

Critical Behavior in Small Particle Combustion

Robert S. Hiers III*

Sverdrup Technology, Inc., Arnold Air Force Base, Tennessee 37389-9900

Small particles combust under free molecular conditions are shown to exhibit critical behavior under conditions of high collision efficiency. At a particular collision efficiency, the particle behavior transitions from noncritical to critical (or runaway) behavior. Noncritical behavior is defined as a finite particle temperature at burnout, whereas critical behavior implies an infinitely increasing particle temperature at burnout. The critical collision efficiency is derived from the governing equations for free molecular combustion of small particles. The critical collision efficiency is shown to be a function of the specific heats of the gas and the particle and is independent of the particle size. Analytic and numerical results are compared. Particle radiation is included in the numerical results. The inclusion of radiation does not effect the critical collision efficiency, although radiation does decrease the rate of particle temperature increase.

Nomenclature

A	= particle surface area
C	= particle specific heat
C_p	= gas-specific heat at constant pressure
C_v	= gas-specific heat at constant volume
\hat{C}_v	= gas-specific heat at constant volume under effusive conditions
D	= particle diameter
E	= particle internal energy
e	= particle specific internal energy
f	= collision efficiency
$h_f^0(0)$	= enthalpy of formation at 0 K
k	= Boltzmann constant
k_r	= spectrally averaged emission coefficient
M_w	= gas molecular weight
m	= gas molecular mass
\bar{m}	= mass of carbon atoms removed from particle per reactive collision
N_A	= Avogadro's number
n	= gas number density
P_∞	= ambient pressure
q_{nr}	= energy transferred to the particle by a nonreactive collision
q_r	= energy transferred to the particle by a reactive collision
\mathcal{R}	= specific gas constant
r	= particle radius
r_0	= initial particle radius
T	= particle temperature
T_0	= reference temperature or initial particle temperature
T_∞	= ambient temperature
T^*	= particle burnout temperature
t	= time
t^*	= particle burnout time
u	= gas thermodynamic internal energy
V	= particle volume
X	= stoichiometric coefficients
Z	= collision frequency
α	= particle surface thermal accommodation coefficient
γ	= gas ratio of specific heats
ϵ	= particle emissivity
λ	= gas mean free path

μ	= gas kinematic viscosity
\bar{v}	= average molecular velocity
ρ	= particle material density
ρ_∞	= ambient gas density
σ	= Stefan–Boltzmann constant
ω	= specific oxidation rate

Introduction

THE term critical behavior is used to describe many different aspects of combustion, for example, ignition vs nonignition, explosion vs nonexplosion, and vigorous vs weak combustion. In general, criticality indicates an abrupt transition from a stable or well-behaved configuration to a completely different, potentially unstable configuration. The critical combustion behavior of spherical carbon particles has been examined previously by Trevino et al.¹ Additionally, Zhang² analyzed bifurcation behavior in a homogeneous–heterogeneous system. In each of these instances, the particle combustion was assumed to occur under continuum conditions. Hiers^{3,4} has shown that the combustion of soot particles occurs under substantially rarefied or free molecular conditions for most practical applications. The objective of this paper is to identify a regime of critical behavior for particles combust under free molecular conditions, indicated by an infinitely increasing particle temperature at burnout.

It has been shown that soot particles are sufficiently small so that they are in rarefied conditions in typical atmospheric pressure laboratory flames.^{3,4} Soot particles in low-pressure flames or ablated from reentry vehicle heat shields at high altitude would experience free molecular flow. The theory presented here is strictly valid only for small particles combust under these high-temperature and relatively low-pressure conditions, where the particle size is smaller than the gas mean free path. Additionally, the process of thermal sublimation (which becomes an important mass removal process for soot at temperatures around 4000 K) is ignored in the current work.

Free Molecular Combustion Model

Complete details of the free molecular combustion model are given in Refs. 3 and 4. A brief derivation is given here. Each term is defined in the Nomenclature. All thermal properties of the particle and the surrounding gas are assumed to be temperature dependent in this derivation. Additionally, the particle is treated as a lumped, one-dimensional spherical system. If we denote the particle thermal energy as E , then E is given by

$$E = \rho V(t) e(T) \quad (1)$$

where ρ is assumed constant, and e is energy per unit mass. Because particle volume is simply $4/3\pi r^3$, then E is a function of both

Presented as Paper 99-0977 at the AIAA 37th Aerospace Sciences Meeting, Reno, NV, 11–14 January 1999; received 29 March 1999; revision received 3 August 1999; accepted for publication 5 August 1999. This material is declared a work of the U.S. Government and is not subject to copyright protection in the United States.

*Chief Engineer for Space and Missile Sciences, Space and Missiles Department, AEDC Group, Arnold Engineering Development Center; robert.hiers@arnold.af.mil. Senior Member AIAA.

particle radius r and particle temperature T . Because both V and T (and thus e) are functions of time, then the rate of change of E is

$$\frac{dE}{dt} = \frac{\partial E}{\partial e} \frac{de}{dt} + \frac{\partial E}{\partial V} \frac{dV}{dt} \quad (2)$$

The partial derivatives are obviously

$$\frac{\partial E}{\partial e} = \rho V \quad (3)$$

$$\frac{\partial E}{\partial V} = \rho e \quad (4)$$

because we are treating the particle material density as a constant. Additionally, we can apply the chain rule to yield

$$\frac{dV}{dt} = \frac{\partial V}{\partial r} \frac{dr}{dt} \quad (5)$$

where

$$\frac{\partial V}{\partial r} = \frac{\partial}{\partial r} \left(\frac{4}{3} \pi r^3 \right) = 4\pi r^2 = A \quad (6)$$

Making these substitutions into Eq. (2) yields

$$\frac{dE}{dt} = \rho V \frac{de}{dt} + \rho e A \frac{dr}{dt} \quad (7)$$

We can write the internal energy as

$$e = \int_{T_0}^T C d\hat{T} + e(T_0) \quad (8)$$

where C is a function of temperature and T_0 is some reference temperature. If we use the thermodynamic properties of graphite (a reference element) for soot, then $e(T_0)$ is defined to be zero. Throughout this paper, the reference temperature T_0 is assumed to be 0 K. Applying Leibnitz's rule yields

$$\begin{aligned} \frac{de}{dt} &= \frac{d}{dt} \int_{T_0}^{T(t)} C(\hat{T}) d\hat{T} \\ &= C[T(t)] \frac{dT(t)}{dt} - C(T_0) \frac{dT_0}{dt} + \int_{T_0}^{T(t)} \frac{\partial}{\partial t} [C(\hat{T})] d\hat{T} \end{aligned} \quad (9)$$

but

$$\frac{dT_0}{dt} = 0 \quad (10)$$

$$\frac{\partial}{\partial t} [C(\hat{T})] = 0 \quad (11)$$

because C is not an explicit function of time. Therefore, Eq. (9) simplifies to

$$\frac{de}{dt} = C \frac{dT}{dt} \quad (12)$$

Substituting Eq. (12) into Eq. (7) yields

$$\frac{dE}{dt} = \rho V C \frac{dT}{dt} + \rho e A \frac{dr}{dt} \quad (13)$$

Furthermore, because

$$V = A(r/3) \quad (14)$$

then Eq. (13) will simplify to

$$\frac{dE}{dt} = A \left[\rho \frac{r}{3} C \frac{dT}{dt} + \rho e \frac{dr}{dt} \right] \quad (15)$$

If we assume we are given the specific oxidation rate ω (g/cm²/s) as a function of temperature and pressure, we can find the rate of change of the particle radius since

$$-\omega A = \rho \frac{dV}{dt} = \rho A \frac{dr}{dt} \quad (16)$$

or

$$\frac{dr}{dt} = -\frac{\omega}{\rho} \quad (17)$$

Substituting Eq. (17) into Eq. (15) yields

$$\frac{dE}{dt} = A \left[\frac{\rho r}{3} C \frac{dT}{dt} - \omega e \right] \quad (18)$$

This is the rate of change of the energy content of the particle.

The free molecular model considers only collisions between gas molecules and the particle surface. Collisions amongst gas molecules are not considered. A collision that results in an exothermic reaction adds energy to the particle. An endothermic reaction removes energy. Nonreactive collisions will either add or subtract energy from the particle: adding if the gas is hotter than the particle, subtracting if the particle is hotter than the gas. Also, if a reaction occurs, mass must be removed from the particle.

If the characteristic body dimension is small compared to the gas mean free path, the body is in free molecular flow, and heat transfer will occur only by direct collisions with the ambient gas molecules (ignoring radiation for the moment). Upon collision with the particle surface, the gas molecules will exchange energy with the surface, either by transferring thermodynamic internal energy and translational energy, or by chemically reacting with the particle surface. The term thermal accommodation refers to the effectiveness of the energy exchange between the gas and the particle during a collision. Perfect thermal accommodation is assumed throughout this work, which means that the energy modes of a gas molecule come to thermal equilibrium at the particle temperature. This is reasonable for low thermal energy collisions with rough surfaces such as those considered here.⁵ We can express the oxidation rate ω as a fraction of the total number of collisions; that is,

$$\omega = Z f \bar{m} \quad (19)$$

where Zf is the frequency of reactive collisions and \bar{m} is the mass removed per reactive collision. Assuming no relative motion between the particle and the gas (dynamic equilibrium), the collision rate Z is given in Ref. 6 as

$$Z = \frac{1}{4} n \bar{v} = \frac{1}{4} (P_\infty / k T_\infty) \sqrt{8 k T_\infty / \pi m} \quad (20)$$

where P_∞ and T_∞ are the pressure and temperature of the ambient gas. The assumption of dynamic equilibrium is valid for small soot particles. The velocity relaxation times are extremely small due to the large drag coefficients present under rarefied conditions. The energy flux at the particle surface due to collisions with gas molecules can, therefore, be given as

$$\frac{dE}{dt_{\text{collisions}}} = [Z f q_r + Z(1 - f) q_{nr}] A \quad (21)$$

The internal energy u of a gas molecule has contributions from translational energy, internal structure (e.g., vibrational and rotational energy), and chemical potential energy (bond energy). We can write the internal energy of the gas molecules as

$$u = u_{\text{translational}} + u_{\text{internal}} + u_{\text{chemical}} \quad (22)$$

Because the particle is smaller than the mean free path, the molecular flux to the particle surface is effusive. Therefore, the average translational energy of the gas molecules incident on the particle surface is $2kT$ (Ref. 7). Also, because the reference temperature is chosen as 0 K, the chemical potential energy is simply the enthalpy of formation at 0 K, or $h_f^0(0)$. Therefore, the internal energy of a gas molecular at any temperature T is shown in Ref. 8:

$$u(T) = 2kT + \int_0^T C_{v,\text{internal}} d\hat{T} + h_f^0(0) \quad (23)$$

The change in the internal energy during a single gas-surface collision is given by

$$\Delta u = u_{\text{products}} - u_{\text{reactants}} \quad (24)$$

or using Eq. (23) is

$$\begin{aligned} \Delta u = & \sum_{i \text{ products}} X_i \left(2kT_i + \int_0^{T_i} C_{v,\text{internal},i} d\hat{T} + h_{f,i}^0(0) \right) \\ & - \sum_{j \text{ reactants}} X_j \left(2kT_j + \int_0^{T_j} C_{v,\text{internal},j} d\hat{T} + h_{f,j}^0(0) \right) \end{aligned} \quad (25)$$

where X are the gas-phase stoichiometric coefficients of the reaction under consideration. Equation (25) can be used to find the change in internal energy for either reactive or nonreactive collisions. By the first law of thermodynamics, the energy transferred to the particle during the collision is simply the negative of the change in internal energy of the collision. Therefore, for a nonreactive collision

$$q_{\text{nr}} = -\Delta u_{\text{nr}} \quad (26)$$

and for a reactive collision

$$q_r = -\Delta u_r \quad (27)$$

Tables of Ref. 9 and associated curve fits of Ref. 10 are used for all specific heats and heats of formation appearing in Eq. (25).

Equation (21) represents the flux of energy at the particle surface due to collisions with ambient gas molecules. The particle will also exchange energy with the environment by radiation. The rate of radiant energy transfer is given by

$$\frac{dE}{dt_{\text{radiation}}} = \varepsilon \sigma (T_\infty^4 - T^4) A \quad (28)$$

where σ is the Stefan-Boltzmann constant. The treatment of small particle radiation is explained in more detail in Appendix D of Ref. 3. Briefly, small particles are mass (or volume) radiators.¹¹ The emissivity ε is, thus, directly proportional to the particle radius. Therefore,

$$\frac{dE}{dt_{\text{radiation}}} = rk_r \sigma (T_\infty^4 - T^4) A \quad (29)$$

where k_r is a function of particle temperature and is derived from the Lee and Tien¹² soot optical properties. The total energy flux at the particle surface is, therefore, the sum of Eqs. (21) and (28), or

$$\frac{dE}{dt_{\text{fluxes}}} = [Zf q_r + Z(1-f)q_{\text{nr}}]A + rk_r \sigma (T_\infty^4 - T^4) A \quad (30)$$

Substituting Eq. (19) into Eq. (18) yields

$$\frac{dE}{dt_{\text{fluxes}}} = A \left[\frac{\rho r}{3} C \frac{dT}{dt} - Zf \tilde{m} e \right] \quad (31)$$

Equating Eqs. (30) and (31) and solving for the rate of change of temperature yields

$$\frac{dT}{dt} = \frac{3Z}{\rho r C} [f(\tilde{m} e + q_r) + (1-f)q_{\text{nr}}] + \frac{3k_r \sigma}{\rho C} (T_\infty^4 - T^4) \quad (32)$$

Note that the particle radius r appears in Eq. (32) as an unknown function of time. However, substituting Eq. (19) into Eq. (17) yields an ordinary differential equation for the particle radius:

$$\frac{dr}{dt} = \frac{-Zf \tilde{m}}{\rho} \quad (33)$$

Because f is also a function of particle temperature, Eqs. (32) and (33) form a coupled set of nonlinear ordinary differential equations for the particle temperature and radius as functions of time. These equations are statements of energy conservation and mass conservation, respectively. In later sections these equations will be integrated in time using a modified implicit Euler method described in Appendix E of Ref. 3.

Critical Combustion Behavior Analysis

Equations (32) and (33) comprise a first-order, nonlinear set of ordinary differential equations for the particle radius and temperature as functions of time. The nonlinearity is due both to the radiation term T^4 and the nonlinear dependence of the various coefficients (collision efficiency, specific heat, etc.) on the particle temperature. The equations can be linearized by neglecting radiation and assuming that all thermal properties are constant. If the thermal properties are assumed constant, then

$$e = CT \quad (34)$$

$$q_{\text{nr}} = (2k + C_{v,\text{internal}})(T_\infty - T) = \hat{C}_v(T_\infty - T) \quad (35)$$

from which the definition of \hat{C}_v is obvious. Making these substitutions in Eq. (32) and neglecting radiation yields

$$\frac{dT}{dt} = \frac{3Z}{\rho r C} [f(\tilde{m} CT + q_r) + (1-f)\hat{C}_v(T_\infty - T)] \quad (36)$$

For constant collision efficiency, the particle mass equation (33) will integrate immediately to yield

$$r(t) = r_0 - (Zf \tilde{m} / \rho) t \quad (37)$$

Equation (36) is a linear, first-order, ordinary differential equation with variable coefficients [because $r = r(t)$] that can be simply integrated using an integrating factor to obtain

$$T(t) = -\beta + (T_0 + \beta)[r_0 / r(t)]^\delta \quad (38)$$

where

$$\beta = \frac{[f q_r + (1-f)\hat{C}_v T_\infty]}{[f \tilde{m} C - (1-f)\hat{C}_v]} \quad (39)$$

$$\delta = 3 \left[1 - \frac{(1-f)\hat{C}_v}{f \tilde{m} C} \right] \quad (40)$$

and T_0 is the initial particle temperature.

This analytic solution was used to validate the numerical method. For these numerical and analytical calculations, the constant coefficients are evaluated at the following conditions: pure molecular oxygen at a pressure of 0.10 atm and temperature of 2500 K, using oxidation rates from Roth et al.¹³ Figure 1 presents a comparison of the analytical solution and the numerical solution [solving Eqs. (32) and (33) using the modified implicit Euler scheme described in Appendix E of Ref. 3] for the temperature rise of particles of various size oxidizing under the conditions just given. The numerical solution has been altered to neglect radiation and to use the same constant properties as the analytic solution.

The analytical and numerical solutions are virtually indistinguishable from each other, except at the smaller particle sizes. The numerical solutions were performed with a constant (10^{-7} s) step size

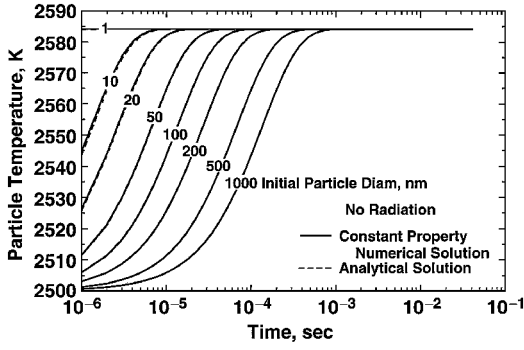


Fig. 1 Comparison of analytical and numerical solutions for particle temperature history.

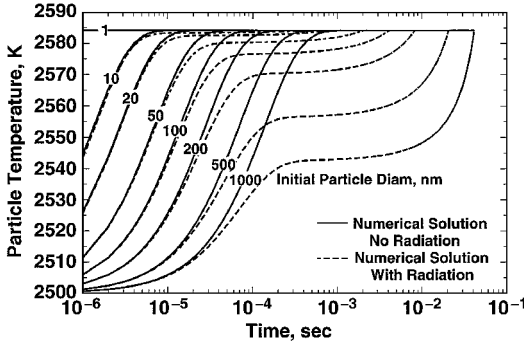


Fig. 2 Comparison of constant property numerical solutions with and without radiation.

that was not small enough to capture the fast rise for the smallest particles. This result validates the bulk of the numerical solution. The only potential errors are in the evaluation of the nonconstant properties and in the treatment of the radiation term. Note in Fig. 1 that the ultimate temperature of the particle is independent of the initial particle size. The initial particle size affects only the rise time.

Including the radiative term in Eq. (36) yields

$$\frac{dT}{dt} = \frac{3Z}{\rho r C} [f(\tilde{m}CT + q_r) + (1 - f)\hat{C}_v(T_\infty - T)] + \frac{3k_r \sigma}{\rho C} (T_\infty^4 - T^4) \quad (41)$$

where k_r is now treated as a temperature-independent constant. Figure 2 presents the same numerical results as Fig. 1, with the addition of the results from the numerical solution, including radiation. The analytical solutions have been removed for clarity. Note that neither the ultimate particle temperature nor the particle lifetime change with the inclusion of the radiation term. Inclusion of the radiation term only increases the time required to reach the ultimate temperature. Physically, the inclusion of the radiation term would be expected to reduce the particle temperature, as Fig. 2 shows. The observation that the inclusion of radiation does not impact the ultimate particle temperature may be theoretically justified by examining Eq. (41). Note that, as the particle size r approaches zero, the coefficient of the first term becomes very large. Therefore, the radiation term can be neglected when the particle size becomes very small, and radiation should cease to have an effect. This is exactly what is observed in Fig. 2. For very small particles, Eqs. (41) and (36) are identical.

Critical Behavior Analysis

The presence of the r_0/r term in Eq. (38) indicates a singularity at burnout, that is, at $r = 0$. The burnout temperature T^* is the particle temperature as this singularity is approached. The time at which the singularity is reached ($t = t^*$) can be found by setting $r(t) = 0$ in Eq. (37):

$$t^* = r_0 \rho / Z f \tilde{m} \quad (42)$$

and so we can define

$$T^* = \lim_{t \rightarrow t^*} [T(t)] \quad (43)$$

The burnout temperature T^* exhibits two distinct behaviors depending on the value of the exponent δ :

$$\delta < 0 \Rightarrow T^* \rightarrow -\beta \quad (44)$$

$$\delta \geq 0 \Rightarrow T^* \rightarrow \infty \quad (45)$$

Allowing the collision efficiency f to vary while considering all other parameters fixed, we can solve Eq. (40) for the critical value of $f = f^*$ that corresponds to $\delta = 0$. This yields

$$f^* = 1/[1 + (\tilde{m}C/\hat{C}_v)] \quad (46)$$

which for the numerical values of the other parameters yields $f^* = 0.401$. This means that

$$f < f^* \Rightarrow \delta < 0 \Rightarrow T^* \rightarrow -\beta \quad (47)$$

$$f \geq f^* \Rightarrow \delta \geq 0 \Rightarrow T^* \rightarrow \infty \quad (48)$$

Physically, the collision efficiency f must be between 0 and 1. Therefore, both behaviors are possible, and a bifurcation exists at $f = f^*$. Results from Eq. (38) are plotted in Fig. 3 for various values of the collision efficiency f . The computations stop one time step before burnout to avoid the infinite temperature at the singularity.

Note the change in the behavior of the slope of the temperature-time history as f becomes larger than f^* . The slope at burnout changes from practically zero to very large as the collision efficiency increases. Figure 4 is a rescaled version of Fig. 3 to show the complete curve at $f = 0.41$. The small f behavior would be typical under most physical conditions. The large f behavior would be approached only under the conditions of very efficient reactive collisions (such as with atomic oxygen) and no nonreactive gases (such as nitrogen). These conditions are not typically found in flames,

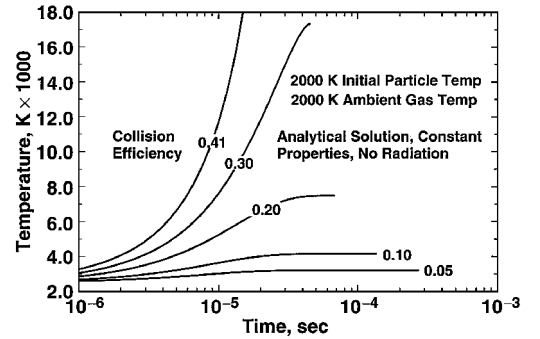


Fig. 3 Analytical solution for temperature history as a function of collision efficiency.

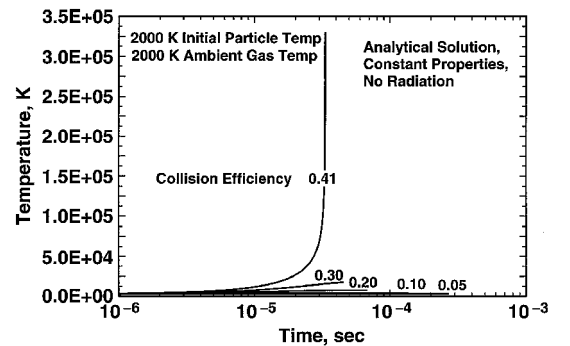


Fig. 4 Analytical solution for temperature history as a function of collision efficiency, rescaled.

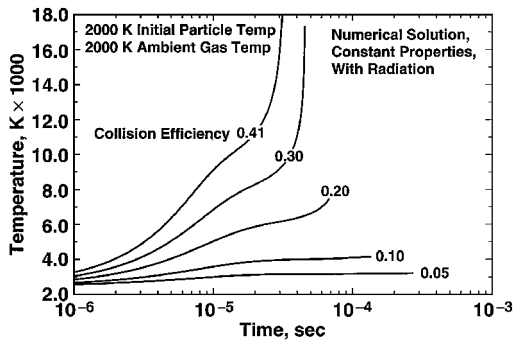


Fig. 5 Numerical solution for temperature history as a function of collision efficiency (with radiation).

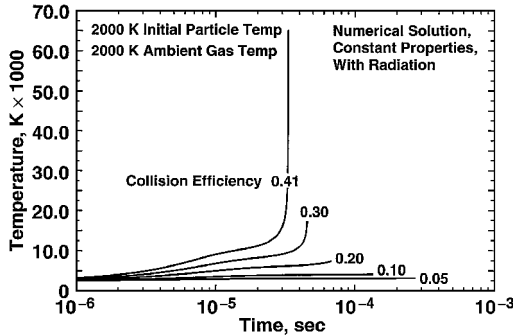


Fig. 6 Numerical solution for temperature history as a function of collision efficiency (with radiation), rescaled.

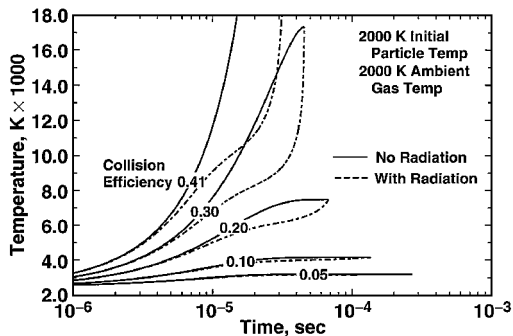


Fig. 7 Comparison of analytical and numerical (with radiation) solution for temperature history as a function of collision efficiency.

shock tubes, or other practical combustion devices. However, these conditions may be encountered in the combustion of ablative materials (such as carbon) in atmospheric reentry.

The large temperatures indicated are not physical because other processes that are ignored here would become important. Two such processes are thermal vaporization (which will continue to be ignored) and radiation. Radiation will now be considered.

Equation (41) is the particle energy equation including radiative loss. Figure 5 shows the numerical solution of Eq. (41) for particle temperature vs time. The collision efficiency f is varied while considering all other parameters fixed.

The small f and large f behaviors noted in Fig. 3 are also seen when including radiative heat loss. Figure 6 is a rescaled version of Figure 5 to show the complete curve for $f = 0.41$. Note that the addition of the radiative term did not change the ultimate particle temperature. Once again, the high temperatures indicated here are not physical because thermal vaporization will become important at about 4000 K. This mechanism would remove mass (and thus energy) from the particle while holding the particle temperature down. As in Figs. 3 and 4, the calculations are stopped one time step before burnout to avoid the singularity that occurs when the particle radius is reduced to zero.

Figure 7 shows the solutions for both the analytical solution without radiation and the numerical solution with radiation. For small

collision efficiencies, the curves are practically indistinguishable, but the radiation term does increase the temperature rise time, as noted in the preceding section. For larger values of the collision efficiency, the slope of the temperature at burnout is practically zero for the no-radiation cases, but is very large for the cases considering radiation. The inclusion of radiation reduces the value of the collision efficiency required to produce a large slope at burnout. The critical value for infinite temperature at burnout is unaffected by the inclusion of radiation.

Conclusions

A bifurcation is seen in the behavior of small particles combusting under free molecular conditions. For relatively low collision efficiencies (or kinetic rates), the particle temperature is bounded as the particle size reduces to zero at burnout. As the collision efficiency is increased, the particle temperature at burnout increases, but still remains bounded. At some critical value of collision efficiency, the particle temperature at burnout is unbounded and increases without limit. Under the assumption of constant thermal properties of both the particle and the surrounding gas, this critical value of the collision efficiency is seen to be a simple function of the gas and particle specific heats and the amount of mass removed per collision. Calculations were presented neglecting and including the effect of particle radiation. The inclusion of radiation increases the time required to reach any given particle temperature, but does not substantially change the critical behavior; that is, the particle temperature at burnout becomes unbounded at the same critical value of collision efficiency, whether radiation is included or neglected.

The impact of this critical behavior will be important in situations involving high collision efficiency, that is, high particle temperatures in extremely oxidizing conditions. For instance, the use of laser-induced incandescence as a soot diagnostic is typically applied in reducing or at most weakly oxidizing conditions. The kinetic timescales are long enough that reactions on the particle surface during the laser pulse and subsequent particle cooldown are typically ignored. If soot (or other small combustible particles) were present in an oxidizing atmosphere (e.g., ablation or intentional particle injection into the boundary layer of a reentry vehicle) and laser-induced incandescence used as a particle concentration diagnostic, the potential for critical vs noncritical combustion behavior would have to be assessed.

For the carbon particles considered here, thermal vaporization (sublimation) is expected to have a major impact on the critical behavior as the particle temperatures approach the vaporization temperature of about 4000 K. Particle vaporization will be added to the model in the near future.

Acknowledgments

The research reported herein was performed by the Arnold Engineering Development Center (AEDC), Air Force Material Command. Work and analysis for this research were performed by personnel of Sverdrup Technology, Inc., AEDC Group, technical services contractor for AEDC. Further reproduction is authorized to satisfy needs of the U.S. Government.

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