ROLE OF CONDENSED-PHASE REACTIONS IN IGNITION AND DEFLAGRATION OF AMMONIUM PERCHLORATE PROPELLANTS*

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ABSTRACT

The contribution of exothermic, condensed-phase reactions to ignition and deflagration of propellants is examined. Measurements of the rates of heat release, thermal diffusivity, burning rate and ignition are combined to demonstrate the role of reactions in propellants made up of powdered ammonium perchlorate and catalysts. By means of a theoretical analysis, it is found that for the propellants under study a thermal runaway in the condensed phase can account for the ignition phenomena observed. Also, at low steady-state deflagration rates the contribution of the solid-phase reactions can be demonstrated. Some of the propellants quenched during deflagration have shown the existence of a subsurface layer, which is located in a zone at which the temperature has reached the level characteristic of the crystal transition of ammonium perchlorate.

Introduction

Ignition and deflagration of a solid propellant involve reactions in the condensed phase, in the gas phase and at the solid-gas interface. In an attempt to elucidate the importance of the various complex reactions, such combustion phenomena as steady-state burning rate and ignition temperature as a function of different parameters have been employed. However, the conclusions reached from these experiments have not been unequivocal because of the large number of separate and interrelated processes involved, such as heat transfer to the surface of the propellant, vaporization and exothermic reaction at its surface, energy transfer into the solid, heat release in the condensed phase, mass transport and mixing of reactants in the gaseous layer and exothermic reactions in the gas phase. Particularly the dominant role of exothermic reactions in the gas phase and in the condensed phase (both homogeneous and heterogeneous) has been debated at some length by a number of authors. Two recent reviews consider in some detail the applicability of the gas- and condensed-phase propellant ignition[1] and propellant burning[2].

We have examined in some detail the potential contribution of reactions in the solid phase to ignition and deflagration of ammonium perchlorate (AP). For this purpose, we selected simulated propellants containing AP, catalysts and in several cases an additional fuel component. The kinetic measurements of exothermic heat release associated with reactions in the solid phase have been reported previously[3,4]. Determinations of (1) ignition by radiant heat sources and (2) steady-state burning were made on propellants of the same composition as employed in the kinetic studies. The contribution of condensed phase reactions to combustion is quantitatively examined in the following report on the basis of the heat-release data and energy transport parameters determined for these particular propellants.

Experimental Details

Burning-rate studies

The burning-rate measurements were carried out with pressed pellets composed of AP and various catalysts. The sample was in the form of a cylinder (28mm in diameter, 8 to 12mm in thickness) pressed at 25,000 psi. It was ignited by means of an electrically heated wire passing through the center of the pellet. With the onset of combustion, radial regression of the solid surface in the outward direction took place at a uniform rate. The burning rate of the material was determined by recording with a high-speed motion picture camera the approach of the inner surface towards the outer edge of the pellet. A Chromel-Alumel thermocouple was embedded in the pellet at a central point approximately 5mm from the outer edge of the pellet. In most experiments, the thermocouple had the following dimensions: wire diameter = 0.003 inch, thermocouple bead = 0.008 inch. However, several studies were performed with smaller thermocouples (wire diameter = 0.001 inch, thermocouple bead = 0.003 inch) in order to obtain better resolution. Coating of the thermocouple with a layer of silicon monoxide evaporated on it demonstrated that the bare thermocouples exerted no catalytic effect. This thermocouple monitored the temperature during the steady-state radial combustion of the pellet. Since the simulated propellants employed in these studies do not sustain steady-state combustion at atmospheric pressure, the propellant wafer, placed in a suitable assembly, was located inside a furnace heated to a specified temperature T_i. A typical temperature history of a sample containing ammonium perchlorate (AP) and copper chromite (CC) is shown in Figure 1.

In a number of experiments the steady-state combustion process was interrupted by rapid quenching brought about by directing a stream of carbon dioxide from a fire extinguisher into the combustion zone. In a narrow band concentric with the burning surface we observed a marked change in the physical appearance of the quenched wafer (Figure 2). In line with the observations made in similar experiments on AP single crystals[5], this subsurface layer is caused by a somewhat disorderly recrystallization of the AP crystallites from the cubic to the orthorhombic form during the quenching process. Since the phase transition of AP from the orthorhombic to the cubic form is known to occur at $513^{0}K$, measurement of the penetration distance of the subsurface layer offers a suitable temperature reference in an analysis of the experimental data.

Ignition studies

The apparatus and materials used in the ignition measurements have been described elsewhere[6]. The arc-image furnace allowed a range of incident energy fluxes up to 120 cal/cm^2sec. Special precautions were taken to obtain within a precision of ±5 per cent the ignition time, i.e., exposure time to radiant energy of a given magnitude which will result in ignition. Experimentally, the criterion for ignition was taken to be deflagration of the sample.

Experimental Results

Burning-rate measurements

Since the purpose of our experimental work is the examination of the role of exothermic condensed-phase reactions in the deflagration of solid propellants, the burning rate studies were limited to those simulated propellant mixtures for which heat-release kinetics had previously been measured. In several publications[7,8] the experimental determinations of the condensed-phase temperature profile in a burning propellant have indicated the existence of a heat-release region close to the burning surface. But interpretation of these observations in terms of condensed-phase reactions was impossible due to lack of data on the properties of these propellants.

Based on a one-dimensional conductive heat transfer analysis in a medium containing distributed heat sources, the heat balance in any plane of the combustion wave may be written as:

$$K(d^2T/dx^2) - r(dT/dx) + \dot{q}/c\rho = 0 \qquad (1)$$

where κ is the thermal diffusivity, T the temperature, x the distance coordinate (the semi-infinite slab of propellant extends $-\infty < x < 0$), r the linear burning recession rate of the surface located at $x = 0$, $\dot{q}$ the rate of temperature rise due to exothermic reaction in the condensed phase, c the specific heat and ρ the propellant density. For constant coefficients, integration of Eq. (1) yields

$$\frac{d \ln (T - T_i)}{dx} = \frac{r}{\kappa} - \frac{1}{\kappa c\rho(T - T_i)} \int_{-\infty}^{x} \dot{q}\, dx \qquad (2)$$

It is apparent, therefore, that any deviation from linearity in a plot of ln $(T - T_i)$ against x may be associated with the existence of reactions in the solid. For exothermic reactions, the integral in Eq. (2) is positive and the slope of the curve in the (T, x) phase plane decreases with the onset of heat release in the medium. In the nonreactive region, i.e., $\dot{q} \to 0$, a plot of ln $(T - T_i)$ versus x yields a straight line of slope r/κ. Therefore, from measurements of the linear recession rate and the temperature variation with distance, the thermal diffusivity of the propellant may be evaluated.

In a typical experiment (Figure 1) three distinct temperature regimes are detectable from the temperature histories of the propellant undergoing steady-state burning in the presence of catalysts. At temperatures below 513°K, the slope of the line yields a thermal diffusivity in good agreement with results obtained by another technique[9]. At temperatures above 513°K, the marked increase in the slope of the straight-line portion of the curve is associated with a pronounced decrease in the thermal diffusivity of the medium as summarized in Table 1. Finally, a region is approached where exothermic heat release becomes detectable as shown by the deviations from the straight line. The conductive heat transfer analysis has been modified to take into account a solid composed of two slabs: one with average diffusivity κ_1 (at $T < 513°K$), the other with average diffusivity κ_2 (at $T > 513°K$) with the transition temperature T_0 defining the boundary between the two adjoining slabs. Under these conditions, the heat conduction equation in the nonreactive region yields the following expression in integrated form

$$(T - \bar{T})/(T_s - \bar{T}) = \exp(rx/\kappa_2) \qquad (3)$$

where $\bar{T} \equiv T_0 - (\kappa_2/\kappa_1)(T_0 - T_i)$ and T_s is the surface temperature. By means of this analysis, the average thermal diffusivity in the region from 515 to 650°K was found to be $0.6 \pm 0.1 \times 10^{-3}$ cm²/sec.

The temperature-distance traces by themselves are unsatisfactory for establishing the surface temperature of the solid. However, for quenched samples the existence of a visible subsurface layer of measurable thickness and a temperature boundary located at 513°K provided us with the additional parameter required for calculation of the surface temperature T_s. The results of these calculations together with the pertinent experimental data derived from our measurements are given in Table 1. In Figure 3, we present a comparison of the experimental temperature profile with one calculated on the basis of Eq. (1) with inclusion of the heat-release kinetics[4]. The agreement is quite satisfactory and emphasizes the finite contribution of exothermic reaction in the condensed phase.

Ignition measurements

In order to examine the experimental ignition data for the contribution of condensed-phase exothermic reaction, a theoretical analysis was made of the nonsteady-state temperature distribution in the interior of a semi-infinite slab of material whose surface ($x = 0$) is exposed to a radiant flux of intensity I_0 for various lengths of time t. The computer solutions were obtained by the method described in reference 10. In this calculation, a moving boundary is included with endothermic reaction due to crystal-phase transition. The one-dimensional heat conduction equation applicable to this model is

$$\partial T/\partial t = \kappa(\partial^2 T/\partial x^2) + \dot{q}/c\rho$$

with the boundary conditions: $\kappa(\partial T/\partial x) = I_0/c\rho$ at $x = 0$, $T = T_0$ at $x = \infty$, and $T = T_0$ at $t = 0$. This equation is a good approximation for a body of finite absorptivity α when the parameter $\kappa\alpha^2 t > 10$. This requirement was met in our experimental conditions. For the $\dot{q}/c\rho$ term, the rate of temperature rise previously observed in adiabatic rate studies was employed[4]; for the thermal diffusivity at $T > 513^{\circ}K$, the value derived from the steady-state burning rates was used (cf. preceding section).

In Figure 4, we have plotted the theoretical surface temperature of the propellant T_s as a function of exposure time t for various radiant flux levels. The chemical composition of the propellant is 95 AP/5CC (weight per cent). The temperature rise due to exothermic chemical reaction is given by the positive deviation from the straight lines in a plot of T_s against $t^{1/2}$. The points marked on these curves as indicative of ignition are located at values of $T_s/T_s' = 1.1$ where T_s' is the surface temperature in the absence of heat release ($\dot{q} = 0$). In other words, we have chosen as a mathematical criterion for ignition that surface temperature which exceeds the nonreactive value by 10 per cent. Such a criterion may appear somewhat arbitrary at first. However, based on theoretical consideration it ensures a runaway reaction because of the experimental nature of the exothermic heat-release term.

For this propellant a comparison of experimental ignition times[6] with the theoretical values is presented in Figure 5. The agreement is quite satisfactory over a range of fluxes of radiant energy from 20 to 110 cal/cm^2 sec. In Table 2, we have given the surface temperature at time of ignition. These values are obtained from the theoretical analysis by feeding into the computer the observed ignition time for a specified radiant flux.

As required by the mathematical analysis, this gradient is equal to the ratio of the radiation flux absorbed at the surface and the thermal conductivity. The last column in Table 2 refers to the amount of energy stored in a surface layer of propellant at time of ignition. It should be noted that the energy contributed by exothermic chemical reaction represents an appreciable portion of the total energy, i.e., radiative and chemical, especially at the lower incident flux levels. At the same time, the net energy per unit area in the surface layer is less than the sum of the radiative and chemical contribution because of the endothermic nature of the phase transition which was included in these calculations as an energy sink with a moving boundary.

Discussion

The experimental results obtained and their correlation with the theoretical analyses emphasize the contribution of condensed-phase exothermic reactions in steady-state burning and ignition of the propellants examined. The condensed-phase processes may be the result of homogeneous reactions in the solid. The disappearance of nucleation as a rate-controlling step in the decomposition of AP due to the addition of catalyst[4] strongly suggests that homogeneous reactions may be involved. At the same time, the qualitative correlation between the efficiency of a catalyst for AP decomposition and ammonia oxidation may be taken as evidence for heterogeneous rate-determining processes occurring at gas-solid interfaces. Further work is required to elucidate the relative importance of each in propellant combustion.

It should be recognized that the existence of such condensed-phase reactions does not preclude gas-phase reactions as an important step in the conversion of chemical energy of the propellant to thermal energy. In ignition, for example, it is apparent that the formation of a visible flame is the result of vapor phase reaction. However, our data suggest that these reactions in the vapor phase are relatively fast and that they are controlled by the rate of generation of vaporized reactants or intermediates at the propellant surface. One may expect that with increasing total gas pressure the already rapid chemical reactions in the gas phase will be further enhanced, so that unless mixing and diffusional transport become rate-determining the exothermic runaway condition in the solid will remain the trigger for ignition. On the other hand, in the case of propellant deflagration an increase in burning rate would be expected to diminish the contribution of condensed-phase reactions because the enhanced recession rate of the propellant surface reduces the time available for exothermic heat release in the solid. However, certain compensating mechanisms may come into play as becomes evident from the data presented in Table 1. By changing the type of catalyst from iron oxide to copper chromite, the burning rate was observed to increase by a factor of two, yet the surface temperature remained practically unaltered. Similar observations were made by Powling and Smith[11] in the burning-rate studies for various AP-catalyst-fuel propellants. For our simulated propellants, the increase in burning rate in the case of AP/CC was partially counterbalanced by the enhanced rate of heat generation due to condensed-phase reactions.

Comparison of some of the physical parameters encountered during ignition and steady-state burning, such as the surface temperature and the temperature profile, indicates that these two processes result in entirely different conditions. The surface temperatures during ignition are considerably higher than those during steady-state burning (Tables 1 and 2), and the temperature gradients at the surface also exhibit similar differences for the same AP catalyst combinations. Thus ignition cannot be interpreted solely as the time required to establish the conditions prevailing during steady-state burning.

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Table 1. Results of burning-rate studies

Propellant Composition (weight per cent)	Linear Recession Rate (cm/sec)	Subsurface Layer Thickness (cm)	Temperature (°K) Initial	Temperature (°K) Surface*	Temperature Gradient at Surface* (°K/cm) x 10^{-3}
95 AP/5 Fe_2O_3	1.83 ± 0.03 x 10^{-2}	0.120	503	673	4.2
			508	595	2.4
95 AP/5 CC	4.07 ± 0.14 x 10^{-2}	0.054	503	675	8.9
			508	592	5.5
97 AP/3 CC	3.13 ± 0.15 x 10^{-2}	0.065	503	635	7.0
			508	574	3.3

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* Computer solution.

Table 2. Physical parameters at ignition
[Propellant: 95 AP/5CC (weight per cent)]

I_0 (cal/cm^{2}sec)	t_i (sec) exptl.	t_i (sec) calc.	T_s (^{0}K)	Energy (cal/cm^2) Radiant	Exothermic	Net*
22	0.124	0.117	800	2.35	0.67	2.37
43	0.040	0.033	824	1.37	0.16	1.35
80	0.015	0.011	856	0.78	0.07	0.75
110	0.0097	0.007	870	0.65	0.05	0.62

* Net surface energy density includes the heat consumed in the endothermic phase transition.

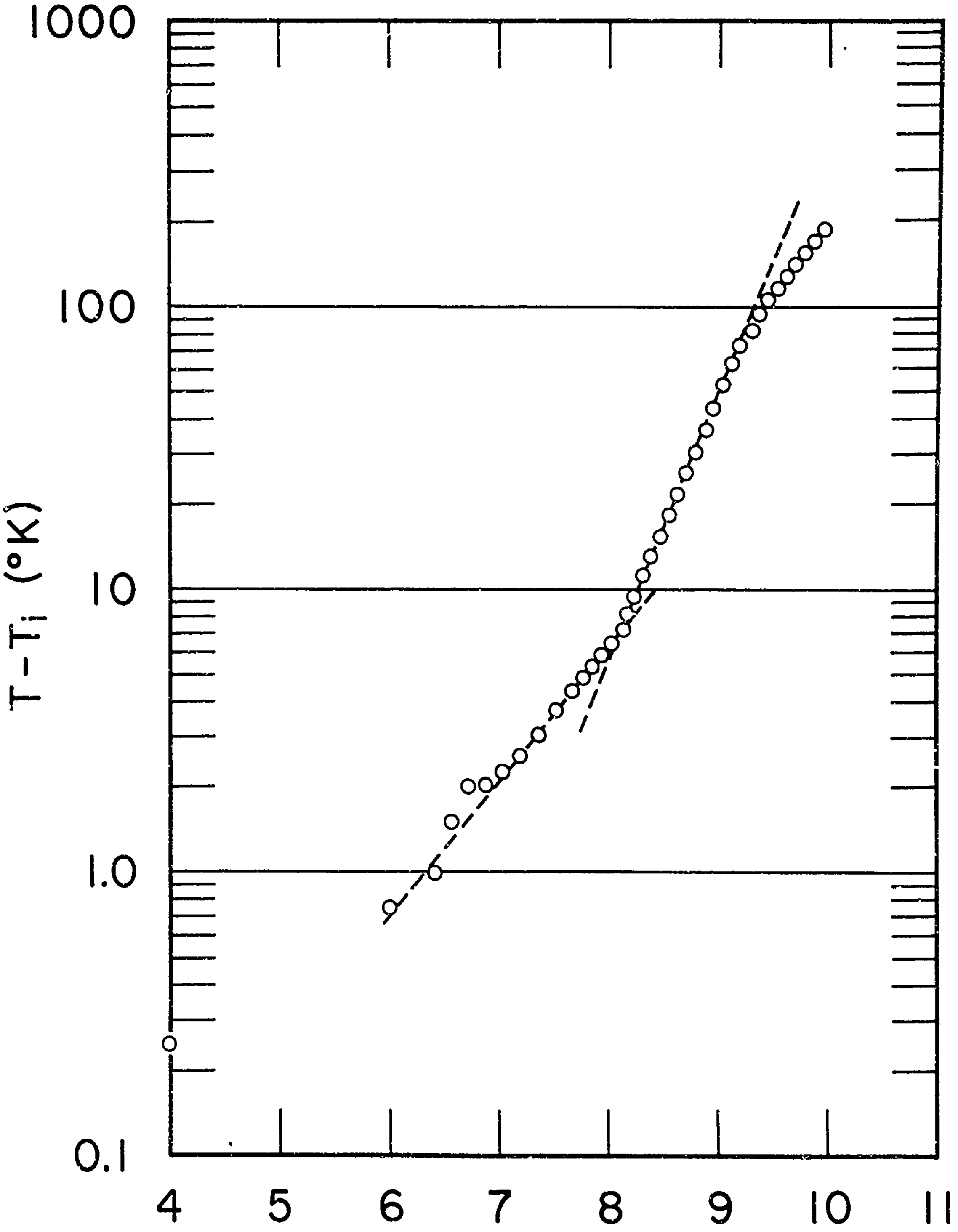

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FIG. 1 TEMPERATURE PROFILE DURING STEADY-STATE DEFLAGRATION OF PROPELLANT [composition: 95 AP/5CC (weight per cent); initial temperature: T_i 504° K; radial burning rate: 4.0×10^{-2} cm/sec]

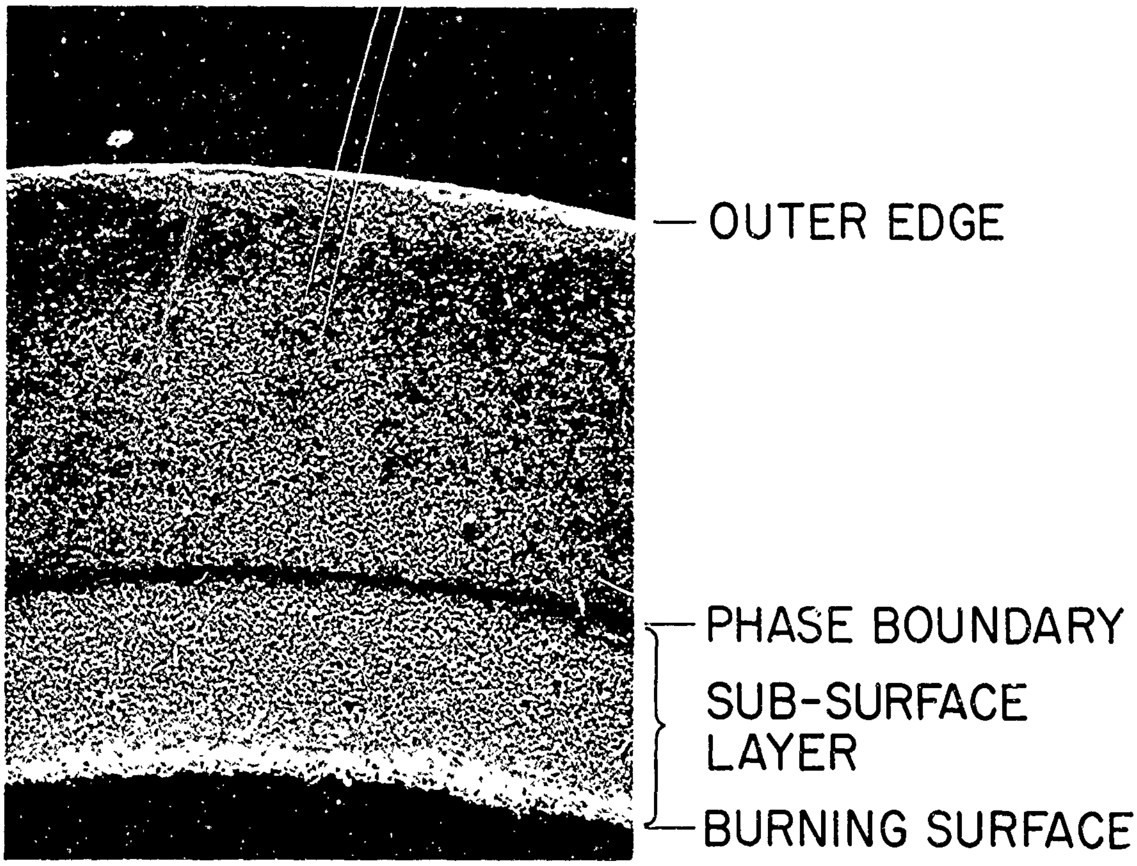

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FIG. 2 PROPELLANT QUENCHED DURING STEADY-STATE DEFLAGRATION [composition: 95 AP/5Fe_2O_3 (weight per cent)]

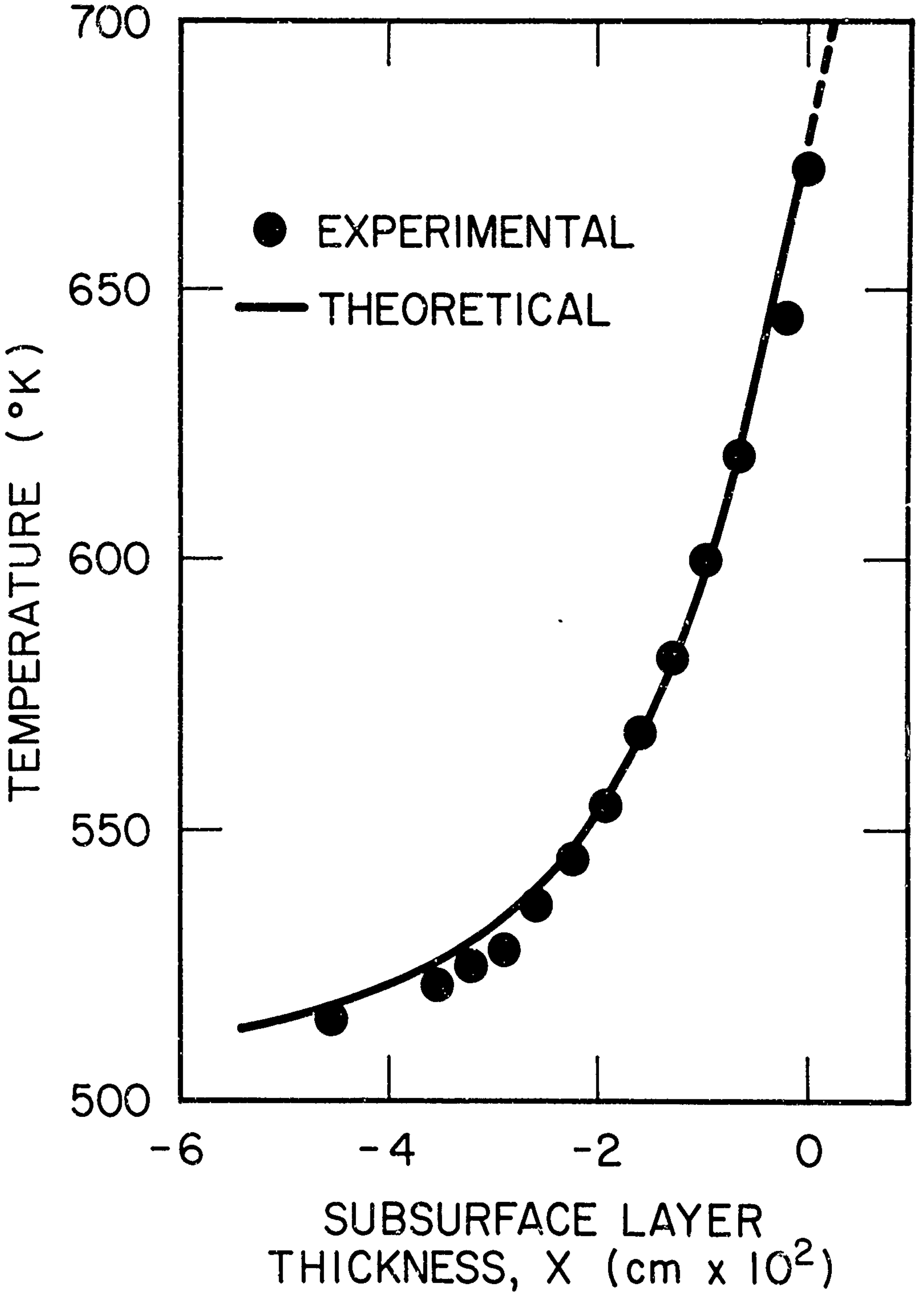

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FIG. 3 COMPARISON OF EXPERIMENTAL AND THEORETICAL TEMPERATURE PROFILE

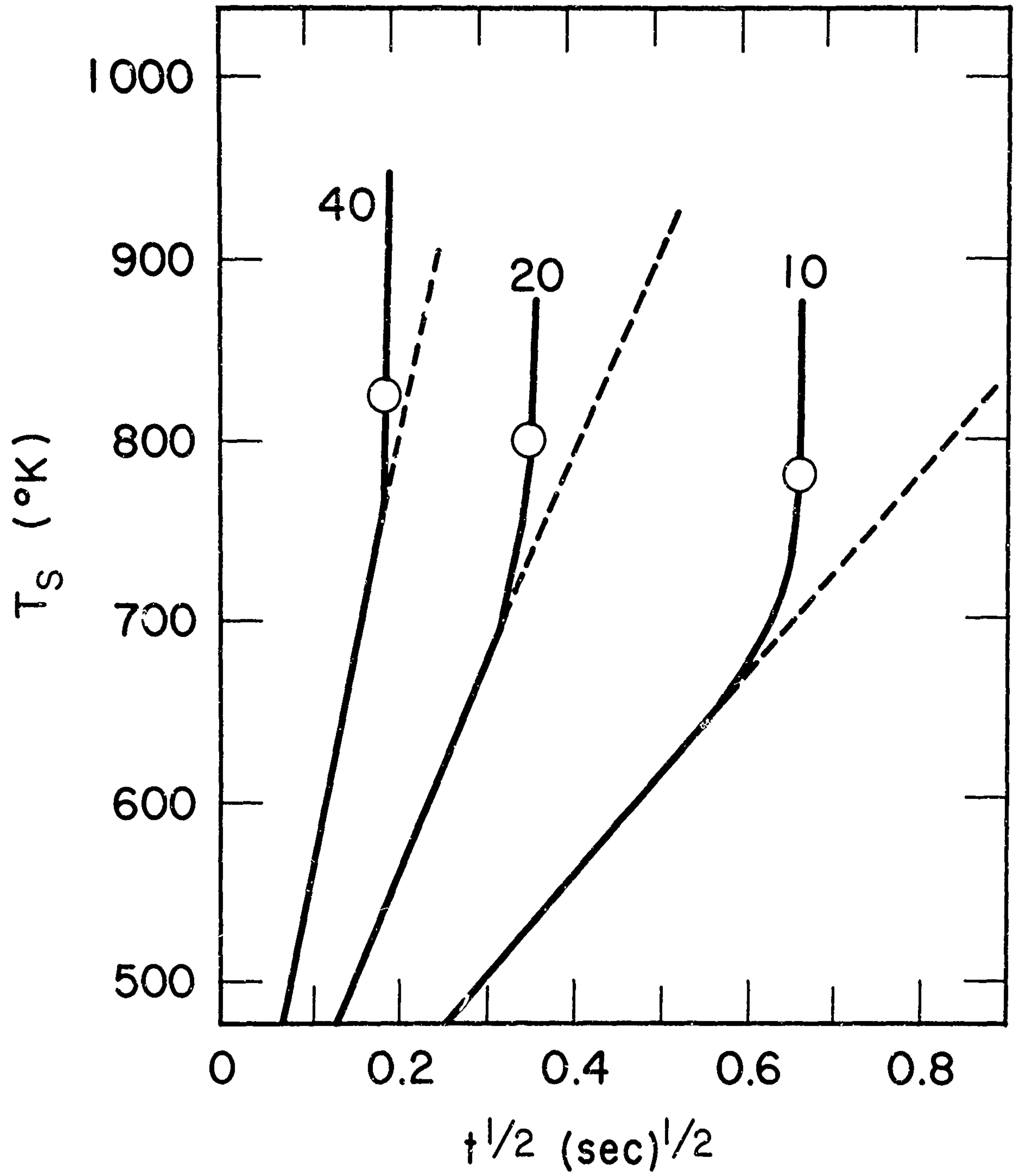

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FIG. 4 SURFACE TEMPERATURE OF PROPELLANT AS A FUNCTION OF EXPOSURE TIME TO RADIANT FLUX [composition: 95 AP/5CC (weight per cent)]

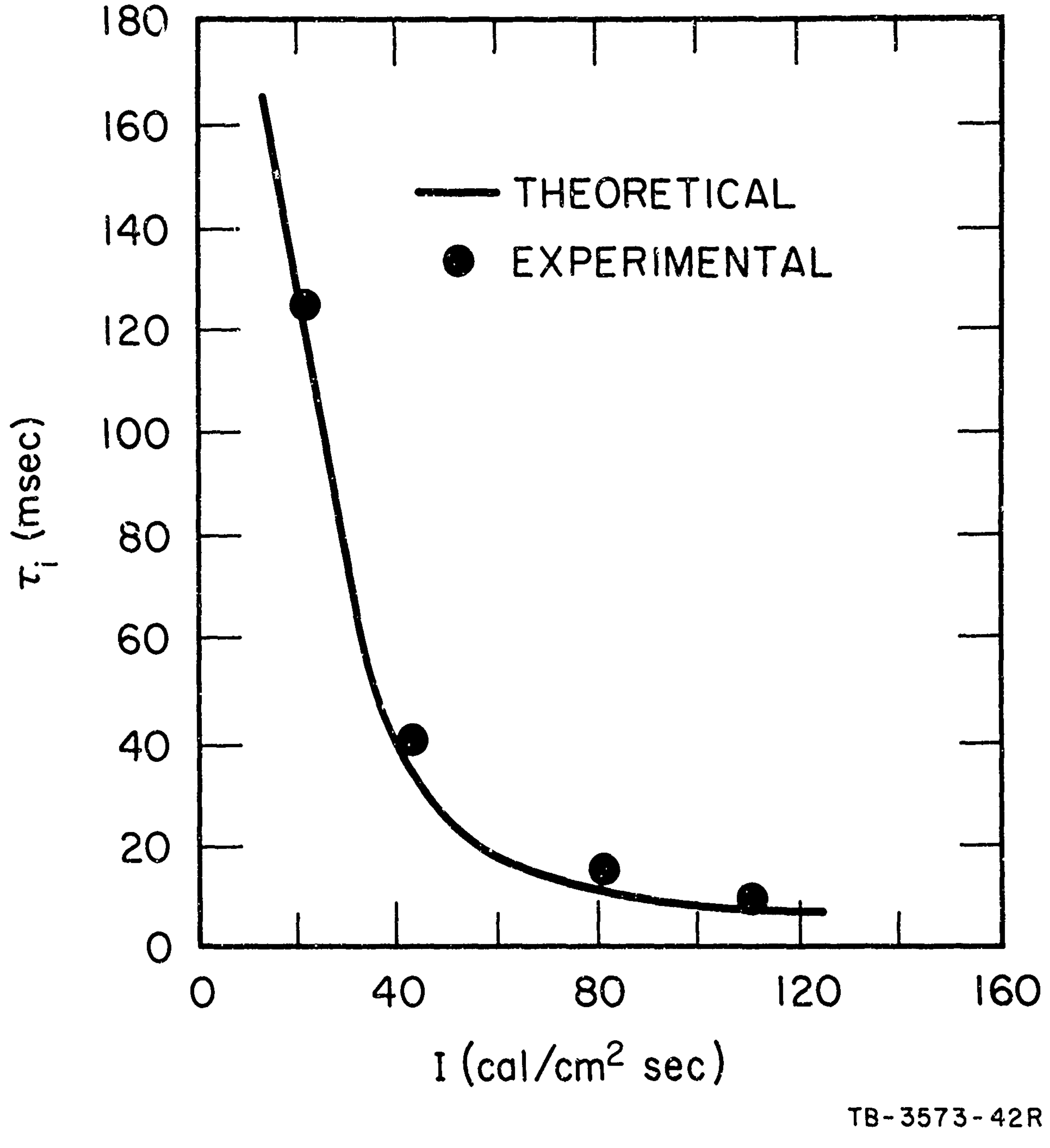

FIG. 5 IGNITION TIME AS A FUNCTION OF RADIANT FLUX [composition: 95 AP/5CC (weight per cent)]

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13. ABSTRACT

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