

The effect of chemical erosion on heat-transfer rates can be derived from the net heat of reaction involved and the resulting effect on wall enthalpy. The convective heating rate can be evaluated using the effective wall-enthalpy/temperature relationship, or the convective heat-transfer rate can be modified to account for the loss or absorption of energy associated with the chemical reaction occurring within the boundary layer.

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Linear Pyrolysis Rate Measurements of Propellant Constituents

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This paper discusses the construction and use of a device to measure linear pyrolysis rates of solid-propellant constituents. The device employs a radiantly heated porous plate. Propellant samples are pressed against the plate, and the pyrolysis rates corresponding to different interface temperatures are measured. The use of a porous plate represents a new approach, which seeks to avoid the problem associated with the obstruction of flow of pyrolysis products that occurs if a solid plate is used. This obstruction results in a gas film between the plate and the sample and, therefore, causes uncertainty in the evaluation of the sample surface temperature. Data for the linear pyrolysis of ammonium chloride and ammonium perchlorate have been obtained with this new device. Although subject to rather poor reproducibility, these data compare favorably with the existing data for these materials obtained with the original hot-plate technique. The data also are compared with similar data for propellant mixtures. In addition, a comparison of these experimental results with vapor-pressure data has allowed estimation of the surface accommodation coefficients. These were found to be of the order of 10^{-2} and 10^{-3} , respectively, for ammonium perchlorate and ammonium chloride.

Introduction

THE initial step in the chain of events occurring during propellant combustion is the conversion of the solid constituents to reactive gases. The description of this step is of prime importance in any theory that attempts to describe the over-all combustion process, since it represents the boundary condition that couples the conservation equations that are written normally for the solid and gaseous phases. Most theorists follow the idea proposed by Daniels¹ that surface gasification can be described as a monomolecular reaction, and that this step controls the over-all burning rate. Thus, the regression rate may be expressed in kinetic terms as

$$r = B \exp(-E/RT_s) \quad (1)$$

where r is the steady-state regression rate, B is the pre-

exponential constant, which depends upon the kinetic frequency factor and the surface concentration of the decomposing molecules, E is the activation energy, R is the gas constant, and T_s is the surface temperature. Penner² has pointed out that, as long as a first-order gasification process occurs, the preceding equation remains valid independently of the interplay of surface and gas-phase reactions.

Shultz^{3,7} and Dekker⁷ extended this line of reasoning to the burning of composite solids, suggesting that gasification of the oxidizer and binder proceed independently, both following a regression rate law of the form of Eq. (1), but each with a different activation energy and pre-exponential factor. As a consequence, the surface temperatures of the oxidizer and fuel must be different if both regress at the same mean rate. This reasoning is the basis for their "two-temperature" theory.

In more recent years, the concept of a surface gasification reaction, described mathematically by an equation of the form of Eq. (1), has been employed in theories for nonsteady-state combustion (e.g., Refs. 4 and 5). The objective of these theories has been the prediction of nonsteady combustion behavior based on a knowledge of more easily measured steady-state burning-rate parameters. In these theories, the surface gasification parameters strongly influence the predicted behavior. Therefore, experimental evaluation of these parameters is of practical interest.

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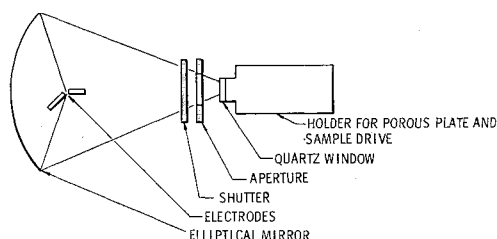


Fig. 1 Schematic of pyrolysis apparatus, arc-image furnace arrangement.

The problem in determining the rate parameters B and E is the measurement of T_s for a known regression rate r . Although the technique of direct measurement with a fine thermocouple imbedded in the propellant has been utilized by several investigators, the data are difficult to interpret because of the extremely high temperature gradients. This method would at best yield average values, since the rates of oxidizer and binder could not be distinguished. Powling and Smith⁶ have employed a technique for measuring the surface temperatures of propellants burning at low pressure that utilizes specific wavelengths of infrared emission. Their data for ammonium perchlorate-weak fuel mixtures indicate that the surface gasification reaction is not rate-controlling at atmospheric pressure, since they measure an approximately constant surface temperature over a wide range of burning rates. Their measurements at less than atmospheric pressure indicate strong dependence of surface temperature upon pressure (again independent of burning rate). Whether or not the same trends continue at pressures typical of rocket motors remains to be ascertained, a task made difficult with their techniques because of gas-phase emission.

The data most often employed in theoretical predictions of nonsteady burning have been obtained by the hot-plate technique that was introduced by Shultz and Dekker⁷ and improved upon by Barsh.⁸ This technique involves simply pressing a sample of the solid against an electrically heated plate and measuring simultaneously the temperature of the plate and the rate of disappearance of the solid. A source of error in this experiment is the gas film that must separate the heated plate from the solid in order for the gaseous pyrolysis products to escape. The importance of considering the temperature drop that occurs across the gas film has been demonstrated by Cantrell.⁹

Williams and Nachbar¹⁰ proposed that the error introduced by the gas film could be eliminated or at least rendered susceptible to precise analytical description by replacing the impervious plate of the Barsh apparatus with a porous plate and constraining the flow of gas away from the sample surface

to be one-dimensional. This paper describes the design and construction of such a porous-plate apparatus. Data obtained for the pyrolysis rates of ammonium chloride and ammonium perchlorate also are presented, and the results are discussed in relation to the data of other investigators. The results also are used to estimate evaporation coefficients.

Experimental Apparatus

Practical consideration of the design of a porous-plate apparatus immediately presented what appeared to be a serious shortcoming, i.e., the problem of maintaining a uniform temperature across the plate. Temperature non-uniformity is a problem because of the transpiration cooling, which occurs when the pyrolysis products are allowed to pass through the plate. If the plate is heated by passing an electrical current through it, as in the Barsh apparatus, either the resistance must be discontinuous at the sample perimeter, or a heat sink must be provided in order to prevent excess temperature at the sample perimeter. This implied a complexity in the fabrication of a suitable plate that was incompatible economically with its expected lifetime. The pyrolysis products of a propellant constituent (such as ammonium perchlorate) are very corrosive, and the porosity of the plate would be expected to change considerably with continued testing of this material. This apparent impasse led to the idea of employing radiative heating with an arc-image furnace.

Figure 1 shows schematically how the arc-image furnace is used for heating, and Fig. 2 shows the construction details of the porous-plate holder and sample feed mechanism. The arc-image furnace is a Strong jet-arc, rated at 160 amp. The radiant flux at the image focus has been calibrated and found to be uniform within $\pm 3\%$ of 30 cal/cm²/sec over an area of approximately 5 cm². Variation of the porous-plate temperature is achieved by shifting the position of the plate with respect to the focal point.

The porous plates that are made by sintering particles of 347 stainless steel were obtained commercially from the Mott Metallurgical Company, Hartford, Conn. Plates having a thickness of 1.6 mm were selected to obtain the data presented here. The density of the plate material is 3.84 g/cc, and the pore size is approximately 40 μ . The permeability of these plates to air flow was measured, and the data are shown in Fig. 3. An insulator formed from aluminum silicate holds the porous plate in position.

An aspirator was used to withdraw the pyrolysis products and create a vacuum on the downstream face of the plate. Radiant heating of the porous plate was accomplished by employing a quartz window in the vacuum chamber. A pressure of approximately 35-mm Hg was maintained on the downstream face of the porous plate for the experiments reported here.

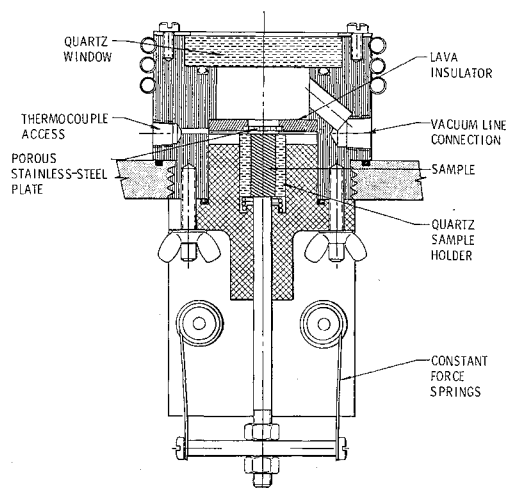


Fig. 2 Assembly drawing of porous-plate holder and sample positioning arrangement.

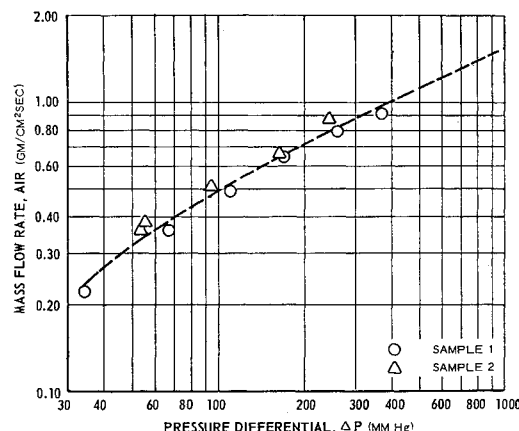


Fig. 3 Permeability data, 0.16-cm-thick porous stainless steel.

Test samples 9.5 mm in diameter are formed by pressing the powdered material [chemically pure (C.P.) grade] under high pressure until densities greater than 95% of crystal density are obtained. The samples are forced against the heated plate by a spring-loaded rod. The pressure at which the sample is pressed against the plate can be varied between 0.8 and 12.9 atm by changing the springs. A pressure of 0.8 atm was selected for these experiments.

The temperature at the interface between the sample and the porous plate is measured with a thermocouple sandwiched between the two surfaces. Chromel-Alumel thermocouples made with 36-gage wire are used. The linear regression rate of the sample is measured with a potentiometer position transducer that is attached to the sample push rod.

The procedure followed for operating the apparatus was to position the sample, release the push rod to apply force to the sample, and then to open the shutter on the arc-image furnace. Outputs from the thermocouple and the position transducer are recorded on an oscillograph. Figure 4 shows an oscillograph trace for an ammonium perchlorate run in which two thermocouples were placed between the sample and the plate. As illustrated in Fig. 4, there is a transient heating period followed by an equilibrium period of the order of 5 sec where the thermocouple output and rate-of-change position are approximately constant. The surface temperature and regression rate data are taken during this equilibrium period. If pyrolysis of ammonium perchlorate is allowed to continue, the porous plate eventually becomes fouled because of oxidation, and the temperature begins to rise.

Experimental Results

Ammonium Chloride Data

Initial experiments were made with ammonium chloride samples. The sublimation of this material previously has been studied both with the Barsh hot-plate apparatus and, at lower temperatures, by the more conventional method in which the sample is heated uniformly in a thermostated, evacuated container.¹¹ Figure 5 shows the data obtained with this material. These results show that the pyrolysis rate changes with temperature in a manner consistent with Eq. (1), but that the reproducibility is rather poor. The scatter is caused by uncertainty in the interface temperature. By placing a second thermocouple junction between the sample and the plate, spaced approximately 4 mm from the first and on the same radius with respect to the axis of the sample, it was observed that the temperatures would differ as much as 40°C between the two thermocouples. Attempts to improve the reproducibility by reducing the radial heat loss from the porous plate were unsuccessful. Figure 6 shows how the data obtained with the porous-plate apparatus compare with the previously reported data.

Ammonium Perchlorate

Pyrolysis data for pressed strands of ammonium perchlorate are presented in Fig. 7. It was observed that the surface temperatures were more reproducible with this material

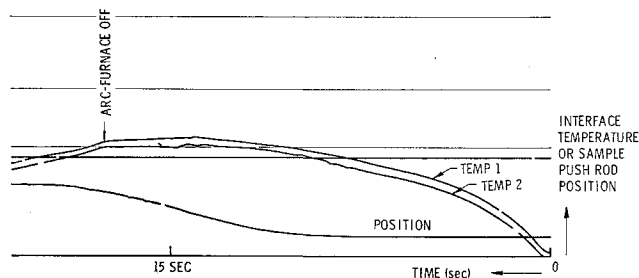


Fig. 4 Oscillograph trace of an ammonium perchlorate run.

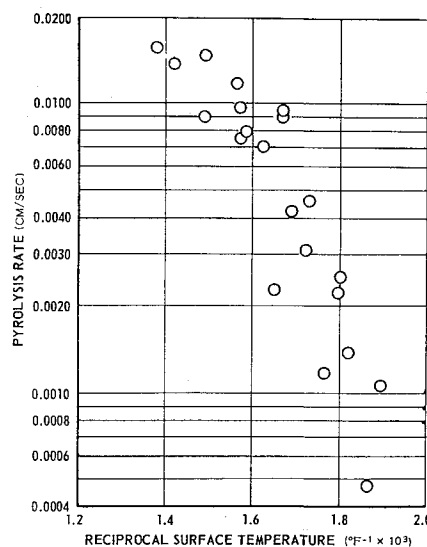


Fig. 5 Ammonium chloride pyrolysis data.

than with the ammonium chloride; however, the reason for this is not evident. Previous results measured with the Barsh apparatus and reported by Anderson and Pesante¹² are included in Fig. 7 for comparison with those obtained in this study.

As indicated in Fig. 7, the observed rates and activation energy for ammonium perchlorate generally were lower than those obtained with the Barsh apparatus. However, the data in Fig. 6 demonstrate an opposite trend. In this study, both the rates and activation energy measured for ammonium chloride are higher than those measured with the Barsh apparatus.

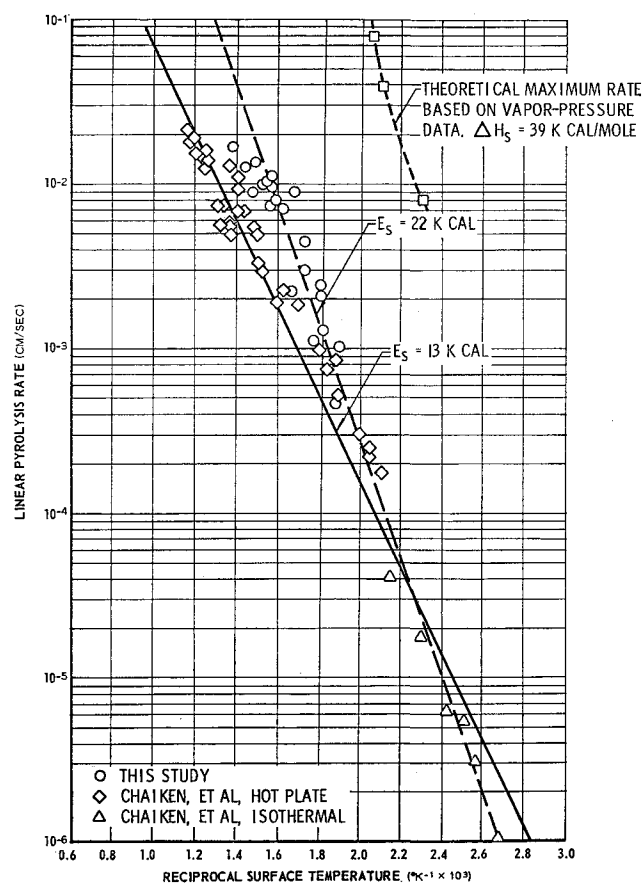


Fig. 6 Comparison of ammonium chloride data with that previously reported by Chaiken et al.¹¹

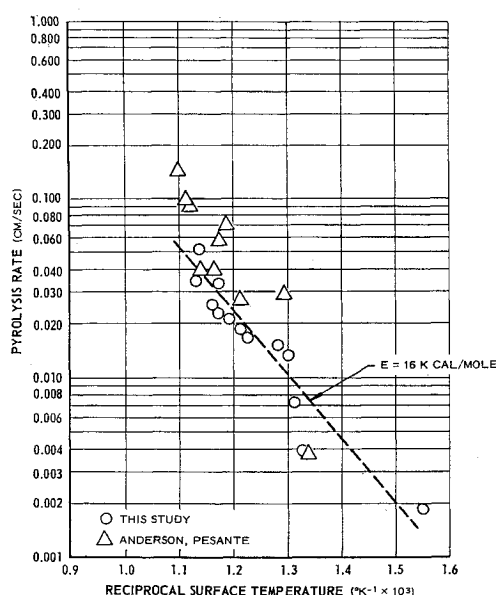


Fig. 7 Ammonium perchlorate pyrolysis data.

Calculation of Evaporation Coefficients

The densities of ammonium chloride and ammonium perchlorate are 1.53 g/cc and 1.95 g/cc, respectively. Therefore, the mass flow rates that correspond to linear pyrolysis rates of 0.1 cm/sec will (as shown in Fig. 3) produce a pressure differential across the porous plate of only about 20-mm Hg. At the surface temperatures corresponding to this regression rate, the vapor pressure of ammonium chloride is well over 1 atm. Therefore, under these conditions, the porous plate provides little restriction to the flow of gases away from the surface of the sample, and, unless the plate acts as a catalyst, the regression rate is much the same as it would be if the plate were not there at all. It is of interest, therefore, to compare the measured vacuum sublimation rates with calculated values for the maximum possible sublimation rate based on vapor-pressure data.

If the vapor pressure for a material is known, a maximum surface regression rate may be calculated, based on the kinetic theory of gases. This calculation has been discussed by Penner.¹⁴ The limiting rate is governed by the speed with which the gaseous molecules can leave the vicinity of the surface. It represents an idealized condition in which the rate of molecular transition from the condensed state to the gaseous state does not limit the over-all evaporation rate. The difference between the maximum theoretical rate and the observed vacuum evaporation rate, therefore, represents a measure of the extent to which the phase transition step or gasification reaction is rate-limiting. For a compound that does not disassociate on gasification, the maximum rate is given by

$$r = 0.0583 [P_{mm}/\rho_c(T_s/M)^{1/2}] \quad (2)$$

where P_{mm} is the vapor pressure in mm Hg, ρ_c is the density of the condensed material in g/cc, T_s is the surface temperature in °K, and M is the molecular weight of the vapor. For compounds such as ammonium chloride and ammonium perchlorate that do dissociate on sublimation, the maximum rate would be given approximately by

$$r = 0.0583 [\frac{1}{2} P_{mm}/\rho_c(T_s/M_1)^{1/2}] [(M_1 + M_2)/M_1] \quad (3)$$

where M_1 is the molecular weight of the heavier gas molecules, and M_2 is the molecular weight of the lighter gas molecules. Equation (3) is derived by extending the kinetic-theory derivation of Eq. (2) that is based on the calculation of the rate at which gaseous molecules at a given temperature and pressure strike a surface. At equilibrium, if each striking

molecule is adsorbed, the striking rate is equal to the rate at which gaseous molecules are being formed and leave the surface. Thus, the maximum gasification rate is related directly to the maximum striking rate at equilibrium which depends upon the concentration and velocity of the gaseous molecules. If two kinds of gaseous molecules are present in equal concentrations, one being heavier than the other, the striking rate of the heavier molecules is less because of lower velocities. Therefore, if both are to be adsorbed at the same average rate, the rate will be governed by the velocity of the slower molecules. Using the assumption that the maximum gasification rate in this case is again equal to the maximum adsorption rate, Eq. (3) is obtained.

The dashed curves in Figs. 6 and 8 represent maximum rates calculated with Eq. 3. In both cases the rate of phase transition, or the gasification reaction, appears to be very small compared with the theoretical maximum rate. An evaporation coefficient, defined as

$$\alpha = \frac{\text{observed vacuum rate}}{\text{maximum theoretical rate}} \quad (4)$$

can be computed from the data presented in Figs. 6 and 7. Calculated evaporation coefficients are given in Table 1. The data corresponding to very low vapor pressures have been corrected to account for flow restriction caused by the pressure drop through the plate. The correction is made by subtracting this pressure drop from the vapor pressure.

The assumption that the measured temperature is the true surface temperature could be in error, and the effect that such an error would have on the calculated evaporation coefficient was considered. Since the thermocouple junction (which is placed between the sample and the plate) has dimensions greater than the pore sizes of the plate, it becomes slightly imbedded in the solid sample during pyrolysis. Therefore, it must sense a temperature equal to or less than the true sample surface temperature, at least for a material such as ammonium chloride, which is not capable of exothermic decomposition. Thus, if a temperature correction were made, the calculated evaporation coefficients would become even smaller than is indicated in Table 1.

Constituent Rates vs Propellant Mixture Rates

In Fig. 8 the hot-plate pyrolysis data for ammonium perchlorate are compared with recent surface temperature meas-

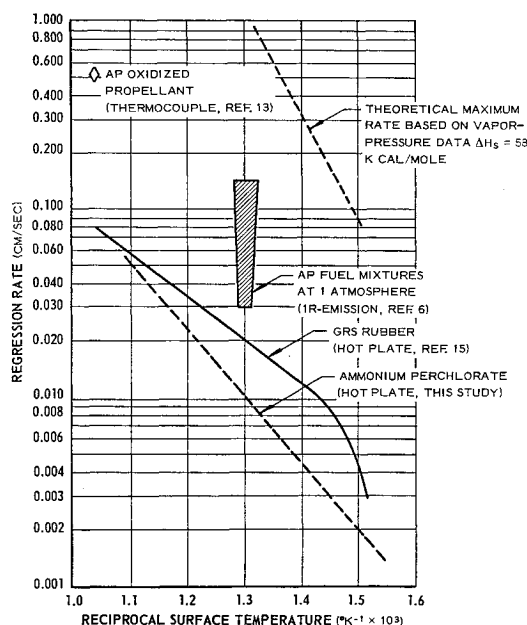


Fig. 8 Comparison of pure constituent regression rates with mixture regression rates.

Table 1 Effective evaporation coefficients α for ammonium chloride and ammonium perchlorate

$T_s, ^\circ\text{C}$	$\alpha, \text{NH}_4\text{Cl}$	$\alpha, \text{NH}_4\text{ClO}_4$
271	1.4×10^{-3}	...
292	1.3×10^{-3}	...
315	1.2×10^{-3}	...
337	1.1×10^{-3}	...
441	...	1.54×10^{-2}
468	...	1.33×10^{-2}
502	...	0.98×10^{-2}

urements of ammonium perchlorate fuel mixtures. Data obtained both by an imbedded thermocouple¹³ and by the infrared emission technique⁶ are shown. In addition, published pyrolysis rates of a material similar to the fuel binder in conventional composite propellants are shown.¹⁵

The difference between the surface temperatures at a given regression rate for the pure constituents as measured by the hot-plate technique and those measured for ammonium perchlorate fuel mixtures (as shown in Fig. 8) indicates that the propellant combustion processes postulated in Refs. 2 and 3 may be oversimplified somewhat. If, indeed, the gasification step of the oxidizer and fuel proceed independently, then, based on the pyrolysis rates of pure ammonium perchlorate and pure fuel binder, the average surface temperature of ammonium perchlorate fuel mixtures would be expected to be higher than observed either by Wenograd¹³ or by Powling and Smith.⁶ The observed rates for the mixtures are of the order of five times those of pure ammonium perchlorate for a given surface temperature, and although data are not available for the particular fuels that were employed, the data shown for GRS rubber indicate that the fuel pyrolysis rates also would be considerably lower than the mixture rate.

This discrepancy between constituent and mixture rates might be attributed to a catalytic effect of the fuel or of the pyrolysis products. The large difference in rates also indicates that further efforts to characterize mathematically the surface gasification rate of a propellant should be done with the propellant mixture itself rather than with the individual constituents.

Summary

An apparatus has been constructed that allows simultaneous measurement of the surface regression rate and temperature of a material that is undergoing surface pyrolysis or sublimation. Energy is supplied, and the temperature is measured without appreciable obstruction of the flow of the pyrolysis products by the use of a radiantly heated porous plate. Experiments conducted thus far with ammonium chloride

and ammonium perchlorate have been analyzed. Calculated evaporation coefficients were found to be small (of the order of 10^{-3} and 10^{-2} , respectively) for the two materials. The measured pyrolysis rates of pure ammonium perchlorate, which substantiate those previously reported, were found to be much lower for a given surface temperature than corresponding burning rates recently published for ammonium perchlorate fuel mixtures. This discrepancy suggests that further work to characterize the kinetics of the surface gasification reaction of burning solid propellants be done with the propellant mixtures rather than with the constituents individually.

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