conveniently, the temperature at several specific time values; 3) in the context of 2), the temperature can be evaluated at a node and/or nodes without requiring calculations to be performed at all nodes; 4) the procedure can be used as a starter for numerical integration techniques for $t > 0$; (this of course, would reduce the numerical degradation of time stepping schemes); and 5) upper bounds are available on possible series truncation errors.

Example

To reveal the capabilities of the present procedure, the time dependent temperature distribution of a laminated slab composed of inherently anisotropic laminae is considered, Fig. 1. The boundary-value problem treated is defined by

$$\text{at } x_1 = x_{1j}; T = T^* \cos\left(\frac{m\pi}{L_2} x_2\right) \cos\left(\frac{n\pi}{L_3} x_3\right) \cos \Omega t$$

$$\text{at } x_1 = x_{1j}; T = 0 \quad (22)$$

In terms of the developments of Ref. 7, an eight node 3-D brick element was used to obtain the spacial distribution for the stated problem. For $t \geq 0$, the exact solution to the stated problem was derived by assuming that $T = \text{Re}\{\zeta(x_1, x_2, x_3) e^{i\Omega t}\}$ where $\zeta(x_1, x_2, x_3)$ was obtained in the manner of Ref. 8. The material properties used for the following numerical experiments were obtained by considering that each lamina of the slab, Fig. 1, consisted of fiber reinforced materials (boron-epoxy).⁸ Figure 1 illustrates the main effect of Ω variations on the time dependent temperature field of an x_1 monoclinic alternately laminated slab ($\theta_{23}, -\theta_{23}, \theta_{23}, -\theta_{23}$). This figure also juxtaposes the "exact" and element

generated results. As can be seen, good agreement was possible over a large range of Ω and for all the positions depicted. To reveal the significant effects of x_3 monoclinic material anisotropy, Fig. 2 illustrates the time dependent temperature field of an alternately laminated slab ($\theta_{12}, -\theta_{12}, \theta_{12}, -\theta_{12}$). Here again, excellent accuracy was possible over the entire range of material anisotropy considered.

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Condensed Phase Reactions in Solid Propellants

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Introduction

MOST of the combustion theories, based on analytical models for describing the steady-state combustion process of solid propellants, consider that oxidizer and binder sublime independently and interact in the gas phase while no significant physical or chemical interactions take place in the condensed phase. However, the importance of the condensed phase reactions has been realized in solid propellant combustion.¹⁻⁵ It is very likely that combustion may be controlled to a varying extent by reactions taking

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place in the gas phase, at the burning surface, or in the solid phase below it. In general, the surface temperature of solid propellants varies around 1000°C and it becomes quite obvious that there should be sufficient temperature below the surface⁶ (which may be in a thin zone due to the poor thermal conductivity of propellants) where the decomposition of the oxidizer and binder may take place leading to various types of reactions inside the porous solid phase. The mixture of the reaction products and primary decomposition products may travel upwards on to the surface for yet another type of heterogeneous reaction giving rise to complex gaseous mixture which finally burns in gas phase.

In a recent work⁷ it has been reported that no significant interaction takes place between the binder and oxidizer in the condensed phase and that the oxidizer and binder decompositions are independent processes in propellant decomposition. Recent differential scanning calorimetric (DSC) studies⁸ on polystyrene (PS) ammonium perchlorate (AP) propellants has shown that heat of thermal decomposition of the propellant is not an additive of the heat of thermal decomposition of PS and AP contained in it. In fact, the heat of decomposition of propellant is much larger than that of the components, suggesting that there does occur some sort of condensed phase reactions during propellant decomposition. It may be noted that DSC records only solid-state reactions, especially when the product gases are allowed to escape out of pan during decomposition.²

The objective of the present investigation is to understand the cause for the difference between the DSC results⁸ and the mass spectrometric studies.⁷ Our mass spectrometric (MS) studies of PS, AP, and propellant show that the mass spectra of the propellant are not additive and are quite different from the sum of the individual mass spectra of PS and AP (Table 1). The difference between our results and those of Ref. 7 may be due to the following factors:

A. Method of Preparation of Propellant

In Ref. 7, the method of preparation was not the usual one where the oxidizer is mixed with the binder when it is viscous and then cured. Solutions of PS and AP, were prepared in toluene and alcohol, respectively, and then mixed the two solutions in appropriate proportions followed by putting the drops of mixture on a hot surface for evaporation of the solvent. We feel that this procedure may give simply a physical mixture rather than a well-bonded, strong, tough propellant.

B. Difference in Experimental Conditions in the Use of Mass Spectrometer (MS)

Korobeinicha et al.⁷ used time of flight mass spectrometer for their studies. The decomposition was carried out by placing the sample only a few millimeters from the electron gun of the mass spectrometer. In this way, sufficient time was not given for the product sublimates to interact with each other and attain equilibrium. In our present studies we have given sufficient time for the sublimate and product gases to interact completely and to give final equilibrium products. The distance between the site of the decomposition and the detector cell was sufficiently large to ensure complete mixing and reaction between the gaseous species. In this Note, we describe some experiments which have been performed in order to shed some light on the dilemma.

Experimental

Commercial grade AP, recrystallized from water, was used. PS and propellant containing 25% of PS binder was prepared in a manner described earlier.⁹ A sharp knife was used to cut the cured propellant/polymer to suitable sizes. A homemade mass spectrometer (MS) of the MS 10 type was used in the study.

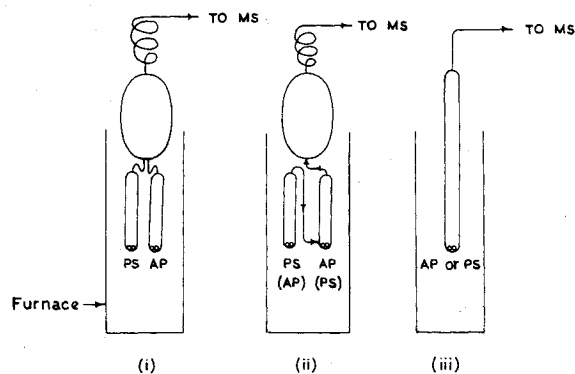


Fig. 1 Glass cells for the decomposition of PS, AP, and propellant.

Table 1 Mass numbers corresponding to the peaks obtained in various decomposition experiments done at 400°C

1	2	3	4	5	6
12	12	12	12	...	12
14	14	14	14	14	14
...	...	15	15	...	15
16	16	16	16	16	16
17	17	17	17	17	...
18	18	18	18	18	...
...	...	22	22
26	26	26	26	...	26
27	27	27	27	...	27
28	28	28	28	28	28
29	29	29
30	30	30	30	30	...
31	...	31
32	32	32	32	32	...
...	35	...
...	36	...
...	37	...
...	38	...
39	39	39	39
44	44	44	44	44	44
...	45
...	50
...	51	51
...	52	52
...	70	...
...	78	72	78
...	92 ^a	74	92
...	104 ^a	104
...	106 ^a

^aThese peak appear with high intensities at initial stages of the decomposition but fade away at the completion of the decomposition.

Special glass cells (see Fig. 1, which is self-explanatory) were used to decompose PS, AP, and propellant. The following experiments were done: 1) Gaseous decomposition products of PS and AP were allowed to mix in a bulb during decomposition [cell (i) was used]. 2) Gaseous decomposition products of AP were allowed to pass through PS during decomposition [cell (ii) was used]. 3) Gaseous decomposition products of PS were allowed to pass through AP during decomposition [cell (ii) was used]. 4) Decomposition of propellant [cell (iii) was used]. 5) Decomposition of AP [cell (iii) was used]. 6) Decomposition PS [cell (iii) was used].

In this set-up, decomposition products get sufficient enough time to mix, interact, and reach equilibrium before they enter MS for analysis. The decomposition studies were carried out in the temperature range of 250°-500°C. The amount of sample taken was between 0.02 and 0.1 gm.

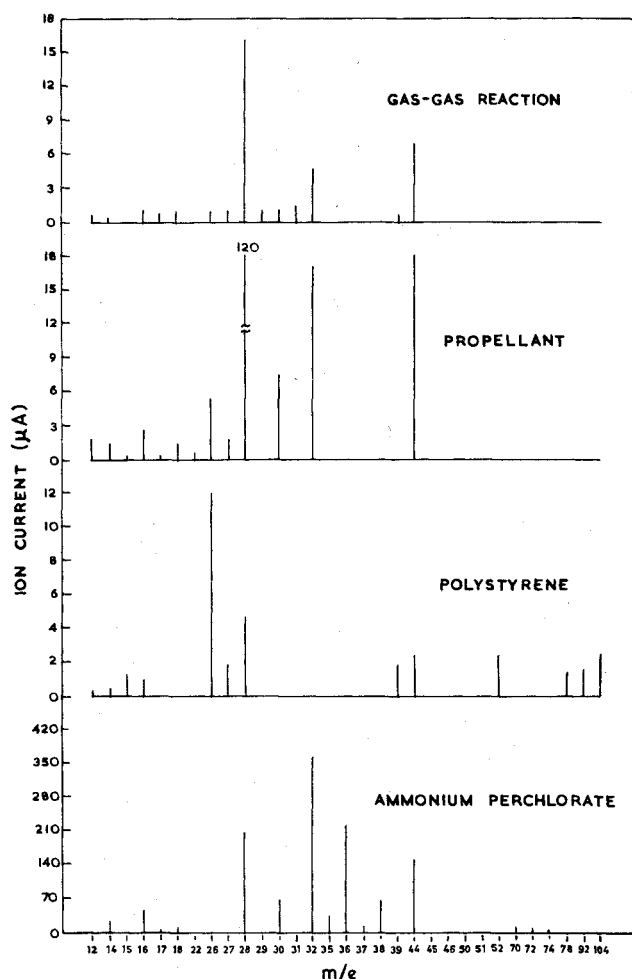


Fig. 2 Mass spectrum of ammonium perchlorate, polystyrene, propellant, and gas-gas reaction.

Results and Discussion

The mass spectra results are shown in Table 1. Although the related analysis of the mass numbers and hence of the products is under investigation, the data in its present form as shown in Table 1, clearly indicate that the propellant decomposition products are different from those of the decomposition products of their individual components. This can be seen better in Fig. 2 where the actual mass spectrograms for AP, PS, and the propellants are displayed.

This therefore suggests that the propellant decomposition is a nonadditive phenomenon. The decomposition products in experiments 1-3 are also different from the additive spectra of the individual spectra of PS and AP. Thus, even a physical mixture of AP and PS does not yield additive decomposition products of its components. This rules out our suspicion that the divergence of our data from that of Ref. 7 is due to the method of preparation. Therefore, the difference may be due to the lack of equilibrium in Ref. 7, which is probably due to the method in which sample was decomposed in MS chamber. A close inspection of our results at first glance suggests a similarity in the mass-spectral data of propellant (4) and gas-gas reaction (1) [see Fig. 2], which apparently supports the conclusion of Ref. 7. All the experimental runs (1-4) leave behind a yellow sublimate on the cooler part of the reaction vessel where the gases interact. Although detailed analysis of the products have not been yet completed, the preliminary analysis suggests that the yellow deposit is an aromatic compound containing chlorine. The presence of chlorine in yellow sublimate explains the mass spectra of propellant (4) and gas-gas reaction (1) in which chlorine peaks are absent. A point of interest here is the fact that although at 400°C the yellow com-

pound is found as a sublimate, yet at 270°C on partial decomposition the entire-nondecomposed residue is intensely yellow-colored throughout the bulk of the solid residue, while no yellow sublimate is formed. On allowing the decomposition to go to completion at 270°C the yellow products, distributed uniformly throughout the bulk of propellant residue, sublimes on the cooler part of the vessel leaving behind a brown residue. This therefore suggests that the yellow compound is initially formed in the condensed phase.

In conclusion, therefore, our results on the identification of the yellow compound in the bulk of propellant suggests a condensed phase reaction and the mass spectral results suggest that final products result from the interaction of the decomposition products of PS and AP individually. Experiments where AP and PS are allowed to decompose separately followed by an interaction of the products in the gas-phase compare favorably with the decomposition of the propellant as a whole thereby suggesting that the interaction of the product in the reaction vessel is similar to the interaction of AP and PS decomposition products in the porous matrix of the propellant. The occurrence of the reaction in the porous "Condensed Phase" of the propellant may explain the larger exothermicity of the propellant compared to the additive heats of decomposition of its components.⁸

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Circular Elastic Membrane Loaded at Concentric Circle

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Nomenclature

- a = outer radius of membrane
 E = Young's modulus
 F = load at circle

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