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COMBUSTION OF BORON PARTICLES AT ELEVATED PRESSURES

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

Combustion of single boron particles, about 75μ in diameter, from a crystalline powder sample has been studied. Particles were ignited by being dropped through a focused laser beam in several oxidizing gases over a range of pressures. In pure oxygen, in air, and in O_2/Ar(20/80), particles were merely preheated to a temperature about 2000°K; ignition took place spontaneously after a measurable induction period. Quantitative values of both the induction period and the subsequent self-sustained combustion period are listed. In air and in the O_2/Ar mixture the burning times decrease from about 45 msec to about 20 msec as the pressure is increased from 1 to 35 atm. In pure O_2 at atmospheric pressure the total burning time is only 6.8 msec. In pure CO_2 and in O_2/N_2(7/93) there is no induction period, no self-ignition, and no steady-state combustion; particles must be brought to a burning regime by an external energy flux, and they are able to maintain that regime for only a limited time before extinguishment.

It is shown that the classical theory of ignition and combustion can account for all three observed burning modes: metastable surface reaction during the pre-ignition period, rapid self-sustained diffusion-combustion, and decaying combustion. Previously reported reaction-rate and ignition-limit data are used for quantitative estimates of parameters pertaining to the three regimes.

LIST OF SYMBOLS

d - particle diameter (cm)

f_D - diffusive flux (cal/cm^{2}sec)

f_L - thermal flux (cal/cm^{2}sec)

f_R - reactive flux (cal/cm^{2}sec)

k - surface reaction rate constant (cm/sec)

n - order of reaction (dimensionless)

t - time (sec)

v - surface reaction rate (mole/cm^{2}sec)

y - partial pressure of oxidant (atm)

A - pre-exponential rate factor (mole/cm^{2}sec)

D - diffusion coefficient (cm^2/sec)

E - activation energy (cal/mole)

Nu - Nusselt number (dimensionless)

Q - heat of reaction (cal/mole)

T - temperature (°K)

Z - pre-exponential rate factor (cm/sec)

α - Sherwood number (dimensionless)

ε - radiant emissivity (dimensionless)

λ - thermal conductivity coefficient (cal/cm degsec)

σ - Stefan-Boltzmann constant (cal/cm^{2}deg^{4}sec)

SUBSCRIPTS

b - burning (steady state)

i - ignition

∞ - gas phase far from particle

I. INTRODUCTION

During the last decade several studies of combustion of boron have been reported in the literature. Three earlier experimental studies are directly relevant to the program reported herein.

Talley and Henderson(1) burned boron cylinders, several centimeters in diameter, in various oxidizing gases at room temperature and at relatively low pressures (0 to 5 atm). They reported quantitative surface reaction rate data both in pure and in moist oxygen over a wide range of temperatures. Addition of water vapor to oxygen was found to increase drastically the reaction rate.

More recently, we reported on ignition and self-sustained combustion of small (30-50μ diameter) single particles of crystalline boron(2). The work was done by a flat-flame burner technique in which particles are burned at atmospheric pressure, but at elevated gas temperatures (2000 to 3000°K). The main results of that work were that ignition temperatures of boron were found to be between 1900 and 1950°K in dry gases, but somewhat lower in moist gases. It was also found that burning rates of particles corresponded roughly to calculated rates of gas-phase diffusion of oxidants from the surroundings to the particle surface.

Uda reported on work done with boron particles ranging in diameter from 30 to 50μ by means of a shock-tube technique(3). It was found that the ignition temperature of boron in air at atmospheric pressure was about 1900°K, in excellent agreement with our flat-flame burner data. The ignition temperature was found to decrease to about 1500°K as the air pressure increased to 15 atm.

The experimental technique described in this paper differs essentially from the previous efforts. Boron particles are ignited by being dropped through a focused laser beam in arbitrary oxidizing atmospheres at arbitrary pressures. This paper deals with combustion experiments with a sample of crystalline boron powder having average particle diameters of about 75μ. Testing was done in pure oxygen, nitrogen-oxygen mixtures, an argon-oxygen mixture, and pure carbon dioxide, at several pressures ranging from 1 to 35 atm.

II. APPARATUS AND EXPERIMENTAL PROCEDURE

The experimental facility consists of a carbon-dioxide gas laser (Coherent Radiation Laboratories, Model 40), and a high-pressure reactor with the associated equipment. The output wavelength of the laser is 10.6μ, and its radiant power is 35 cal/sec over an area of about 1 cm^2. In most experiments the beam was focused down to about 0.5 mm, at which point the radiant flux intensity was of the order of 10^4 cal/cm^2 sec.

A schematic representation of the reactor is shown in Figure 1. The reactor is a vertically positioned stainless-steel cylinder 40cm long and having an inner diameter of about 3cm. When relatively high flow-velocities of gases in the reactor were desirable, the inner diameter was narrowed down by inserts. For observation purposes a quartz window runs almost over the entire length of the reactor.

The particle-dispensing device is located inside, near the top of the reactor. The main part of the dispenser is a vibrating diaphragm from which single particles of the powder are dropped in a cascading fashion into a hypodermic needle, and thence into the laser beam immediately (ca. 1mm) underneath. Sufficent powder can be introduced into the dispenser before pressurization for prolonged continuous operation of the system.

The laser beam enters the reactor horizontally through a lens of 10cm focal length, which closes off a side-arm of the reactor. The lens is made of IRTRAN-4 (Kodak), a material which is stated to transmit 85% of the laser radiation. A concave mirror of the same focal length is inside another side-arm, located directly opposite the lens. The laser beam, having traversed the reactor, is reflected back into its focus. Thus the particle fed into the focus is exposed to radiant flux from two directions.

During the tests it was desirable to have a continuous downward flow of the oxidizing gas, which was therefore introduced at the top and removed at the bottom of the reactor. A mesh-screen was placed inside the reactor about 0.5cm above the laser beam to break up turbulence. Gas velocities were usually 50 to 100 cm/sec. Igniting and burning particles were thus entrained in a laminar gas flow.

Boron powder used in this program was pure crystalline material screened between 62 and 88μ; thus the average particle diameter was roughly 75μ. Since the particle-diameter effect was not studied, no effort was made to ascertain the exact average diameter. Simple energy-absorption estimates indicate that boron particles of that size, exposed to our focused laser beam, should heat up at the rate of several thousand degrees per millisecond. Indeed, we found experimentally that the time necessary to heat particles to a temperature of roughly 2000°K. (see Sections III and IV) was always less than 1 msec. It must be pointed out here that residence times of different particles in the beam, and therefore the amounts of radiant energy absorbed by particles, are not uniform. This is so, because there is no assurance that each particle traverses the center of the beam, and a grazing traverse will evidently lead to a relatively small absorption of energy. But whatever the exact residence time in the beam, this time was always negligible compared to the subsequent self-sustained combustion which usually persisted for 10 to 100 msec.

The phenomena of ignition and combustion were observed by photographic time-exposures with a magnification factor of 1.5 on the negative. Burning times were measured by interposition of a stroboscopic disk (2,860/sec -- see Reference 2) between the camera and the particle. The accuracy of individual determinations was usually $\pm$ 0.5 msec.

III. RESULTS

Combustion of boron particles was studied in the following five oxidizing gases: pure oxygen, pure carbon dioxide, air, a mixture consisting of 7% oxygen and 93% nitrogen, and a mixture consisting of 20% oxygen and 80% argon.

We found that in pure oxygen, in air, and in the oxygen-argon mixture the laser beam may be used merely to preheat the particle to a temperature at which a relatively slow surface reaction is initiated. Ignition, evinced by transition from a dull glow to a bright flame, takes place spontaneously only after a measurable induction period. The feature of spontaneous ignition taking place substantially after the particle has emerged from the laser beam is very important, because it allows the particle to ignite and to burn freely in a self-sustained flame without being force-burned in an external radiant flux for any period of time. Thus it appears likely that the exact mode of ignition, even if it does affect the pre-ignition induction period, will not affect the subsequent combustion (see below). The feature also removes all uneasiness about the effect of unusual excited species which the intense laser radiation may conceivably generate in the ambient gas.

The effect of pressure on the induction period t_i is curious. At low pressures, up to about 10 atm, t_i is relatively short and fairly reproducible from particle to particle in a given gaseous environment. At higher pressures, on the other hand, the average value of t_i increases very substantially. Even more striking, the individual values of t_i become highly non-uniform. These effects are illustrated in Figures 2 and 3, which show photographs of burning boron particles in an oxygen-argon mixture at 7.8 and 35.0 atm respectively. Uniformity of post-ignition burning times t_b in both

photographs stands in sharp contrast to the wide scatter of induction periods evident in Figure 3. The cause of the scatter has not been ascertained. An obvious explanation is to ascribe it to the parameter which is known to be uncontrolled, namely the residence time of the particle in the laser beam.

Results of particle combustion in the two weak oxidizing atmospheres, pure CO_2 and $O_2/N_2(7/93)$, are markedly different. Visible burning traces in these mixtures are so short that they can be explained only by incomplete combustion. It is also most interesting that in these mixtures there is no induction period and no self-ignition: boron particles must be brought to a burning regime by an external energy flux, and they are able to maintain that regime only for a limited time before extinguishment. Important implications of this result will be discussed in Section IV.

Quantitative induction and burning-time data obtained in five different gases at varying pressures will now be detailed.

a. Oxygen/Argon (20/80)

Combustion of single boron particles was studied at four different pressures: 1.0, 7.8, 21.4, and 35.0 atmospheres. As explained above, two readings were made: t_i, measuring the period from the laser beam to self-ignition; and t_b, measuring the subsequent period of bright burning. The data are collected in Table I, which lists average values of t_i and t_b obtained from records similar to those shown in Figures 2 and 3. The number of particles from which the averages were computed is listed in the second column.

Results at 1.0 and 7.8 atm conform to the pattern of Figure 2, i.e., values of both t_i and t_b are reasonably uniform. Deviations given in the third and the fourth columns are probable errors for averages at the 95% confidence level. Results at 21.4 and 35.0 atm show approximately the same reproducibility for t_b, but values of t_i are essentially random:

at 21.4 atm, they range from 11 to 47 msec; at 35.0 atm, they range from 6 to 113 msec! These results, of course, are not surprising in view of the appearance of Figure 3. No deviations are therefore listed for $\bar{t}_i$ at 21.4 and 35.0 atm.

b. Air

Data for combustion in air are listed in Table II. Total pressures, again, ranged from 1.0 to 35.0 atm. The results are quite analogous to those given in Table I, but the values of $\bar{t}_b$ are somewhat higher, and the scatter of the data is wider.

c. Oxygen

Combustion in pure oxygen was studied at 1 atm only. Reproducibility of both t_i and t_b was found to be very good. The data are collected in Table III.

d. Carbon Dioxide

As explained previously, the pattern of combustion in CO_2 and in oxygen-deficient mixtures is quite different from patterns described in Sections III a-c, since only one brief stage is visible.

The data for CO_2 are collected in Table IV. Comparison with Tables I and II makes it clear that these are only partial burning times. In addition, we observed that the duration of combustion depends somewhat on the flow-velocity of the gas in the reactor. (Such a dependence was not observed in any of the tests with oxygen-rich gases, the results of which are listed in Tables I-III). Two series of tests, in which the flow-velocity differed by a factor of two, were therefore run at each of the three pressures. At 1.0 and at 7.8 atm, the burning times at the low flow velocities are substantially longer. The difference does not appear at 4.4 atm, but the data are few and fairly scattered, especially at low flow velocity, so that no firm conclusion can be drawn.

e. Oxygen/Nitrogen (7/93)

The data are collected in Table V. As in the case of the results obtained in carbon dioxide, these are one-stage data representing partial combustion. While the calculated deviations indicate that all four entries are not statistically identical, the average burning times do not vary much with pressure.

IV. DISCUSSION

The data presented in Section III reveal three distinct modes of combustion of boron particles. The classical combustion theory accounts for these different modes, and sufficient quantitative information is available for an approximate determination of fundamental parameters (temperatures, reaction rates) governing all three modes. The theory, of course, can retain its simplicity only when dealing with spherical particles. The following treatment assumes that our boron particles are equivalent to spherical particles of diameter d. It is important to emphasize that the exact numerical value of d is not crucial.

The theory can be conveniently formulated in terms of three energy fluxes (4,5). When a spherical particle is maintained by reactive self-heating at a temperature exceeding the ambient gas temperature, the rate of its heat loss is:

$$f_L = \frac{Nu\ \lambda}{d} (T - T_\infty) + \varepsilon \sigma T^4 \qquad (1)$$

where λ is thermal conductivity and T_∞ the ambient gas temperature; other symbols have their usual meanings. The rate of heat generation at the surface is:

$$f_R = Q\ v = Qky^n \qquad (2)$$

where v is the actual rate, k is the specific reaction rate, y is the partial pressure of the gaseous reactant (oxidant) just above the surface, and Q is the heat of reaction. The mass flux of oxidant to the surface is equivalent to an energy flux

$$f_D = \frac{\alpha\, DQ}{dRT} \quad (y - y_\infty) \qquad (3)$$

where D is the diffusion coefficient; α is 2 in a stagnant regime, and it increases with the Reynolds number. Steady-states obtain when $f_L = f_R = f_D$.

The general form of the solution is sketched graphically in Figure 4, where curves $f_L = f_R$ and $f_L = f_D$ are shown in the y-T plane. For a given set of ambient conditions y_∞ and T_∞, steady-states are given by intersections of the two curves. Depending on the specific values of y_∞ and T_∞, there may be either one or three intersections. Curves are dotted in the regions where quantitative data are not available for boron particles. At low temperatures the lines $f_L = f_D$ are straight, but as temperature increases they begin to curve for two reasons: heat loss by radiation becomes substantial, and the value of Q decreases because of dissociation of the reaction product.

When the ambient temperature is low compared to temperatures at which significant surface reaction takes place, as in our present application, the conditions are represented by Figure 4A. Two different cases, both physically realistic, are possible.

(a) If $y_\infty > y_c$ there are three steady states. The upper state ($T = T_F$, $y \sim 0$) and the lower state ($T \sim T_\infty$, $y \sim y_\infty$) are stable, the intermediate state ($T = T_M$) is metastable. Thus if the particle is immersed in a gas at $T = T_\infty$ and $y_\infty = y_1$ it will continue to stagnate at the lower steady state, virtually indistinguishable from the point $y = y_\infty$, $T = T_\infty$. If, by whatever means, its temperature is raised above T_M, it will find its way to the upper, diffusion-controlled steady state.

(b) If $y_\infty < y_c$ there is only one, trivial, steady state near the abscissae. A particle pre-heated to any temperature along the line $f_L = f_D$ based at $y_\infty < y_c$, must tend toward extinction.

In what follows it will be shown that realistic temperature and reaction rate data can be obtained from the available experimental information to account in an approximate, but quantitative, way for three observed combustion modes of boron: the bright combustion in O_2, in air, and in O_2/Ar(20/80), which corresponds to the upper steady state in Figure 4A; the weak pre-ignition reaction in these oxidizing gases, which corresponds to the metastable state; and the combustion in O_2/N_2(7/93) and in CO_2, which is an unstable (decaying) regime corresponding to $y_\infty = y_2 < y_c$.

a. The Kinetic Parameters

The most important parameter requiring quantitative determination is the surface reaction rate preceding ignition. According to previous interpretations (1, 2) the surface reaction will take place in the presence of a liquid layer of B_2O_3; thus the surface temperature will be below the boiling point of B_2O_3 (2316°K). Talley and Henderson (1) found that surface oxidation, even in the presence of pure oxygen at 1 atm, becomes appreciable only above about 1500°K, thus bracketting the range of interest between 1500 and 2300°K. Further, Maček and Semple(2) and Uda(3) found that the ambient gas temperature (1 atm total, y=0.2-0.4 atm O_2) necessary for ignition of boron particles is about 1900°K. Thus, the particle temperature even in the case of such high ambient temperatures is near 2000°K. In the case of combustion at low ambient temperatures, which is the experimental condition of the present study, the particle surface temperature just below ignition must be somewhat in excess of 2000°K (see Section IVb for a closer estimate).

Since throughout the pre-ignition reaction described in Section III, the particle surface is no doubt near the ignition temperature (indeed, any brightening of the particle trace leads to immediate ignition), we shall now compute the heat loss of the particle in the pre-ignition stage by means of Equation 1 assuming that its surface temperature is 2000°K.

Other parameters in the equation are known: T_∞ = 300°K, d = 7.5×10^{-3}cm, Nu$\sim$2.5, and thermal conductivity of air at the logarithmic mean between 300 and 2000°K is $\lambda = 1.6 \times 10^{-4}$ cal $cm^{-1} deg^{-1} sec^{-1}$. The rate of heat loss then is 80 cal/cm^2sec by convection and 11 cal/cm^2sec by radiation (for ε=0.5). The corresponding rate of the surface reaction, $2B(c) + 3/2\ O_2(g) \rightarrow B_2O_3(g)$, Q = 135 kcal/mole O_2, required to keep the particle at constant temperature is

$$v = 7 \times 10^{-4} \text{mole } (O_2)/cm^2\text{sec} = 1{,}300 \text{ mg}/cm^2\text{min}.$$

The rate so calculated evidently is not the result of any assumed form of temperature dependence (such as the Arrhenius equation); moreover, it does not depend in any significant way on the assumed value of surface temperature. The rate is roughly proportional to surface temperature, so that an assumed change of that temperature as large as 500° would change the calculated rate only by about 25%. The particle-diameter effect is equally insignificant. We conclude that this rate is a good experimental estimate of the actual reaction rate during the pre-ignition stage.

Utilization of the data of Talley and Henderson (1) allows further quantitative calculations. These investigators found that in the temperature range of 1500 to 2300°K, the oxidation rate is

$$v = Ae^{-E/RT} \tag{4}$$

where E = 77kcal/mole, corresponding to the heat of vaporization of B_2O_3, and $A = 1.3 \times 10^{10} mgO_2/cm^2min = 7 \times 10^3 mole/cm^2sec$. These values were found valid for oxidation rate through a fairly thick oxide layer in 1 atm of oxygen.

If one now assumes for the sake of concreteness that the surface reaction rate is proportional to the concentration of oxygen in the gas, $[O_2] = y/RT$, Equation 4 can be rewritten:

$$v = k[O_2] = Z[O_2]e^{-E/RT} \text{mole}/cm^2\text{sec} \tag{4a}$$

The numerical value of Z from Equations 4 and 4a is 1.3×10^9cm/sec. If a

different oxidant-concentration dependence were assumed, the dimension and numerical value of Z would differ, but the qualitative discussion below would remain analogous.

The exponential dependence of the reaction rate on temperature allows an analytical definition of self-ignition, which will occur if T_∞ is sufficiently high. The y - T relationship for a system having such a high value of T_∞ (i. e. a value at which the surface rate is substantial) is depicted in Figure 4B. The portion of the graph to the left of $y_\infty = y_3$ is entirely analogous to Figure 4A, and its significance has already been discussed. However, in the case of high T_∞, a new possibility arises. A particle introduced into a gas with $T = T_\infty$ and $y_\infty > y_3$, has only one steady state available to it, namely that at $T = T_F$. Evidently, $T = T_\infty$ and $y_\infty = y_3$ are critical ambient conditions for self-ignition. (In principle, a peninsula, bounded by $f_R = f_L$, exists also in Figure 4A, but the corresponding hypothetical value of y_3 would be so immensely large that it is not practical to speak about it.)

In view of the fact that, at ignition (tip of peninsula in Figure 4B), the partial pressure of oxygen at the surface is virtually the same as in the gas phase, a simplified theory neglecting diffusion is entirely satisfactory for determination of ignition conditions (6). These conditions are given by $f_L = f_R$ (Equ. 1) and $df_L/dT = df_R/dT$ (equ. 5):

$$\frac{Nu\ \lambda}{d} + 4\varepsilon\sigma T^3 = QA\frac{E}{RT^2}\, e^{-E/RT} \qquad (5)$$

Phenomena which follow ignition, discussed briefly in Section IVc, of course, depend crucially on gas-phase diffusion of oxygen, and cannot be described by Equations 1 and 5 alone.

Since measured self-ignition temperatures for boron particles from two entirely different experimental techniques are in excellent agreement,

Equation 5 can be compared with the experiment. According to both Reference 2 and Reference 3, 0.2 atm of O_2 at 1 atm total pressure demands a T_∞ of 1900 - 1950°K for self-ignition of particles 30 - 50μ in diameter. When the numerical parameters from Equation 4 are substituted into Equation 1 and 5, the gas temperature necessary for ignition is T_∞ = 2070°K, i. e. it is about 150° too high; the corresponding particle temperature is 2190°K. Conversely, if one specifies the value of T_∞ necessary for ignition to be 1900 - 1950°K (experiment), the theory demands a surface rate about 4 times higher than that given by Equation 4. This is not unreasonable, because Talley and Henderson(1) report having observed a liquid oxide layer up to 10μ thick covering the surface. (The layer thickness was found to be invariant with time at a constant temperature, but it presumably varies with the temperature.) In the case of small particles used by Uda(3), and Maček and Semple(2), it is reasonable to expect a thinner layer and a higher oxidation rate.

b. The Pre-Ignition Regime

Experimental results described in Section III show that heating of boron particles in the presence of sufficient amounts of oxygen in the gas phase initiates a metastable regime, which, as a rule, changes spontaneously into rapid high-temperature combustion. We suggest here that this metastable state corresponds to the point T_m in Fig. 4A. We shall also show now that a rough estimate of the temperature during the metastable pre-ignition regime can be made on the basis of data discussed in Section IVa.

Two numerical values obtained in Section IVa are of relevance. First, it was shown that, whatever the actual rate function, an oxidation rate of 7×10^{-4} mole O_2/cm^2sec is required to keep the particle at a steady state. Second, if one assumes the temperature dependence found by Talley and Henderson (1), the rate function consistent with the independently determined experimental ignition data (2,3) is $v = 3 \times 10^4 e^{-E/RT}$ mole/cm^2sec (i.e. four times the value given in Equation (4). Equating the two values, one obtains a

steady-state (metastable) pre-ignition temperature of about 2200°K, which appears reasonable.

It must be strongly emphasized that these quantitative estimates are reasonable largely because they are in fact only small extrapolations of direct experimental measurement of ignition conditions. Equation (4) certainly should not be used indiscriminately for calculations of boron particle surface temperature, oxidation rate, etc. The reason is twofold. First, as mentioned previously, these rate data were obtained in the presence of an oxide layer of considerable thickness which one cannot expect to be matched in particle-ignition experiments. Second, the rate data were obtained in 1 atm of O_2, and the effect of oxygen pressure (partial or total) on kinetics is not known. Therefore, no quantitative estimates will be made for either reaction rates or pre-ignition temperatures at elevated pressures. Qualitatively, one should expect the rate to increase and the pre-ignition temperature to decrease with increasing partial pressures of oxygen. There is sound experimental support for that statement: first, direct measurement in air shows lower ignition temperatures at high pressures (3); second, an inspection of our high-pressure photographs, such as Figure 3, shows very weak pre-ignition streaks persisting for long times (up to 100msec), suggesting metastable states at relatively low temperatures.

c. Decaying Combustion

Inspection of Figure 4A shows that once the curve $f_R=f_L$ is defined, the critical value y_c, below which there can be no self-sustained combustion, can be calculated. For T_∞ = 300°K, d = 75μ, and the first-order rate parameters given in Section IVa, a value of the order of 0.1atm O_2 is obtained for y_c. Experimentally (see Tables II and V), we found that, at 1 atm total pressure, 0.20 atm of oxygen will sustain combustion, but 0.07 atm will not. While this close agreement of theory with the experiment may well

be fortuitous --- indeed, a quest for quantitative agreement would be out of place at the current knowledge of rate parameters --- it is important to note that the theory does predict a critical value y_c, and therefore it offers a logical explanation of failure of boron particles to sustain combustion in atmospheres containing small amounts of oxygen.

d. Steady-State Combustion

The upper intersection in Figure 4A and B corresponds to rapid steady-state combustion controlled by diffusion. This regime has previously been studied in far more mechanistic detail than that afforded by the phenomenological sketch of Figure 4. The general theory for a number of metals was treated by Brzustowski and Glassman(7); specific burning rate data for boron, obtained in hot ambient gases, were discussed by Macek and Semple(2). Only a brief comparison of our new results with the data of Reference 2 will be made here.

It was found previously(2) that the observed burning rates of crystalline boron particles, ca. 40μ in diameter, were about twice higher than the estimated rates of diffusion of oxygen from the surrounding gases to the surface. Two possible explanations were suggested: (a) carbon dioxide, present in large amounts, could be responsible for increased burning rates; (b) gas-phase reactions of volatile intermediates with incoming oxidants could enhance the burning rate.

Our current data (Section III, Tables I and II) again show burning rates higher than estimated diffusion rates by a factor of 2 to 2.5. Since no oxidants other than oxygen were present, the first of the two previous explanations does not apply, and this fact makes the hypothesis of a combustion mode taking place partly in the gas phase even more probable. In addition, an accelerating effect due to the particle velocity relative to the gas should be expected (the calculation in Ref. 2 was made for a stagnant system in accordance with the experimental conditions). A particle of about 75μ diameter falling in the field of gravity has a Reynolds number of about unity, so that the coefficient α in Equation 3 will be 2.5 to 3.

Inspection of Tables I and [illegible] also shows a small but clear increase of burning rates with increasing pressure (about a factor of 2 over a 35-fold pressure increase). According to the simple theory, diffusion rates should be invariant with pressure. A gradual change of mechanism (e.g. of relative contributions of various gas species instrumental in combustion) with pressure appears possible, especially in view of the fact that the flame temperature T_F no doubt increases with pressure.

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TABLE I

Combustion in O_2/Ar(20/80)

Pressure (atm)	No. Particles	$\bar{t}_i$ (msec)	$\bar{t}_b$ (msec)
1.0	19	7.3 ± 0.9	41.3 ± 2.7
7.8	23	8.4 ± 0.9	34.3 ± 2.6
21.4	28	24	28.5 ± 2.5
35.0	22	70	20.5 ± 1.7

TABLE II

Combustion in Air

Pressure (atm)	No. Particles	$\bar{t}_i$ (msec)	$\bar{t}_b$ (msec)
1.0	33	5.0 ± 1.7	50.0 ± 5.6
7.8	29	5.3 ± 1.0	40.8 ± 4.1
21.4	16	26	39.6 ± 5.8
35.0	24	71	21.6 ± 2.2

TABLE III

Combustion in Oxygen

Pressure (atm)	No. Particles	$\bar{t}_i$ (msec)	$\bar{t}_b$ (msec)
1.0	40	1.8 ± 0.2	6.8 ± 0.5

TABLE IV

Combustion in CO_2

Pressure (atm)	Flow Velocity	No. Particles	$\bar{\tau}_b$* (msec)
1.0	Low	14	2.5 ± 0.3
1.0	High	7	1.0 ± 0.4
4.4	Low	9	4.7 ± 1.8
4.4	High	16	4.7 ± 1.0
7.8	Low	25	15.1 ± 1.8
7.8	High	39	9.4 ± 1.2

*Partial (decaying) combustion

TABLE V

Combustion in O_2/N_2(7/93)

Pressure (atm)	No. Particles	$\bar{t}_b$ *
1.0	21	16.8 ± 1.7
7.8	22	13.6 ± 1.1
21.4	28	18.6 ± 2.3
35.0	60	14.5 ± 1.1

*Partial (decaying) combustion

LEGENDS FOR FIGURES

Figure 1. The high-pressure reactor.

Figure 2. Photograph (time-exposure) of six single boron particles ca. 75μ diameter, ignited by laser, in O_2/Ar(20/80) at 7.8 atm total pressure. Superposed stroboscope frequency: 2,860/sec.

Figure 3. Photograph of 26 single boron particles ca. 75μ diameter, ignited by laser in O_2/Ar(20/80) at 35.0 atm total pressure. Superposed stroboscope frequency: 2,860/sec.

Figure 4. Theoretical representation of fluxes determining ignition and combustion of spherical boron particles: f_L - conductive flux; f_D - diffusive flux; f_R - reactive flux.

A. Low ambient temperature T_∞.

B. High ambient temperature T_∞.

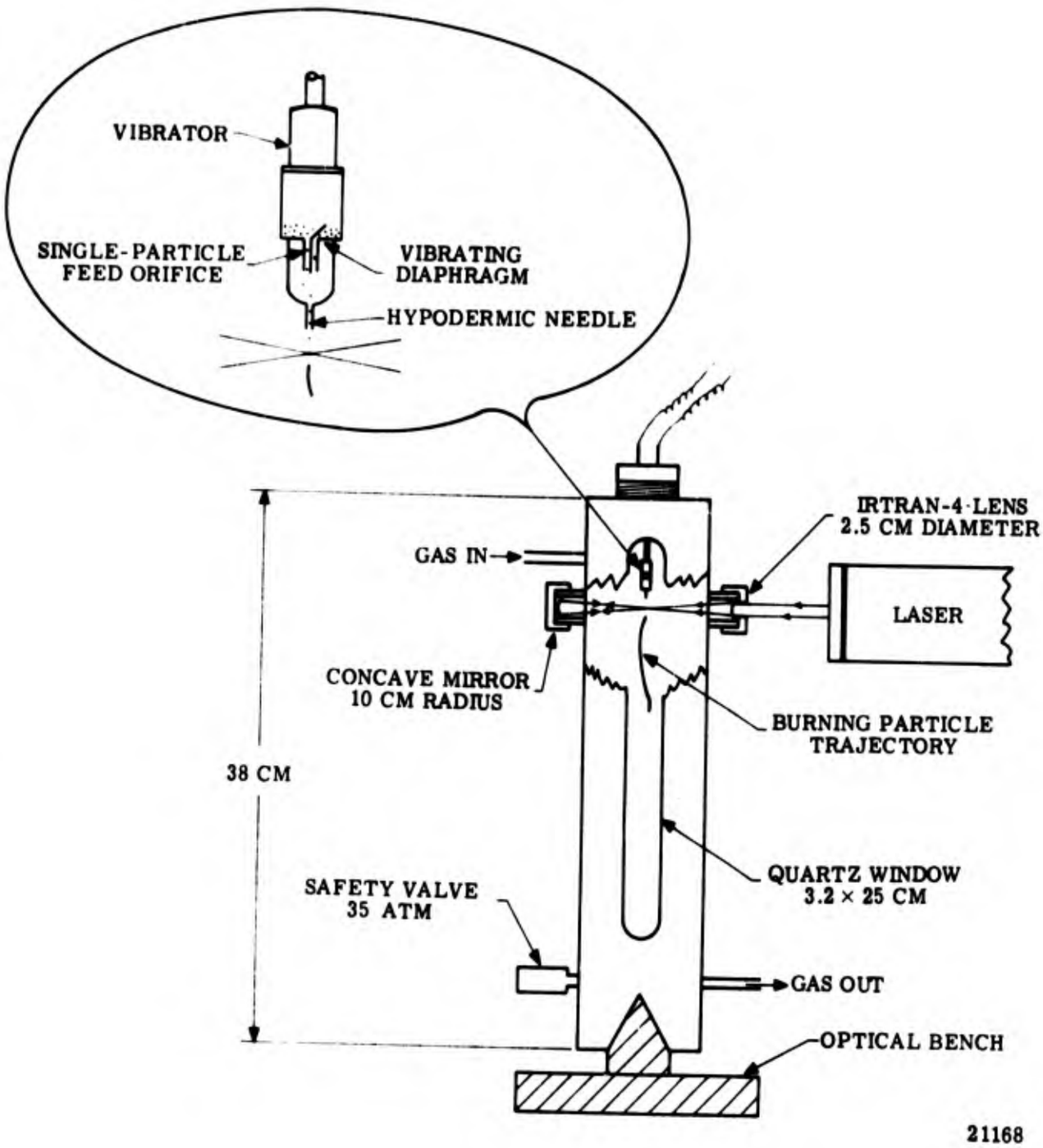
VIBRATOR
SINGLE-PARTICLE FEED ORIFICE
VIBRATING DIAPHRAGM
HYPODERMIC NEEDLE
GAS IN
IRTRAN-4 LENS 2.5 CM DIAMETER
LASER
CONCAVE MIRROR 10 CM RADIUS
BURNING PARTICLE TRAJECTORY
38 CM
QUARTZ WINDOW 3.2 × 25 CM
SAFETY VALVE 35 ATM
GAS OUT
OPTICAL BENCH
21168

Figure 1

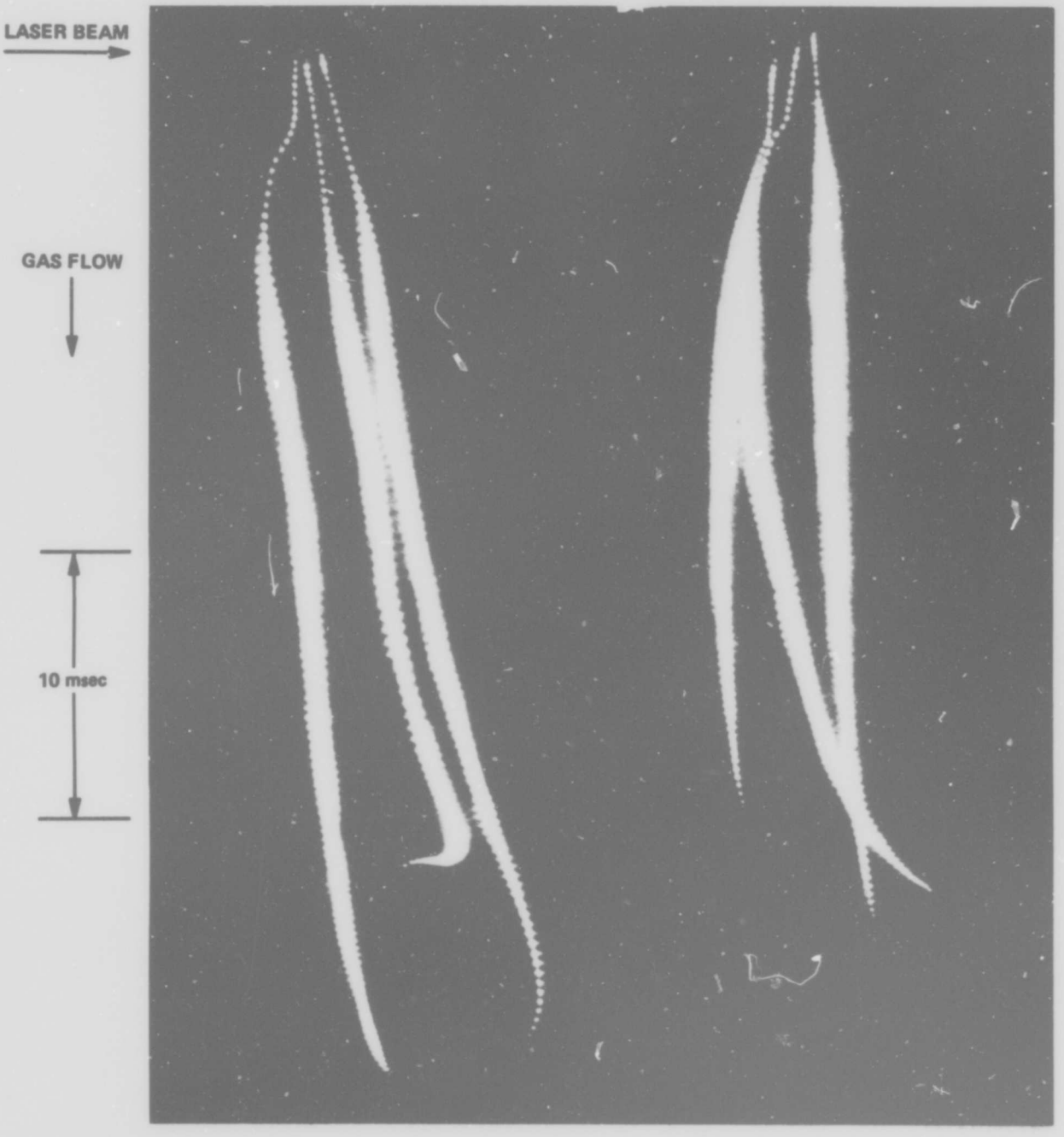

Figure 2

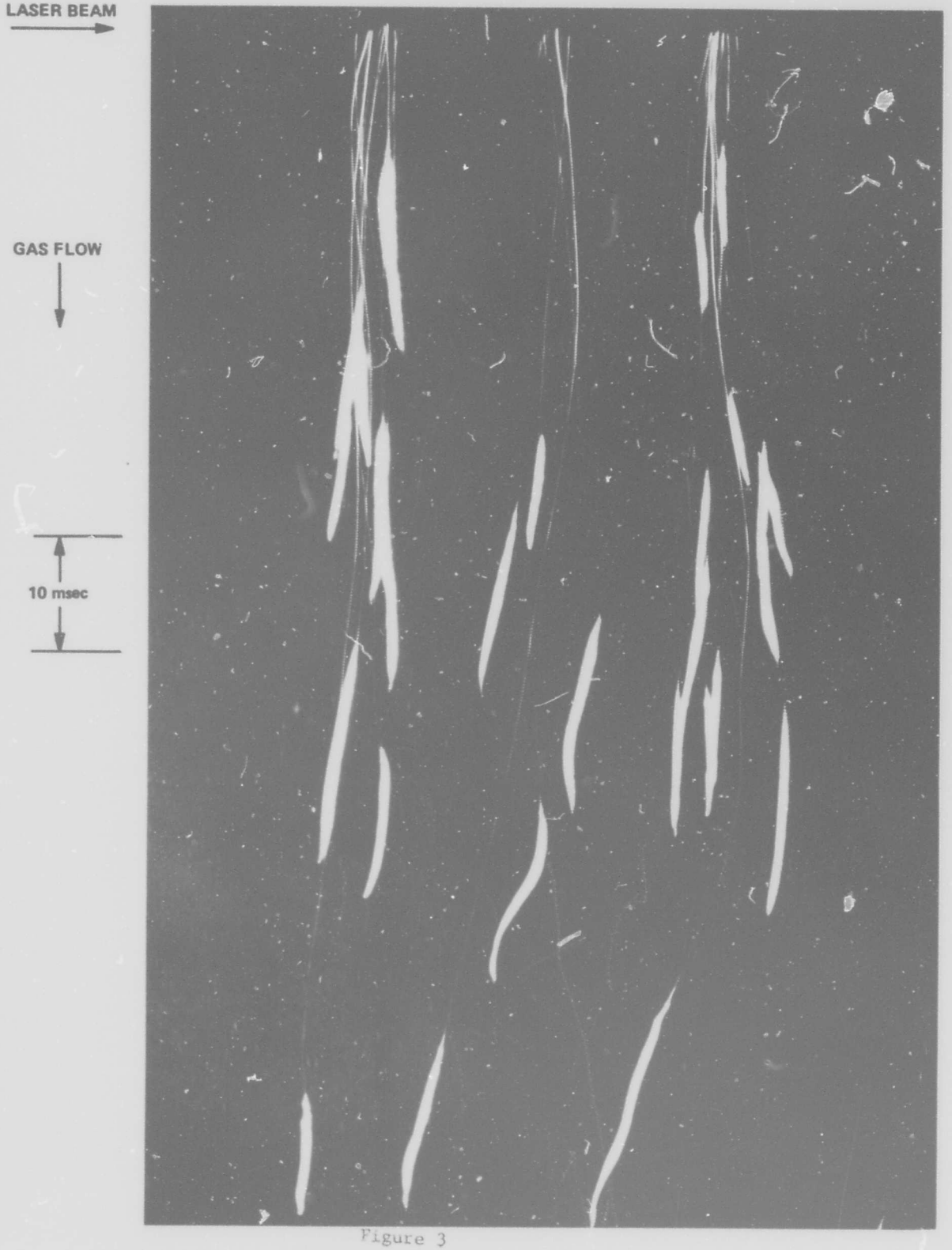

Figure 3

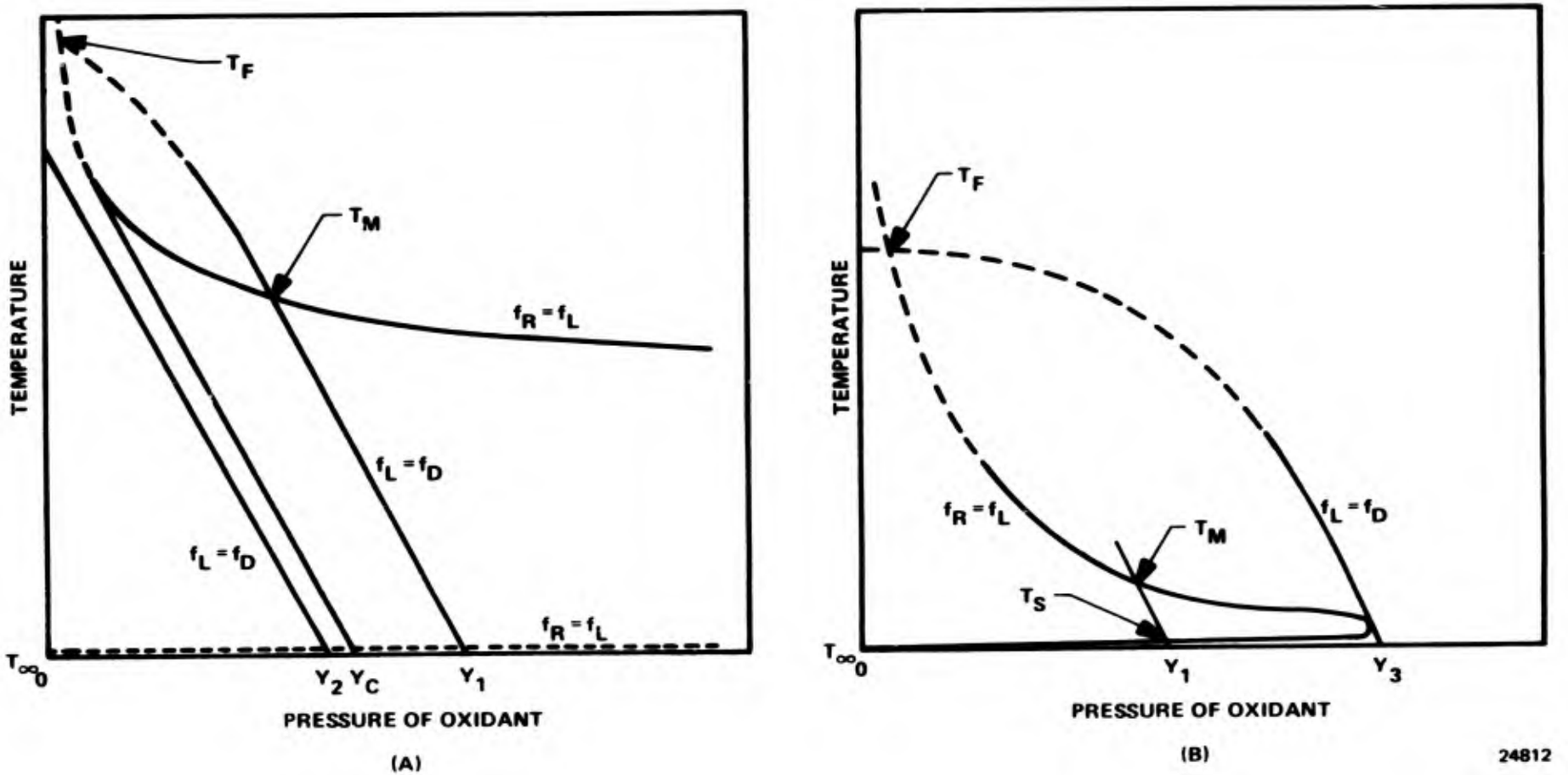
TEMPERATURE
T_F
T_M
$f_R = f_L$
$f_L = f_D$
$f_L = f_D$
$f_R = f_L$
T_{∞_0}
Y_2 Y_C
Y_1
PRESSURE OF OXIDANT
(A)
TEMPERATURE
T_F
$f_R = f_L$
$f_L = f_D$
T_M
T_S
T_{∞_0}
Y_1
Y_3
PRESSURE OF OXIDANT
(B)
24812

Figure 4

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13 ABSTRACT

Combustion of single boron particles, about 75μ in diameter, from a crystalline powder sample has been studied. Particles were ignited by being dropped through a focused laser beam in several oxidizing gases over a range of pressures. In pure oxygen, in air, and in O_2/Ar(20/80), particles were merely preheated to a temperature about 2000°K; ignition took place spontaneously after a measurable induction period. Quantitative values of both the induction period and the subsequent self-sustained combustion period are listed. In air and in the O_2/Ar mixture the burning times decrease from about 45 msec to about 20 msec as the pressure is increased from 1 to 35 atm. In pure O_2 at atmospheric pressure the total burning regime by an external energy flux, and they are able to maintain that regime for only a limited time before extinguishment.

It is shown that the classical theory of ignition and combustion can account for all three observed burning modes: metastable surface reaction during the pre-ignition period, rapid self-sustained diffusion-combustion, and decaying combustion. Previously reported reaction-rate and ignition-limit data are used for quantitative estimates of parameters pertaining to the three regimes.

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14. KEY WORDS	LINK A		LINK B		LINK C	
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Metal combustion						
Metal particles						
Ignition						
Droplet combustion						
Propellant ingredient combustion						
Burning rates						
Diffusion-controlled combustion						