

is no way of operating the argon cold-cathode discharge at arbitrary combinations of current and voltage. The power supply impedance fixes the operating point. On the other hand, with a thermionic cathode, a second control parameter is available, i.e., the heater power. This permits selection of both voltage and current over rather wide ranges and allows the discharge parameters to be adjusted to match the desired mass flow and specific impulse.

### References

- <sup>1</sup> Kilpatrick, W. D., Mullins, J. H., and Teem, J. M., "Propulsive applications of the modified Penning arc plasma ejector," *AIAA J*, 1, 806-813 (1963).
- <sup>2</sup> Salz, F., Meyerand, R. G., Lary, E. C., and Walch, A. P., "Electrostatic potential gradients in a Penning discharge," *Phys Rev Letters* 6, 523-525 (1961).
- <sup>3</sup> Meyerand, R. G., Salz, F., Lary, E. C., and Walch, A. P., "Electrostatic potential gradients in a non thermal plasma," *Proceedings of the International Conference on Ionization Phenomena in Gases* (North-Holland Publishing Co., Amsterdam, 1962), Vol. II.
- <sup>4</sup> Lehnert, B., "Diffusion processes in the positive column in a longitudinal magnetic field," *Proc. 2nd United Nations Conf. Peaceful Use of Atomic Energy* 32, 349-357 (1958).
- <sup>5</sup> Kadomtsev, B. B. and Nedospasov, A. V., "Instability of the positive column in a magnetic field and the 'anomalous' diffusion effect," *J. Nucl. Energy* 1, 230-235 (1960).
- <sup>6</sup> Davis, J. W., Walch, A. P., Meyerand, R. G., Salz, F., and Lary, E. C., "Theoretical and experimental description of the oscillating electron ion engine," IAS-ARS Preprint 61-103-1797 (June 1961).
- <sup>7</sup> Davis, J. W., Angelbeck, A. W., and Pinsley, E. A., "Research on the oscillating-electron plasma source," *Aeronaut. Res. Labs. Rept. ARL 62-471*, Wright-Patterson Air Force Base, Ohio (December 1962).

## Comment on "Matrices for the Direct Stiffness Method"

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REFERENCE 1 may well be a vital contribution leading toward the second generation of stiffness methods for structural analysis. An academic attitude seems appropriate, because obviously no method is trustworthy unless the solution is accurate using small elements. Melosh presents new criteria governing the shape functions (displacement functions of Ref. 1) to ensure this. Perhaps he could comment on an alternative to his subdivision criterion. Suppose a shape function gives zero shear stress near a node and appreciable shear stress elsewhere. Such shape functions may look very smooth. But as the element size is reduced, the stress continues to oscillate violently instead of converging to a continuous function. Conversely, if the shape functions are chosen so that they can describe any necessary state of constant stress or curvature (for small elements at least), then the true physical situation is faithfully represented in the limit. This criterion is included in that of Melosh. It does not necessarily insure monotonic convergence, except perhaps near the limit, whereas the Melosh criterion will ensure monotonic convergence even for large elements.

Another reason why a solution may converge to the wrong values is that rigid body motions are not represented. Then, as Melosh observes, equilibrium conditions are falsified. This elementary observation had not been published previously,

to the authors' knowledge, let alone received the attention it deserves; yet in practice it is the most difficult criterion to satisfy. Shape functions are invented rather than derived, and despite the criteria there is no unique choice. The authors submitted a note to the *AIAA Journal* some months ago, discussing shape functions for a thin curved beam and for a flat quadrilateral plate in bending. The difficulties suggested that further progress would be limited without an alternative and simpler technique.

A straightforward method of ensuring equilibrium is proposed. Assume the deflections are

$$\sum_{i=1}^N \alpha_i \varphi_i(x, y, z) = [\varphi'] \{\alpha\}$$

Here the  $\varphi_i$  are vector functions defined over the element. They are generalized shape functions, chosen without regard for the nodal deflections. The  $\alpha_i$  are scalar multipliers known as generalized deflections. They are related to the nodal deflections  $x_i$ ; thus

$$\{x\} = [T] \{\alpha\}$$

where  $[T]$  is easily calculated as an  $n \times N$  rectangular matrix, where  $N \geq n$ . Using either orthodox methods or numerical integration, the strain energy may be expressed in terms of a generalized stiffness matrix  $[S]$ :

$$\frac{1}{2} \alpha' [S] \alpha$$

The information latent in  $[T]$  and  $[S]$  is interpreted as follows:

$$\begin{bmatrix} -S & T' \\ T & 0 \end{bmatrix}^{-1} = [Z]^{-1} \\ = \begin{bmatrix} G & t' \\ t & K \end{bmatrix}$$

$[K]$  is the required nodal stiffness. No use for  $[G]$  has been found, but  $[t]$  is needed in deriving stresses, etc.;  $\{\alpha\} = [t'] \{x\}$ .

The following conditions are sufficient for nonsingular  $[Z]$ , and are independent of whether  $[K]$  is singular.

1) It may be possible to select many subsets of  $n$  generalized shape functions which give independent nodal deflections. At least one subset must satisfy further conditions.

2) The remaining  $(N - n)$  shape functions give  $(N - n)$  different systems of stresses. These must be mutually independent; that is, they cannot be combined to give zero total strain energy.

3) The  $n$  stress systems under 1 must not combine with any individual stress system under 2 to give zero total strain energy.

Thus, shape functions under 1 which are pure translations and rotations are not forbidden, so long as they are independent. The proposal is that the first few shape functions should represent the necessary rigid body motions. The remainder should then represent the types of deformation envisaged, preferably with minimum rigid-body displacement.

Another question which interests the authors concerns natural frequencies. Just as the strain energy is expressed in terms of the stiffness matrix, so the kinetic energy may be expressed in terms of a nondiagonal mass matrix, based on the shape functions. These two matrices can be combined in an eigenvalue calculation. The question is, do the resulting frequency estimates converge monotonically as the mesh is subdivided? One would expect this, because the Melosh criterion means that simple constraints are progressively relaxed. In a similar way, work done against second order strains may be written in matrix form. The eigenvalue calculation then gives the buckling load. Since only the largest eigenvalue is significant, this case seems clearer.

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## Reference

- <sup>1</sup> Melosh, R. J., "Basis for derivation of matrices for the direct stiffness method," AIAA J. 1, 1631-1637 (1963)

## Comments on "Gas-Film Effects in the Linear Pyrolysis of Solids"

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THE recent excellent paper by Cantrell<sup>1</sup> reiterates the known complexities of the measurement of the surface temperature in studying the thermal decomposition of solids by the linear pyrolysis (LP) technique, and also makes a valuable contribution toward a solution of the problem. However, this paper, if taken too literally by workers unacquainted with the field, can tend to discredit certain (generally accepted) hypotheses regarding propellant combustion and solid decomposition which have been developed from the experimental data and concept of LP kinetics. The purpose of this note is to emphasize that many of these hypotheses are relatively insensitive to the absolute values of the experimental rate data, so that their validity is essentially unaffected by treatments such as that of Cantrell. The note also appraises in some detail the general validity of the published LP data.

First it should be pointed out that the LP technique has undergone a continuous process of evolution and improvement since its original development by Schultz and Dekker.<sup>2</sup> LP data cannot, therefore, be analyzed in toto but must be related to the particular design of the apparatus that was used to obtain it. Thus, in the early studies,<sup>2-5</sup> sample surface temperature ( $T$ ) was measured by a small flattened thermocouple interposed between the hot plate and the sample. In the latest version of the LP apparatus,<sup>6,7</sup>  $T$  is measured by a thermocouple junction imbedded in the hot plate. Unlike the temperatures recorded by the external thermocouple, which were of some value between the hot-plate temperature (too hot) and the sample temperature (too cold), the temperature recorded by the thermocouple junction is amenable to theoretical analysis, such as that published recently by Cantrell, Nachbar, and Williams<sup>8</sup> and by Chaiken et al.<sup>9</sup> Also, LP data obtained in some of the earliest experiments, when a hot wire was used as the heat source,<sup>2</sup> have since been shown to be somewhat in error as a result of a cutting action exerted by the hot wire on the sample.<sup>10</sup>

It was recognized in the early studies that the LP rate of a material was a function of the loading force pushing the sample against the hot plate, and that the rate became independent of force for sufficiently large forces. However, it was not recognized until much later<sup>9</sup> that the "ultimate" loading force was itself a function of pyrolysis rate. At the higher LP rates, then, a considerably larger force was necessary in order for the pyrolysis rate to be independent of loading force than was required at lower rates.

Although the absolute validity of the experimental rate data of the early studies using the external thermocouple should be in doubt, these studies gave kinetic data for the sublimation of ammonium chloride which were in substantial agreement with the results obtained by the more conventional high-vacuum weight-loss technique. Recent studies by Chaiken et al.<sup>9</sup> of the sublimation rates of  $\text{NH}_4\text{F}$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{Br}$ , and  $\text{NH}_4\text{I}$ , by both the weight-loss technique and the LP technique using the thermocouple junction, also showed the rates

by both techniques to be consistent with each other. The published theoretical treatments suggest this to be largely the result of the relatively low LP rates involved. Schultz and Dekker had argued<sup>2</sup> that the pyrolysis of ammonium chloride involves dissociative sublimation, that the rate-controlling step consists of the desorption of  $\text{NH}_3$  and  $\text{HCl}$  gases from a complex of these gases adsorbed on the surface, and that the activation energy for pyrolysis should be equal to the sum of the heats of sublimation of the two gases. The studies by Chaiken et al. disclosed that the activation energies for the pyrolysis of all four ammonium halides follow this rule within experimental error. The more classical explanation of the relatively low activation energy of  $\text{NH}_4\text{Cl}$  is that a diffusion process is rate-controlling.<sup>11</sup> The activation energy obtained for the LP of ammonium nitrate was about 7.1 kcal/mole,<sup>5</sup> and it was hypothesized that the decomposition consisted of a dissociative sublimation process. The activation energy of ammonium nitrate should then be about 14.8 kcal/mole (about twice that measured) if it also follows the preceding rule. An activation energy slightly greater than 7 kcal/mole (and a corresponding increased frequency factor) would be even more in agreement than 7 kcal with the experimental grain burning detonation reaction time of ammonium nitrate,<sup>12</sup> particularly if the detonation reaction temperature is lower than previously used, which appears probable. The analysis of gas-film effects by Nachbar and Williams,<sup>8</sup> although very interesting and informative, is not necessarily valid in their theoretical correction of the ammonium nitrate pyrolysis rates, since a thermocouple of finite thickness had been used for the temperature measurements. Thus, the value of 14.8 kcal appears more reasonable than their computed value of about 30 kcal/mole. However, the presence of a liquid melt suggests that the decomposition mechanism may be more complex than merely dissociative sublimation.

The concept of linear surface pyrolysis kinetics, together with some preliminary experimental data, led Schultz and Dekker to hypothesize<sup>13</sup> that, in a burning composite propellant, the average burning surface temperatures of the oxidizer and binder (fuel) differ from each other since their Arrhenius kinetic parameters (activation energy and frequency factor) will usually differ, but the propellant burns at a constant velocity. This postulated "two-temperature" theory of composite propellant burning thus views the initial decomposition of the solid oxidizer and binder in a burning propellant as essentially independent processes. A subsequent study on ammonium-nitrate-based propellants<sup>4,5</sup> supported these views, and various contemporary works on propellant combustion now employ the same postulate.

The large differences between the LP rate of ammonium nitrate and various binders for a given temperature (ammonium nitrate is the faster) led to the conclusion<sup>4</sup> that, during the burning of ammonium nitrate composite propellants, the binder is pyrolyzed out in the flame of the burning pyrolysis products of the monopropellant ammonium nitrate and that there is on the average a relatively large distance between the surfaces of the pyrolyzing ammonium nitrate and the pyrolyzing binder. This distance should prevent the heat from the reaction between the diffusing oxidizer and binder pyrolysis products (diffusion flame) from having much influence on the pyrolysis of the solid ammonium nitrate and, hence, on the burning rate of the propellant. Thus, most inert binders should have little influence on the burning rate of ammonium nitrate composite propellants; this is fully supported by experiment. On the other hand, ammonium perchlorate has an LP rate slower than or comparable to those of many binders at a given temperature,<sup>4,14</sup> and, therefore, the binder in an ammonium perchlorate composite propellant is pyrolyzed either ahead of or on nearly the same surface plane as the oxidizer; the diffusing binder pyrolysis products can, therefore, influence substantially the flame of the monopropellant, ammonium perchlorate. Thus, the burning rate of the propellant can either increase or decrease from that of

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