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

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THE recent excellent paper by Cantrell[1] 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 unaquainted 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 [2] 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,[2–5] 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, [6, 7] 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[8] and by Chaiken et al [9] Also, LP data obtained in some of the earliest experiments, when a hot wire was used as the heat source,[2] have since been shown to be somewhat in error as a result of a cutting action exerted by the hot wire on the sample [10]

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[9] 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 [9] of the sublimation rates of NH_4F, NH_4Cl, NH_4Br, and NH_4I, 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[2] that the pyrolysis of ammonium chloride involves dissociative sublimation, that the rate-controlling step consists of the desorption of NH_3 and 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 NH_4Cl is that a diffusion process is rate-controlling [11] The activation energy obtained for the LP of ammonium nitrate was about 7 1 kcal/mole,[5] 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,[12] particularly if the detonation reaction temperature is lower than previously used, which appears probable The analysis of gas-film effects by Nachbar and Williams,[3] 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[13] 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[4 5] 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[4] that, during the burning of ammounium 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,[4 14] 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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the pure ammonium perchlorate, depending on whether the binder products produce fast reaction or dilution effects [15] That the binder can have strong influence on the burning rate of an ammonium perchlorate propellant is well known experimentally

The latest study of the LP rate of polymethylmethacrylate (PMM)[10] showed that the activation energy is large at the lower temperatures, but changes to a constant value of about 11 kcal/mole at high temperatures (i e , the LP mechanism changes) This contrasts with the larger values obtained earlier at the higher temperatures using a hot wire[2] and an external thermocouple [4] The hypothesis was made that vaporization (desorption) of the monomer was rate-controlling This hypothesis is then in line with that of the ammonium halides in that a desorption step is rate-controlling This hypothesis is especially attractive with regard to understanding the pyrolysis of various plastics and polymers at high temperatures However, it requires further verification for both PMM and other plastics An unpublished study by Nishibayashi, Codner, and the author on the LP of Teflon has disclosed the same general behavior as for PMM The activation energy at the higher temperatures is approximately consistent with the vaporization energy of the dimer or trimer or with a mixture of small multiple monomer units However, the gas-film corrections vary according to the theoretical treatment used, and the general conclusions are still in doubt It is interesting that the experimental data did not differ appreciably using both an external thermocouple and a thermocouple junction Surface pyrolysis kinetics of plastics and polymers are of importance to both propellant combustion theory [4, 13] and ablation theory [16]

Studies[4, 14] on the LP kinetics of ammonium perchlorate showed an activation energy at high temperatures of about 22 kcal/mole, which is essentially the same as the sublimation energy of ammonium perchlorate It was hypothesized that ammonium perchlorate undergoes dissociative sublimation during its high-temperature pyrolysis Nachbar and Williams[8] have argued that the sublimation process may be nondissociative However, a paper by Inami, Rosser, and Wise[17] indicates that the sublimation of ammonium perchlorate is accompanied by dissociation The pyrolysis data of ammonium perchlorate in Ref 14 are adequate to explain the grain-burning detonation reaction time of ammonium perchlorate [18] They are also essentially consistent with the high-pressure surface temperature of deflagrating ammonium perchlorate which was measured by Friedman, Levy, and Rumbel,[19] with the correlation of the deflagration rates of ammonium perchlorate by the theory of Johnson and Nachbar,[20] and with the theoretical linearity of the shear stress in the surface of ammonium perchlorate burning at high pressures [21] However, there is some latitude in all of the correlations, and it is quite possible that the activation energy (and frequency factor) of the ammonium perchlorate pyrolysis rate expression may be a little higher than measured because of gas-film effects [8]

The LP of ammonium perchlorate does not follow the Arrhenius rate law throughout its decomposition range The publications[4, 10] treating the LP of ammonium perchlorate have not discussed this point, and it seems desirable to do so here, since certain confusion has resulted Above about 800°K (measured) surface temperature, the LP of ammonium perchlorate follows an Arrhenius rate law with an activation energy of about 22 kcal/mole The rate process is believed to be dissociative sublimation However, below about 800°K the linear pyrolysis characteristics change A "chuffing" type of pyrolysis behavior occurs in which for a given surface temperature the sample surface will alternatively regress (decompose) very rapidly and then remain more stationary for a short period of time The effect is most pronounced at the lower temperatures, where the surface regression distance vs time looks like a flight of stairs As the surface temperature is increased, the regression distance during the former stationary period becomes finite, and the very rapid regression period becomes less rapid This behavior increases as the surface temperature is further increased Finally, at a sufficiently high temperature, the LP rate becomes linear, with a constant activation energy The explanation for this low-temperature decomposition behavior is not known, but possibly involves the reaction of the intermosaic phase of the ammonium perchlorate followed by a collapsing of the remainder of the sample surface under the applied loading force The decomposition mechanism of ammonium perchlorate at low temperatures differs from that at high temperatures and is possibly related to the surface temperatures of ammonium perchlorate burning at low pressures observed by Powling and Smith [22]

The results of both theory and experiment indicate that it is possible to obtain valid LP data if a sufficient loading force is applied to make the rate independent of the force Thus, the large corrections found necessary by Cantrell in the LP of dry ice would not have been necessary if a higher loading force has been used The author and Barsh[23] studied the LP rate of dry ice, using an external thermocouple for the surface temperature measurement Although there was a relatively large scatter in the rate data, the measured activation energy in the temperature range of about 205° to 270°K was consistent with theory The absolute rates are about a factor of 6 greater than those obtained by Cantrell for the same temperature

In conclusion, the concept of linear surface decomposition kinetics and the data obtained by the LP technique have led to new and interesting hypotheses regarding solid decomposition under high heat flux, the mechanism of ablation, grain-burning detonation, and composite propellant combustion These hypotheses generally require further verification, however Much of the original experimental data requires refinement using the published theoretical treatments to help correct for gas-film effects For substances such as ammonium perchlorate which react chemically while undergoing pyrolysis, it is possible that further corrections are necessary In any event, the evolutionary nature of science suggests that the LP technique will be a useful scientific tool of the future

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Reply by Author to W H Andersen

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In the preceding comment, Andersen[1] surveys the published data in the linear pyrolysis (LP) field and comments on the author's recent paper The author appreciates Andersen's generally kind appraisal but wishes to comment on four specific criticisms: 1) that the conclusions might mislead persons unfamiliar with the history of the LP field; 2) that the theoretical results differ from those of Chaiken et al ; 3) that the predicted rate of pyrolysis depends on weight loading; and 4) that the experimental results on dry ice LP require too great a temperature correction

With regard to misleading conclusions, the author agrees with Andersen's statement that hypotheses, which are independent of absolute rate data, may be correctly deduced from existing LP data It is indeed possible to draw correct qualitative conclusions from inexact quantitative data! However, the author intended primarily to assert that the quantitative results of many LP experiments are subject to question because of the failure of most authors to consider gas-film effects Andersen acknowledges this point

The author[2] and Chaiken et al [3] have presented theoretical models by which the gas-film temperature correction to LP data may be calculated As Andersen notes, these theories give different corrections It is, therefore, appropriate to determine which model, if either, is suitable for calculation of the gas-film temperature correction of existing LP data The data of Chaiken et al [3] contain sufficient information to make numerical comparisons Before discussing these data, an important criterion for the validity of a theory must be noted Most theories (including those under discussion) contain explicit and implicit assumptions based on the magnitudes of various dimensionless parameters The ranges of the parameters involved must be consistent with the theoretical model chosen

As a numerical example, the following data point (in the notation of Ref 2) from Fig 4 and Table III of Chaiken et al [3] is examined†: $m = 1\ 6(10)^{-2}$ g/cm^2-sec, $T_0 = 750$°K, $p_{av} =$ 6 03 atm, and $p_\infty = 1$ atm From the theory of Chaiken et al ,[3] the calculated temperature correction and film thickness are $(T_1 - T_0) = 4\ 2$°K and $z_1 = 5\ 58(10)^{-5}$ cm For the calculated film, the reduced Reynolds number given by Schlichting[4] is‡ $R = mz_1/\mu = 2\ 26(10)^{-3}$ The magnitude of this parameter is inconsistent with the constant film pressure assumption of Chaiken et al ,[3] so that the applicability of their theorectical treatment to the present case is subject to objection The author's theory[2] is developed for a cylindrical specimen, and so, for purposes of comparison, an effective radius b is chosen Thus, the cylindrical cross sectional area $\pi b^2 = 0\ 5$ cm is identical to the rectangular area in the experiments of Chaiken et al The dimensionless weight $W = (p_{av} - p_\infty)/p_\infty = 5\ 03$, and the Sommerfeld number $S = 79\ 5$ With these additional parameters, the viscosity‡ $\mu =$ 3 95$(10)^{-4}$ g/cm-sec, the calculated temperature correction and film thickness are $(T_0 - T_1) = 41$°K, and $z_1 = 5\ 54(10)^{-4}$ For these calculations, the magnitude of the Reynolds number is consistent with the assumption of a pressure gradient However, two inconsistencies with the assumptions of the author's theory do arise The calculated average radial velocity at $r = b$ is 3 28$(10)^4$ cm/sec, which is almost the speed of sound [5 40$(10)^4$ cm/sec at average film temperature] The pressure at $r = b$ is, therefore, not p_∞ as assumed Also, the equilibrium pressure (p_{eq}) for the calculated surface temperature according to data extrapolated from Ref 5 is approximately 7 atm, so that $(p_{eq} - p_{av})/p_{eq} \approx \frac{1}{7}$, which would indicate that considerable condensation occurs Thus the pyrolysis rate could not closely approximate the vacuum sublimation rate

The author's reply to Andersen's objections to the theoretical dependence on weight loading and to the large temperature correction for dry ice LP must reiterate portions of Ref 2, where it is stated that faster rates of evaporation result in channel formation on the evaporating surface (see Fig 11 of Ref 2) and where it is speculated that channel formation might result in the independence of pyrolysis rate on weight loading, as observed by Andersen and his associates Channel formation is clearly inconsistent with the assumptions of any current theory Andersen notes that Barsh and Schultz[6] report significantly larger dry ice LP rates than the author at comparable temperatures It is noteworthy that Barsh and Schultz use an external thermocouple that measures some temperature between plate temperature and ambient temperature in the solid If extrapolation of the author's data is permissible, evaporation rates of $20(10)^{-3}$ g/cm^2-sec would occur at 249°K, which is not significantly greater than the calculated temperatures

In conclusion, at least two courses of action seem feasible for future interpretation of LP data on solid propellant materials: 1) perform additional experiments under suitable conditions (weight loading, ambient pressure pyrolysis rate, etc) such that the parameters are consistent with some existing theory; and 2) develop additional theory to include the necessary range of parameters, as the author noted might be

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† Since the data are partially determined from a graph, they may not agree exactly with the original data However, they are well within the experimental scatter

‡ In the calculations, a viscosity of 3 95$(10)^{-4}$ g/cm-sec is used This value is arbitrarily chosen so that the Prandtl number $(c_p\mu/\lambda)$ is 0 75 when the thermal conductivity (2 0 $\times 10^{-4}$ cal/cm sec-°K) of Chaiken et al is used and where the specific heat (c_p) of the gas is identical to the specific heat of the solid