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I am submitting herewith a dissertation written by Robert Smith Hiers III entitled "Rarefaction Effects in Small Particle Combustion." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Mechanical Engineering.

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Rarefaction Effects in Small Particle Combustion

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Abstract

The standard theories of particle combustion rely upon continuum gas dynamic relationships. These theories predict that small reacting particles are always essentially in thermal equilibrium with the ambient gas phase. This is a consequence of three results from continuum theory: 1) the convective loss is inversely proportional to particle size, 2) the convective loss is independent of pressure, and 3) the convective loss depends upon the thermal conductivity of the ambient gas. Because soot particles are smaller than the mean free path of the ambient gas under typical combustion conditions, the author believed that rarefaction effects may be important in establishing the particle temperature relative to the gas temperature. Therefore, this dissertation began with the derivation of the energy and mass conservation equations assuming free molecular conditions about a single particle. Under these assumptions, the convective loss was shown to be independent of particle size, dependent on the ambient pressure, and independent of the gas phase thermal conductivity; precisely the opposite from the continuum case. These equations were solved numerically for a variety of $O_2/O/N_2$ gas mixtures, pressures, and temperatures. High O_2 mole fractions at low pressure resulted in significant gas/particle thermal nonequilibrium; the particle surface temperature was shown to elevate significantly above the gas temperature. This result contradicted the theoretical behavior of small reacting particles as predicted by continuum theory.

High ambient gas temperature was shown to favor thermal nonequilibrium by increasing the oxidation rate. The presence of small amounts of atomic oxygen also raised the particle temperature significantly. Once the theory for rarefaction effects on particle temperature was developed, and the numerical method tested, soot oxidation in flames by OH, O, and O₂ was evaluated with the new model. The model results were compared to experimental data from a premixed lean, low pressure, flat methane/air flame. The computed particle temperatures turned out to be low when compared to the measurements, which show a temperature overshoot behavior that the currently formulated model cannot capture. It was concluded that additional effects, such as exothermic surface catalyzed recombination chemistry, were responsible for the measured particle temperature behavior. Alternately, the measurements might be in error due to calibration or other problems. A simpler shock tube experiment was designed by the author to isolate and quantify the effect of rarefaction on the temperature of small combusting soot particles. This experiment, or others of a similar nature, are required to resolve the issues concerning rarefaction effects on small particle heat transfer and combustion.

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Nomenclature

A	= mass mean particle surface area
$\tilde{A}$	= true particle surface area
BET	= Brunauer-Emmett-Teller adsorption theory for 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_p	= diameter of primary particle in aggregate
D	= particle diameter
D_f	= Hausdorf (or fractal) dimension
E	= particle internal energy
e	= particle specific internal energy
f	= collision efficiency
G	= geometry-dependent heat transfer factor
h	= convective heat transfer coefficient
h_{fm}	= free molecular convective heat transfer coefficient
$h_f^o(0)$	= enthalpy of formation at 0 K
k	= Boltzmann constant
k_f	= gas film thermal conductivity

k_r	= spectrally-averaged emission coefficient
L	= length of shock tube low pressure section
m	= gas molecular mass
$\tilde{m}$	= mass of carbon atoms removed from particle per reactive collision
M_w	= gas molecular weight
n	= gas number density
N	= number of primary particles in fractal aggregate
N_A	= Avogadro's number
Nu	= Nusselt number
P_{O_2}	= oxygen partial pressure
Pr	= Prandtl number
P_∞	= ambient pressure
$\dot{Q}$	= heat transfer rate from gas to particle
q_{nr}	= energy transferred to the particle by a nonreactive collision
q_r	= energy transferred to the particle by a reactive collision
$\mathfrak{R}$	= specific gas constant
R_g	= radius of gyration of fractal aggregate
r	= particle radius
r_0	= initial particle radius
$\bar{r}$	= non-dimensional particle radius
t	= time

t_i	= elapsed time at incident shock conditions
t_r	= elapsed time at reflected shock conditions
$\bar{t}$	= scaled time
t^*	= particle burnout time
T	= particle temperature
T_0	= reference temperature or initial particle temperature
T_∞	= ambient temperature
T^*	= particle burnout temperature
$\bar{T}$	= non-dimensional particle temperature
$\bar{T}^*$	= non-dimensional particle temperature at burnout
u	= gas thermodynamic internal energy
u_1	= incident shock velocity
u_2	= velocity behind incident shock
u_5	= reflected shock velocity
u_p	= contact surface velocity
V	= particle volume
v	= gas or particle velocity
$\bar{v}$	= average molecular velocity
x_o	= observation station in shock tube
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

ρ = particle material density

ρ_{∞} = ambient density

σ = Stefan-Boltzmann constant

ω = specific oxidation rate

Chapter 1. Introduction

Soot is a ubiquitous by-product of hydrocarbon combustion. Soot radiation is an important consideration in base heat transfer and infrared signature for kerosene-fueled rockets. In industrial furnaces, the presence of soot is beneficial, since it increases the radiative heat transfer. However, due to environmental concerns, it is desirable that the soot be oxidized completely before the exhaust is released to the atmosphere. The negative impact of soot on health has long been recognized. Soot was identified by medical researchers in 1775 as the agent responsible for scrotal cancer in London chimney sweeps [1]. The harmful effect of soot and other small particulates on the respiratory system is also obvious. The control of soot emissions requires a fundamental understanding of both the formation and oxidation of soot particles. A very instructive comment made in a review of soot by Hamins [2] in 1993 holds true today:

There have been a great number of experimental measurements conducted in the last twenty years on the soot formation processes in premixed flames, nonpremixed flames, shock tubes, engines, and flow reactors. These studies have focused on the chemical kinetics associated with fuel pyrolysis, molecular growth chemistry and particle growth. Yet, only a handful of studies have been performed on soot oxidation processes. Further studies are needed to unravel this very fundamental flame process.

The intent of this dissertation is to concentrate on one aspect of soot oxidation - the effect of rarefaction on the temperature of the soot particle during oxidation.

History of Small Particle Combustion

Most previous developments of the governing equations of soot oxidation have focused on either the diffusion controlled (large particle, high temperature) or kinetically controlled (small particle, low temperature) limits [3-7]. In a seminal paper, Libby and Blake [8] have developed the general kinetic and diffusive equations governing the oxidation of carbon spheres. In the limit of small particles, all these developments predict that the particles are essentially in thermal equilibrium with the gas. Figure 1 illustrates the theoretical temperature profiles resulting from diffusionally and kinetically limited combustion when considering only heterogeneous (surface) reactions. For large particles (diffusion limit) the particle temperature can rise significantly above the ambient gas temperature. The temperature gradient through the particle can also be significant for large particles. For small particles (kinetic limit), the thermal conduction loss to the surrounding gas is predicted to overwhelm the energy release at the particle surface. Also, for small particles, the temperature is essentially uniform throughout the particle - indicating that the particle Biot number is less than 0.1. It should be noted that the consideration of homogeneous gas phase chemistry changes the temperature profiles shown in Figure 1 significantly. Specifically, a flame sheet forms some distance away from the particle. However, for a particle combusting in free molecular conditions, no such flame sheet can form, since in the free molecular limit, collisions between gas molecules are ignored.

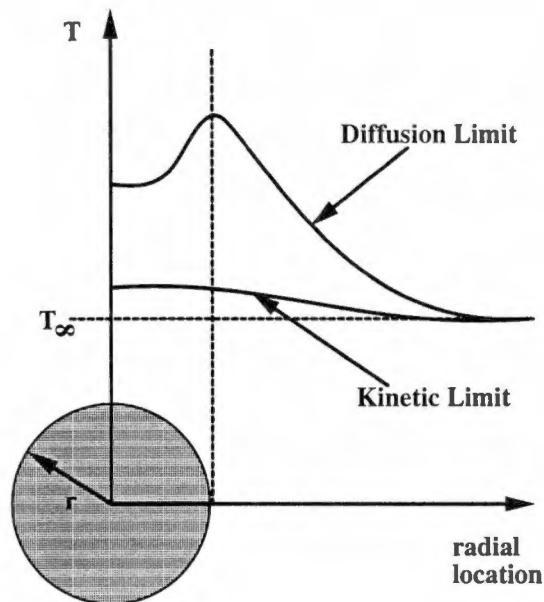


Figure 1 Theoretical temperature profiles for a particle experiencing either kinetically or diffusionally controlled combustion.

Annamalai and Durbetaki [9] developed a comprehensive model for the combustion behavior of carbon particles. They considered both homogeneous and heterogeneous reactions. Initial particle size was treated as a parameter, with no restriction on particle size noted. Makino and Law [10] analyzed the transient response of a carbon particle burning in an O_2/CO_2 /inert gas environment. They extended the approach of Libby and Blake to include finite-rate, gas-phase kinetics and radiation. Particle size was treated as a parameter through various Damkohler numbers, and no restriction on particle size is noted. The Damkohler number of interest was proportional to particle size and inversely proportional to the gas phase thermal conductivity. Trevino, Higuera, and Linan [11] determined the critical

conditions for vigorous burning of carbon particles. They determined that, for low Damkohler numbers (that is, for small particles), the combustion was kinetically controlled, with negligible particle temperature rise. At some critical Damkohler number, the combustion behavior transitioned from a kinetically controlled regime to a diffusion controlled regime, with substantial particle temperature increases. In their theory, the initial particle size was treated as a parameter, and the particle radius size was reduced to zero as combustion progresses and the particle burns out. No mention is made of a critical particle size below which the governing continuum equations became invalid. Lee, Yetter, and Dryer [12] developed the governing equations for spherical carbon particle combustion using detailed transport properties, a comprehensive gas-phase reaction mechanism, and a five-step heterogeneous surface reaction mechanism. Their calculations resulted in predictions of typical, diffusion controlled behavior for large particles and the kinetically controlled behavior for small particles. In their transient response analysis, the particle size regressed to zero. No mention was made of any possible rarefaction effects due to small particles or low pressure.

It is interesting to trace the inclusion of rarefaction effects in the development of the Laser Induced Incandescence (LII) technique for measuring soot concentration. In the founding paper by Eckbreth [13], rarefaction effects were ignored when considering the thermal response of a laser heated particle. In a later paper by Melton [14], the effect of rarefaction was included in the convective loss term by using a method by McCoy and Cha [15]. This method does approach the

free molecular limit at very large Knudsen numbers. However, as is shown in a following section entitled **Knudsen Number Scaling**, their method underestimates the heat transfer coefficient at all Knudsen numbers. In a later work on LII, Roth [16] explicitly uses the free molecular heat transfer coefficient, albeit with constant specific heats for the gas and the particle.

In most shock tube studies [17-20] of soot oxidation the experimenters assumed that the particle temperature could be computed from the shock tube relations. Roth [19] explicitly states: "The particle surface temperature was assumed to be equal to the gas phase temperature. This assumption seems to be reasonable for nm-size shock-heated, reacting particles." It is precisely this assumption that is investigated in the present work.

Outline of Dissertation

In Chapter 2, the continuum and free molecular heat transfer coefficients are developed and compared. Soot particles (50-nm diameter) are shown to be smaller than the gas mean free path under typical conditions, and thus are considered to be in free molecular flow. Knudsen number scaling laws are explored to relate the continuum and free molecular limits. Finally, the Nusselt number is shown to be an inappropriate scaling parameter for heat transfer in free molecular flow.

In Chapter 3, the particle energy and mass conservation equations are derived. The flux of energy to the particle surface by collisions with gas molecules and by radiation is analyzed. The particle size regression rate is related to measured

oxidation rates. Oxidation rates for molecular and atomic oxygen are given in Chapter 4.

In Chapter 5, the energy and mass conservation equations are solved for a variety of ambient conditions and oxidation rates. Gas-particle thermal nonequilibrium is predicted - unlike the expectations of continuum theory under similar conditions. The numerical method is validated by comparison to analytic solutions that neglect radiative heat transfer. A phase plane analysis is performed that shows the particle temperature is always predicted to approach its ultimate temperature monotonically, with no under- or overshoot.

Chapter 6 explores the possibility that previous shock tube measurements of soot oxidation rates are contaminated by gas-particle thermal nonequilibrium. The calculations show little thermal nonequilibrium at the experimental conditions, since the experiments were performed in test gases highly diluted with argon.

The model is applied in Chapter 7 to predict particle temperatures observed in a flame experiment. Soot oxidation by OH is added to the model. Because of initially poor comparisons to the experimental data, excursions in oxidation rates and particle size are considered, as well as the effect of rough particle surfaces. However, satisfactory comparisons to the experimental data are never achieved. It is concluded, along with the authors of the original experimental paper, that some other mechanism is responsible for the observed gas-particle thermal nonequilibrium.

In Chapter 8, a shock tube experiment is designed to isolate and quantify the effect of rarefaction on small particle combustion. A brief review of shock tube theory is given, and a specific series of test conditions chosen. Particle combustion calculations show significant gas-particle thermal nonequilibrium is achieved at several test conditions. The diagnostics required for this experiment are briefly discussed.

The limitations of the current model are discussed in Chapter 9. Consequences of the free molecular assumptions are enumerated, and the uncertainties in the input oxidation rates are noted. The potential influence of fractal soot agglomerates on the optical properties and the combustion behavior of soot particulates is discussed. Finally, conclusions and recommendations are given in Chapter 10.

Chapter 2. Convective Heat Transfer Coefficients

Continuum Theory for Particle Heat Transfer

Consider a non-reacting sphere undergoing convective heat transfer with a surrounding gas. The governing heat transfer equation is

$$\dot{Q} = hA(T_{\infty} - T) \quad (1)$$

where $\dot{Q}$ is the heat transfer rate from the gas to the particle, h is the convective heat transfer coefficient, A is particle surface area, T is the particle temperature, and T_{∞} is the ambient temperature. Throughout this work it is assumed that there is no relative motion between the particle and the gas. This means that either quiescent ambient conditions are established, or that the particles are so small that they track the gas motion with no lag. If continuum conditions are assumed (as is done in Refs. [1-6]) then the Nusselt number (Nu) will be approximately 2 since the particle is undergoing free convection [21-23]. Details of the derivation of the limiting value of Nu can be found in Appendix A. Since Nu is defined as

$$Nu = \frac{hD}{k_f} \quad (2)$$

where D is the particle diameter and k_f is the gas film thermal conductivity, then we have the classic result

$$h = \frac{k_f}{r} \quad (3)$$

where r is the particle radius. For small particles the convective coefficient is extremely large and forces the particle temperature to rapidly approach the gas temperature. This is the result cited frequently in the literature to justify thermal equilibrium for small particles, even in the presence of energy addition by oxidation. Recall that the thermal conductivity of a gas is not dependent on pressure [24]. Therefore, the continuum convective heat transfer coefficient is independent of pressure.

Free Molecular Theory for Particle Heat Transfer

If the characteristic body dimension is small compared to the mean free path of the ambient gas molecules, the body is in free molecular flow, and the convective heat transfer is given by [25,26]

$$-\dot{Q} = \alpha \rho_\infty \mathcal{R} T_\infty \sqrt{\frac{\mathcal{R} T_\infty}{2\pi}} \left[\frac{\gamma}{\gamma-1} - \frac{\gamma+1}{2(\gamma-1)} \frac{T}{T_\infty} - \frac{1}{2} \right] A \quad (4)$$

where α is the surface thermal accommodation coefficient, ρ_∞ is the ambient density, $\Re$ is the specific gas constant, and γ is the ratio of specific heats. This assumes a Maxwellian velocity distribution in the gas as a whole and no mean relative velocity between the gas and the particle. It also assumes that the internal energy modes are fully excited and in equilibrium with the translational energy. By rearranging and invoking the ideal gas law we arrive at

$$\dot{Q} = \frac{\alpha}{2} \frac{P_\infty}{T_\infty} \sqrt{\frac{\Re T_\infty}{2\pi}} \frac{\gamma+1}{\gamma-1} A (T_\infty - T) \quad (5)$$

This is in agreement with an early work of Simmons and Spadaro [27]. Throughout this work, the ambient gas molecules are assumed to undergo sufficient collisions with each other (far from the particle) so as to maintain a Maxwellian velocity distribution - thus justifying the use of the ideal gas law for the ambient gas. By comparison with (1) we can define a free molecular convective heat transfer coefficient (h_{fm}) as

$$h_{fm} = \frac{\alpha}{2} \frac{P_\infty}{T_\infty} \sqrt{\frac{\Re T_\infty}{2\pi}} \frac{\gamma+1}{\gamma-1} \quad (6)$$

Comparing (6) with (3) we see that the $1/r$ dependence does not appear in the free molecular heat transfer coefficient. Therefore, small particle size does not result in

large convective coefficients under free molecular conditions. Indeed, the free molecular heat transfer coefficient is independent of particle size but is instead dependent on pressure (or, on more physical grounds, density). Also note that the gas thermal conductivity does not appear. On the other hand, the continuum heat transfer coefficient is independent of pressure and strongly dependent on the gas thermal conductivity. Therefore, significantly different behavior might be expected under free molecular conditions.

We can now make a direct comparison of the free molecular and continuum convective heat transfer coefficients by forming the ratio h/h_{fm} (Equation (3) divided by Equation (6)) and plotting this ratio as a function of temperature and pressure (see Figure 2). A 50-nm diameter particle immersed in molecular oxygen was used for this calculation. The NASA Equilibrium Code with Transport Properties [28] was used to compute the temperature dependent ratio of specific heats as well as the thermal conductivity of the molecular oxygen. The accommodation coefficient was assumed to be unity. For these conditions, the free molecular convective heat transfer coefficient is always significantly less than the continuum convective coefficient. At 0.1-atm, the continuum coefficient is 500-1000 times larger than the free molecular coefficient. If the particle is actually in free molecular conditions, the use of the continuum heat transfer coefficient will significantly over-predict the heat transfer rate from the particle, implying an under-prediction of the particle temperature.

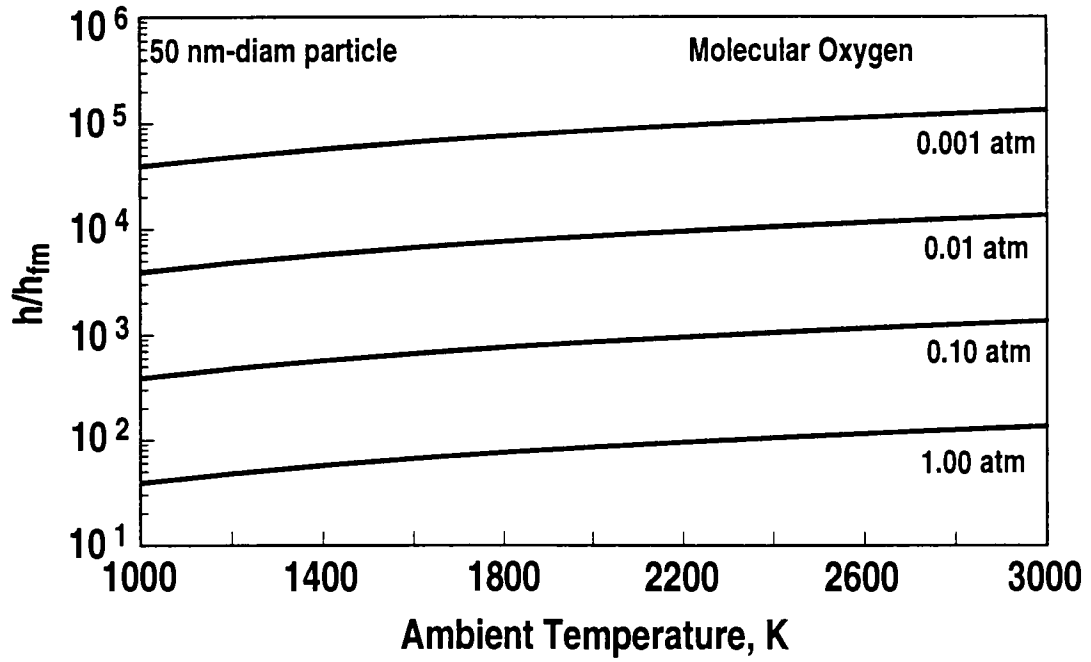


Figure 2 Ratio of convective heat transfer coefficients.

Soot Particle Knudsen Number

The particle Knudsen number (Kn) is defined as the ratio of the mean free path of the gas to the particle diameter [29], or

$$Kn = \frac{\lambda}{D} \quad (7)$$

where λ is the mean free path defined by

$$\lambda = \frac{2\mu}{P_\infty} \left(\frac{\pi k T_\infty}{8m} \right)^{\frac{1}{2}} \quad (8)$$

where k is the Boltzmann constant, m is the gas molecular mass, P_∞ is the ambient pressure, and μ is the gas viscosity. The definition of flow regimes is problem dependent, but in general for low relative velocities [30]:

$Kn < 0.1$	Continuum Flow
$0.1 < Kn < 2.0$	Slip Flow
$2.0 < Kn < 10.$	Transitional Flow
$Kn > 10.$	Free Molecular Flow.

Assuming again that the particle is immersed in pure molecular oxygen, Kn was calculated as a function of temperature and pressure for a baseline particle diameter of 50-nm, and is plotted in Figure 3. The NASA Equilibrium Code with Transport Properties was used to determine the viscosity. This will be a baseline Knudsen number only, since the particle size is held constant. The particle size will of course decrease with oxidation, causing an increase in the Knudsen number. Note that the particle Knudsen number is always much greater than 1.0, even at atmospheric pressure. At 0.1-atm, the Knudsen number is greater than 100. Therefore, soot-sized particles are always in transitional to free molecular flow. Rarefaction effects will always be important, and continuum relations may be inappropriate in predicting particle heat transfer.

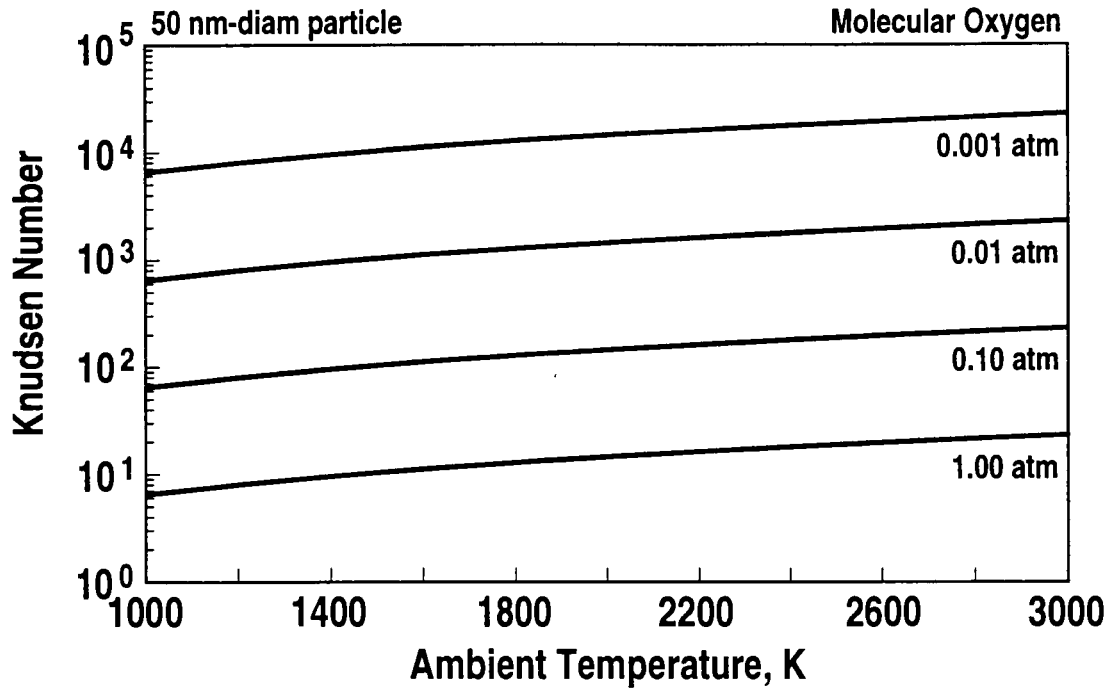


Figure 3 Particle Knudsen number.

Knudsen Number Scaling

By combining Equations (3), (6), (7), and (8), a non-dimensional parameter can be derived relating the continuum heat transfer coefficient, the free molecular heat transfer coefficient, and the Knudsen number. Dividing Equation (3) by both Equations (6) and (8), and recognizing that

$$\mathfrak{R} = \frac{R}{M_w} = \frac{kN_A}{mN_A} = \frac{k}{m} \quad (9)$$

where R is the universal gas constant, M_W is the gas molecular weight, and N_A is Avogadro's number yields

$$\frac{h/h_{fm}}{Kn} = 8 \frac{k_f}{\mu} \frac{1}{\alpha} \frac{\gamma-1}{\gamma+1} \frac{m}{k} \quad (10)$$

We also have the relationships

$$Pr = \frac{C_p \mu}{k_f} \quad (11)$$

or

$$\frac{k_f}{\mu} = \frac{C_p}{Pr} \quad (12)$$

and

$$\frac{m}{k} = \frac{1}{\Re} \quad (13)$$

and

$$C_p = \frac{\Re \gamma}{\gamma - 1} \quad (14)$$

where Pr is the Prandtl number and C_p is the specific heat at constant pressure.

Making these substitutions into Equation (10) and rearranging yields a non-dimensional parameter, GKn , the ratio of the continuum to the free molecular heat transfer coefficients:

$$\frac{h}{h_{fm}} \equiv GKn = \left[\frac{8}{\alpha} \frac{\gamma}{\gamma + 1} \frac{1}{Pr} \right] Kn \quad (15)$$

where G is defined as the quantity in brackets. Equation (15) can be rearranged as

$$h_{fm} = \frac{h}{GKn} \quad (16)$$

For typical values of the parameters ($\alpha \approx 1$, $\gamma \approx 1.3$, and $Pr \approx 0.7$) G takes the value of

$$G \approx 6.5 \quad (17)$$

This value and Equation (15) give a quick estimate of the importance of rarefaction in heat transfer from spheres. For example, soot particles in a 0.10 atmosphere

flame have Kn on the order of 100. Therefore, the continuum heat transfer coefficient is 650 times larger than the free molecular heat transfer coefficient.

The parameter G is also used in the correlation developed by McCoy and Cha [15] to bridge the continuum and free molecular regimes for sphere heat transfer. They refer to the parameter G as a “geometry-dependent heat transfer factor.” Their expression for the Knudsen number dependent heat transfer coefficient is

$$h(Kn) = \frac{k_f}{r} \frac{1}{[1 + GKn]} \quad (18)$$

where k_f / r is the continuum heat transfer coefficient and G is defined in Equation (15). The behavior in the limit of small and large Knudsen number is

$$h(Kn \rightarrow 0) = \frac{k_f}{r} \quad (19)$$

which is the correct continuum limit, and

$$h(Kn \rightarrow \infty) = \frac{k_f}{r} \frac{1}{GKn} \quad (20)$$

which obviously agrees with the free molecular limit (Equation (16)) above.

However, it will now be shown that the McCoy and Cha formulation underestimates the heat transfer coefficient at all Knudsen numbers between the limits. Dividing the heat transfer coefficient provided by the McCoy and Cha formulation by the continuum limit yields

$$\frac{h(Kn)}{h(Kn \rightarrow 0)} = \frac{\frac{k_f}{r} \frac{1}{[1+GKn]}}{\frac{k_f}{r}} = \frac{1}{[1+GKn]} \leq 1 \quad (21)$$

which shows that (except at the limit of $Kn=0$) the McCoy and Cha heat transfer coefficient is less than the continuum heat transfer coefficient. Dividing instead by the free molecular limit yields

$$\frac{h(Kn)}{h(Kn \rightarrow \infty)} = \frac{\frac{k_f}{r} \frac{1}{[1+GKn]}}{\frac{k_f}{r} \frac{1}{GKn}} = \frac{GKn}{[1+GKn]} \leq 1 \quad (22)$$

which shows that (except at the limit of $Kn=\infty$) the McCoy and Cha heat transfer coefficient is less than the free molecular heat transfer coefficient. Therefore, even though it has the correct limit behavior, the McCoy and Cha formulation

underestimates the heat transfer coefficient at all intermediate Kn . Numerical details of the McCoy and Cha correlation are shown in Appendix B.

Failure of the Nusselt Number in Free Molecular Flow

The concept of the Nusselt number as the correlating heat transfer parameter breaks down in free molecular flow. Continuum heat transfer theory is based on the observation that the convective heat transfer to a body is controlled by the thermal conductivity of the boundary layer surrounding the particle which is often treated as a film of gas molecules that builds up on the body surface. This is the genesis of the "film coefficient". This film is created by molecules striking the surface, which then reflect from the surface and collide with other incoming molecules and are directed back toward the surface. These secondary and tertiary collisions near the surface create the "film". Continuum flow is dominated by these collisions of incoming molecules with the surface film. In free molecular flow, the molecules which collide with the surface are reflected back into the bulk gas without ever encountering another incoming molecule. It is this fact that allows us to derive relatively simple relationships for free molecular flow. Therefore, since in free molecular flow there exists no film, the film thermal conductivity plays no role in free molecular heat transfer. As shown above, free molecular heat transfer is independent of the gas thermal conductivity. Although kinetic theory is used to deduce the form of the gas thermal conductivity, it is essentially a continuum concept. In the classic derivations involving heat transfer between two plates at

different temperatures [31], the assumption is made that the separation of plates is much greater than the mean free path. Therefore, molecules will undergo many collisions with each other before striking the surface. This is not the case in free molecular flow. Therefore, since free molecular heat transfer is independent of the gas thermal conductivity, the Nusselt number is an inappropriate correlating parameter for heat transfer in free molecular flows.

Chapter 3. The Particle Energy Equation

Particle Energy Content

In this section, a complete derivation of the energy equation is given. All thermal properties of the particle and the surrounding gas are assumed to be temperature dependent. Additionally, the particle is treated as a lumped, one-dimensional system since the Biot number of the particle is less than 0.1 (see Appendix C for details on the Biot number analysis). If we denote the particle thermal energy as E , then E is given by

$$E = \rho V(t)e(T) \quad (23)$$

where ρ is the material density (assumed constant), V is the particle volume, and e is the particle specific internal energy (energy per unit mass). Since particle volume is simply $4/3\pi r^3$, then E is a function of both particle radius, r , and particle temperature, T . Since both V and T (and thus e) are functions of time, then the rate of change of E is

$$\frac{dE}{dt} = \frac{\partial E}{\partial e} \frac{de}{dt} + \frac{\partial E}{\partial V} \frac{dV}{dt} \quad (24)$$

The partial derivatives are obviously

$$\frac{\partial E}{\partial e} = \rho V \quad (25)$$

and

$$\frac{\partial E}{\partial V} = \rho e \quad (26)$$

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

$$\frac{dV}{dt} = \frac{\partial V}{\partial r} \frac{dr}{dt} \quad (27)$$

where

$$\frac{\partial V}{\partial r} = \frac{\partial}{\partial r} \left(\frac{4}{3} \pi r^3 \right) = 4\pi r^2 = A \quad (28)$$

where A is the particle surface area. Making these substitutions into Equation (18) yields

$$\frac{dE}{dt} = \rho V \frac{de}{dt} + \rho e A \frac{dr}{dt} \quad (29)$$

We can write the internal energy as

$$e = \int_{T_0}^T C d\hat{T} + e(T_0) \quad (30)$$

where C is the particle specific heat (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

$$\frac{de}{dt} = \frac{d}{dt} \int_{T_0}^{T(t)} C(\hat{T}) d\hat{T} = C(T(t)) \frac{d}{dt} T(t) - C(T_0) \frac{d}{dt} (T_0) + \int_{T_0}^{T(t)} \frac{\partial}{\partial t} [C(\hat{T})] d\hat{T} \quad (31)$$

but

$$\frac{d}{dt} (T_0) = 0 \quad (32)$$

and

$$\frac{\partial}{\partial t}[C(\hat{r})] = 0 \quad (33)$$

since C is not an explicit function of time. Therefore, Equation (31) simplifies to

$$\frac{de}{dt} = C \frac{dT}{dt} \quad (34)$$

Substituting Equation (34) into Equation (29) yields

$$\frac{dE}{dt} = \rho VC \frac{dT}{dt} + \rho e A \frac{dr}{dt} \quad (35)$$

Furthermore, since

$$V = A \frac{r}{3} \quad (36)$$

then Equation (35) will simplify to

$$\frac{dE}{dt} = A \left[\rho \frac{r}{3} C \frac{dT}{dt} + \rho e \frac{dr}{dt} \right] \quad (37)$$

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

$$-\omega A = \rho \frac{dV}{dt} = \rho A \frac{dr}{dt} \quad (38)$$

or

$$\frac{dr}{dt} = -\frac{\omega}{\rho} \quad (39)$$

Substituting Equation (39) into (37) and yields

$$\frac{dE}{dt} = A \left[\frac{\rho r}{3} C \frac{dT}{dt} - \omega e \right] \quad (40)$$

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

Reactive and Non-Reactive Collisions

The free molecular model is one of collision-counting. A collision which results in an exothermic reaction adds energy to the particle. An endothermic reaction removes energy. Non-reactive 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 [32]. We can express the oxidation rate (ω) as a fraction of the total number of collisions; i.e.

$$\omega = Zf\tilde{m} \quad (41)$$

where Z is the total collision frequency, Zf is the frequency of reactive collisions, f is termed the collision efficiency, and $\tilde{m}$ 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 by [33]

$$Z = \frac{1}{4} n \bar{v} = \frac{1}{4} \frac{P_{\infty}}{k T_{\infty}} \sqrt{\frac{8 k T_{\infty}}{\pi m}} \quad (42)$$

where k is Boltzmann's constant, $\bar{v}$ is the average molecular velocity, n is the number density, m is molecular mass, and P_{∞} and T_{∞} are the pressure and temperature of the ambient gas. The energy flux at the particle surface due to collisions with gas molecules can therefore be given as

$$\frac{dE}{dt}_{\text{collisions}} = [Z f q_r + Z(1-f) q_{nr}] A \quad (43)$$

where q_r is the energy transferred to the particle by a reactive collision and q_{nr} is the energy transferred by a non-reactive collision. 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

$$u = u_{\text{translational}} + u_{\text{internal}} + u_{\text{chemical}} \quad (44)$$

Since the particle is smaller than the mean free path, the energy flux to the surface is effusive, and thus the translational contribution is $2kT$ rather than the typical $(3/2)kT$ [34]. Also, since the reference temperature is chosen as 0 K, the chemical potential

energy is simply the enthalpy of formation at 0 K, or $h_f^o(0)$. Therefore, the internal energy of a gas molecular at any temperature T is [35]

$$u(T) = 2kT + \int_0^T C_{v, internal} d\hat{T} + h_f^o(0) \quad (45)$$

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

$$\Delta u = u_{products} - u_{reactants} \quad (46)$$

or, using Equation (45),

$$\Delta u = \sum_{i \text{ products}} X_i \left(2kT_i + \int_0^{T_i} C_{v, internal} d\hat{T} + h_f^o(0) \right) - \sum_{j \text{ reactants}} X_j \left(2kT_j + \int_0^{T_j} C_{v, internal} d\hat{T} + h_f^o(0) \right) \quad (47)$$

where X denotes the stoichiometric coefficients of the reaction under consideration.

Equation (47) can be used to find the change in internal energy for either reactive or non-reactive 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 non-reactive collision

$$q_{nr} = -\Delta u_{nr} \quad (48)$$

and for a reactive collision

$$q_r = -\Delta u_r \quad (49)$$

The JANAF Thermochemical Tables [36] and associated curve fits [37] are used for all specific heats and heats of formation appearing in Equation (47).

Small Particle Radiation

Equation (43) 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

$$\frac{dE}{dt}_{\text{radiation}} = \varepsilon \sigma (T_{\infty}^4 - T^4) A \quad (50)$$

where σ is the Stefan-Boltzmann constant. The treatment of small particle radiation is explained in more detail in Appendix D. Briefly, small particles are mass (or volume) radiators [38]. The emissivity (ε) is thus directly proportional to the particle radius. Therefore

$$\frac{dE}{dt}_{\text{radiation}} = rk_r \sigma (T_\infty^4 - T^4) A \quad (51)$$

where k_r (the spectrally-averaged emission coefficient) is a function of particle temperature, and is derived from the Lee and Tien [38] soot optical properties.

Free Molecular Energy Equation

The total energy flux at the particle surface is therefore the sum of Equations (43) and (50), or

$$\frac{dE}{dt}_{\text{fluxes}} = [Zfq_r + Z(1-f)q_{nr}]A + rk_r \sigma (T_\infty^4 - T^4) A \quad (52)$$

Substituting Equation (41) into Equation (40) yields

$$\frac{dE}{dt}_{\text{fluxes}} = A \left[\frac{\rho r}{3} C \frac{dT}{dt} - Zf\tilde{m}e \right] \quad (53)$$

Equating (52) and (53) and solving for the rate of change of temperature yields

$$\frac{dT}{dt} = \frac{3Z}{\rho r C} [f(\tilde{m}e + q_r) + (1-f)q_{nr}] + \frac{3k_r \sigma}{\rho C} (T_\infty^4 - T^4) \quad (54)$$

In free molecular flow, the heat transfer is independent of the gas phase thermal conductivity, whereas the continuum heat transfer rate is linearly dependent on the thermal conductivity. In free molecular flow, there is no extra $(1/r)$ term on the convective loss rate. Therefore, the convective loss term will not automatically dominate the heat addition term for small particles. Heat transfer processes (except radiation) are limited by the collision rate (Z). This means that the free molecular convective heat transfer is linearly dependent on pressure, whereas in continuum flow, the convective heat transfer is independent of pressure.

Note that the particle radius r appears in Equation (54) as an unknown function of time. However, substituting (41) into (39) yields an ordinary differential equation for the particle radius

$$\frac{dr}{dt} = \frac{-Zf\tilde{m}}{\rho} \quad (55)$$

Since f is also a function of particle temperature, (54) and (55) form a coupled set of 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.

Chapter 4. Soot Oxidation Rates

Oxidation by Molecular Oxygen

A summary of soot oxidation rate measurements over a wide range of oxygen partial pressure appears in Figure 4. The data have been cast into the form of collision efficiency, assuming the reaction

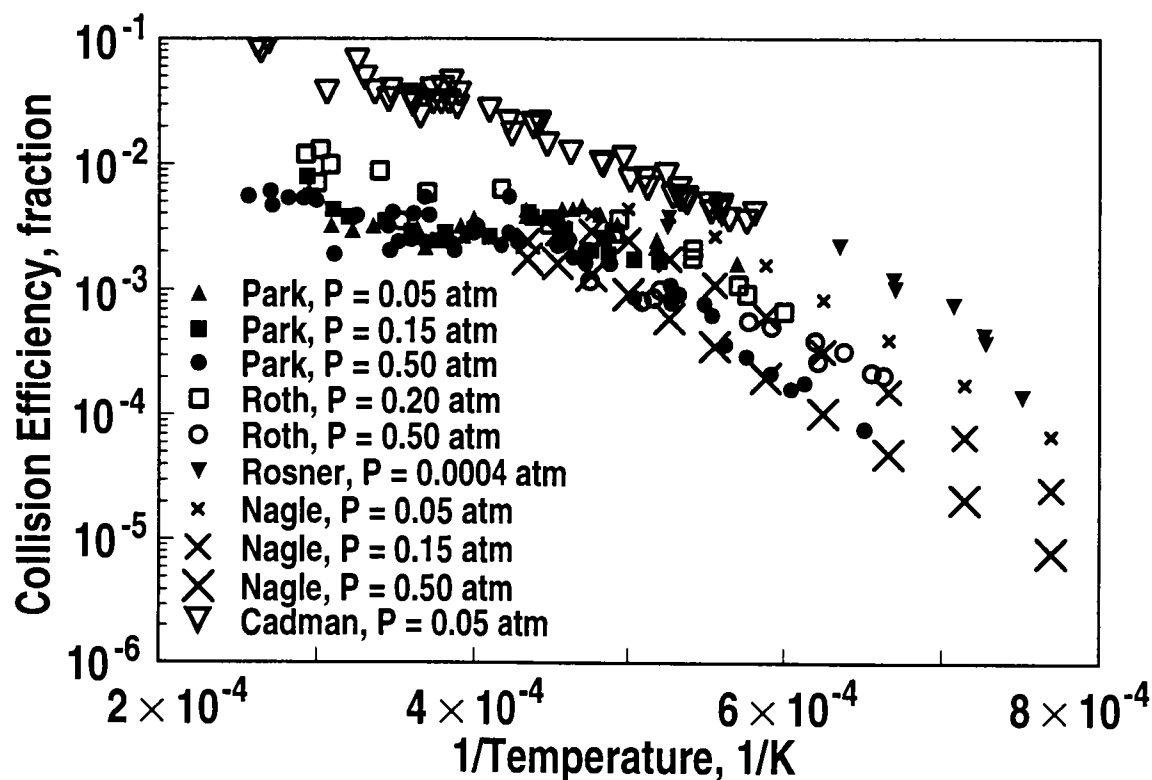


Figure 4 Collision efficiency for $2C + O_2 = 2CO$.

Shock tube data from Park and Appleton [39], Roth et al. [40], and Cadman et al. [41], are compared with the carbon rod data from Nagle and Strickland-Constable [42] and the low pressure flow tube data of Rosner and Allendorf [43]. Park and Appleton, Roth et al., and Cadman et al. used thermal or lamp black particles, and Rosner and Allendorf used graphite filaments. Roth et al. and Olander et al.[44-45] independently confirmed that the reaction forming CO is much more likely than that forming CO₂. Roth et al. used laser absorption to confirm the presence of CO and the absence of CO₂. Olander et al. used mass spectrometry to determine that the reaction forming CO was at least 2 orders of magnitude more probable than that forming CO₂. The Cadman et al. data lies well above most of the other data, but (perhaps coincidentally) fair in nicely with the much lower pressure Rosner and Allendorf measurements. Figure 5 presents the Cadman et al. and Roth et al. data (at oxygen partial pressures of 0.05- and 0.5-atm, respectively) along with a fit to this data using an equation of the Nagle and Strickland-Constable [42] form. This form is derived from surface reaction theory, and will be discussed in more detail in the following chapter.

$$f = \frac{\omega}{Z\tilde{m}} = 12 \left[\left(\frac{k_A P_{O_2}}{1 + k_Z P_{O_2}} \right) \chi + k_B P_{O_2} (1 - \chi) \right] \text{ (dimensionless)} \quad (57)$$

where

$$\chi = \left[1 + \frac{k_T}{k_B P_{O_2}} \right]^{-1},$$

$$k_A = 20 \exp(-15100/T), \text{ gm cm}^{-2} \text{ sec}^{-1} \text{ atm}^{-1},$$

$$k_B = 0.2 \exp(-7640/T), \text{ gm cm}^{-2} \text{ sec}^{-1} \text{ atm}^{-1},$$

$$k_T = 1.51 \times 10^5 \exp(-48800/T), \text{ gm cm}^{-2} \text{ sec}^{-1},$$

and

$$k_Z = 21.3 \exp(2060/T), \text{ atm}^{-1}.$$

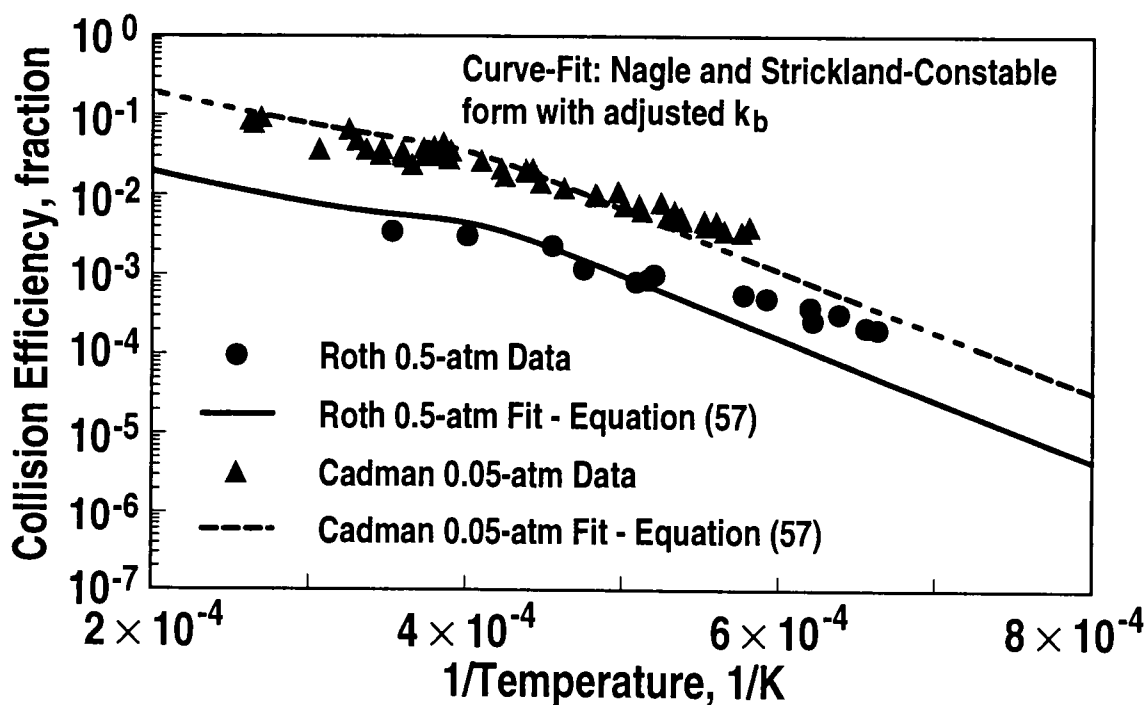


Figure 5 Curve fit of collision efficiency for $2C + O_2 = 2CO$.

The coefficients given in Equation (57) fit the Cadman et al. data. The Roth et al. data are well fit with a coefficient on k_B of 0.02. In the original Nagle and Strickland-Constable work, the coefficient on k_B is 0.00446. These are the only change to the original Nagle and Strickland-Constable fit required to fit the various data sets. The curve fits of these oxidation rates will be used in particle combustion calculations in subsequent sections.

Oxidation by Atomic Oxygen

Rosner and Allendorf [43] measured the rate of O-atom attack on pyrolytic graphite surfaces in a flow tube at low pressure. These data were fit with an exponential/polynomial curve fit of the form

$$f = \exp\left[\frac{a + cT + eT^2}{1 + bT + dT^2}\right] \quad (58)$$

where

$$\begin{aligned} a &= -2.319 \\ b &= -0.00123 \\ c &= 0.00277 \\ d &= 4.404 \times 10^{-7} \\ e &= -8.553 \times 10^{-7} \end{aligned} \quad (59)$$

The data along with the curve fit are shown in Figure 6. These collisions are extremely efficient, with a reaction probability near 1.0. Rosner and Allendorf [46] also confirmed that the product of the reaction of atomic oxygen with the carbon surface was CO, not CO₂. Since the atomic oxygen collisions are so efficient, and since the expected atomic oxygen content is small, this collision efficiency is assumed to be independent of atomic oxygen partial pressure.

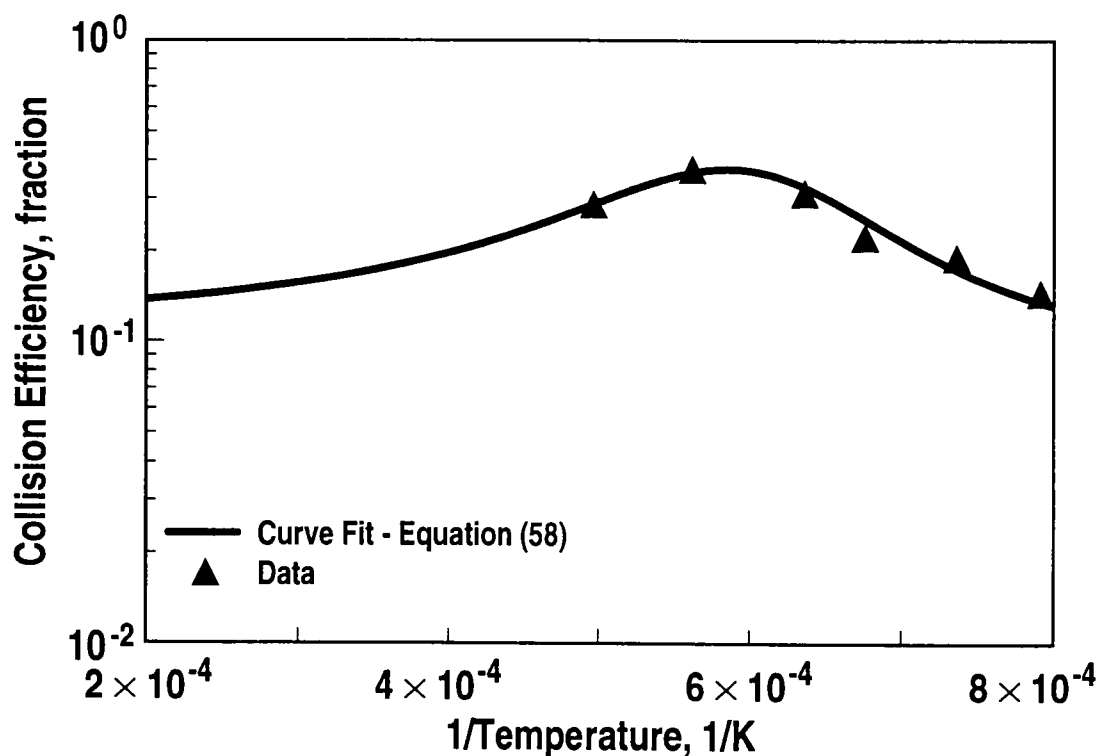


Figure 6 Rosner and Allendorf collision efficiency for $C + O = CO$.

Chapter 5. Model Results

Mass and Energy Equations for Multiple Collision Partners

Now that collision efficiencies for more than one reaction have been determined, the energy and mass conservation equations, Equations (54) and (55), must be extended to consider more than one collision partner. Assuming simple superposition of the collisions yields

$$\frac{dT}{dt} = \frac{3}{\rho r C} \sum_i Z_i \left[f_i (\tilde{m}_i e + q_{ri}) + (1 - f_i) q_{nri} \right] + \frac{3k_r \sigma}{\rho C} (T_\infty^4 - T^4) \quad (60)$$

and

$$\frac{dr}{dt} = \frac{-1}{\rho} \sum_i (Z f \tilde{m})_i \quad (61)$$

where the summation is taken over the number of collision partners. Equations (60) and (61) represent the current model for a soot particle reacting in an arbitrary gas mixture. These equations were solved numerically using a modified implicit Euler scheme detailed in Appendix E. Three collision partners were considered in the following calculations: O₂, O, and N₂. Every collision with N₂ was non-reactive, i.e.

f is identically zero for N_2 . Reactive collisions with OH will be considered in later sections.

Due to the competition among the reactive collision partners for active sites on the surface of the soot particle, superposition is not precisely valid. However, it does provide an upper bound on the reaction rate for a mixture of reactive collision partners and thus an upper bound on the predicted particle temperatures.

Oxidation in O_2 , O_2/N_2 , and O_2/O Mixtures

Figure 7 presents the calculated temperature history for a 50-nm initial diameter soot particle oxidizing in pure O_2 at a pressure of 0.02-atm.

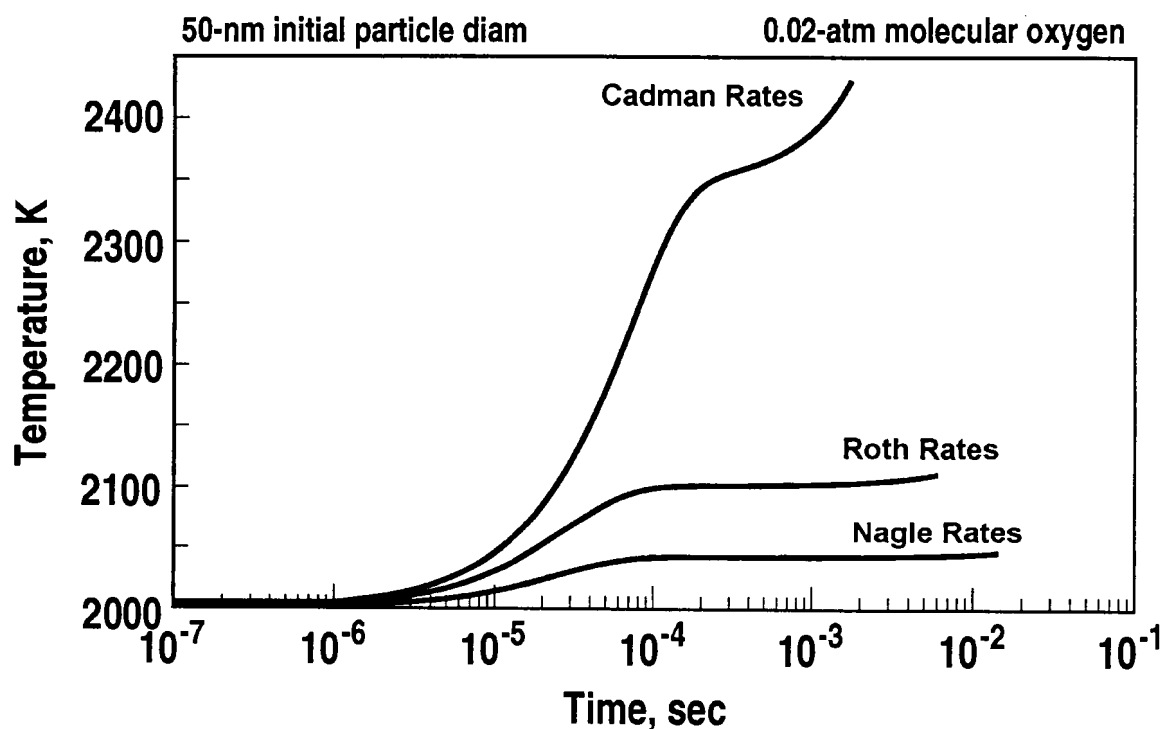


Figure 7 Particle Temperature History.

The particle is assumed initially to be in equilibrium with the 2000 K bath gas. The curve fits of the oxidation rates of Cadman et al. [41], Roth et al. [40], and Nagle and Strickland-Constable [42] were used. The Cadman et al. rates produced the maximum particle temperature. Note that the maximum temperature elevation of the particle temperature above the gas temperature is over 400 K when the Cadman et al. rates are used. The corresponding reduction in particle diameter as a function of time is shown in Figure 8. Note that the temperature elevation is over 300 K when the particle has lost less than 50% of its mass for the Cadman et al. rates.

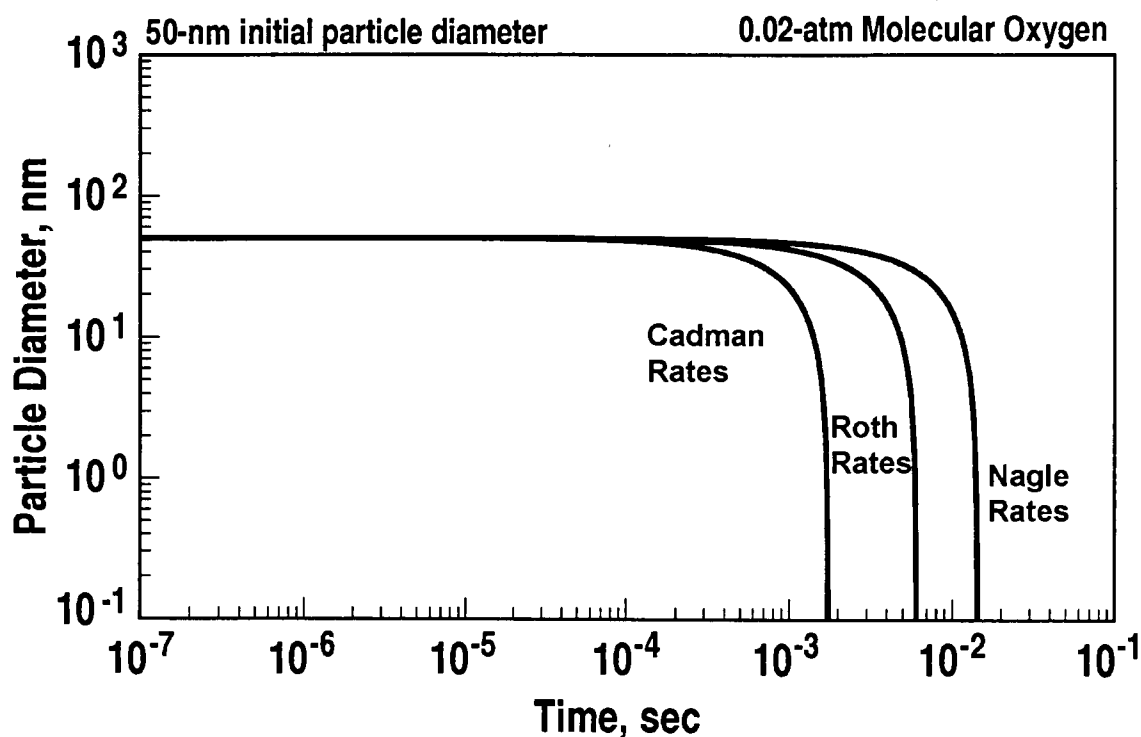


Figure 8 Particle size history.

Even for the Nagle and Strickland-Constable rates the particle temperature elevation is about 50 K. It is important to note that, if the typical continuum mass and energy conservation equations are used, the computed temperature elevation is a few degrees at most for particles of this size. Therefore, small particle size does not guarantee gas/particle thermal equilibrium for reacting particles. In fact, it is the small particle size that allows thermal nonequilibrium, if rarefaction effects are properly taken into account. This result contradicts the small particle limit predicted by the continuum theory in Refs. [3-12].

Figure 9 presents the particle temperature elevation at burnout for a 50-nm initial diameter particle oxidizing in various O_2/N_2 mixtures at 1.00-atm.

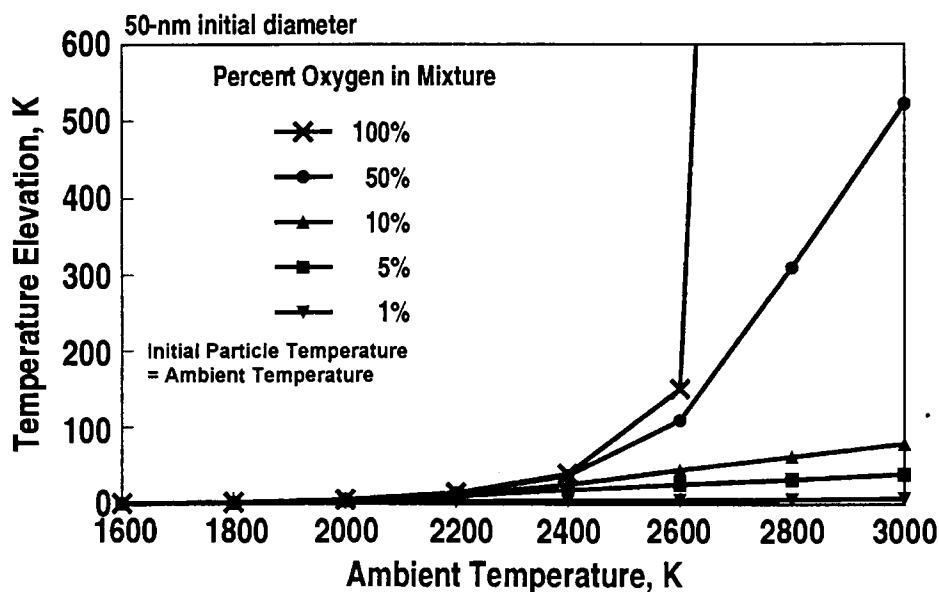


Figure 9 Particle temperature elevation at burnout for 1.00-atm O_2/N_2 mixtures.

Here, particle burnout is defined as the time at which the particle diameter is reduced to 0.5-nm. The particle is assumed to be initially in thermal equilibrium with the bath gas. These and all later calculations in this section use the Cadman et al. rates for O₂ oxidation since they are the fastest and will give an upper bound on the particle thermal nonequilibrium. The particle temperature elevation is seen to increase with increasing ambient temperature and with increasing oxygen concentration. Negligible particle temperature elevation is seen below about 2200 K, due to the decrease in collision frequency below this temperature.

Figures 10 and 11 show similar results for 0.1- and 0.01-atm, respectively.

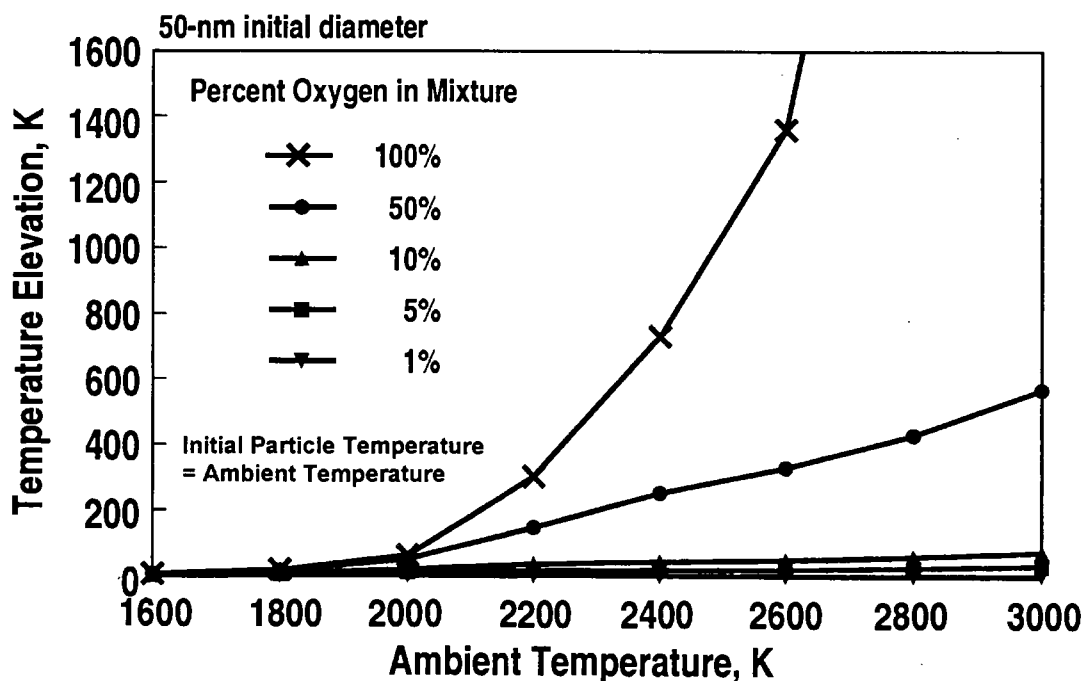


Figure 10 Particle temperature elevation at burnout for 0.10-atm O₂/N₂ mixtures.

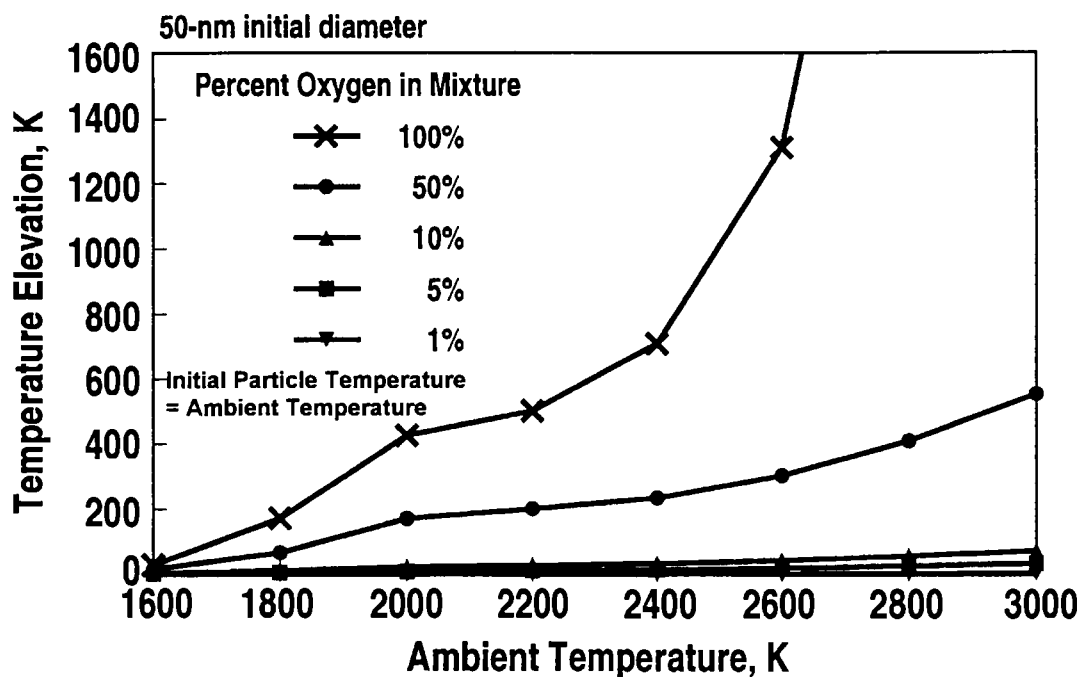


Figure 11 Particle temperature elevation at burnout for 0.01-atm O₂/N₂ mixtures.

Note the change in the temperature elevation scale from Figure 9 to Figures 10 and 11, indicating that the particle temperature elevation increases with decreasing pressure. At the lowest pressure, substantial particle temperature elevation is predicted at temperatures as low as 1600-1800 K ambient temperature.

The pressure dependence of the particle temperature elevation is shown directly in Figure 12. This figure shows a 50-nm diameter particle combusting with pure O₂ at 1.0-, 0.1-, and 0.01-atm. The particle is assumed to be initially in thermal equilibrium with the 2200 K bath gas.

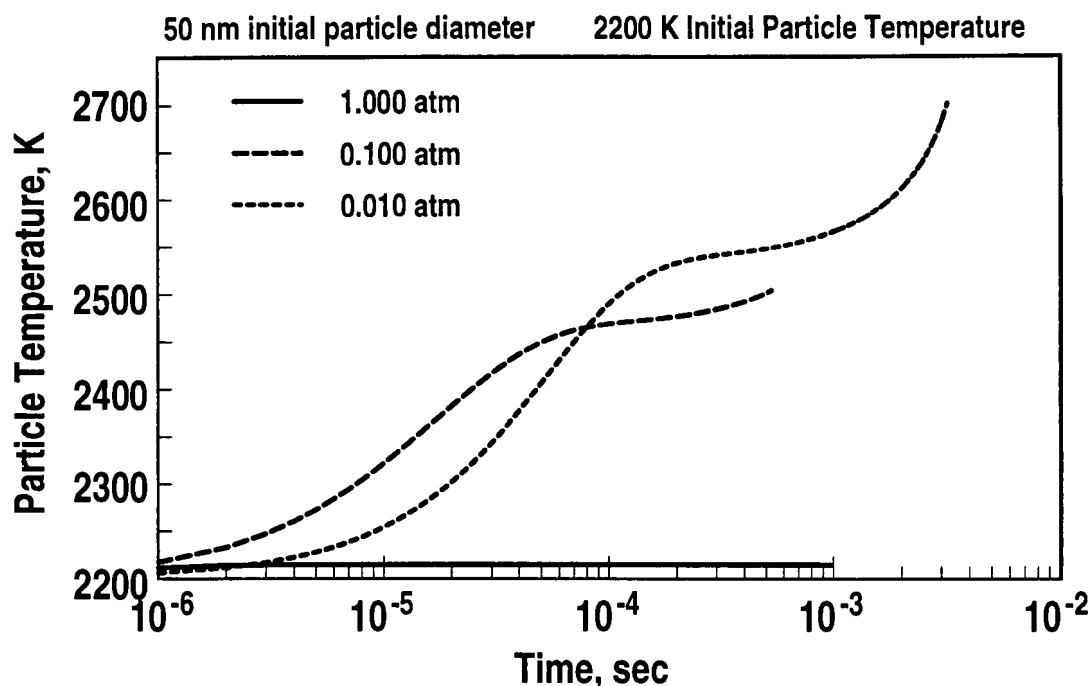


Figure 12 Particle temperature history in O₂ as a function of pressure.

At 1.0-atm, there is negligible particle temperature increase. At 0.1-atm, the particle temperature reaches a plateau at about 250 K above the gas temperature, with a small increase at burnout. At 0.01-atm, the particle temperature reaches a plateau at about 300 K above the ambient gas temperature, with a rapid increase at burnout. It is interesting to note that the particle burns out faster at 0.1-atm than at 1.0-atm, even though the collision frequency is an order of magnitude greater at 1.0-atm. This seemingly counter-intuitive behavior is explained by the particle temperature elevation at 0.1-atm. As the particle temperature rises, the collision efficiency increases (see Figure 5), which produces still higher temperatures. This feed-forward process causes the collision efficiency-collision frequency product to be

greater at 0.1-atm than at 1.0-atm. Therefore, the particle lifetime is shorter at 0.1-atm. This complicated pressure-dependence of particle lifetime would be completely missed by a continuum model.

Figure 13 shows the particle temperature history of a 50-nm diameter particle oxidizing in two ambient gas compositions: 100% O_2 and 98% O_2 /2% O . The Cadman et al. [41] rates are used for O_2 and the Rosner and Allendorf [43] rates are used for O . The particle is assumed to be initially in equilibrium with the 2200 K bath gas. The addition of this small amount of atomic oxygen causes an increase of 200 K in the particle temperature. Collisions with O are efficient and very exothermic.

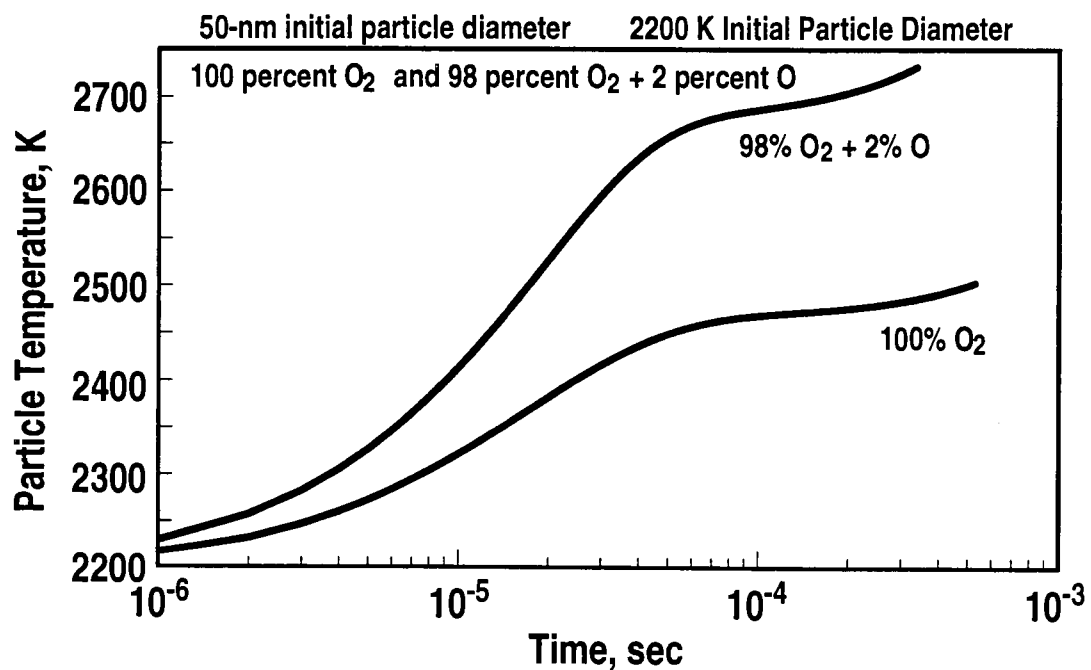


Figure 13 Particle temperature history in O_2 and O_2/O mixture.

The calculations in this section show that significant particle thermal nonequilibrium can exist for small combustng particles, if rarefaction effects are properly taken into account. Thermal nonequilibrium is favored by high particle temperatures and low pressures - conditions which create high collision efficiencies.

Extrapolation of the Nagle and Strickland-Constable Rate Expression to Low Pressure

The carbon oxidation rates of Nagle and Strickland-Constable [42] are routinely applied in the flame literature to determine soot oxidation by molecular oxygen. These rates were experimentally determined at temperatures from 1000-2000° C (1273-2273 K) and at oxygen partial pressures from 0.1-0.6 atm and then curve fit. For typical laboratory flames, oxygen partial pressures may be significantly lower than 0.1-atm. Frequently, researchers will extrapolate the Nagle and Strickland-Constable curve fit to these lower oxygen partial pressures to determine the molecular oxygen contribution to the overall soot oxidation rate. It has been shown [47] that the Nagle and Strickland-Constable curve fits exhibit nonphysical behavior at pressures below 0.05-atm (depending on the temperature.) This behavior is revealed when the oxidation rates are transformed to collision efficiencies. At a fixed temperature, the oxidation rate drops faster than the collision rate as the pressure is reduced. At typical flame conditions, extrapolation of the Nagle and Strickland-Constable curve fits yields collision efficiencies that may be an order of magnitude too low.

In order to fit their data, Nagle and Strickland-Constable used a modification of the surface reaction theory of Blyholder, Binford, and Eyring [48]. This theory states that the number of active sites on the surface is a function of temperature only, and is explicitly independent of pressure. Active sites are occupied by oxygen molecules (or atoms) for a finite time, rendering these sites temporarily inactive. If the collision frequency is high enough, the molecules occupying the active sites will interfere with other molecules arriving at the surface. Therefore, increasing pressure causes an *apparent* decrease in the number of active sites on the soot surface. This is reflected as a decrease in the collision efficiency. The number of active sites on the surface is fixed by the temperature, but the availability of an active site is affected by the collision frequency. At high collision frequency, molecules collide with the soot surface faster than the occupied sites are cleared. This means that, at a given temperature, the collision efficiency must be a monotonically increasing function with decreasing pressure. As seen on Figure 14, at 2000 K the collision efficiency computed from the Nagle and Strickland-Constable expression is not a monotonically increasing function with decreasing pressure. The efficiency has a maximum at about 0.02-atm and then decreases with further decrease in pressure. This decrease is not physical. It is caused simply by extrapolating the Nagle and Strickland-Constable expression beyond its range of validity. At 1250 K, the collision efficiency computed from the Nagle and Strickland-Constable expression is a monotonically increasing function of decreasing pressure. This is the expected behavior, if the number of active sites on the surface is independent of pressure.

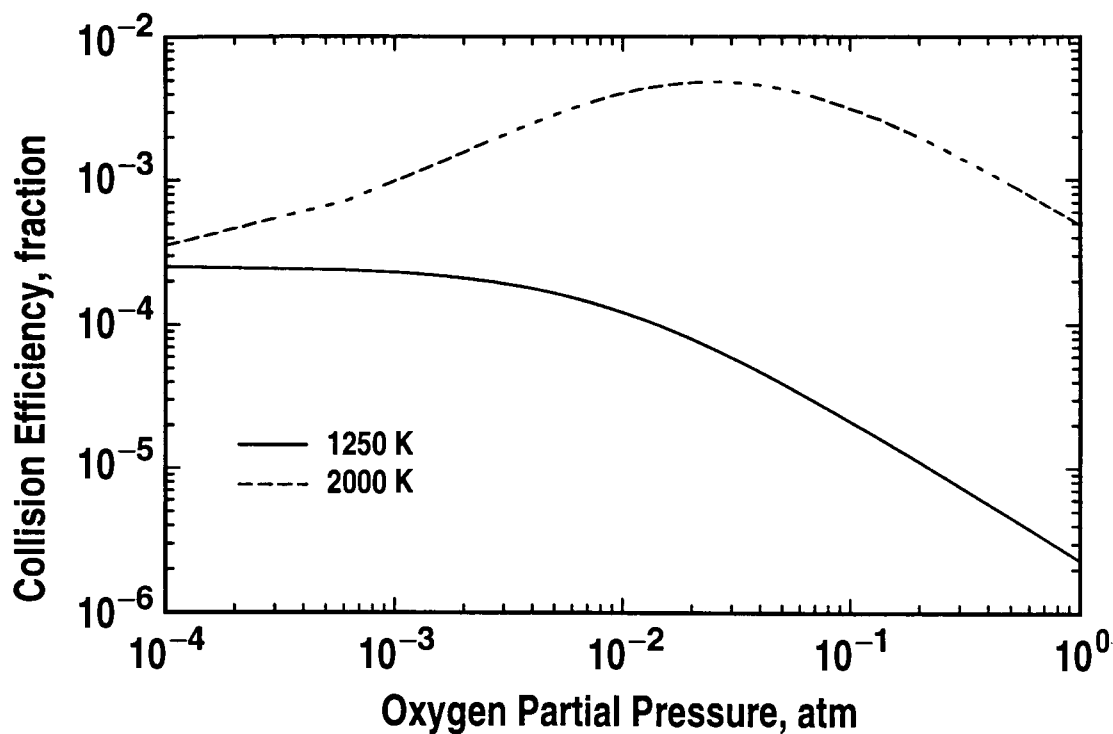


Figure 14 Pressure dependence of Nagle and Strickland-Constable collision efficiency.

An alternate way to describe this situation is that the Blyholder, Binford, and Eyring theory limits the order of the reaction to between zero order and first order. It can be shown that the rate expression of Nagle and Strickland-Constable allows reaction orders higher than unity. More details are available in the paper by Hiers [47].

The effect of this nonphysical behavior is illustrated in Figure 15, which shows burnout temperature as a function of pressure.

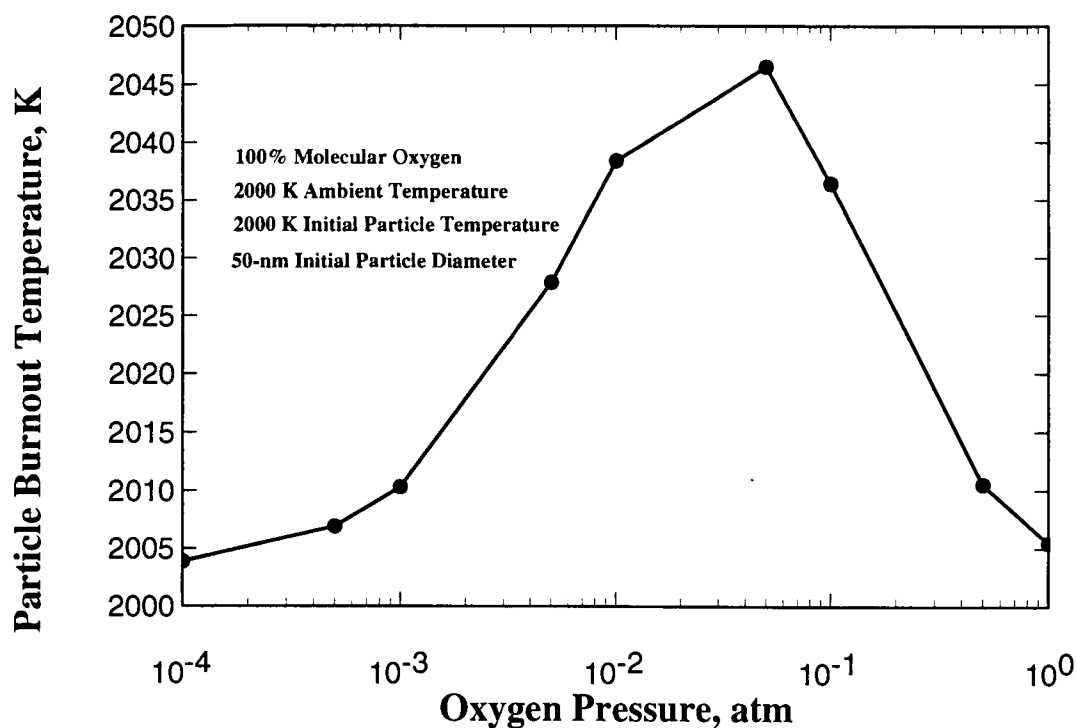


Figure 15 Pressure dependence of particle burnout temperature at 2000 K.

The Nagle and Strickland-Constable rates were used, fit with their rate expression (Equation (57)). The conditions for these calculations are: 50-nm initial particle diameter; pure molecular oxygen; and an ambient temperature (and initial particle temperature) of 2000 K. Note the peak in the burnout temperature. The burnout temperature should increase as a function of decreasing pressure, to some low pressure limit. The temperature elevation maximum seen in Figure 15 is nonphysical, and is caused by the reasons stated above. As stated in [47], the Nagle and Strickland-Constable rate expression should be modified to limit the pressure dependence to first-order or less. Figure 16 shows the particle burnout temperature

as a function of pressure at an ambient temperature of 1250 K. The burnout temperature is a monotonically increasing function of decreasing pressure, as are the collision efficiencies at 1250 K shown in Figure 14. This demonstrates that the pressure dependence of the Nagle and Strickland-Constable rate expression is also temperature dependent. At low temperature, the pressure dependence is between zero- and first-order, while at higher temperatures, the pressure dependence is higher than first order. This monotonic increase in burnout temperature with decreasing pressure is the expected physical behavior if the number of active sites on the surface is independent of pressure.

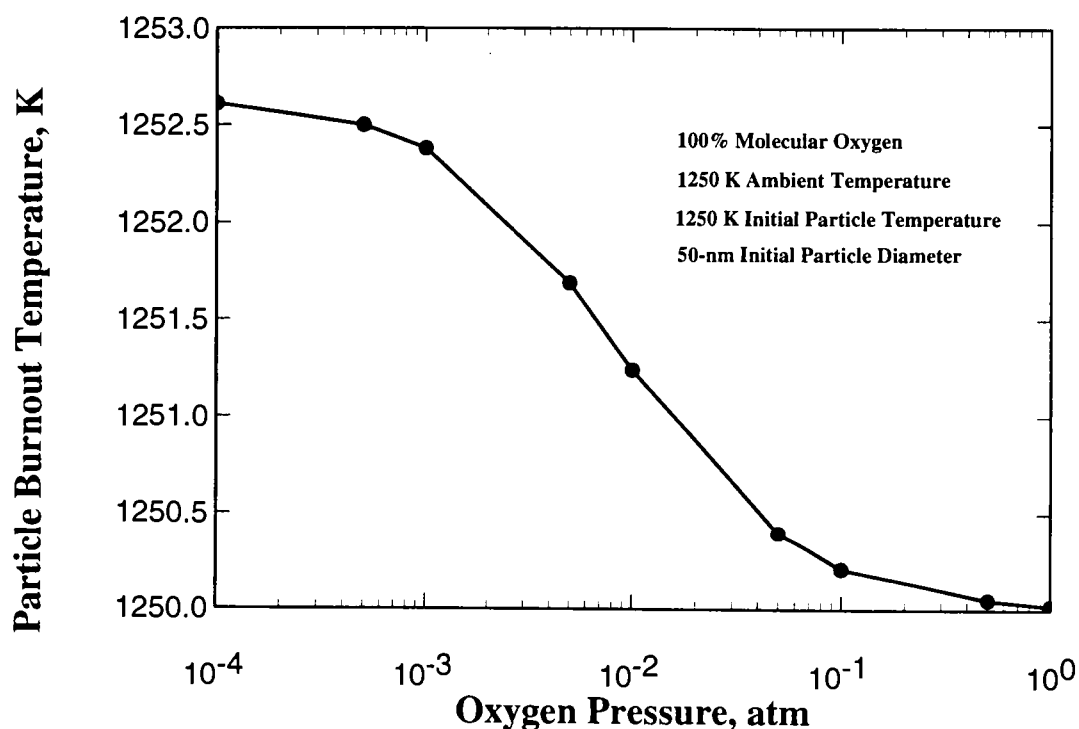


Figure 16 Pressure dependence of particle burnout temperature at 1250 K.

Comparison to Analytical Solutions

The particle energy and mass equations (Equations (54) and (55)) are first-order, non-linear, ordinary differential equations. The non-linearity is due both to the radiation term (T^4) and the non-linear 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

$$e = CT \quad (62)$$

and

$$q_{nr} = (2k + C_{v, internal})(T_\infty - T) = \hat{C}_v(T_\infty - T) \quad (63)$$

from which the definition of $\hat{C}_v$ (the gas specific heat at constant volume under effusive conditions) is obvious. Making these substitutions in Equation (54) (and neglecting radiation) yields

$$\frac{dT}{dt} = \frac{3Z}{\rho r C} [f(\tilde{m}CT + q_r) + (1-f)\hat{C}_v(T_\infty - T)] \quad (64)$$

For constant collision efficiency, the particle mass equation (Equation (55)) will integrate immediately to yield

$$r(t) = r_0 - \frac{Zf\tilde{m}}{\rho}t \quad (65)$$

where r_0 is the initial particle radius. Equation (64) is a linear, first-order, ordinary differential equation with variable coefficients (since $r = r(t)$) which can be simply integrated using an integrating factor to obtain

$$T(t) = -\beta + (T_0 + \beta) \left(\frac{r_0}{r(t)} \right)^\delta \quad (66)$$

where

$$\beta = \frac{[fq_r + (1-f)\hat{C}_v T_\infty]}{[f\tilde{m}C - (1-f)\hat{C}_v]} \quad (67)$$

and

$$\delta = 3 \left[1 - \frac{(1-f)\hat{C}_v}{f\tilde{m}C} \right] \quad (68)$$

and T_0 is the initial particle temperature. For the subsequent calculations, the constant coefficients are evaluated at the following conditions: pure molecular oxygen at a pressure of 0.10-atm, temperature of 2500 K, using the Roth et al. [40] oxidation rates. Figure 17 presents a comparison of the analytical solution and the numerical solution (solving Equations (60) and (61) using the modified implicit Euler scheme described in Appendix E) for the temperature rise of particles of various size oxidizing under the conditions given above. The numerical solution has been altered to neglect radiation and to use the same constant properties as the analytic solution.

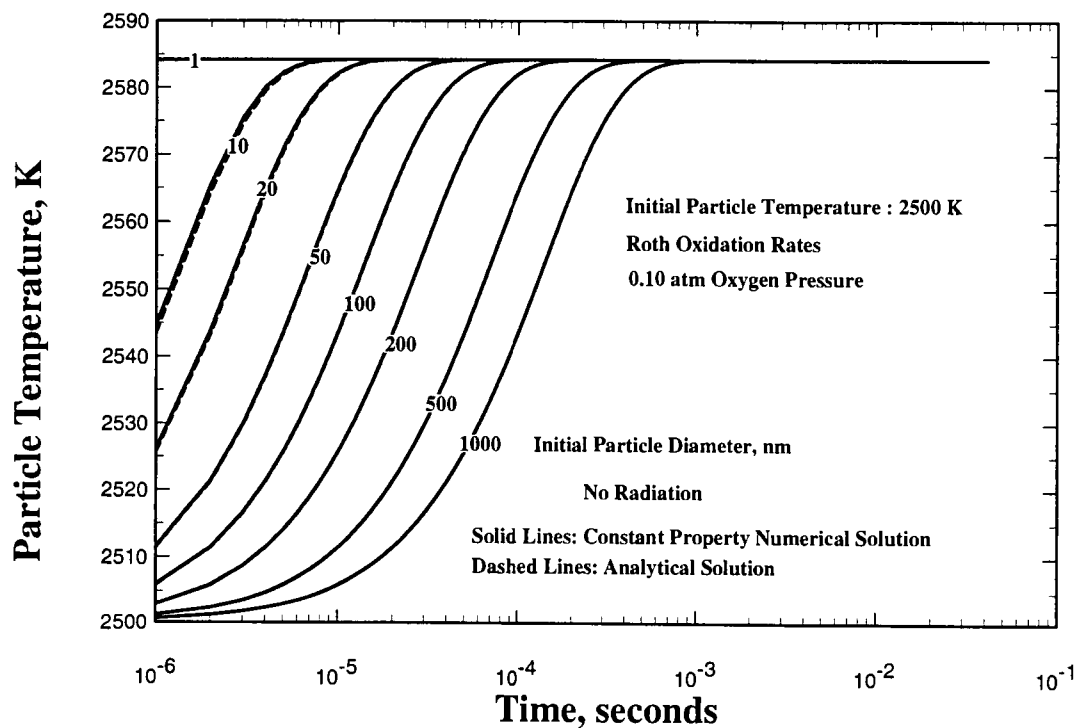


Figure 17 Comparison of analytical and numerical solutions for particle temperature history.

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} sec) step size which 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 non-constant properties and the in the treatment of the radiation term. Note in Figure 17 that the ultimate temperature of the particle is independent of the initial particle size. The initial particle size effects only the rise time. This will be discussed in further detail in a later section.

Including the radiative term in Equation (64) yields

$$\frac{dT}{dt} = \frac{3Z}{\rho r C} \left[f(\tilde{m}CT + q_r) + (1-f)\hat{C}_v(T_\infty - T) \right] + \frac{3k_r\sigma}{\rho C} (T_\infty^4 - T^4) \quad (69)$$

where k_r is now treated as a temperature-independent constant. Figure 18 presents the same numerical results as Figure 17, 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.

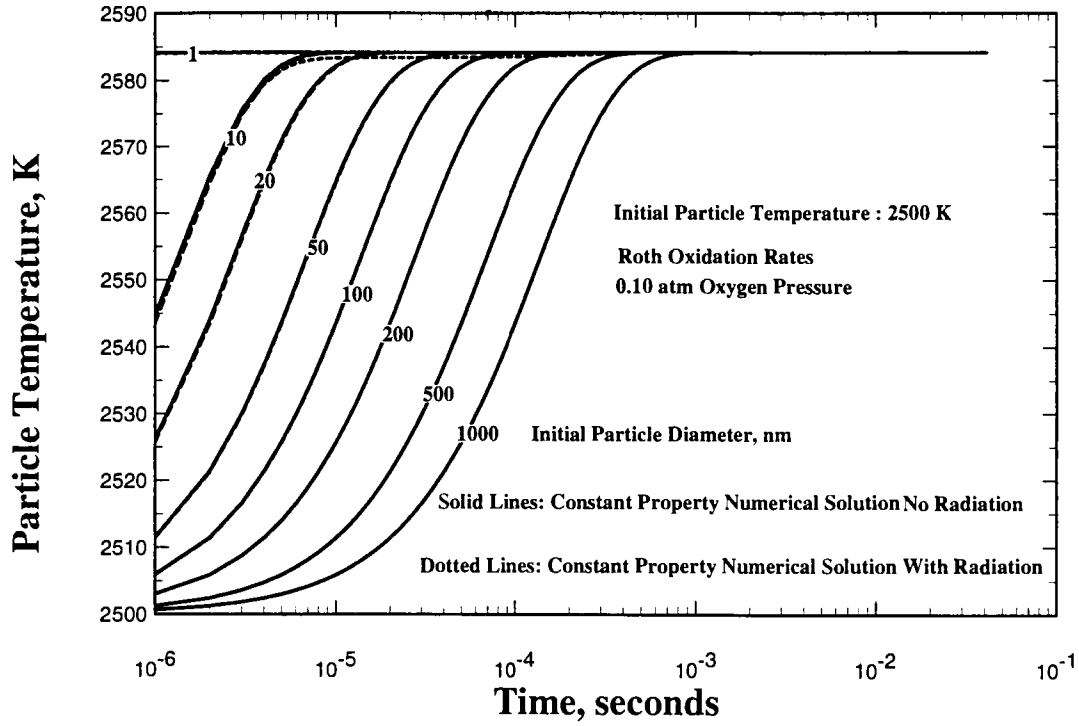


Figure 18 Comparison of constant property numerical solutions with and without radiation.

The presence of the r_0/r term in Equation (66) indicates a singularity at burnout (i.e. 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 Equation (65):

$$t^* = \frac{r_0 \rho}{Z f \bar{m}} \quad (70)$$

and so we can define

$$T^* = \lim_{t \rightarrow t^*} [T(t)] \quad (71)$$

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

$$\delta < 0 \Rightarrow T^* \rightarrow -\beta \quad (72)$$

$$\delta \geq 0 \Rightarrow T^* \rightarrow \infty \quad (73)$$

Allowing the collision efficiency (f) to vary while considering all other parameters fixed, we can solve Equation (68) for the critical value of $f = f^*$ that corresponds to $\delta=0$. This yields

$$f^* = \frac{1}{1 + \frac{\tilde{m}C}{\hat{C}_v}} \quad (74)$$

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

$$f < f^* \Rightarrow \delta < 0 \Rightarrow T^* \rightarrow -\beta \quad (75)$$

$$f \geq f^* \Rightarrow \delta \geq 0 \Rightarrow T^* \rightarrow \infty \quad (76)$$

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 Equation (66) are plotted in Figure 19 for various values of the collision efficiency f . The computations stop one time step before burnout to avoid the infinite temperature at the singularity.

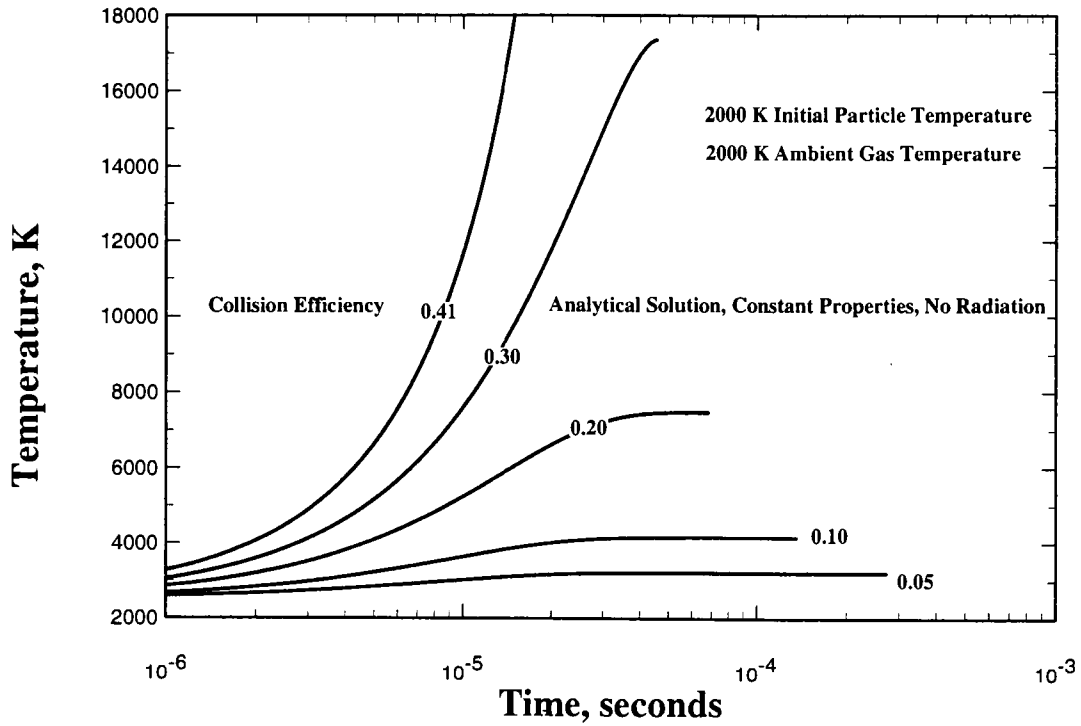


Figure 19 Analytical solution for temperature history as a function of collision efficiency.

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 20 is a re-scaled version of Figure 19 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 collisions (such as atomic oxygen) and no non-reactive gases (such as nitrogen). These conditions are not typically found in flames or shock tubes.

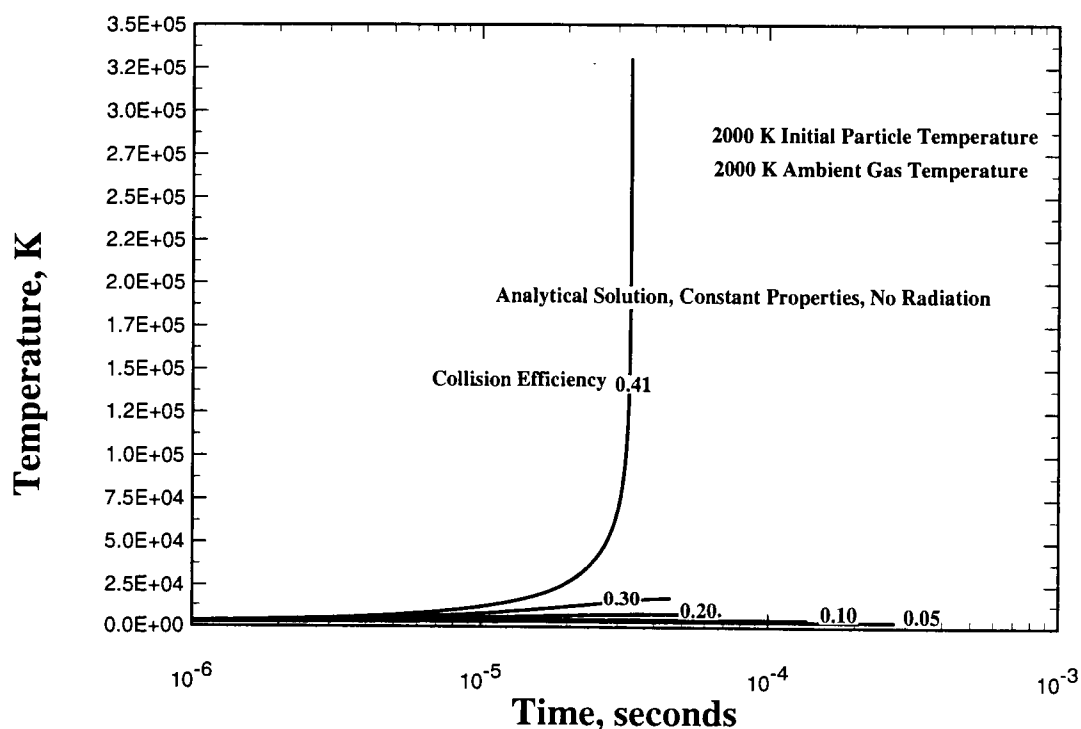


Figure 20 Analytical solution for temperature history as a function of collision efficiency - rescaled.

The large temperatures indicated are not physical, since 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 (69) is the particle energy equation including radiative loss. Figure 21 shows the numerical solution of Equation (69) for particle temperature versus time. The collision efficiency (f) is varied while considering all other parameters fixed.

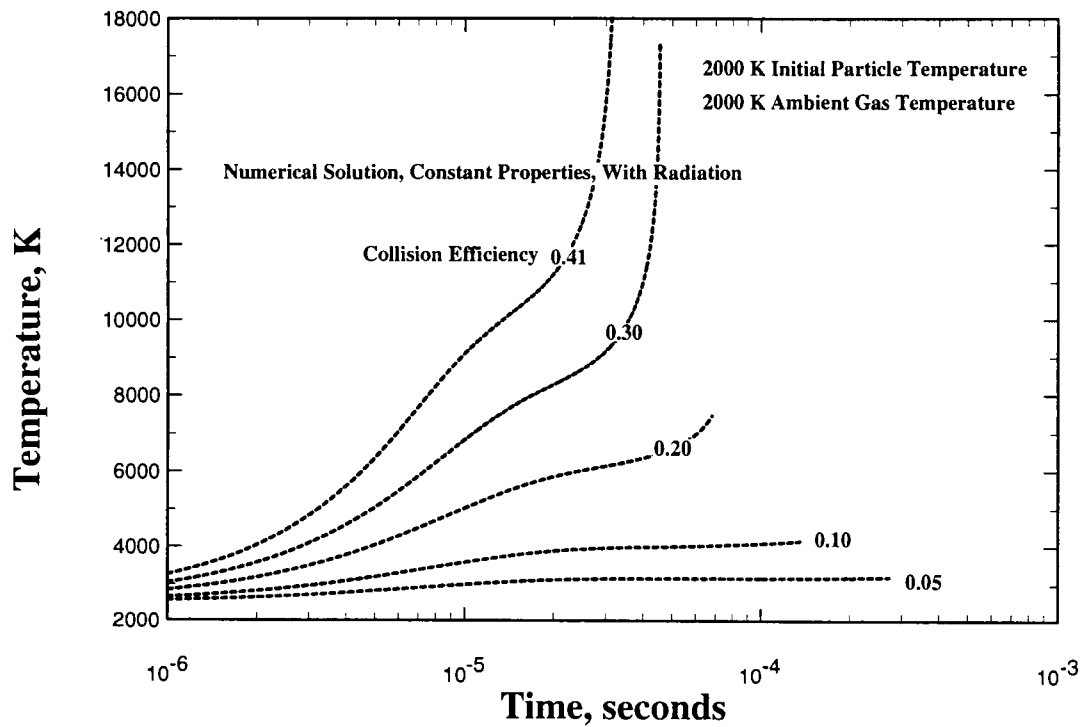


Figure 21 Numerical solution for temperature history as a function of collision efficiency (with radiation).

The “small f ” and “large f ” behaviors noted in Figure 19 are also seen when including radiative heat loss. Figure 22 is a re-scaled version of Figure 21 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, since 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 Figures 19 and 21, the calculations are stopped one time step before burnout to avoid the singularity which occurs when the particle radius is reduced to zero.

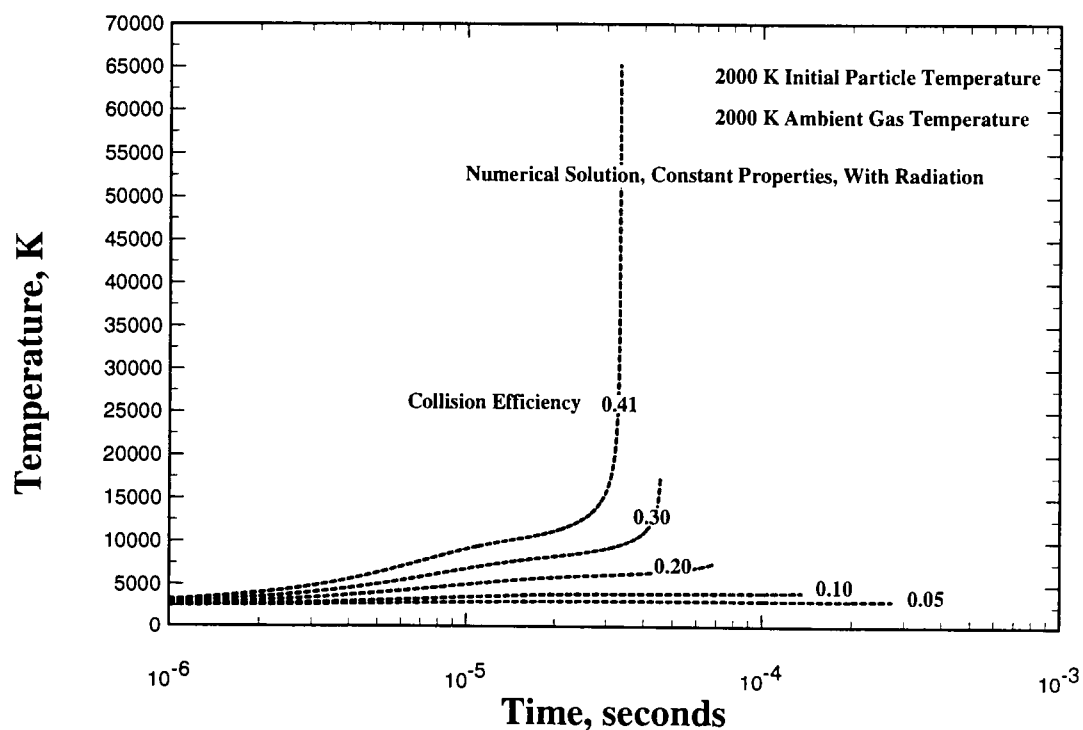


Figure 22 Numerical solution for temperature history as a function of collision efficiency (with radiation) - rescaled.

Figure 23 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 previous 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 “critical value” for a large slope at burnout. The critical value for infinite temperature at burnout is unaffected by the inclusion of radiation.

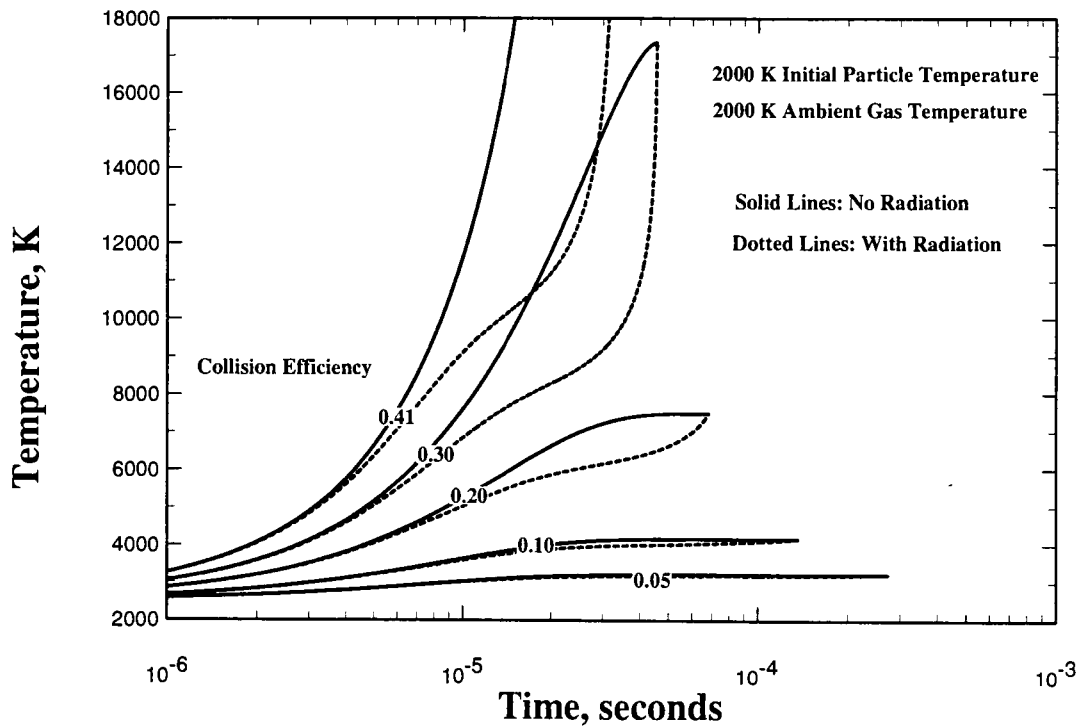


Figure 23 Comparison of analytical and numerical (with radiation) solution for temperature history as a function of collision efficiency.

Phase Plane Analysis

A phase plane analysis of the governing system of ordinary differential equations can reveal behaviors not apparent in the physical plane. Before computing the phase plane for the system of differential equations, it will be convenient to non-dimensionalize Equations (69) and (55). Dividing both sides of Equation (69) by T_∞ and rearranging yields

$$\frac{d\bar{T}}{dt} = \frac{3Z}{\rho r C} \left[f\tilde{m}C\bar{T} + (1-f)\hat{C}_v(1-\bar{T}) + fq_r \right] + \frac{3k_r\sigma}{\rho C} T_\infty^3 [1-\bar{T}^4] \quad (77)$$

where

$$\bar{T} = \frac{T}{T_\infty} \quad (78)$$

Dividing both sides of Equation (55) by r_0 yields

$$\frac{d\bar{r}}{dt} = -\frac{Zf\tilde{m}}{\rho r_0} \quad (79)$$

where

$$\bar{r} = \frac{r}{r_0} \quad (80)$$

Multiplying and dividing the first term in Equation (77) by r_0 yields

$$\frac{d\bar{T}}{dt} = \frac{3Z}{\rho\bar{r}C} \frac{1}{r_0} \left[f\tilde{m}C\bar{T} + (1-f)\hat{C}_v(1-\bar{T}) + fq_r \right] + \frac{3k_r\sigma}{\rho C} T_\infty^3 [1-\bar{T}^4] \quad (81)$$

Equations (81) and (79) are the non-dimensional particle energy and mass conservation equations, respectively. Multiplying both sides of these equations by r_0 and defining a new scaled time as

$$\bar{t} = \frac{t}{r_0} \quad (82)$$

yields

$$\frac{d\bar{T}}{d\bar{t}} = \frac{3Z}{\rho\bar{r}C} \left[f\tilde{m}C\bar{T} + (1-f)\hat{C}_v(1-\bar{T}) + fq_r \right] + r_0 \frac{3k_r\sigma}{\rho C} T_\infty^3 [1-\bar{T}^4] \quad (83)$$

and

$$\frac{d\bar{r}}{d\bar{t}} = -\frac{Zf\tilde{m}}{\rho} \quad (84)$$

as the particle energy and mass conservation equations. If the radiation term is neglected, the initial particle radius does not appear as a parameter. Therefore, the behavior in the $(\bar{r}, \bar{T})$ phase plane should be independent of initial particle size. This is confirmed in Figure 24, which shows this phase plane for a variety of initial particle sizes and temperatures, ignoring the radiation term. The conditions for these calculations are: ambient temperature of 2500 K, initial particle temperatures of 100, 1000, 2500, 5000, and 9000 K (corresponding to $\bar{T} = 0.04, 0.4, 1.0, 2.0$, and 3.6 respectively), initial particle diameters of 50-, 500-, and 1000-nm, and constant thermal properties.

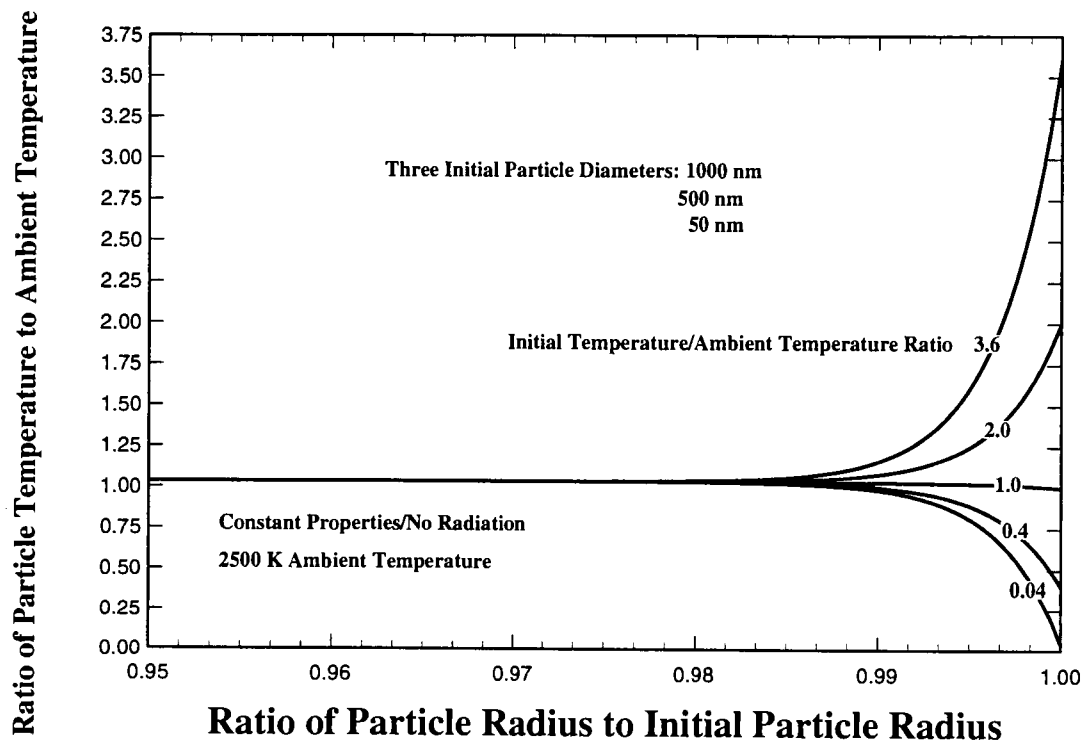


Figure 24 Non-dimensional phase plane for analytical solution.

Three initial particle sizes are shown for each initial particle temperature. However, these lines are indistinguishable from each other, confirming that the behavior of the solution in the phase plane is indeed independent of the initial particle size. Note that it is also obvious in the phase plane that the ultimate temperature is independent both of initial temperature and initial particle size. The abscissa is truncated at 0.95, showing that, under these conditions, the particle reaches the ultimate temperature before a significant amount of mass is lost.

The inclusion of the radiation term complicates the behavior of the solution in the $(\bar{r}, \bar{T})$ phase plane since now the initial particle size is a parameter. This is shown in Figures 25-27.

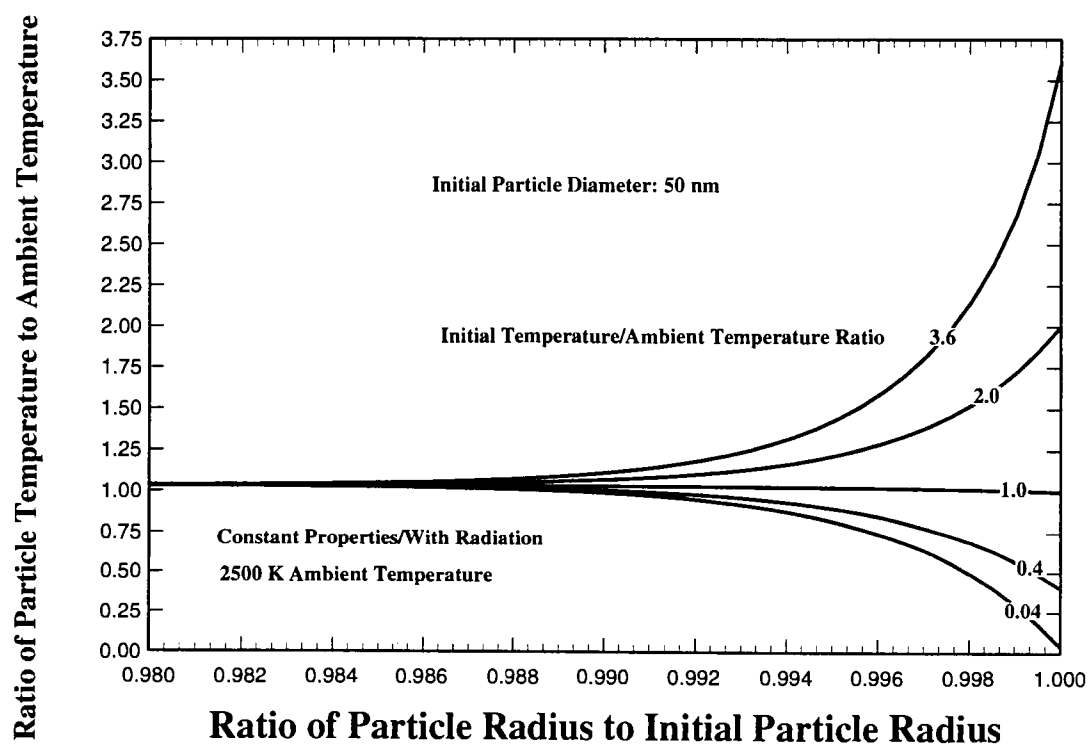


Figure 25 Phase plane for numerical solution - 50-nm initial particle diameter.

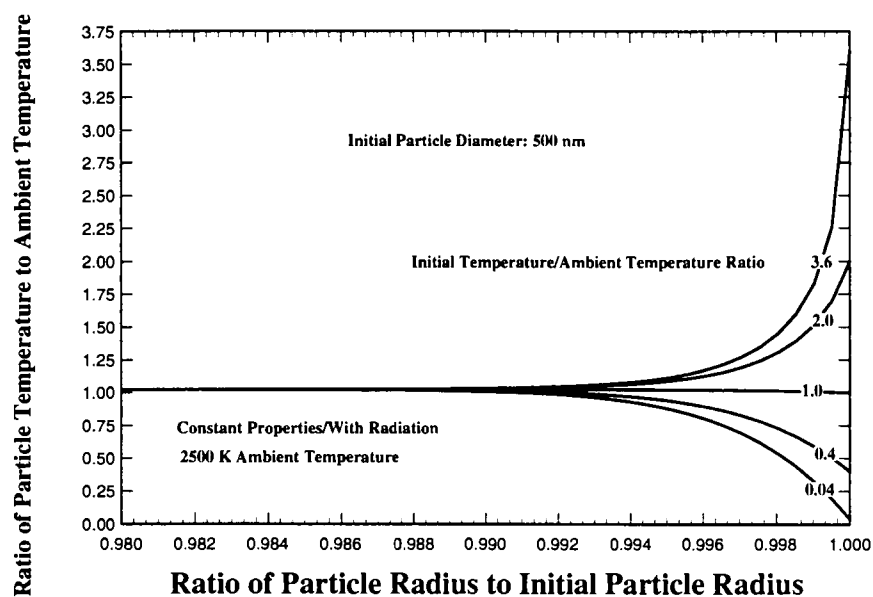


Figure 26 Phase plane for numerical solution - 500-nm initial particle diameter.

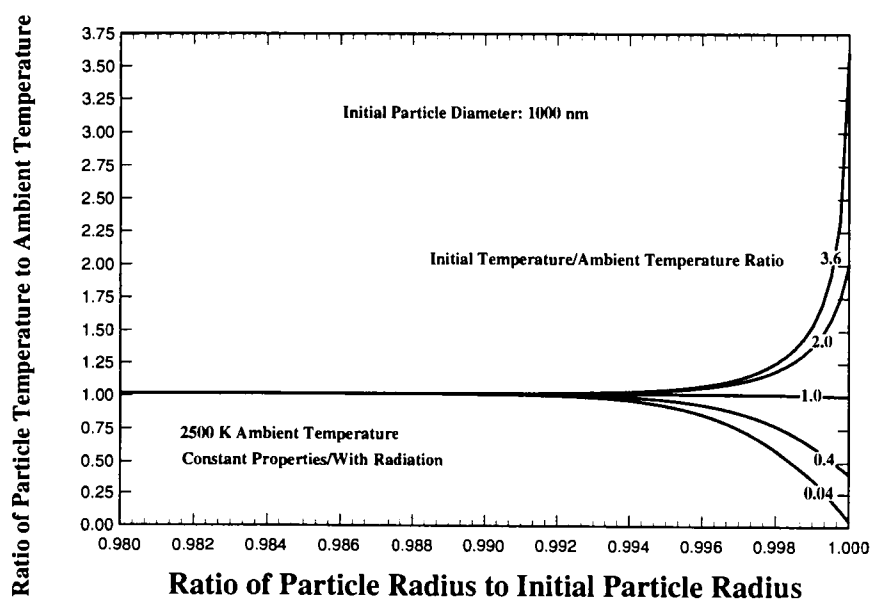


Figure 27 Phase plane for numerical solution - 1000-nm initial particle diameter.

The solution is shown in the phase plane for various initial temperatures for one initial particle size per plot. Figure 25 shows results for a 50-nm initial diameter particle, while Figures 26 and 27 show results for 500- and 1000-nm particles, respectively. Note that the abscissa is truncated in all these figures, indicating that, under these conditions, the particles reach the ultimate temperature before a significant amount of mass is lost. The same ambient temperature and initial temperatures used in Figure 24 are used here - i.e. ambient temperature of 2500 K, and initial particle temperatures of 100, 1000, 2500, 5000, and 9000 K (corresponding to $\bar{T} = 0.04, 0.4, 1.0, 2.0, \text{ and } 3.6$ respectively).

Figure 28 shows the phase plane behavior for a single initial temperature, but several particle sizes. The ambient temperature for this calculation is 2500 K, and the initial temperature is 9000 K, yielding a $\bar{T}$ of 3.6. This plot confirms that the initial particle size is a parameter in the phase plane when the radiation term is included. The smaller particles lose more mass (relatively) than do larger particles before reaching the ultimate temperature. However, the abscissa is truncated at 0.98, showing that whether radiation is included or neglected, negligible mass is lost before the ultimate temperature is reached.

The behavior in the phase plane also shows that the particle temperature asymptotically approaches its ultimate temperature $\bar{T}^*$ (the particle temperature at burnout) with no over- or undershoot. In other words, if the initial temperature is above the ultimate temperature, the particle temperature monotonically decreases to the ultimate temperature.

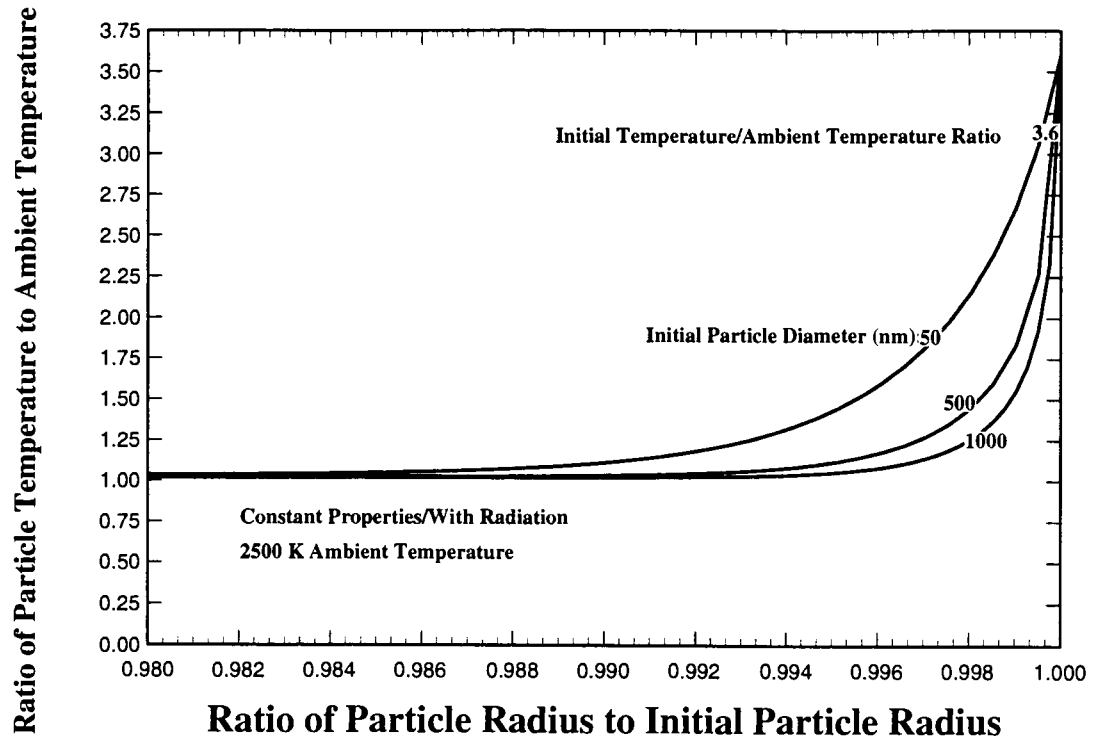


Figure 28 Non-dimensional phase plane for numerical solution - 50-, 500-, and 1000-nm initial particle diameters.

If the initial temperature is less than the ultimate temperature, the particle temperature monotonically increases until the ultimate temperature is reached. This asymptotic approach also implies that

$$\frac{d\bar{T}}{d\bar{t}} \rightarrow 0 \quad (85)$$

as the particle approaches burnout, i.e. as

$$\bar{r} \rightarrow 0 \quad (86)$$

Of course, as the particle approaches burnout

$$\bar{T} \rightarrow \bar{T}^* \quad (87)$$

Note that this discussion of asymptotic behavior at burnout is valid only for the more typically encountered “small f ” behavior discussed in the previous section. As the particle approaches burnout, the $1/\bar{r}$ in the first term in Equation (83) grows without bound, meaning we can neglect the radiation term in comparison to the first term. Assuming also that Equation (85) holds, Equation (83) becomes (at burnout)

$$\frac{d\bar{T}}{dt} = 0 = \frac{3Z}{\rho \bar{r} C} \left[f \tilde{m} C \bar{T}^* + (1-f) \hat{C}_v (1 - \bar{T}^*) + f q_r \right] \quad (88)$$

which can be solved directly for the ultimate temperature, $\bar{T}^*$:

$$\bar{T}^* = \frac{f q_r + (1-f) \hat{C}_v}{(1-f) \hat{C}_v - f \tilde{m} C} \quad (89)$$

which shows that the ultimate temperature is indeed independent of particle size, initial particle temperature, and the inclusion/neglect of the radiation term. It should be stated again that this value of the ultimate temperature is valid only for the “small f ” limit. If the collision efficiency increases above some critical value, the slope at burnout is essentially infinite, which invalidates the assumption of zero slope made in Equation (85). Therefore, care must be used when applying this approximation for the ultimate particle temperature.

It is important to note that all the conclusions drawn from the behavior of the solution in the phase plane apply only to steady ambient conditions. Time-varying ambient conditions can cause different behavior. The equations are modified in subsequent sections to include time-varying ambient conditions.

Chapter 6. Thermal Nonequilibrium in Shock Tube Measurements of Soot Oxidation Rates

As shown above, gas-particle thermal nonequilibrium is increased by higher temperature and lower pressure. As stated in the section **History of Small Particle Combustion** of **Chapter 1**, in most shock tube studies of soot oxidation rates, the experimenters assumed that the particle temperature could be computed from the shock tube relations. That is, they assumed the particles were in thermal equilibrium with the gas. The measured oxidation rates are assigned to the computed gas temperature, not a measured or computed particle temperature. This section will address the possible extent of thermal nonequilibrium in measurements such as these.

It is desirable to measure the oxidation rate at the lowest obtainable oxygen partial pressures, since typical oxygen partial pressures in the soot laden regions of rich flames are in the 0.004 - 0.02 atm range. Shock tube studies typically operate at reflected shock pressures of 4-6 atm. Therefore, to obtain oxygen partial pressures on the order of fractions of an atmosphere, an inert buffer gas must be added to the driven section of the shock tube. This buffer gas is typically argon [39], [40], [41]. Figure 29 presents the computed temperature elevation at burnout for a 50-nm particle as a function of reflected shock gas temperature and argon buffer gas pressure.

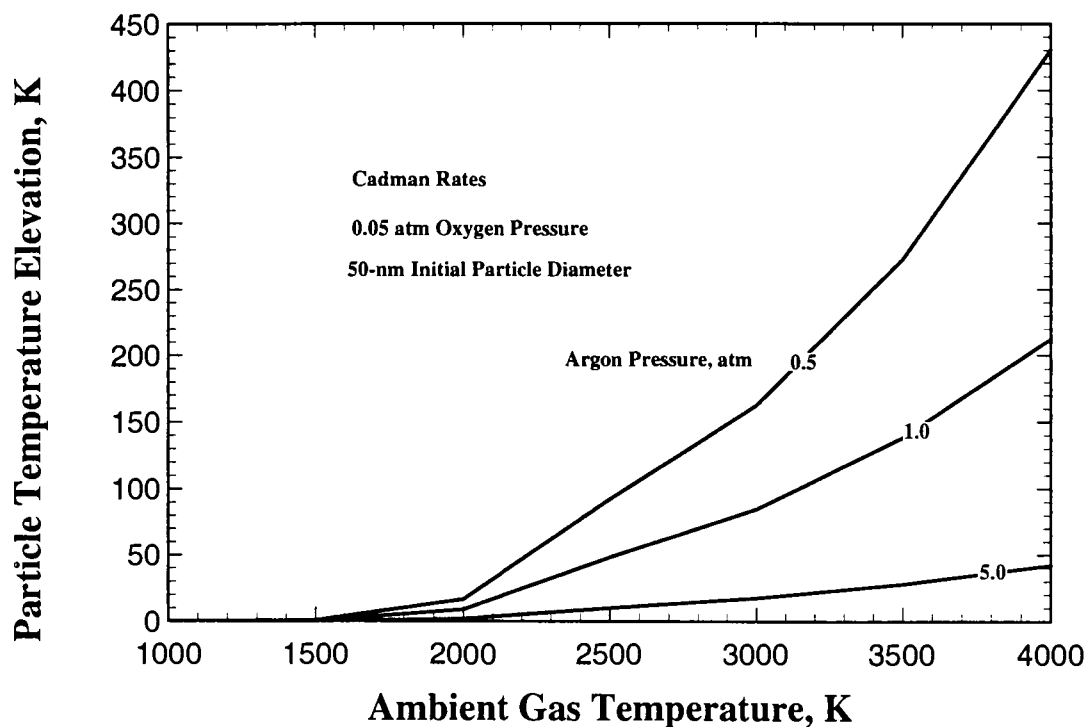


Figure 29 Particle temperature elevation at burnout for shock tube conditions using Cadman rates.

These results are obtained by numerically solving Equations (60-61). The oxygen partial pressure was held fixed at 0.05-atm. The rates of Cadman et al. [41] were used for the computations shown on this figure. These are the fastest rates in the literature and yield the highest ultimate temperature. Note that 5-atm of argon buffer gas pressure results in less than 50 K of particle temperature elevation at burnout for all ambient gas temperatures. Similar results are shown in Figure 30 using the rates of Roth et al. [40]. These rates represent something of an average of the rates in the literature (see Figure 4). For these rates, the addition of 1.0-atm

argon buffer gas results in less than 40 K of particle temperature elevation at all ambient gas temperatures. The results shown on these two figures indicate that particle thermal nonequilibrium is probably insignificant in shock tube measurements of soot oxidation rates, since argon buffer gas pressures are typically on the order of 5.0-atm. However, the computation of significant gas/particle thermal nonequilibrium at low argon buffer gas pressures indicates that perhaps a shock tube experiment could be used to generate validation data for the free molecular model. This idea is explored in **Chapter 8, Design of Shock Tube Validation Experiment.**

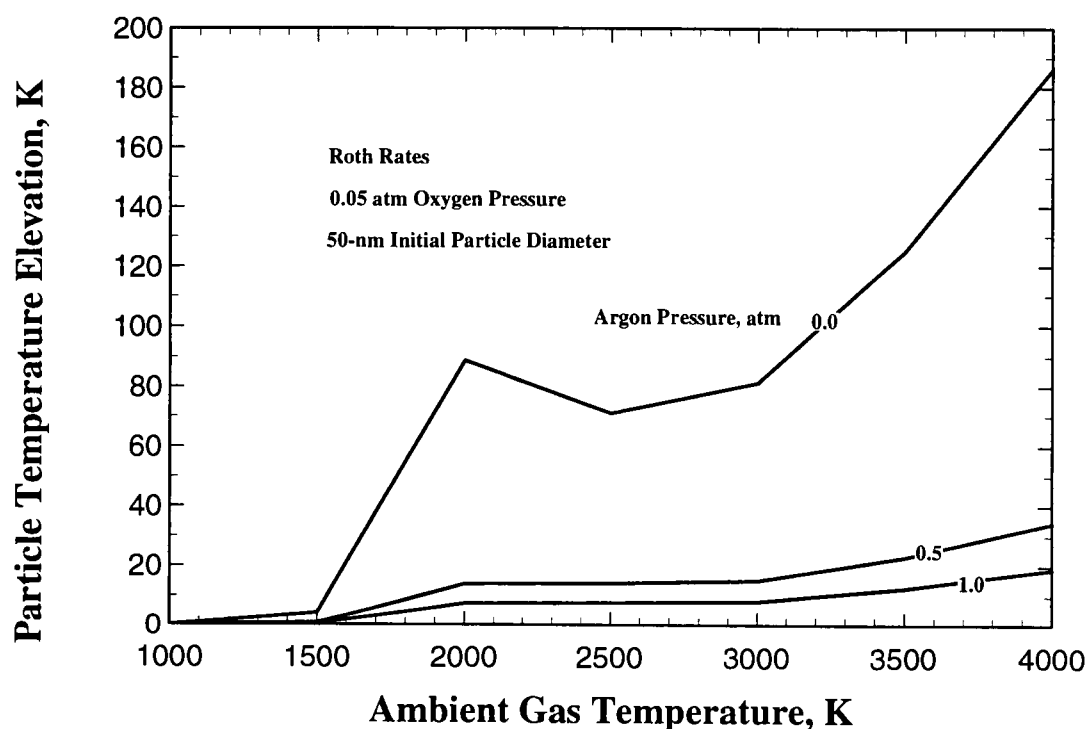


Figure 30 Particle temperature elevation at burnout for shock tube conditions using Roth rates.

Chapter 7. Application of Model to the Bradley Flame Experiment

Bradley et al. [49] entrained fine graphite powder into a flat, laminar, lean, low pressure (0.142-atm), methane-air flame. Gas temperature, particle temperature and velocity, and particle size were measured. The mean particle diameter was approximately 4 μm , much larger than flame soot. Under these conditions, the particle Knudsen number is on the order of unity, which is probably close to the limit of applicability of the free molecular model. The particle temperature was seen to rise above the gas temperature on the order of 250-300 K in the flame reaction zone. A numerical study was undertaken by the experimenters to compute the particle temperature. Reactions of the graphite with O, OH, H, CO₂, H₂O, and O₂ were considered. The treatment of the heat loss from the particle used the continuum (i.e. $Nu = 2$) limit. They attempted to determine which reaction or group of reactions was responsible for the particle temperature elevation. No reaction set was found that was sufficiently exothermic to account for the observed particle temperature elevation. Therefore, they concluded that some other mechanism was responsible. In particular, they postulated that the particles might be heated by exothermic surface-catalyzed radical recombination reactions occurring on the particle surface. In this chapter, the influence of rarefaction on the particle temperature will be investigated.

Streamline Tracing and Unsteady Ambient Conditions

All calculations in the previous sections have considered only steady ambient conditions. To trace the particle through the flame requires the addition of unsteady ambient conditions, since a particle will experience various ambient conditions as it traverses through the flame. Fortunately, the modified implicit Euler method used to solve the governing equations is easily adaptable to unsteady ambient conditions. The energy and mass conservation equations are given by Equation (60) and (61) and are repeated here:

$$\frac{dT}{dt} = \frac{3}{\rho r C} \sum_i Z_i [f_i (\tilde{m}_i e + q_{ri}) + (1 - f_i) q_{nri}] + \frac{3k_r \sigma}{\rho C} (T_\infty^4 - T^4) \quad (60)$$

and

$$\frac{dr}{dt} = \frac{-1}{\rho} \sum_i (Z f \tilde{m})_i \quad (61)$$

Recognizing from Equation (42) that

$$Z_i = Z_i [T_\infty, P_\infty, [X_i]_\infty] \quad (90)$$

where $[X_i]_\infty$ is the mole fraction of the i^{th} species in the ambient gas, and (from Equation (47)) that

$$q_{nr_i} = q_{nr_i} [T_\infty] \quad (91)$$

it is obvious that the required unsteady ambient conditions are simply

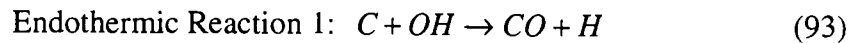
$$T_\infty(t), P_\infty(t), [X_i]_\infty(t) \quad (92)$$

In other words, we require that the ambient temperature, pressure and composition be known functions of time. The particles are assumed to be small enough that they track the gas streamlines exactly with no velocity lag. Bradley et al. [49] make this same assumption. Therefore, there is no need to change from a time-marching scheme to a space-marching scheme as is usually done in multi-phase flow calculations [50]. The modified implicit Euler scheme used here is time-marching. An explicit time step is taken, and the resulting implicit steps in particle temperature and size are computed. Therefore, for unsteady ambient conditions, the only modification required is to ensure that the ambient properties are properly evaluated at the time-advanced step. This is shown in detail in Appendix E.

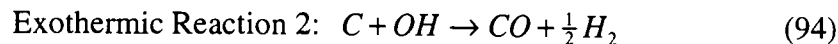
Oxidation by OH

Soot oxidation in flames by OH has been considered by Neoh, Howard, and Sarofim [51], and Puri, Santoro, and Smyth [52]. Neoh et al. derived a collision efficiency of 0.13. Puri et al. determined the OH collision efficiency to be in the range of 0.03 - 0.2 depending on the position in the flame and the fuel/oxidizer combination. Roth [53-54] measured soot oxidation by OH in a shock tube and derived collision efficiencies in the range 0.1 - 0.5. Based on the spread of data in the literature, a collision efficiency of 0.3 was chosen as a baseline value for use in this study. Since no pressure or temperature dependence of the collision efficiency is apparent in the literature, the collision efficiency was assumed to be invariant with pressure and temperature. This lack of pressure or temperature dependence is probably not physical.

The products produced from the surface reaction of soot with OH have not been experimentally determined. Two obvious candidate reactions are:



and



Reaction 1 is endothermic and Reaction 2 is exothermic. The heat of reaction and free energy of reaction for both reactions (derived from the JANAF Thermochemical Tables [36]) are plotted as a function of temperature in Figure 31. Note that equilibrium favors Reaction 2 at temperatures up to almost 4000 K. Therefore, only the exothermic Reaction 2 is considered in the following flame calculations.

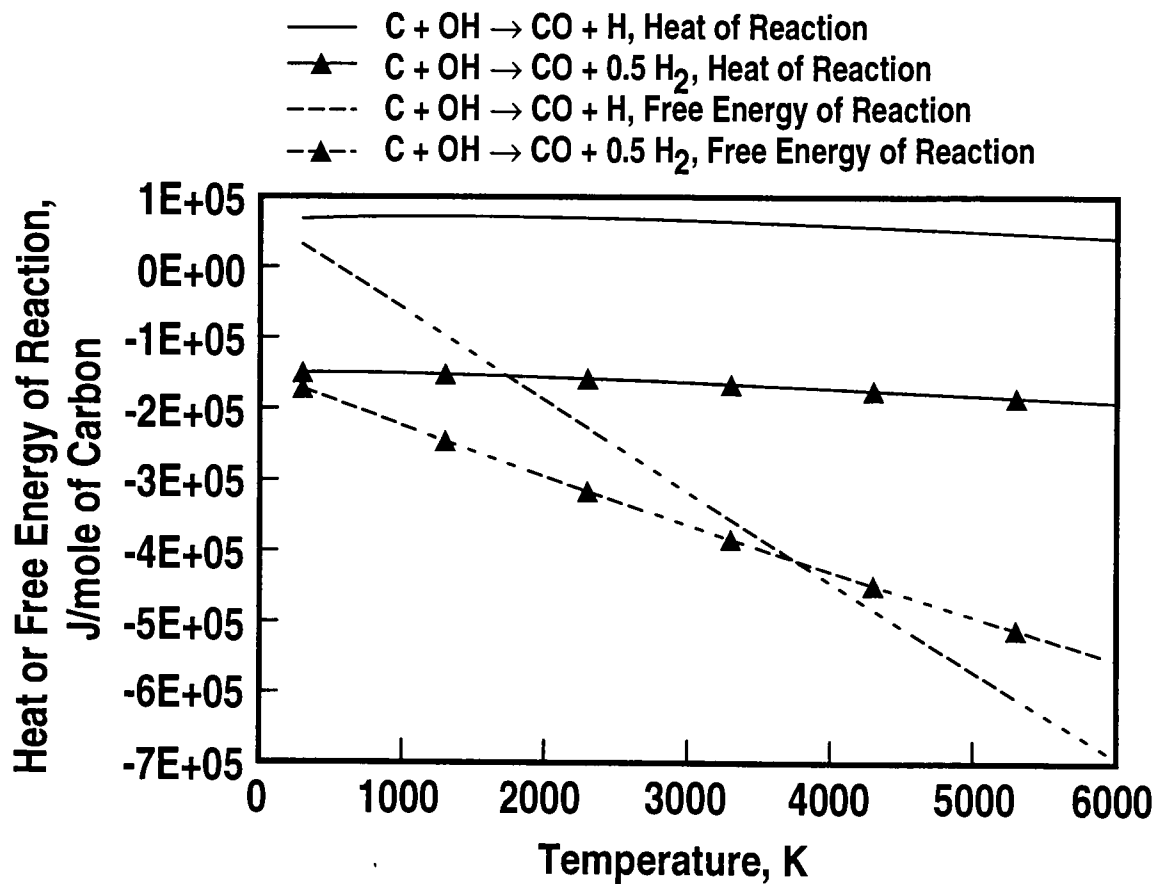


Figure 31 Thermodynamics of soot oxidation by OH.

Bradley Flame Data

Bradley et al. [49] measured flame gas temperature with thermocouples, particle temperature with two-color pyrometry, particle velocity with laser doppler velocimetry (LDV) and mean particle size with scattering from the LDV signal. All measurements were taken on the axis of the flame and are plotted versus height above the burner face. The gas and particle temperature data are shown in Figure 32. The increase of the particle temperature over the gas temperature in the reaction zone is obvious.

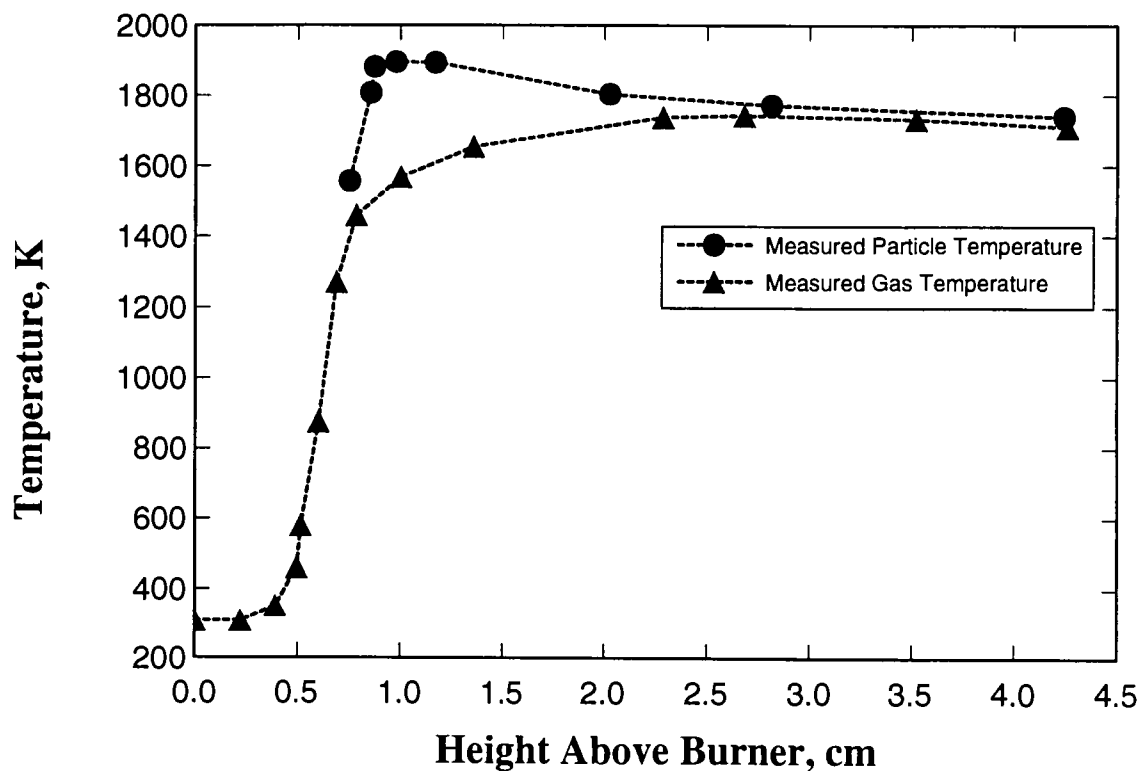


Figure 32 Measured particle and gas temperature in Bradley's flame.

Note also that the particle temperature begins to decrease even though the gas temperature continues to increase. This particle temperature overshoot behavior will be discussed later. Bradley et al. reported no estimate of uncertainties for any of the measurements. The mean particle size data are shown in Figure 33. The mean particle size decreases rapidly in the flame reaction zone and less rapidly in the post-flame gas. The particle velocity data are shown in Figure 34.

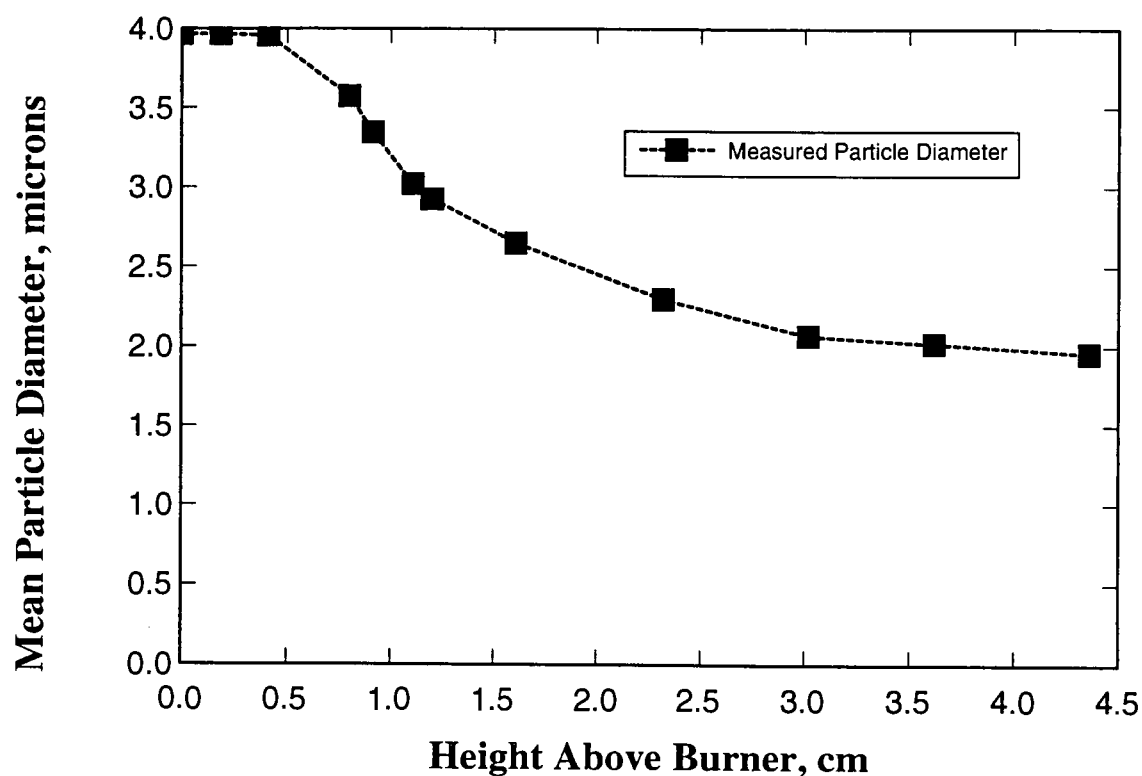


Figure 33 Measured mean particle diameter in Bradley's flame.

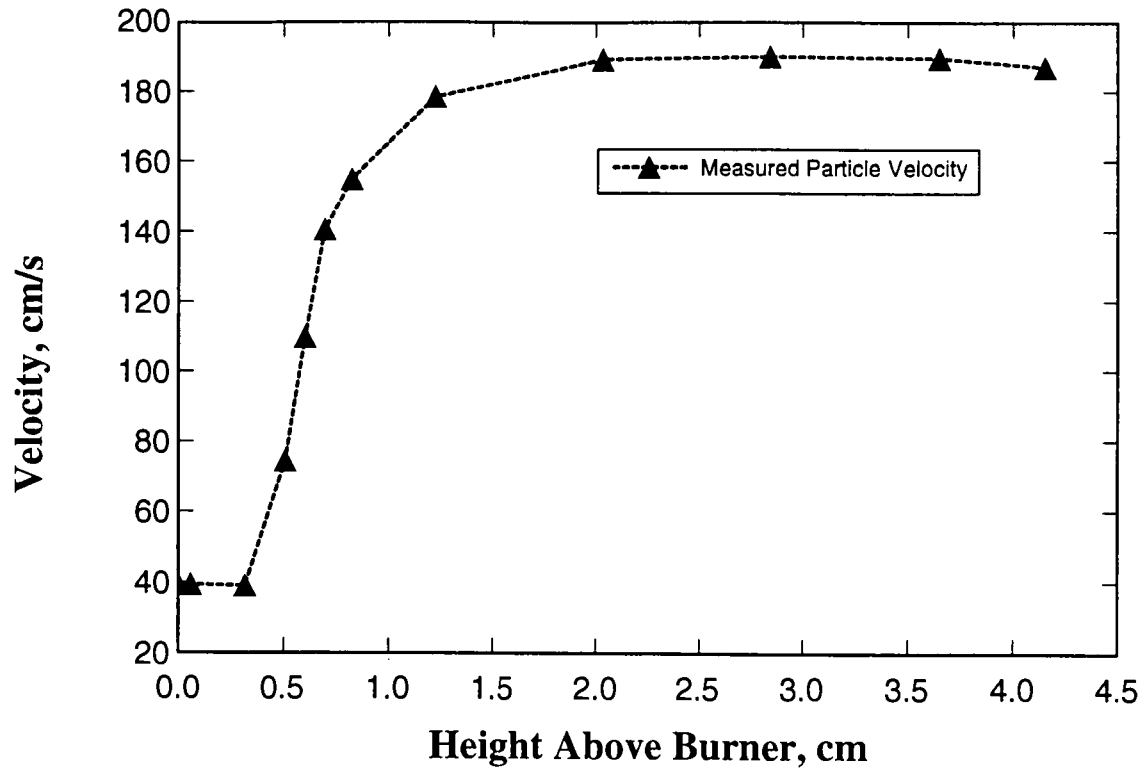


Figure 34 Measured particle velocity in Bradley's flame.

The gas velocity is assumed in this work (along with Bradley et al.) to be equal to the measured particle velocity.

The model requires the input of ambient temperature, pressure, and species concentration as functions of time. However, the Bradley et al. data are given as functions of space (i.e. height above the burner.) The gas velocity (Figure 34) is used to transform the spatial distributions to temporal distributions. If v_i is the gas velocity, x_i the spatial location, and t_i the elapsed time at the i^{th} spatial location above the burner face, then

$$t_i = t_{i-1} + \frac{x_i - x_{i-1}}{\frac{1}{2}[v_i + v_{i-1}]} \quad (95)$$

where time is assumed to start at zero at the burner face and increasing i implies increased distance from the burner. The pressure is assumed to be constant (0.142-atm) throughout the flame.

No composition measurements were made in this flame. Bradley et al. used their flame initial conditions and the measured gas temperature profile as input to a flame model of Dixon-Lewis et al. [55]. In the current study the same inputs were used with the latest version of CHEMKIN [56] along with the most current chemical rates [57]. Figure 35 shows the mole fractions of the oxidizing species O, OH, and O₂ as functions of the height above the burner. The Bradley et al. computations (not shown here) are similar, but the current calculations result in approximately 20-30% more O and OH, presumably due to differences in the chemical mechanisms. The current mechanism has been validated (at least for OH concentration) in methane/air flames [58]. Note also that the concentrations of O and OH are practically equal. This is not the case in a rich flame where soot would occur naturally. The concentration of O drops off rapidly as the equivalence ratio increases (i.e. as the flame becomes rich.)

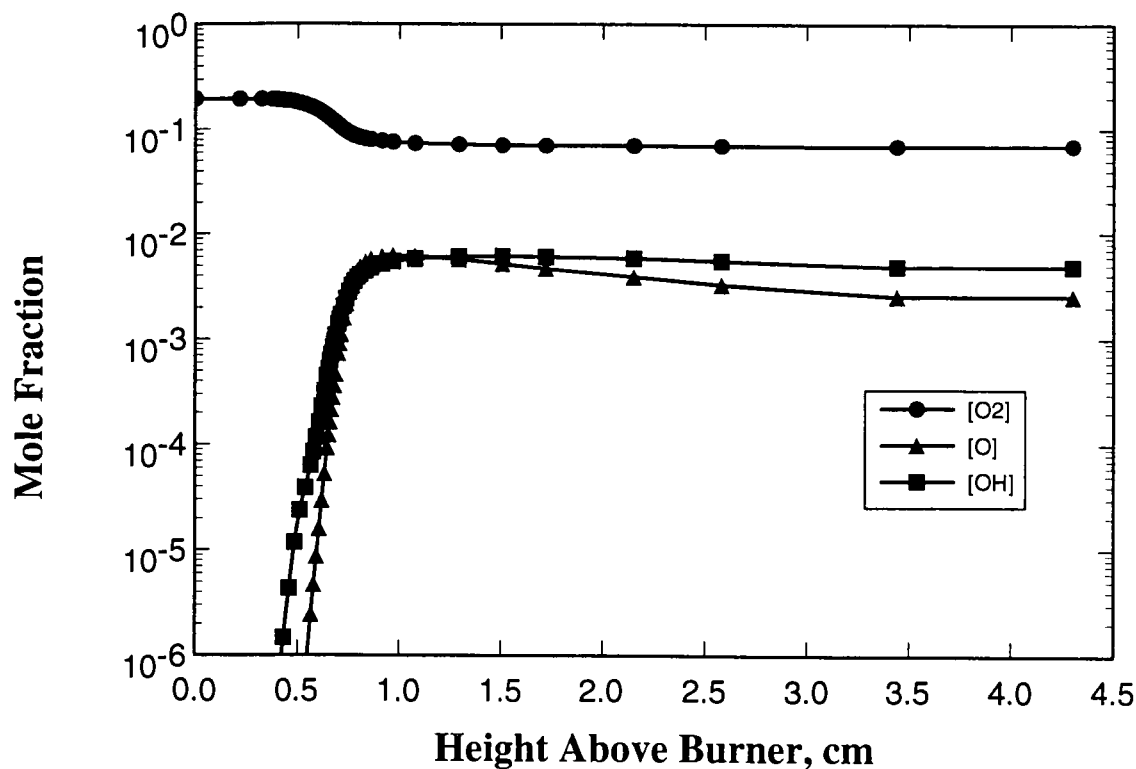


Figure 35 Computed oxidizing species mole fractions for Bradley's flame.

Baseline Comparisons

The present model results for particle temperature are compared to the experimental data in Figure 36. These calculations used the rates of Roth et al. [40] for oxidation by molecular oxygen, a collision efficiency of 0.3 for OH, and the rates of Rosner and Allendorf [43] for atomic oxygen. The model results represent the numerical solution of Equations (60-61). Note that the computed particle temperature is indeed hotter than the gas, although by only about 30 K.

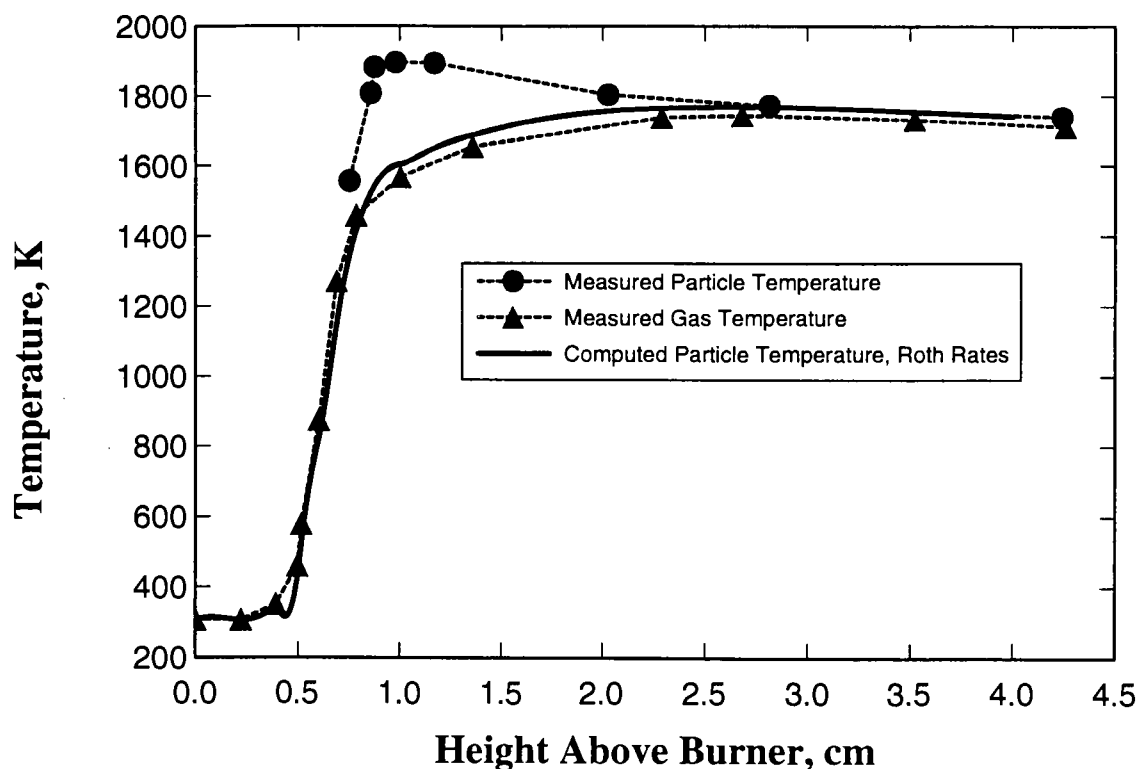


Figure 36 Comparison of measured and computed particle temperature - baseline rates.

The computed particle temperature shows no hint of the overshoot behavior evident in the experimental data. The model results for particle size are shown in Figure 37. Note that the particle size recession rate is greatly underpredicted. In the following sections, attempts will be made to simultaneously match the measured particle temperature and size. Excursions in the oxidation rates of O_2 , O , and OH will be considered. The effect of a rough particle surface will be investigated, and the influence of the presence of smaller particles will be considered.

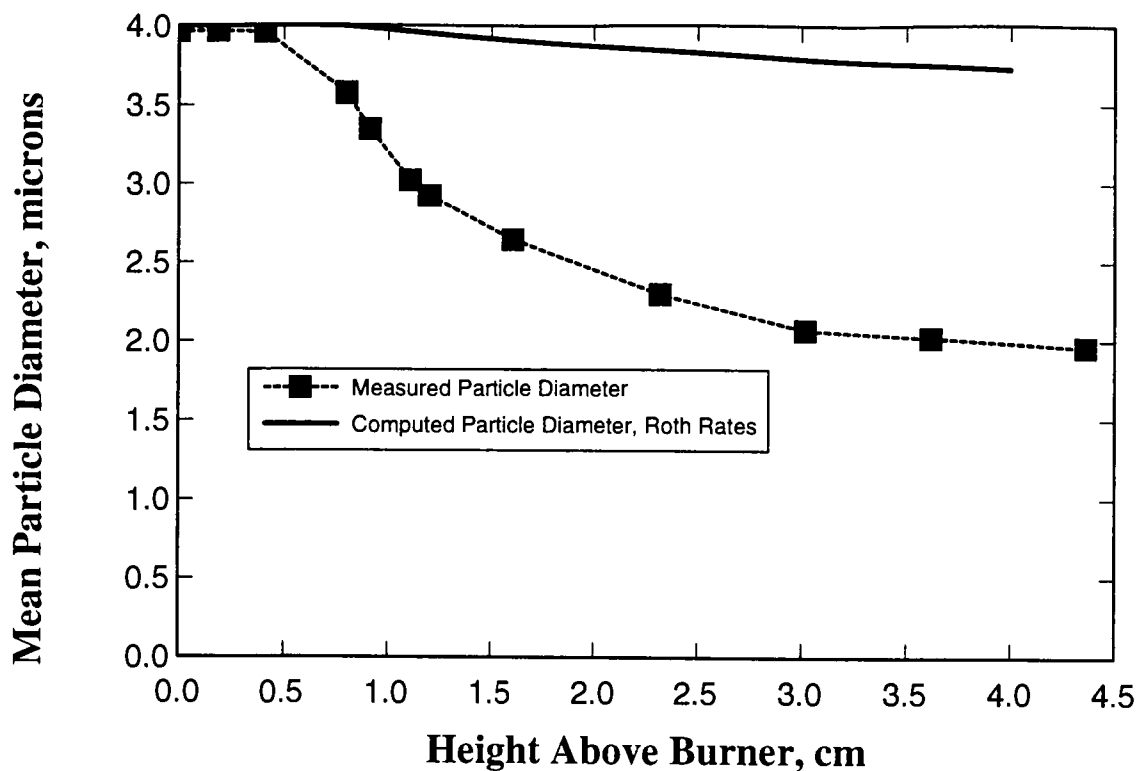


Figure 37 Comparison of measured and computed particle diameter - baseline rates.

Oxidation Rate Excursions

The results of Figures 36 and 37 are repeated in Figures 38 and 39, now showing additional calculated results using the rates of Nagle and Strickland-Constable [42] and Cadman et al. [41] for oxidation by molecular oxygen. Note that both the particle temperature and the particle size recession rate are insensitive to the rates used for molecular oxygen. This indicates that oxidation by OH and O is the dominant mechanism in this flame. Henceforth, the rates of Roth et al.[40] are used.

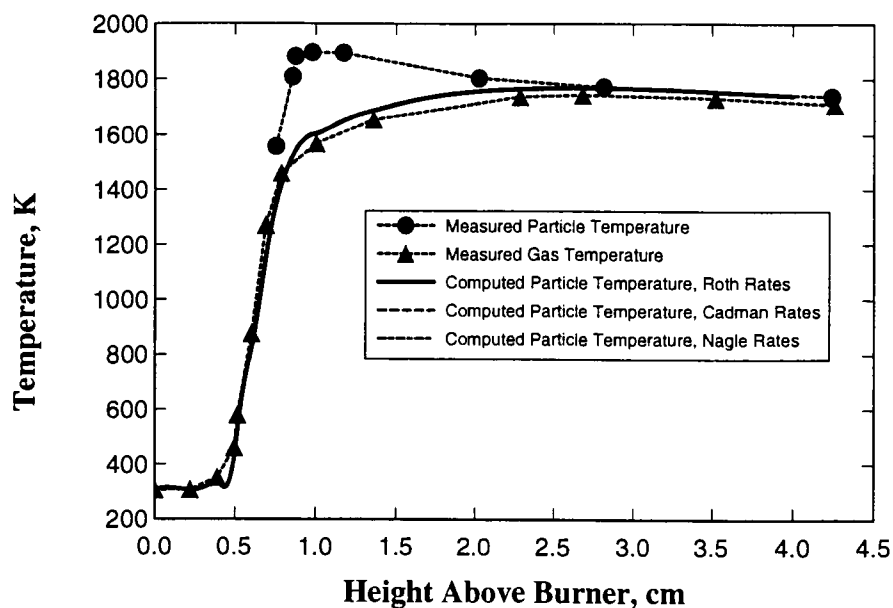


Figure 38 Comparison of measured and computed particle temperature as a function of molecular oxygen oxidation rates.

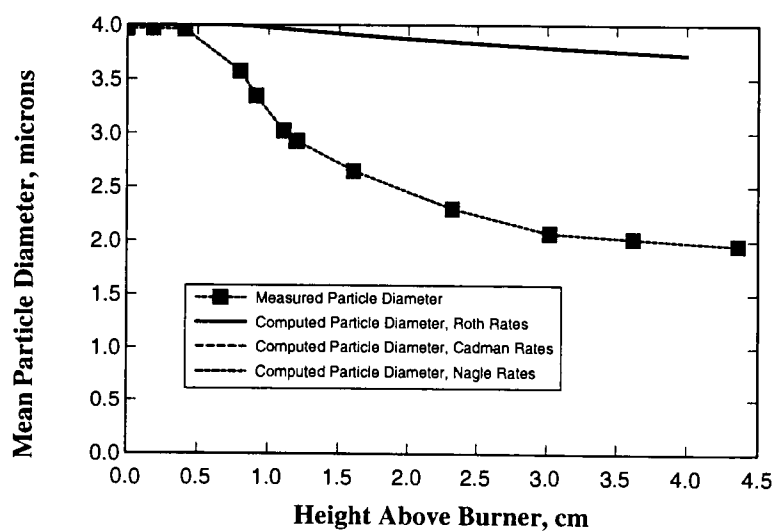


Figure 39 Comparison of measured and computed particle diameter as a function of molecular oxygen oxidation rates.

The results of Figures 36 and 37 are repeated in Figures 40 and 41, now showing additional calculated results using gaskinetic rates for oxidation by O and OH. That is, the collision efficiency is assumed to be unity for O and OH. Note the increase in computed particle temperature. The particle temperature is now on the order of 100 K hotter than the gas, which is still significantly less than the experimental particle temperature data and still no hint of the overshoot. The particle size recession rate is faster than before, but still much slower than the experimental results.

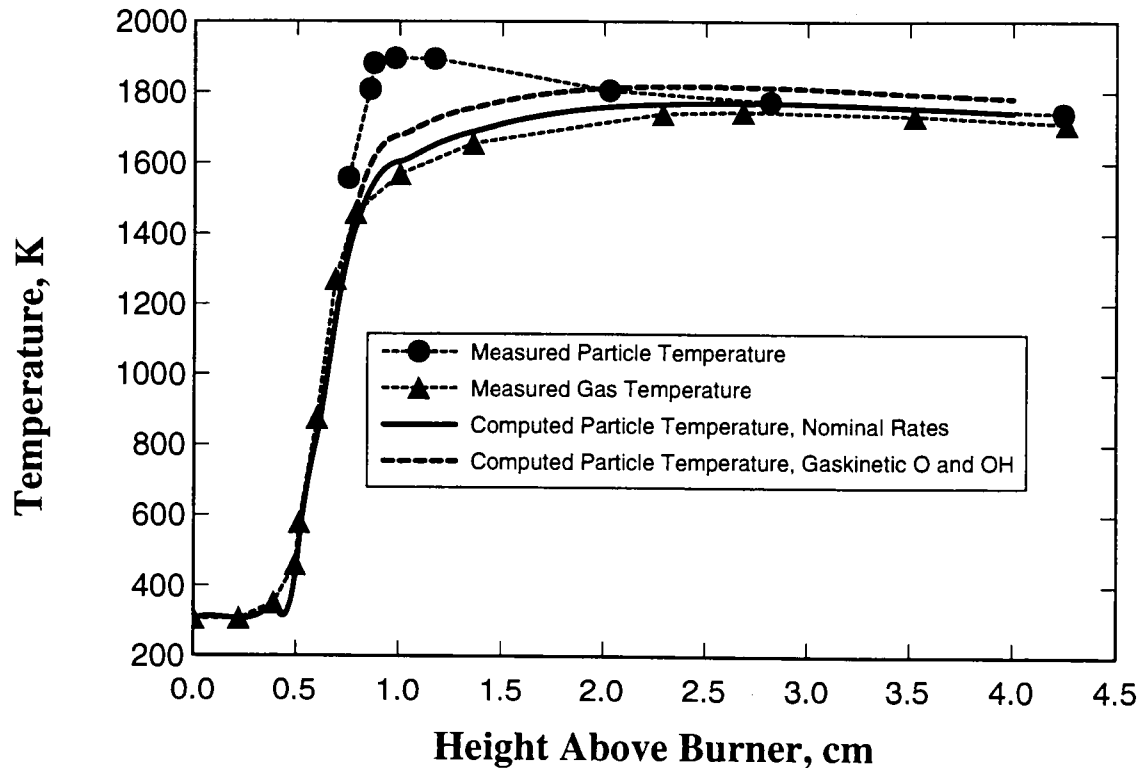


Figure 40 Comparison of measured and computed particle temperature - gaskinetic O and OH oxidation rates.

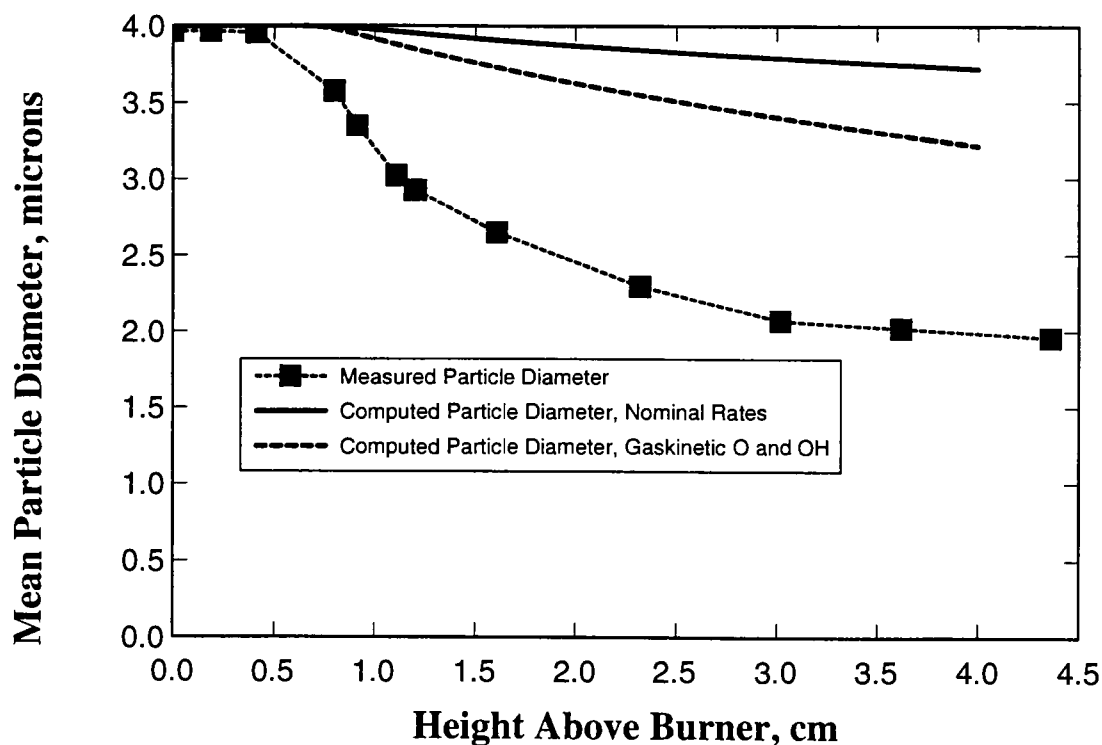


**Figure 41 Comparison of measured and computed particle diameter -
gaskinetic O and OH oxidation rates.**

These comparisons seem to indicate that the disagreement between the measured and computed particle temperatures is not due to uncertainties in the oxidation rates. The increase in the collision efficiencies of O and OH from the experimental values to unity could be viewed instead as an increase of the mole fractions of O and OH by a factor of 3-10. Therefore, the comparisons could also be viewed as indicating that the disagreement in computed and measured particle temperature is not due to errors in the concentrations of O or OH.

Approximate Fractal Corrections to Mass and Energy Equations

The model assumes that the oxidizing particles are perfect, solid spheres with absolutely smooth surfaces. This is obviously not the case in practice. Particles may be porous with rough, extremely irregular surfaces. An approximate correction may be made to the mass and energy conservation equations to account for these rough surfaces. A nominally spherical particle with a rough, fractal surface has more surface area than a perfectly smooth particle of the same mass. This means, that in some sense, a particle with a fractal surface has too much surface area for its mass or volume. Define M as the particle mass, and A as the particle surface area corresponding to the particle mass, i.e.

$$M = \rho V = \rho \frac{4}{3} \pi r^3 \quad (96)$$

so the mass mean particle radius is

$$r = \left[\frac{3M}{4\pi\rho} \right]^{1/3} \quad (97)$$

and therefore A is

$$A = 4\pi r^2 = 4\pi \left[\frac{3M}{4\pi\rho} \right]^{2/3} \quad (98)$$

If we define $\tilde{A}$ to be the actual surface area of the particle, then a particle with a fractal surface will have

$$\frac{\tilde{A}}{A} > 1 \quad (99)$$

The mass and energy conservation equations will now be re-derived considering this fractal effect. In the derivation, all particle mass or volume related quantities will vary proportionally to A . All surface flux quantities will vary proportionally to $\tilde{A}$. The derivation is very similar to that presented in Chapter 3, so only an abbreviated version is given here. Starting with the energy equation

$$E = \rho V(t) e(T) \quad (100)$$

applying the chain rule yields

$$\frac{dE}{dt} = \frac{\partial E}{\partial e} \frac{de}{dt} + \frac{\partial E}{\partial V} \frac{dV}{dt} \quad (101).$$

The partial derivatives are obviously

$$\frac{\partial E}{\partial e} = \rho V \quad (102)$$

and

$$\frac{\partial E}{\partial V} = \rho e \quad (103)$$

since we are treating the particle density as a constant. Substituting Equation (102) and (103) into Equation (101) yields

$$\frac{dE}{dt} = \rho V \frac{de}{dt} + \rho e \frac{dV}{dt} \quad (104)$$

Applying the chain rule again we find

$$\frac{dV}{dt} = \frac{\partial V}{\partial r} \frac{dr}{dt} = A \frac{dr}{dt} \quad (105)$$

Substituting Equation (105) into Equation (104) yields

$$\frac{dE}{dt} = \rho V \frac{de}{dt} + \rho e A \frac{dr}{dt} \quad (106)$$

Now, since the particle oxidation rate is a surface flux related quantity, we must rewrite the mass conservation equation (Equation (38)) as

$$-\omega\tilde{A} = \rho \frac{dV}{dt} = \rho A \frac{dr}{dt} \quad (107)$$

or

$$\frac{dr}{dt} = -\frac{\omega}{\rho} \frac{\tilde{A}}{A} \quad (108)$$

which is the mass conservation equation corrected for a fractal surface. Substituting Equation (108) into Equation (106) yields

$$\frac{dE}{dt} = \rho V \frac{de}{dt} - \rho e A \left(\frac{\omega}{\rho} \frac{\tilde{A}}{A} \right) = \rho V \frac{de}{dt} - \tilde{A} \omega e \quad (109)$$

Also, since the particle volume V can be written as

$$V = A \frac{r}{3} \quad (110)$$

and, as was shown earlier

$$\frac{de}{dt} = C \frac{dT}{dt} \quad (111)$$

and

$$\omega = Zf\tilde{m} \quad (112)$$

we can rewrite Equation (109) as

$$\frac{dE}{dt} = \rho AC \frac{r}{3} \frac{dT}{dt} - \tilde{A} Z f \tilde{m} e \quad (113)$$

which is the rate of change of the energy content of the particle including the first order fractal correction. Equation (113) must now be balanced by the external energy fluxes due to collisions and reactions with the ambient gas molecules and radiation. The ambient gas molecules are assumed to collide with the true surface area. This may not be completely correct, since some of the true surface area may be shielded from direct collisions with gas molecules. However, making this assumption, the energy transferred by collisions (Equation (43)) must be modified as

$$\frac{dE}{dt}_{\text{collisions}} = [Zf q_r + Z(1-f) q_{nr}] \tilde{A} \quad (114)$$

The radiation from small particles is proportional to the particle mass, not the particle surface area, so the radiative flux term (Equation (51)) remains unchanged

$$\frac{dE}{dt}_{\text{radiation}} = rk_r \sigma (T_{\infty}^4 - T^4) A \quad (115)$$

Therefore, the total external flux of energy to the particle surface is the sum of Equations (114) and (115), or

$$\frac{dE}{dt}_{\text{fluxes}} = [Zfq_r + Z(1-f)q_{nr}] \tilde{A} + rk_r \sigma (T_{\infty}^4 - T^4) A \quad (116)$$

Equating Equations (116) and (113) and solving for the rate of change of particle temperature yields the energy conservation equation corrected for first order fractal effects

$$\frac{dT}{dt} = \frac{3Z}{\rho r C} \frac{\tilde{A}}{A} [f(\tilde{m}e + q_r) + (1-f)q_{nr}] + \frac{3k_r \sigma}{\rho C} (T_{\infty}^4 - T^4) \quad (117)$$

which is the same as the previous energy conservation equation (Equation (54)) with the exception of the area ratio term $(\tilde{A}/A)$. The fractally-corrected mass conservation equation (Equation(108)) is also the same as the uncorrected equation (Equation (55)) with the exception of the same area ratio term. Equations (108) and

(117) form a new set of coupled differential equations for the particle size and temperature that will be solved with the same modified implicit Euler solver as previously used. We now need some knowledge of the magnitude of the area ratio term.

Effect of Particle BET

A measure of the true particle surface area is given by the Brunauer, Emmett, and Teller (BET) theory [59]. This is an extension of the Langmuir adsorption isotherm theory. In the BET theory, the surface area is determined by exposing a sample to an adsorbing gas. The adsorbate pressure drops with time as the adsorption process continues. Measuring the pressure yields (after some manipulations, see Ref. 59, pp. 22-23) the total surface area. BET measurements are typically quoted as the specific surface area, i.e. the surface area per unit mass of material.

Bradley et al. [49] report the measured specific surface area (BET) of the 4 μm diameter particles used in their experiment as $18.3 \text{ m}^2\text{-g}^{-1}$. Since the BET gives the ratio of the actual surface area to mass of the particle we can write

$$BET = \frac{\tilde{A}}{M} = \frac{\tilde{A}}{\rho V \frac{A}{A}} = \frac{\tilde{A}}{\rho \frac{4}{3} \pi r^3 \frac{A}{4\pi r^2}} = \frac{3\tilde{A}}{\rho r A} \quad (118)$$

or

$$\frac{\tilde{A}}{A} = BET \frac{\rho r}{3} \quad (119)$$

Therefore, the measured BET gives some measure of the fractal nature of the particle surface. This ignores the fact that some of the total surface area is due to particle porosity, not surface roughness. However, as a first approximation, it is assumed that the surface is non-porous.

The density of the graphite was measured as 2.25 g-cm^{-3} . Using the measured BET, density, and initial particle size in Equation (119) gives $\tilde{A} / A \approx 26.4$. Since surface area is proportional to r^2 , this area ratio means that the effective particle size is approximately 5 times greater than the geometric particle size. The particle surface area ratio derived from the BET is treated as a constant when solving Equations (108) and (117).

The particle temperature and size results including the effects of particle BET are shown in Figures 42 and 43, respectively. The nominal oxidation rates defined in the previous sections are used - that is, the Roth [40] rates for oxidation by O_2 , the Rosner and Allendorf [43] rates for oxidation by O, and a collision efficiency of 0.3 for OH. The inclusion of the BET raises the maximum thermal nonequilibrium from about 50 to 100 K - still not approaching of the measurement of 250-300 K.

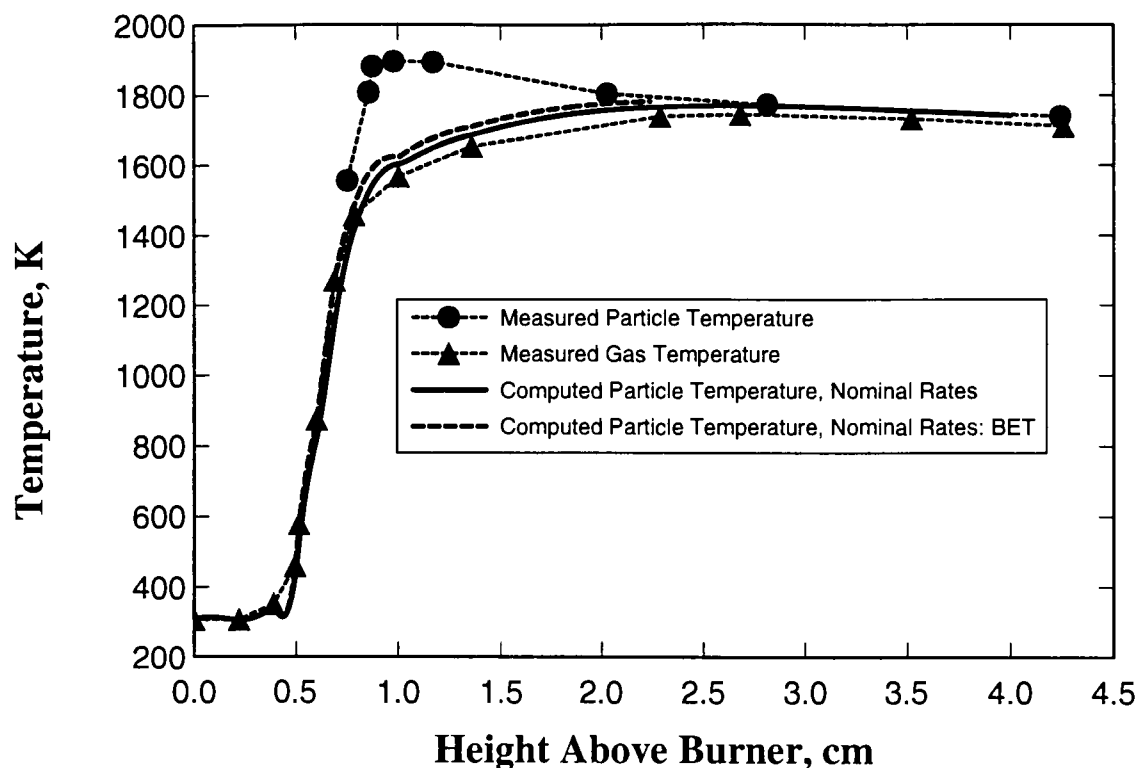


Figure 42 Comparison of measured and computed particle temperature including the effect of particle BET.

Note that the temperature results (including BET) stop at a height of 2.5 cm above the burner. This indicates particle burnout. This is seen more dramatically in Figure 43, which gives the particle size results. The computed particle diameter decreases much faster than the measured particle diameter. These results indicate that the influence of fractal surface effects are in the proper directions (higher temperature, faster surface recession) but of the wrong magnitude. It would be possible to define some radius-dependent area ratio that precisely matches the particle size measurements in Figure 43.

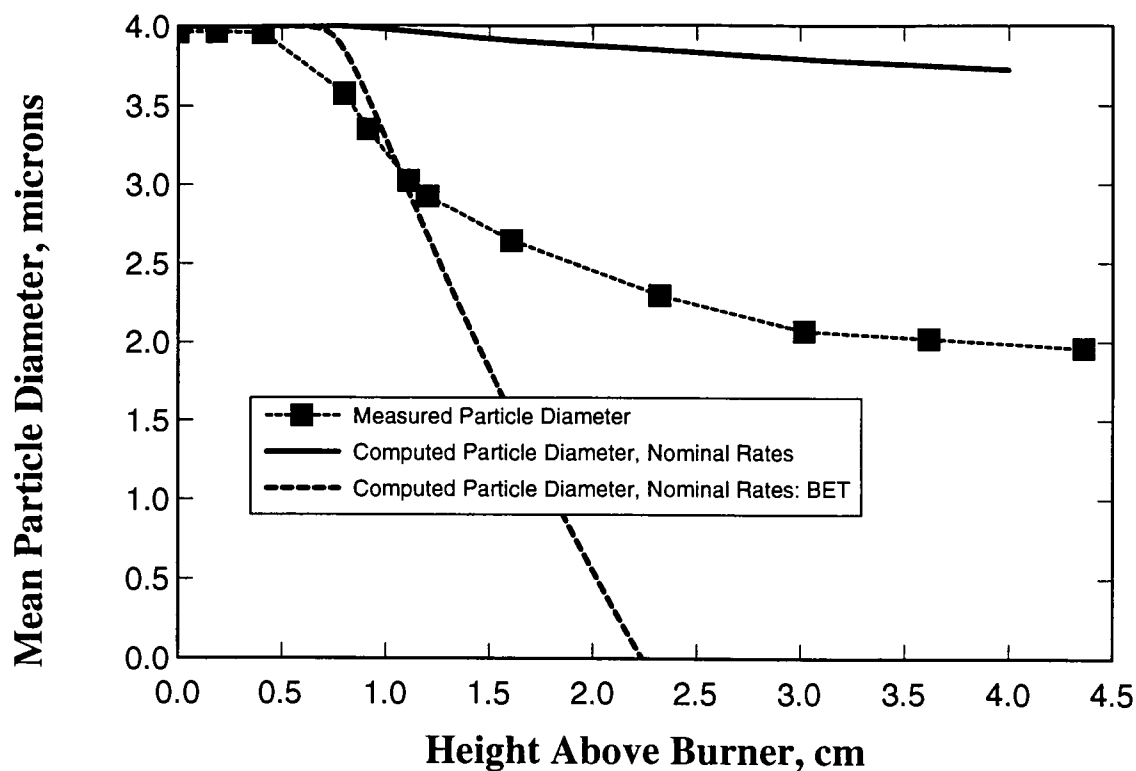


Figure 43 Comparison of measured and computed particle diameter including the effect of particle BET.

However, the resulting particle temperature profile would greatly underpredict the particle temperature measurements in Figure 42 - and would not predict the temperature overshoot seen in the data. Therefore, it would seem that the large amount of particle thermal nonequilibrium evident in the data is not due to fractal surface effects.

Particle Size Excursions

It was concluded in Chapter 5 that small particles heat up faster than large particles. Under steady ambient conditions, small and large particles reach the same ultimate temperature. However, it is possible, with unsteady ambient conditions such as this flame, that small particles may rise locally to a higher temperature than large particles. Therefore, we should consider the possibility that the observed particle thermal nonequilibrium is due to a particle size distribution which contains a significant fraction of particles smaller than 4 μm . A series of calculations were done assuming initial particle diameters of 4., 2., and 0.1 μm . Gaskinetic oxidation rates were used to maximize the thermal nonequilibrium. The particle temperature results are shown in Figure 44.

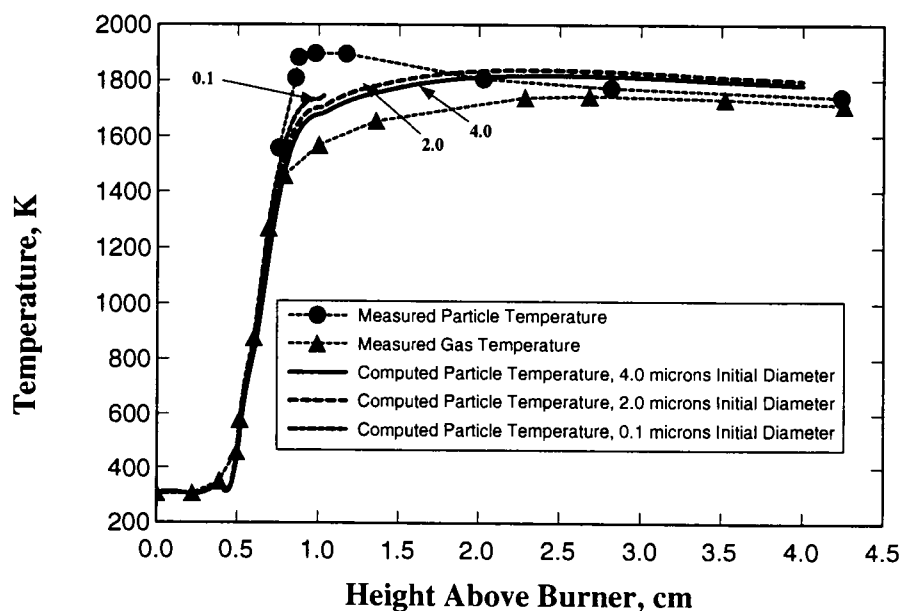


Figure 44 Comparison of measured and computed particle temperature over a range of initial particle diameters.

The maximum thermal nonequilibrium increases with decreasing particle size.

However, even for the 0.1 μm particle, the maximum thermal nonequilibrium is on the order of 200 K, not 300 K as in the data. Also, the 0.1 μm particle burns out at a height of 1.0 cm above the burner face. This indicates that smaller particles would burn out at even lower heights in the flame. Even the smallest reasonable particle sizes coupled with gaskinetic oxidation rates do not produce the observed maximum thermal nonequilibrium. The presence of small particles is probably not responsible for the observed maximum particle temperature.

Chapter Conclusions

None of the calculations presented above matched the magnitude of the observed particle thermal nonequilibrium. Excursions in oxidation rate and particle size showed that smaller particles and faster oxidation rates favored higher levels of thermal nonequilibrium, but never reached the magnitude observed in the data. Consideration of possible fractal surface effects by using a BET model did result in higher thermal nonequilibrium (though still lower than the data) but resulted in particle size recession rates much higher than those observed in the data. None of the calculations exhibited the overshoot behavior evident in the particle temperature data. The calculated particle temperature continued to rise with the gas temperature, but the measured particle temperature begins falling while the gas temperature continues to rise. From the phase plane discussion in Chapter 5, it is unlikely that any combination of rates, BET, etc., would result in this overshoot behavior. Given

this, and the fact that no combination of rates, BET, etc., could simultaneously match the temperature and particle size data, it appears that the thermal nonequilibrium evident in the data is not due primarily to rarefaction effects. Some other mechanism that adds energy to the particle without removing mass could potentially explain the extent of thermal nonequilibrium observed in the data. This conclusion is also supported by consideration of Knudsen number scaling presented in Chapter 2. The Knudsen number of a 4 μm particle at these flame conditions is approximately unity. Therefore, we conclude from Equation (15) that the free molecular heat transfer coefficient is only on the order of 6.5 times smaller than the continuum value. Therefore, the continuum analysis performed by Bradley et al. [49] should be practically adequate. They also concluded that some other mechanism must be at work. Specifically, they theorized that surface-catalyzed exothermic recombination reactions could be responsible for the large thermal nonequilibrium. The model developed in the present work is not capable of considering this type reaction. The present results suggest that rarefaction is not principally responsible for the particle thermal nonequilibrium observed in the Bradley et al. flame data. Therefore, this is not an appropriate validation experiment to either confirm the existence or quantify the magnitude of rarefaction effects in small particle combustion.

Chapter 8. Design of Shock Tube Validation Experiment

In this section, an experiment is proposed to demonstrate the existence of thermal nonequilibrium in small particle combustion. As shown above, nonequilibrium is favored by high temperature and low pressure. Also, the gaseous composition should be kept simple to minimize the influence of possible competing mechanisms such as surface recombination reactions. Conditions such as these are easily established in shock tubes.

Shock Tube Basics

Shock tubes are routinely used to provide high temperature conditions for chemical rate experiments. A shock tube generally consists of a high pressure (or driver) section, and a low pressure (or driven) section, separated by a diaphragm. A schematic of a shock tube and an $x-t$ wave diagram are shown in Figure 45. When the diaphragm bursts, the incident shock propagates from the driver into the driven section at velocity u_I in the laboratory reference frame. Note that the velocity is simply the inverse of the slope of the lines on Figure 45. The contact surface (which divides the driver and driven gases) propagates into the driven section at velocity u_p . The incident shock reflects from the endwall of the driven section as a reflected shock, which propagates back towards the driven section at velocity u_5 in the laboratory reference frame. Quiescent conditions are established behind the reflected shock, and persist until the arrival of the contact surface.

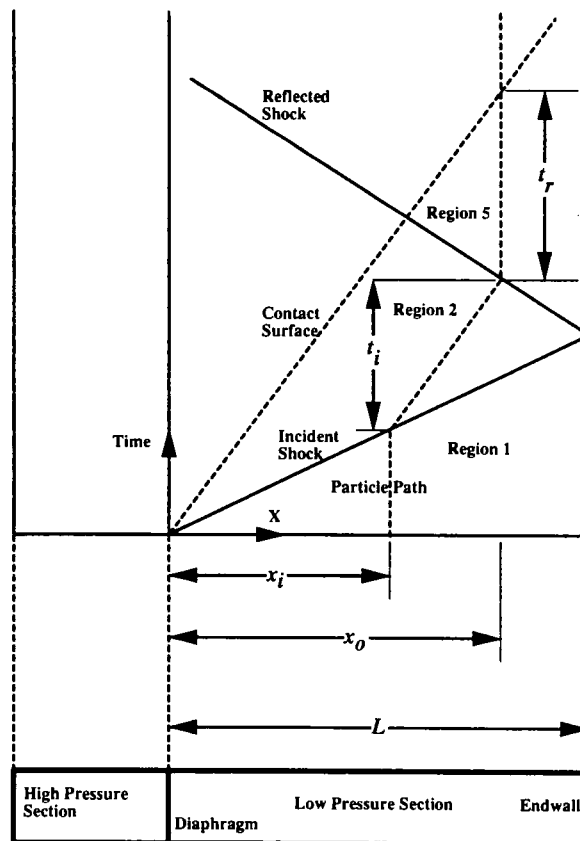


Figure 45 Shock tube schematic and wave diagram.

The arrival of the contact surface terminates the usable test time. As shown on Figure 45, particles (or gas) initially at position x_i remain stationary until the arrival of the incident shock wave. The particles are then transported at velocity u_p until the reflected shock intersects the particle path at position x_o . The particles remain stationary at this location until the arrival of the contact surface. Therefore, if optical measurements are to be taken at station x_o , the gas and particles observed

behind the reflected shock at this station have experienced incident shock conditions for a time of t_i . The gas and particles then experience reflected shock conditions for a time of t_r . The expansion fan that propagates into the high pressure section and the resulting reflections are omitted from Figure 45 for clarity. Details of shock tube theory are found in a NAVORD report by Glass and Hall [60].

Shock Tube Experiments

The appropriate validation experiment should provide:

1. significant gas/particle thermal nonequilibrium
2. reasonable gas temperature/pressure
3. time scales of 100 μ sec or longer
4. uniform aerosol clouds

As noted in Chapter 4, shock tubes have been used extensively to measure soot oxidation rates. The most current work is being done by Roth at the Institute for Combustion and Gas Dynamics, University of Duisberg, Germany. Brandt, Rajathurai, and Roth [61] developed a unique particle delivery system to establish a uniform aerosol in the reflected shock region. A small conventional shock tube is used to generate an aerosol, which is then drawn into the main shock tube by a vacuum pump. A homogenous distribution of particles is established along the

entire length of the driven tube before the diaphragm is burst. A homogeneous mixture is desirable, particularly when making optical measurements.

The time scales are determined by the length of the shock tube (L), the location of the measurement station (x_o) and the various velocities. Using the definitions in the preceding section (and referring to Figure 45) it can be shown that the incident test time is given by

$$t_i = \frac{L}{u_1} + \frac{L - x_o}{u_5} - \frac{\left[\frac{L}{u_1} + \frac{L - x_o}{u_5} - \frac{x_o}{u_p} \right]}{\frac{1}{u_1} - \frac{1}{u_p}} \frac{1}{u_1} \quad (120)$$

and the reflected test time is given by

$$t_r = \frac{x_o}{u_p} - \left[\frac{L}{u_1} + \frac{L - x_o}{u_5} \right] \quad (121)$$

For all calculations, a shock tube driven section length (L) of 20 meters and an observation station (x_o) of 19.75 meters is used.

The initial pressure, temperature, and composition in the driver and driven sections determine the incident shock speed, which in turn determines the reflected shock speed. Typically, reflected shock temperatures from 1000-5000 K and reflected shock pressures from 0.1 - 10 atm are easily attainable [60]. The NASA

Equilibrium code [28] can be used to compute the incident and reflected shock properties as a function of driven gas initial conditions and incident shock speed. For all calculations, initial conditions in the driven section were a temperature of 300 K and a composition of 100% O₂. A series of chemical equilibrium shock tube calculations were performed that yielded a constant reflected shock pressure of 0.1-atm. Chemical equilibrium reflected shock temperatures varied from 2700 to 3000 K. The equilibrium conditions, shock speeds, and test times are tabulated in Table 1. In typical shock tube nomenclature, a subscript 1 refers to initial conditions in the driven section, a subscript 2 refers to conditions behind the incident shock, and a subscript 5 refers to conditions behind the reflected shock.

Note that the equilibrium O₂ dissociation is significant at all temperatures. However, the test times may not be sufficient to allow the gas mixture to reach chemical equilibrium. This was assessed by using the NASA Lewis LSENS code [62]. The LSENS code includes the capability of computing the relaxation behind incident shocks (note that a reflected shock can be transformed into an incident shock by simply changing to a shock-fixed coordinate system). The shock jump conditions are computed first by assuming frozen chemistry (i.e. no dissociation) and then finite rate chemistry is used to compute the relaxation of the chemistry and gasdynamics behind the shock until equilibrium is reached. The oxygen dissociation rates of Bortner [63] are used in all LSENS shock calculations shown here.

Table 1 Equilibrium shock tube conditions and test times.

Conditions	Case 1	Case 2	Case 3	Case 4
T_1 , K	300	300	300	300
P_1 , atm	0.00035	0.00030	0.00022	0.00016
u_1 , m/sec	1880.	2021.	2209.	2440.
T_2 , K	1878.	2063.	2244.	2388.
P_2 , atm	0.0137	0.0136	0.0124	0.0110
u_2 , m/sec	302.	307.	306.	296.
u_p , m/sec	1578.	1714.	1903.	2143.
T_5 , K	2700	2800	2900	3000
P_5 , atm	0.1	0.1	0.1	0.1
u_5 , m/sec	407.	400.	393.	388.
$[O]_5$, fraction	0.11	0.15	0.22	0.31
$[O_2]_5$, fraction	0.89	0.85	0.78	0.69
t_i , msec	1.9	2.0	2.2	2.5
t_r , msec	1.7	1.5	1.2	0.8

The initial conditions (T_I, P_I, u_I) in Table 1 are used as input to LSENS. An incident shock calculation is performed, and relaxation is allowed to occur for the incident test time, t_i . The static conditions and composition at this point are then used as input to LSENS for another incident shock calculation. The appropriate input velocity upstream of the shock is ($u_5 + u_p$) from Table 1. This transforms the velocities from the laboratory frame (in which the reflected shock moves subsonically) to a shock-fixed frame, in which the velocity upstream of the (now stationary) reflected shock is supersonic.

Figure 46 shows the gas temperature as a function of time for the condition for Case 4 in Table 1: 3000 K equilibrium reflected shock temperature; 0.1-atm reflected shock pressure. Note that the time axis is shifted so that the arrival of the reflected shock corresponds to time zero. The dissociation of O_2 behind the reflected shock is so slow that the reflected shock temperature at the end of the test time (0.8 msec) is significantly above the equilibrium value - 3600 K versus 3000 K.

Figure 47 shows the pressure as a function of time for Case 4. The pressure at the end of the test time is slightly less than the equilibrium value - 0.09-atm versus 0.1-atm. This indicates that neither the thermodynamics nor the gas dynamics are fully relaxed to equilibrium at the end of the test time. Additionally, the pressure can never reach the predicted equilibrium value because of entropy generated by the finite-rate chemistry. It will now be shown that the chemistry has also not reached equilibrium at the end of the test time.

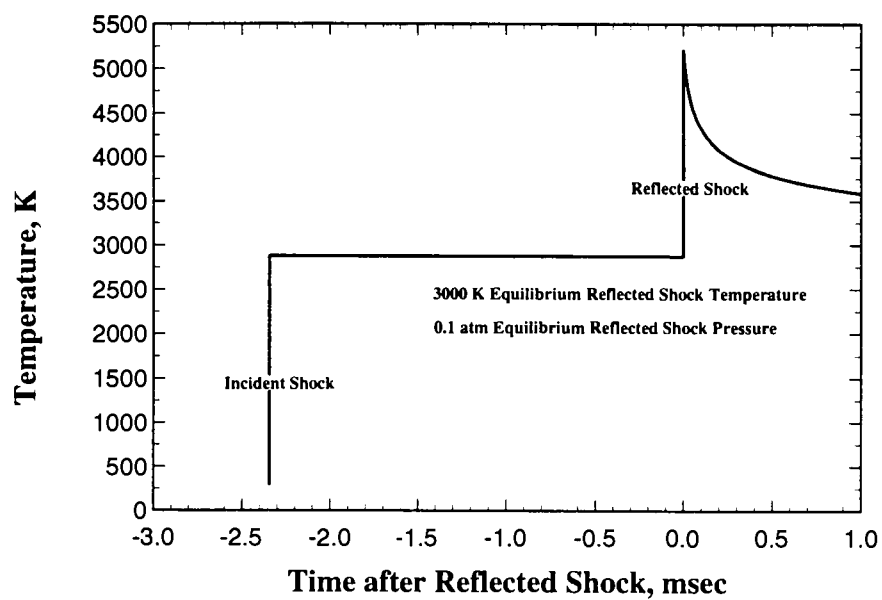


Figure 46 Temperature versus time for Case 4 - 3000 K equilibrium reflected shock temperature.

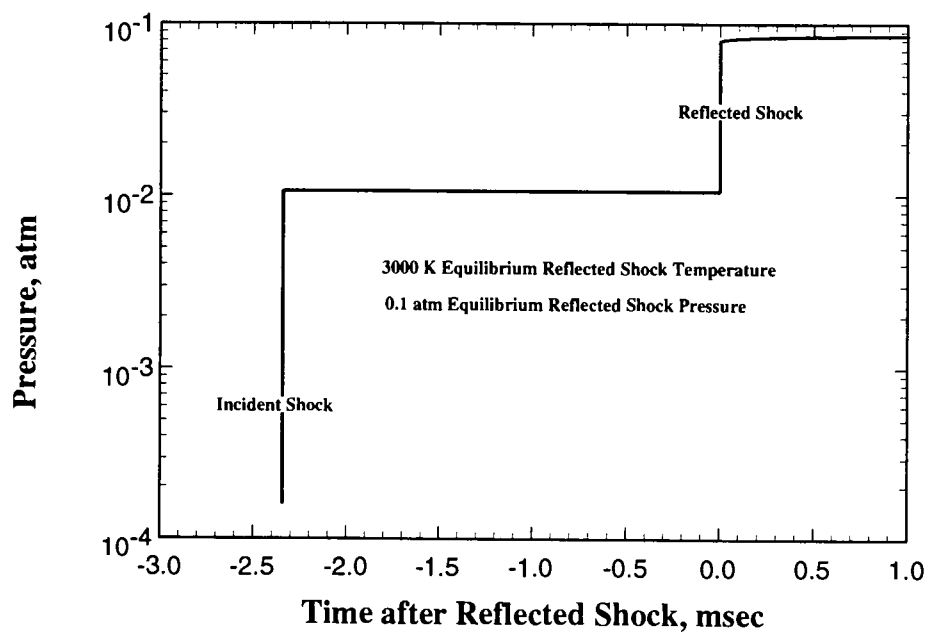


Figure 47 Pressure versus time for Case 4 - 3000 K equilibrium reflected shock temperature.

Figure 48 shows the molecular and atomic oxygen mole fractions versus time. These results indicate insignificant dissociation behind the incident shock. There is significant dissociation behind the reflected shock. However, the O-atom mole fraction at the end of the test time is less than the equilibrium value; 0.25 versus 0.31. This indicates that dissociation is incomplete at the end of the test time. Similar computations were made for Cases 1-3 with similar results, with the lower temperature cases resulting in less dissociation of O_2 in O. It should be noted that no exhaustive survey of O_2 dissociation rates was performed.

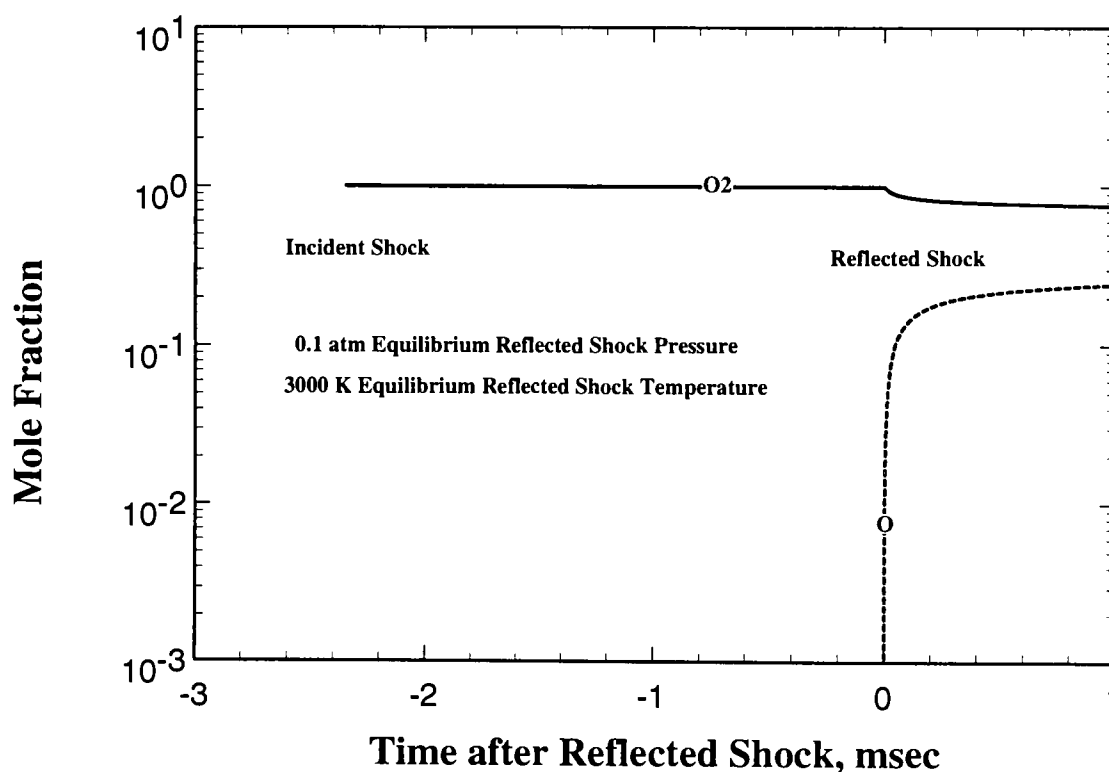


Figure 48 Molecular and atomic oxygen mole fractions versus time for Case 4 - 3000 K equilibrium reflected shock temperature.

Particle Combustion Calculations

The time histories of temperature, pressure, and composition are now used as ambient conditions for the particle combustion model. It is assumed that the addition of very small amounts of soot to these flowfields will not alter either the gas-phase chemistry or the gasdynamics significantly. The initial particle conditions are 300 K initial particle temperature and 50-nm initial particle diameter for all calculations shown here. The Roth et al. [40] oxidation rates are used for molecular oxygen, and the Rosner and Allendorf [43] rates are used for atomic oxygen. Figure 49 shows the particle and gas temperature as functions of time for Cases 1-4.

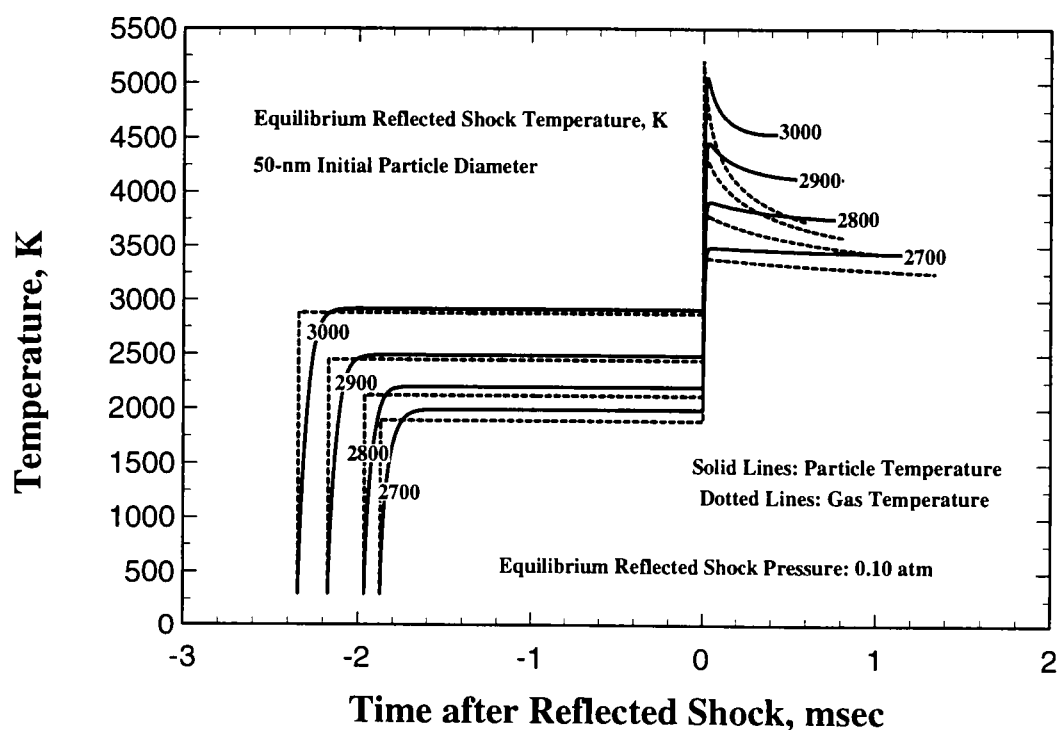


Figure 49 Particle and gas temperature histories at realistic shock tube conditions.

After a very steep rise in temperature from the 300 K initial particle temperature, there is very little gas/particle thermal nonequilibrium in the incident shock. There is very significant nonequilibrium behind the reflected shock. Figure 50 repeats these results, but only shows times after the arrival of the reflected shock. Note that the calculations cease at particle burnout, and that burnout occurs before the end of the test times shown in Table 1 for all cases. Note that Cases 3 and 4 result in particle temperatures exceeding 4000 K. This corresponds approximately to the sublimation temperature of graphite [64]. Therefore, the particle temperature will be somewhat less than that indicated on the figure, as will the burnout time.

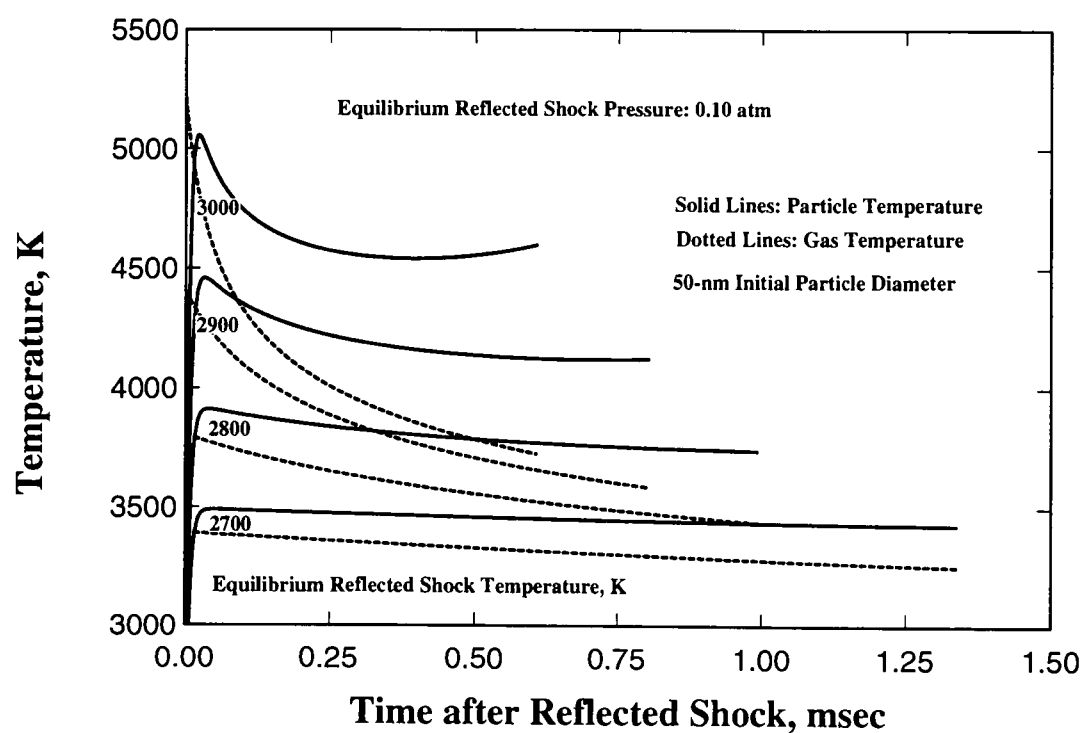


Figure 50 Particle and gas temperature histories at realistic shock tube conditions - for times after arrival of reflected shock.

The particle temperature elevation is shown in Figure 51. Case 1 (2700 K equilibrium reflected shock temperature) exhibits particle temperature elevation of approximately 200 K at burnout. Case 2 (2800 K equilibrium reflected shock temperature) shows approximately 300 K of elevation at burnout. Cases 3 and 4 are somewhat suspect due to the influence of sublimation, but show elevations of 500 and 900 K at burnout, respectively. This level of thermal nonequilibrium should be easily measurable - perhaps by using non-reactive particles to establish a baseline. Potential diagnostic instrumentation is discussed in a following section.

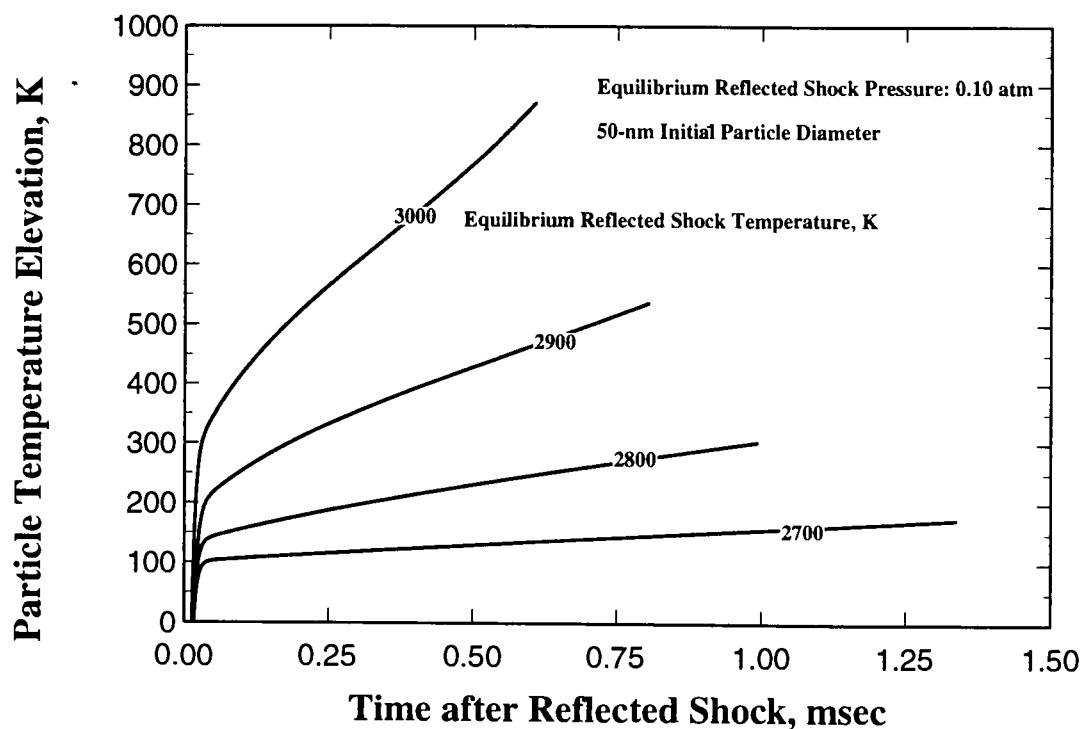


Figure 51 Particle temperature elevation at realistic shock tube conditions - for times after arrival of reflected shock.

The presence of O atoms in the above calculations suggest that previous shock tube measurements of soot oxidation rates (which are purported to be due to molecular oxygen) could be contaminated by an atomic oxygen contribution at high temperature. Park and Appleton [39] and Cadman et al. [41] report the oxidation rate as the oxidation rate by O_2 , without ever referring to the possibility of O_2 dissociation. Roth [40] transforms the measured oxidation rate to collision efficiency of O_2 , implying that no dissociation was present. All these shock tube determined oxidation rates are faster than the Nagle and Strickland-Constable correlation at high temperatures. Perhaps the presence of O atoms in the shock tube measurements is part of the explanation.

Shock Tube Diagnostics

Optical measurements of particle temperature have been routinely made in shock tubes [41], [65], [66]. These measurements typically rely on observing particle emission at several wavelengths and using known particle optical properties to compute particle temperature - essentially the same procedure used by Bradley et al. [49] but at much shorter time scales. Optical measurements of gas temperature in shock tubes have been made by the addition of a trace quantity of a gas with well known and strong absorption features. One candidate is sulfur dioxide (SO_2), which is extremely stable at high temperatures and has a strong absorption feature at 7.3 μm [67]. If a sufficient quantity of SO_2 is used, the emission at 7.3 μm will be saturated, and the gas temperature can then be calculated directly from the Planck

function. However, for a chemical system with well-known kinetics (such as O_2 dissociation) a direct measurement of gas temperature would not be absolutely required. If desired, a measurement of O-atom concentration can be made using the atomic resonance absorption spectrophotometry technique [68], [69]. Standard shock tube diagnostics such as fast time response pressure gauges (Kistler® piezo-electric type) or thin film heat transfer gauges to measure shock arrival times should also be used.

Effect of the Boundary Layer on Shock Tube Test Times

As shown in Figure 45, the distance between the incident shock and the contact surface increases linearly with time. This behavior is predicted considering inviscid flow in the shock tube. The inclusion of the wall boundary layer has the effect of increasing the speed of the contact surface and decreasing the speed of the shock [70], [71]. In fact, the mass loss to the wall boundary layer causes the contact surface and the shock to approach the same velocity - i.e. the paths of the contact surface and the incident shock on Figure 45 would become parallel given sufficient time. These changes in velocity cause a decrease in test time [72] and an increase in the stagnation temperature and pressure behind the incident shock [73]. The decrease in test time can be on the order of a factor of 5 [72].

Given this potential decrease in test time, the results on Figure 51 should be re-examined. The test times indicated in Table 1 range from 0.8 - 1.7 msec (recall that the termination of the lines on Figure 51 indicate particle burnout - not the

termination of test time). Dividing these test times by a factor of 5 yields a range of test times from 160 - 340 μ sec. Figure 51 shows that this is sufficient time to develop substantial thermal nonequilibrium behind the reflected shock. Therefore, although the reduction of test time due to the influence of the boundary layer could be substantial, the predicted magnitude of gas-particle thermal nonequilibrium behind the reflected shock should still be detectable.

Chapter 9. Limitations of the Free Molecular Combustion Model

Free Molecular Assumptions

The combustion model developed here is valid for a single, isolated, spherical particle oxidizing under free molecular conditions. For free molecular conditions to exist, the Knudsen number must be significantly greater than unity. This requires either low gas densities or very small bodies. Another, perhaps less obvious, assumption of the model is that only a single collision between an ambient gas molecule and the surface is allowed. This implies that, for free molecular flow in general, the body surface must be convex. It also implies that, if more than one body is present, the separation distance between the bodies must be very large compared to the gas mean free path. No molecules that collide with one body may then undergo further collisions with another body. The gas molecules that collide with the bodies are assumed to come from infinite, ambient conditions. After a collision with a surface, the internal and translational energy of the gas molecule is no longer representative of the ambient conditions.

Physical Limitations

The uncertainty in the carbon or soot oxidation rates is a very significant limitation to the application of the model. At any given condition, the rates for oxidation by O_2 in the literature span an order of magnitude. The rates for carbon oxidation by O and OH are usually within a factor of 2-3.

The lack of a thermal sublimation model in the current theory limits the validity of the current model to particle temperatures less than about 4000 K. Above this temperature, sublimation can have a significant contribution to the particle mass loss. The LII model of Melton [14] includes a sublimation model, which could be added to the particle combustion model developed here.

A minor limitation is the assumption of a unity thermal accommodation coefficient. The energy equation could easily be altered to allow for non-unity values. However, for low energy thermal collisions on rough surfaces, experiments show accommodation coefficients above 0.95 are typical.

The model assumes that the particle is massive enough compared to the gas molecules that it is not moved by collisions - that is, momentum transfer during collisions is neglected. The particle is also assumed to be massive enough that its mean relative translational velocity is essentially zero. As the particle approaches burnout, these assumptions no longer hold. The particle becomes essentially a large gas molecule, with a non-zero thermal translational velocity. This in turn changes the collision frequency between the gas molecules and the particle. Equation (42) for the collision frequency no longer holds. Therefore, the model is valid only when the particles are much smaller than the gas mean free path, but much larger than molecular sizes.

Influence of Fractal Soot Agglomerates

The combustion model treats only single, compact, spherical, non-porous particles. Soot does not typically exist in flames as isolated spherical particles. Small (50-nm diameter) spherical primary particles agglomerate into aggregates. In sooting flames, these aggregates consist of 200-600 primary particles chained together in an open, rather than a compact structure. This has important implications for the optical properties of soot, since large agglomerates will violate the Rayleigh scattering approximation, and the open structure prohibits treating the agglomerate as an equivalent compact sphere using Mie scattering theory [74], [75], [76].

Although the aggregates exist over a wide size range, they seem to always exhibit mass fractal-like behavior with a Hausdorff or fractal dimension, $D_f < 2$. This is extremely important, since the scattering per primary particle continues to grow for $D_f > 2$, but asymptotes to a constant value for $D_f < 2$ [77]. This greatly simplifies the treatment of the optical properties. The fractal dimension is defined as

$$N \propto (R_g/d_p)^{D_f} \quad (122)$$

where N is the number of primary particles in the aggregate, R_g is the radius of gyration of the aggregate, and d_p is the diameter of the primary particle.

Measurements of flame soot, as well as stochastic simulations of the aggregation process yield fractal dimensions in the range of 1.7-1.8 [74], [78], [79].

In the combustion model, the Rayleigh scattering approximation is used to compute the particle emissivity. Therefore, if the agglomerates are large enough, the Rayleigh approximation will be invalid. However, since the influence of radiation on the particle burnout temperature is relatively small, this is a probably a second-order effect.

As the size of the agglomerate grows, the effective Knudsen number (based on the size of the agglomerate) decreases, creating more continuum-like conditions. Gas-gas collisions will become important at lower pressures than for a single isolated particle - violating the most basic assumption of the free molecular model.

The fractal, open nature of the soot agglomerates creates the possibility of trapping gas molecules within the agglomerate. A gas molecule could undergo collisions with many of the primary particles comprising the agglomerate. This violates the single collision assumption of the current model. The agglomerated nature of soot will tend to create more continuum-like combustion behavior. This effect should be investigated by developing either a free molecular or a direct simulation Monte Carlo (DSMC) technique to track gas molecule trajectories as they collide and rebound throughout the agglomerate. The DSMC technique could consider collisions between gas molecules, while these collisions would be ignored in the free molecular treatment. Heat conduction between primary particles throughout the agglomerate should also be considered.

Chapter 10. Final Conclusions and Recommendations

Soot particles will experience significant rarefaction effects while oxidizing at moderate pressure conditions. The conclusion that small oxidizing soot particles will remain in thermal equilibrium with the surrounding gas is shown to be invalid. This conclusion follows from the assumptions of continuum flow, which predict that the convective heat transfer coefficient is independent of pressure, inversely proportional to particle size, and dependent on the gas thermal conductivity. For sufficiently small particle size, the particle Knudsen number is large and the particles experience free molecular flow. For free molecular flow the convective heat transfer coefficient is dependent on pressure, and independent of particle size and gas thermal conductivity. Under these conditions, energy release by oxidation can overcome the convective loss and drive the soot particle temperature above the ambient gas temperature.

Small particle thermal nonequilibrium is favored by low pressure, high ambient temperature, and high relative concentrations of the oxidizing species. Collisions with inert species such as N_2 and Ar are very effective at reducing the particle temperature. Small amounts of atomic oxygen can cause large increases in particle temperature.

Further experimental work needs to be done to determine the correct temperature- and pressure-dependent collision efficiencies for important oxidizing species such as O_2 , O, and OH. The pressure dependence of the Nagle and

Strickland-Constable oxidation rate expression was shown to be invalid when extrapolated to low pressures. Reaction rates of OH with soot have been derived, but no unambiguous measurements of the products have been made. Without knowledge of the products, no conclusive statement about the exothermicity or endothermicity of the reaction can be made.

Oxidation is not the only mechanism for energy release on the surface of soot particles. Soot particles present a potential catalytic surface for the exothermic recombination of flame radicals. The free molecular energy equation removes the dominance of the convective loss and implies that the determination of soot particle temperature may be subject to more effects than previously recognized.

Soot oxidation and catalytic recombination should be studied in low pressure flames to confirm and quantify the rarefaction effects. Shock tube studies of soot oxidation rates should include emission measurements to infer particle temperature as well as absorption measurements to infer particle consumption rates.

A low pressure shock tube experiment has been designed to isolate and quantify soot particle thermal nonequilibrium. Calculations indicate substantial nonequilibrium exists at experimentally attainable conditions. These calculations also indicate the possibility that previous shock tube measurement of soot oxidation by O_2 may be contaminated by O-atoms at high temperatures.

Finally, it is important to note that this theory is fully free molecular. No gas-gas collisions are considered. Only direct collisions with the surface are allowed, and only convex bodies can be considered. Direct Simulation Monte Carlo

(DSMC) calculations should be done to assess the importance of gas-gas collisions for a variety of particle Knudsen numbers and temperatures. A DSMC model should also be developed to treat the multiple collision environment around and throughout a fractal soot agglomerate.

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Appendices

**Appendix A. Nusselt Number for Spheres in the Pure Conduction
Limit**

Appendix A. Nusselt Number for Spheres in the Pure Conduction

Limit

Consider a solid sphere of radius r_1 embedded in a larger spherical shell of outer radius r_2 and inner radius r_1 as shown in Figure A-1. The inner sphere, and thus the inner surface of the spherical shell, is held at a constant temperature, T_1 . The outer surface of the spherical shell is held at a constant temperature, T_2 . The thermal conductivity of the outer spherical shell is k_2 which is assumed to be constant.

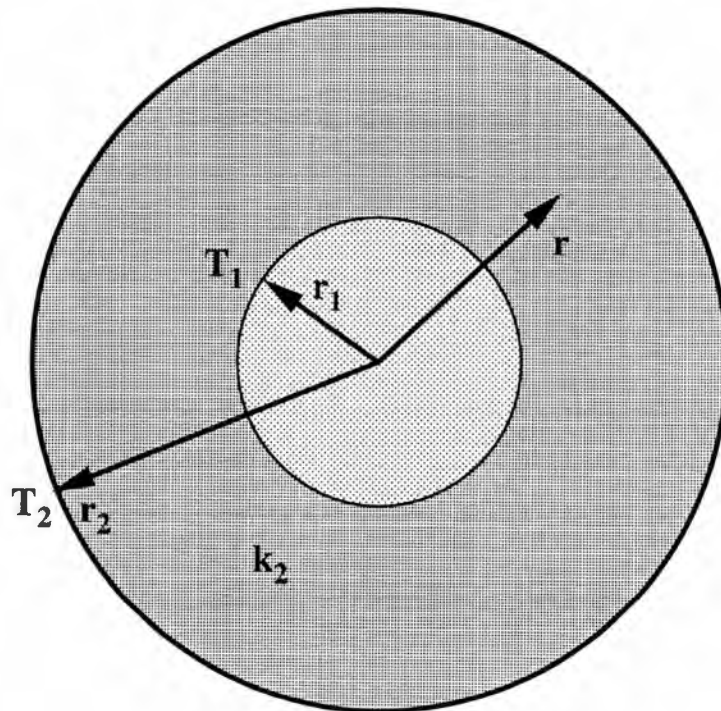


Figure A-1 Geometry for heat transfer in spheres.

The spherically symmetric steady heat conduction equation is

$$\frac{d^2 T}{dr^2} + \frac{2}{r} \frac{dT}{dr} = 0 \quad (\text{A-1})$$

or

$$\frac{d}{dr} \left(r^2 \frac{dT}{dr} \right) = 0 \quad (\text{A-2})$$

The boundary conditions are

$$T(r_1) = T_1 \quad \text{and} \quad T(r_2) = T_2 \quad (\text{A-3})$$

Integrating Equation (A-2) twice yields

$$T(r) = -\frac{C_1}{r} + C_2 \quad (\text{A-4})$$

Imposing the boundary conditions yields the temperature distribution in the outer spherical shell:

$$T(r) = T_1 + \frac{(T_1 - T_2)}{1/r_2 - 1/r_1} \left(\frac{1}{r_1} - \frac{1}{r} \right), \quad r_1 \leq r \leq r_2 \quad (\text{A-5})$$

The rate of heat transfer into the inner sphere is found by applying Fourier's law of heat conduction at the outer surface of the inner sphere (i.e. at $r = r_1$) [A-1]:

$$\dot{Q} = k_2 A \frac{dT}{dr} = k_2 4\pi r_1^2 \frac{(T_2 - T_1)}{r_1^2 (1/r_1 - 1/r_2)} \quad (\text{A-6})$$

or

$$\dot{Q} = k_2 4\pi \frac{(T_2 - T_1)}{(1/r_1 - 1/r_2)} \quad (\text{A-7})$$

Let r_2 approach infinity, and rename T_2 as T_∞ . Making these substitutions in Equation (A-7) yields

$$\dot{Q} = k_2 4\pi r_1 (T_\infty - T_1) \quad (\text{A-8})$$

Introduce the convective heat transfer coefficient (h) by writing the heat transfer to the inner sphere as

$$\dot{Q} = hA\Delta T = h4\pi r_1^2 (T_\infty - T_1) \quad (\text{A-9})$$

Equating (A-8) and (A-9) and solving for the convective heat transfer coefficient yields

$$h = \frac{k_2}{r_1} \quad (\text{A-10})$$

or, in the nomenclature of Chapter 2,

$$h = \frac{k_f}{r} \quad (\text{A-11})$$

where k_f is the thermal conductivity of the fluid surrounding the particle, and r is the radius of the particle. Therefore, Equation (A-10) or (A-11) gives the convective heat transfer coefficient for a particle of radius r immersed in a fluid of thermal conductivity k_f , assuming that heat transfer occurs only by conduction. This is the pure conduction limit for spheres undergoing convective heat transfer in infinite ambient conditions. The Nusselt number [A-2] is defined as

$$Nu = \frac{hD}{k_f} \quad (\text{A-12})$$

where D is the particle diameter. Substituting Equation (A-11) into (A-12) yields

$$Nu = \frac{hD}{k_f} = \frac{\frac{k_f}{r}(2r)}{k_f} = 2 \quad (\text{A-13})$$

Therefore, for spheres undergoing pure conduction with a surrounding gas, the Nusselt number is 2. For spheres undergoing forced convection, the Nusselt number is given by

$$Nu = 2 + f(Re, Pr) \quad (\text{A-14})$$

where Re and Pr are the Reynolds number and the Prandtl number, respectively. For spheres undergoing buoyancy-induced free convection, the Nusselt number is given by

$$Nu = 2 + f(Gr, Pr) \quad (\text{A-15})$$

where Gr is the Grashof number. This shows that heat transfer to spheres for both free and forced convection starts with the pure conduction limit ($Nu=2$) and then is enhanced by the transport of the ambient fluid [A-2].

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Appendix B. The McCoy and Cha Heat Transfer Correlation

Appendix B. The McCoy and Cha Heat Transfer Correlation

McCoy and Cha [B-1] developed a heat transfer correlation to bridge the continuum and free molecular regimes. As shown in the Chapter 2, their correlation is

$$h = \frac{k_f}{r} \left[\frac{1}{1 + GKn} \right] \quad (\text{B-1})$$

where k_f / r is the continuum heat transfer coefficient, Kn is the Knudsen number, and G is defined as

$$G = \frac{8}{\alpha} \frac{\gamma}{\gamma + 1} \frac{1}{Pr} \quad (\text{B-2})$$

where α is the thermal accommodation coefficient, γ is the ratio of specific heats, and Pr is the Prandtl number. The three heat transfer coefficients under consideration (continuum, free molecular, and the McCoy and Cha correlation) can now be compared as a function of Knudsen number. As a reminder, these coefficients are:

$$h_{\text{continuum}} = \frac{k_f}{r} \quad (\text{B-3})$$

$$h_{\text{fm}} = \frac{h_{\text{continuum}}}{GKn} \quad (\text{B-4})$$

(as was shown in Chapter 2, G is approximately 6.5) and Equation (B-1) for the McCoy and Cha bridging correlation. These three heat transfer coefficients are plotted as a function of Kn in Figure B-1. For ease of comparison, each heat transfer coefficient was normalized by the continuum heat transfer coefficient.

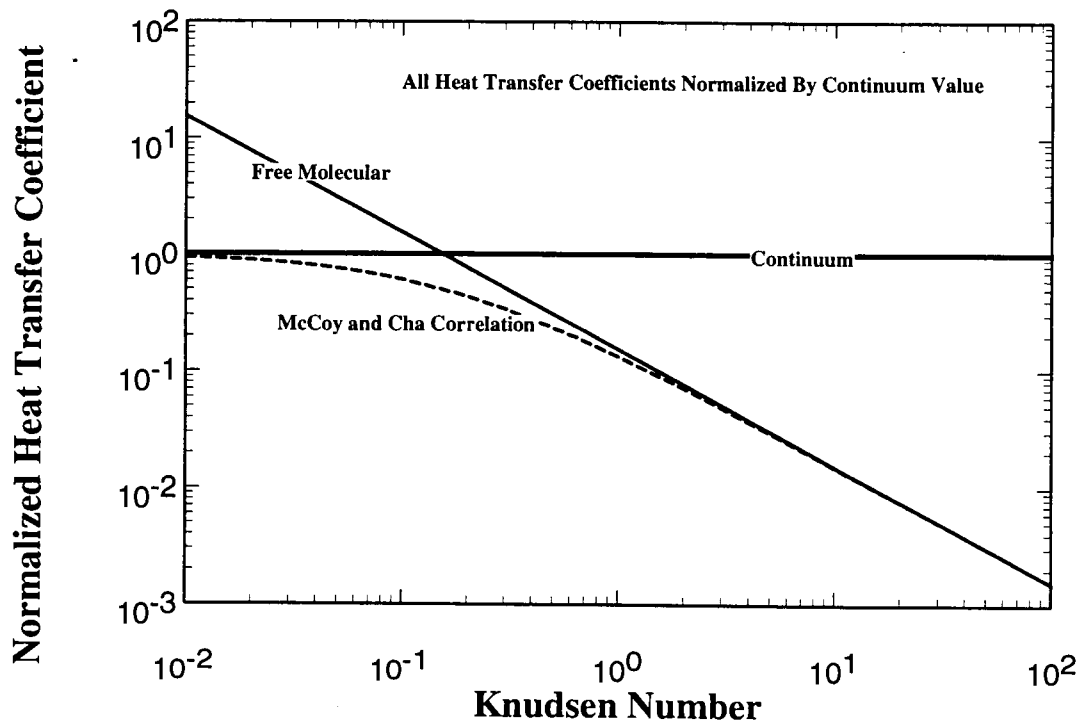


Figure B-1 Comparison of the continuum and free molecular heat transfer coefficients with the McCoy and Cha correlation.

This also removes the necessity to choose a single particle size or value thermal conductivity to consider. The Knudsen number on the ordinate can be considered to be a function of particle size or ambient density or both. The normalized continuum heat transfer coefficient is of course simply unity at all Knudsen numbers. The free molecular heat transfer coefficient is considerably higher than the continuum value at low Knudsen numbers (where it is invalid) and considerably lower at large Knudsen numbers. The McCoy and Cha correlation smoothly bridges the gap between the continuum regime (low Knudsen number) and the free molecular regime (high Knudsen number). Note that, as stated in Chapter 2, the McCoy and Cha correlation results in lower heat transfer coefficients than either the continuum or the free molecular values at all Knudsen numbers. The percent differences between the McCoy and Cha correlation and both the continuum and free molecular values are plotted as a function of Knudsen number in Figure B-2. At $Kn = 10$, the McCoy and Cha correlation results in a value about 2% lower than the free molecular value. At $Kn = 50$, the percent difference drops to about 0.3%. The McCoy and Cha correlation seems to be adequate in the free molecular regime. However, at $Kn = 0.02$ (usually considered to be continuum) the McCoy and Cha correlation produces a value about 10% lower than the continuum value. Even at $Kn = 0.002$, the correlation is about 1% below the continuum value. The McCoy and Cha correlation is probably adequate in the free molecular regime, but results in lower than expected heat transfer coefficients in the continuum and near-continuum regimes.

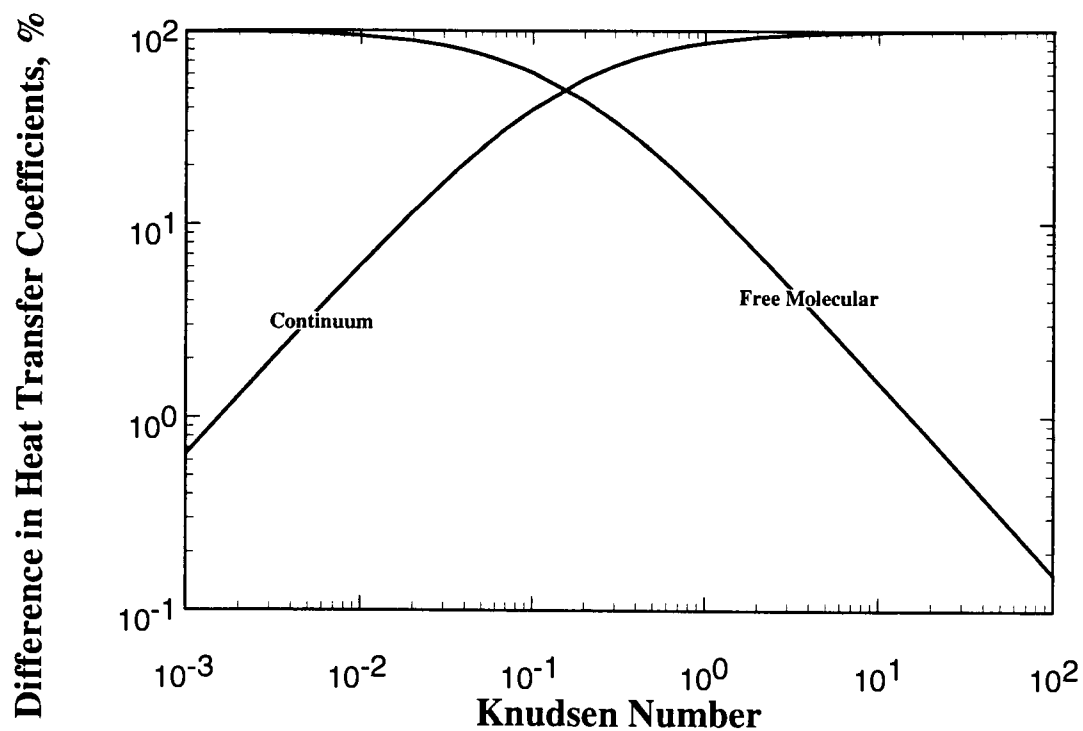


Figure B-2 Percent difference between the McCoy and Cha correlation and the continuum and the free molecular heat transfer coefficients.

References

- B-1. McCoy, B. J., and Cha, C. Y., "Transport Phenomena in the Rarefied Gas Transport Regime," *Chemical Engineering Science*, **29**, 381, 1974.

**Appendix C. Biot Number for Spheres in the Pure Conduction and
Free Molecular Limits**

Appendix C. Biot Number for Spheres in the Pure Conduction and Free Molecular Limits

The Biot number (Bi) is the dimensionless quantity that relates the rate of heat transfer to a body (usually, a convective flux) to the rate of heat transfer within the body by conduction [C-1]. The Biot number is defined as

$$Bi = \frac{hL}{k} \quad (C-1)$$

where h is the convective heat transfer coefficient, L is a characteristic length, and k is the thermal conductivity of the body. If $Bi \ll 1$, the resistance to heat transfer within the body by conduction is much less than the resistance to heat transfer to the body. The assumption of a lumped parameter system (i.e. a uniform temperature distribution throughout the body) is therefore reasonable if Bi is small. The characteristic length, L , is defined as

$$L \equiv \frac{V}{A_s} \quad (C-2)$$

where V is the volume and A_s is the surface area of the body under consideration. For spherical particles, therefore

$$L = \frac{\frac{4}{3}\pi r^3}{4\pi r^2} = \frac{r}{3} \quad (C-3)$$

where r is the particle radius. As shown in Appendix A, for spheres in the pure conduction limit of continuum free convection

$$h = \frac{k_f}{r} \quad (C-4)$$

where k_f is the thermal conductivity of the gas “film” surrounding the particle.

Substituting Equations (C-3) and (C-4) into Equation (C-1) yields

$$Bi = \frac{\frac{k_f}{r} \frac{r}{3}}{k} = \frac{1}{3} \frac{k_f}{k} \quad (C-5)$$

Therefore, in the limiting case of spheres in pure conduction with a surrounding media, Bi is independent of the particle size, which might not be intuitively obvious. The NASA Equilibrium Code with Transport Properties [C-2] gave the thermal conductivity of molecular oxygen as 0.125 W/m-K. The conductivity of amorphous carbon was found to be 1.6 W/m-K [C-1]. The Biot number in this case is, therefore

$$Bi = \frac{1}{3} \frac{0.125}{1.6} = 0.026 \quad (C-6)$$

which is much less than unity. In Chapter 2, it was shown that the free molecular heat transfer coefficient is orders of magnitude less than the continuum heat transfer coefficient under the same conditions. The free molecular Biot number is therefore much less than the continuum Biot number under the same ambient conditions. Since Equation (C-6) shows that the Biot number is sufficiently small to justify a lumped parameter treatment under continuum assumptions, it is apparent that the justification is even stronger under free molecular assumptions. Therefore, in this work, the temperature distribution throughout the particle was assumed to be uniform.

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Appendix D. Emissivity of Small Particles

Appendix D. Emissivity of Small Particles

Buckius and Tien [D-1] measured the spectral absorption of soot in polystyrene flames. Using this data and a dispersion model based on the electronic band structure, Lee and Tien [D-2] computed the real and the imaginary parts of the complex refractive index (m) of soot,

$$m = n - ik \quad (\text{D-1})$$

where n is the real part and k the imaginary. Both n and k are given as functions of wavelength and temperature. If the Rayleigh parameter (x) is small, i.e. if

$$x = \frac{2\pi r}{\lambda} < 1 \quad (\text{D-2})$$

where r is the particle radius and λ the wavelength of light, then the absorption efficiency (Q_{abs}) or the emissivity (ϵ_λ) of the particle is given by the Rayleigh-limit [D-3] expression

$$\epsilon_\lambda = Q_{abs} = -4 \operatorname{Im} \left\{ \frac{m^2 - 1}{m^2 + 2} \right\} x \quad (\text{D-3})$$

For a cloud of particles with a non-uniform size distribution, the spectral absorption coefficient (κ_λ) is

$$\kappa_\lambda = \pi \int_0^\infty Q_{abs} r^2 n(r) dr = -4 \operatorname{Im} \left\{ \frac{m^2 - 1}{m^2 + 2} \right\} \int_0^\infty \left(\frac{2\pi r}{\lambda} \right) \pi r^2 n(r) dr \quad (D-4)$$

where n is the number of particles of radius r in the size distribution. The volume fraction (f_v) of the cloud is defined as

$$f_v = \int_0^\infty \frac{4}{3} \pi r^3 n(r) dr \quad (D-5)$$

The spectral absorption coefficient can be written in terms of the volume fraction by substituting Equation (D-5) into Equation (D-4) to yield

$$\kappa_\lambda = -\operatorname{Im} \left\{ \frac{m^2 - 1}{m^2 + 2} \right\} \frac{6\pi f_v}{\lambda} \quad (D-6)$$

Dividing Equation (D-3) by (D-6) yields

$$\frac{Q_{abs}}{\kappa_\lambda} = \frac{\frac{4}{3} r}{f_v} \quad (D-7)$$

or

$$Q_{abs} = \frac{\frac{4}{3}\kappa_{\lambda}r}{f_v} \quad (D-8)$$

It can be shown [D-2] that the spectral absorption coefficient is also given by

$$\kappa_{\lambda} = \frac{36\pi n k f_v}{\lambda \left[(n^2 - k^2 + 2)^2 + 4n^2 k^2 \right]} \quad (D-9)$$

Note that the spectral absorption coefficient is independent of the particle size. This is because, in the Rayleigh limit, self-absorption by the particle is negligible.

Internal atoms participate in radiative exchange as efficiently as those near the particle surface. Soot particle emissivity is thus a *volumetric*, rather than a *surface*, process. Since n and k are temperature dependent, κ_{λ} is also temperature dependent.

Substituting Equation (D-9) into (D-8) yields

$$Q_{abs} = \frac{4}{3} \frac{36\pi n k}{\lambda \left[(n^2 - k^2 + 2)^2 + 4n^2 k^2 \right]} r = k_{r,\lambda} r \quad (D-10)$$

where

$$k_{r,\lambda} = \frac{4}{3} \frac{36\pi n k}{\lambda \left[(n^2 - k^2 + 2)^2 + 4n^2 k^2 \right]} \quad (\text{D-11})$$

so the spectral emissivity is obviously

$$Q_{abs} = \epsilon_{\lambda} = k_{r,\lambda} r \quad (\text{D-12})$$

Since the emission from the particle is of interest here, the Rayleigh criterion ($x < 1$) must be satisfied in the spectral range responsible for most of the particle emission. Assuming a Rayleigh parameter (x) of 1.0 and a particle radius of 25 nm (0.025 μm) yields 0.16 μm as the minimum wavelength that satisfies the Rayleigh criterion. The wavelength at which peak emission from a blackbody occurs is given by Wien's displacement law [D-4]

$$\lambda_{\max} T = 2898 \mu\text{m} \cdot \text{K} \quad (\text{D-13})$$

which implies that for peak emission to occur at 0.16 μm , the particle temperature must be greater than 18,000 K. Since temperatures of interest in this work are less than 5000 K, it is obvious that most of the particle emission will occur at wavelengths much longer than 0.16 μm . Therefore, the particle emission does indeed occur under Rayleigh-limit conditions.

Since only the total (rather than spectral) emission of the particle is of concern, the spectral emissivity must be integrated to find the total extinction coefficient. Since the total power emitted from a particle at temperature T proportional to [D-5]

$$\int_0^{\infty} k_{r,\lambda}(T) B_{\lambda}(T) d\lambda \quad (\text{D-14})$$

where B_{λ} is the Planck spectral blackbody function, the total emissivity (ϵ) is proportional to

$$k_r(T) = \frac{\int_0^{\infty} k_{r,\lambda}(T) B_{\lambda}(T) d\lambda}{\int_0^{\infty} B_{\lambda}(T) d\lambda} \quad (\text{D-15})$$

where k_r is the spectrally-averaged (or total) emission coefficient. This temperature dependent function was derived from the Lee and Tien determination of n and k by applying Equations (D-11) and (D-15). These results, along with a curve fit of the form

$$k_r(T) = \frac{4}{3} \left[\frac{a + cT + eT^2 + gT^3}{1 + bT + dT^2 + fT^3} \right] \quad (\text{D-16})$$

where

$$\begin{aligned}a &= -964.4 \\b &= -3.190 \times 10^{-4} \\c &= 7.463 \\d &= 4.175 \times 10^{-7} \\e &= 6.647 \times 10^{-3} \\f &= -4.932 \times 10^{-11} \\g &= -1.154 \times 10^{-8}\end{aligned}\tag{D-17}$$

are plotted in Figure D-1.

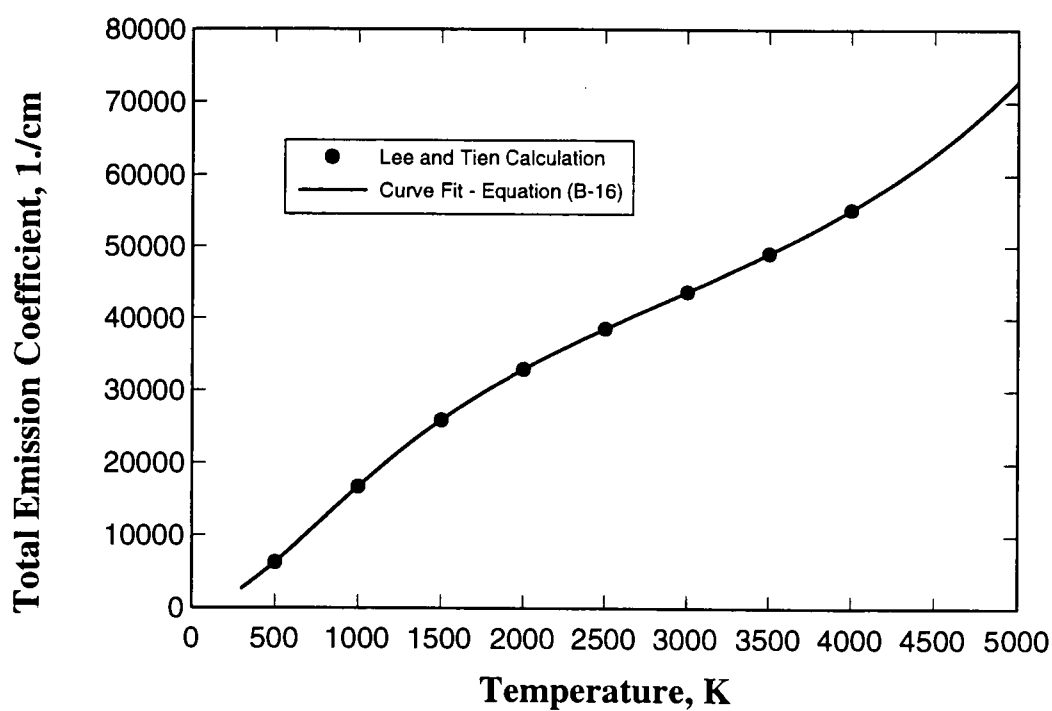


Figure D-1 Lee and Tien total emission coefficient and curve fit.

From Equations (D-12) and (D-15) the temperature-dependent total emissivity is simply

$$\varepsilon = k_r r \quad (\text{D-18})$$

The radiative heat transfer from the particle is given by

$$\dot{q}_{\text{radiation}} = \varepsilon \sigma A T^4 = k_r r \sigma (4\pi r^2) T^4 = 3k_r \sigma \left(\frac{4}{3} \pi r^3 \right) T^4 = 3k_r \sigma V T^4 \quad (\text{D-19})$$

where σ is the Stefan-Boltzmann constant, A is the particle surface area, and V is the particle volume. This demonstrates that the particle radiation is indeed proportional to the volume of the particle, rather than the surface area. Kokhanovsky and Zege [D-6] give a similar development for Rayleigh-sized particles in a general review of aerosol optical properties.

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Appendix E. The Modified Implicit Euler Scheme

Appendix E. The Modified Implicit Euler Scheme

Given a vector of functions $\mathbf{F}$ and an ordinary differential equation

$$\frac{d}{dt}\mathbf{Y} = \mathbf{F} \quad (\text{E-1})$$

we can approximate the time derivative of $\mathbf{Y}$ (the vector of unknowns) as the average value of $\mathbf{F}$, or

$$\frac{\Delta\mathbf{Y}}{\Delta t} = \frac{1}{2}[\mathbf{F}(t_i, \mathbf{Y}_i) + \mathbf{F}(t_{i+1}, \mathbf{Y}_{i+1})] \quad (\text{E-2})$$

where the subscripts i and $i+1$ refer to the current conditions and the next time-advanced step, respectively. This representation is referred to as the trapezoidal rule [E-1], [E-2]. If the governing equations were partial differential equations, this would be identical to the Crank-Nicolson scheme. Linearizing about the current conditions yields

$$\frac{\Delta\mathbf{Y}}{\Delta t} = \frac{1}{2}\left[\mathbf{F}(t_i, \mathbf{Y}_i) + \mathbf{F}(t_{i+1}, \mathbf{Y}_i) + \frac{\partial\mathbf{F}}{\partial\mathbf{Y}}(t_{i+1}, \mathbf{Y}_i)\Delta\mathbf{Y}\right] \quad (\text{E-3})$$

which can be rearranged as

$$\left[\mathbf{I} - \frac{1}{2} \mathbf{J}(t_{i+1}, \mathbf{Y}_i) \Delta t \right] \Delta \mathbf{Y} = \frac{\Delta t}{2} [\mathbf{F}(t_i, \mathbf{Y}_i) + \mathbf{F}(t_{i+1}, \mathbf{Y}_i)] \quad (\text{E-4})$$

where $\mathbf{I}$ is the identity matrix and the Jacobian matrix $\mathbf{J}$ is given by

$$\mathbf{J} = \frac{\partial \mathbf{F}}{\partial \mathbf{Y}} \quad (\text{E-5})$$

Given an explicit time step Δt , the right hand side of Equation (E-4) is known. Note that $\mathbf{F}$ is evaluated at steps i and $i+1$, whereas $\mathbf{Y}$ is only evaluated at the i^{th} step. If we can find the Jacobian matrix (either numerically or analytically) then the left hand side of Equation (E-4) is known except for the vector $\Delta \mathbf{Y}$. This vector contains our desired unknowns - the implicit steps in the components of $\mathbf{Y}$. Equation (E-4) can be solved for $\Delta \mathbf{Y}$ by any convenient matrix solver. Once $\Delta \mathbf{Y}$ is known, then the vector $\mathbf{Y}$ at the time-advanced step is

$$\mathbf{Y}_{i+1} = \mathbf{Y}_i + \Delta \mathbf{Y} \quad (\text{E-6})$$

The energy and mass conservation equations developed in Chapters 3 and 5 are

$$\frac{dT}{dt} = \frac{3}{\rho r C} \sum_i Z_i \left[f_i (\tilde{m}_i e + q_{ri}) + (1 - f_i) q_{nri} \right] + \frac{3k_r \sigma}{\rho C} (T_\infty^4 - T^4) \quad (\text{E-7})$$

and

$$\frac{dr}{dt} = \frac{-1}{\rho} \sum_i (Z f \tilde{m})_i \quad (\text{E-8})$$

respectively. For the notation used above, this means

$$\mathbf{Y} = \begin{bmatrix} T \\ r \end{bmatrix} \quad (\text{E-9})$$

and

$$\mathbf{F} = \begin{bmatrix} F_1 \\ F_2 \end{bmatrix} = \begin{bmatrix} \frac{3}{\rho r C} \sum_i Z_i \left[f_i (\tilde{m}_i e + q_{ri}) + (1 - f_i) q_{nri} \right] + \frac{3k_r \sigma}{\rho C} (T_\infty^4 - T^4) \\ \frac{-1}{\rho} \sum_i (Z f \tilde{m})_i \end{bmatrix} \quad (\text{E-10})$$

and the Jacobian matrix is given by

$$\mathbf{J} = \frac{\partial \mathbf{F}}{\partial \mathbf{Y}} = \begin{bmatrix} \frac{\partial F_1}{\partial T} & \frac{\partial F_1}{\partial r} \\ \frac{\partial F_2}{\partial T} & \frac{\partial F_2}{\partial r} \end{bmatrix} \quad (\text{E-11})$$

The indicated partial derivatives are all evaluated analytically. The system is solved for $\Delta \mathbf{Y}$ by an LU decomposition and back-substitution scheme [E-3] where

$$\Delta \mathbf{Y} = \begin{bmatrix} \Delta T \\ \Delta r \end{bmatrix} \quad (\text{E-12})$$

and thus

$$\begin{bmatrix} T_{i+1} \\ r_{i+1} \end{bmatrix} = \begin{bmatrix} T_i \\ r_i \end{bmatrix} + \begin{bmatrix} \Delta T \\ \Delta r \end{bmatrix} \quad (\text{E-13})$$

This technique is used to solve for the time history of the particle size and temperature for both steady and unsteady ambient conditions. The Jacobian and the vector $\mathbf{F}$ must be evaluated properly. The Jacobian is evaluated only at the time-advanced step, while $\mathbf{F}$ is evaluated at both the current time step and the time-advanced step. Components of both $\mathbf{F}$ and $\mathbf{J}$ contain the ambient conditions, e.g. T_∞ . If the ambient conditions are time-dependent, then both $\mathbf{F}$ and $\mathbf{J}$ are explicitly time-dependent.

The accuracy of the method is demonstrated in Figure 17 in Chapter 5 which compares the numerical and analytic solutions of the constant-property mass and energy equations (ignoring radiation). The stability of the method was assessed by testing the sensitivity of the solution to the time step. The result is illustrated in Figure E-1 below. The conditions for these calculations are: pure molecular oxygen, 50-nm initial particle diameter, 0.10-atm oxygen pressure, and 2500 K ambient temperature. The oxidation rates of Roth are used. The equations solved are Equations (E-7) and (E-8) - the full nonlinear, variable property equations including radiation. Note that burnout temperature and time are insensitive to the step size.

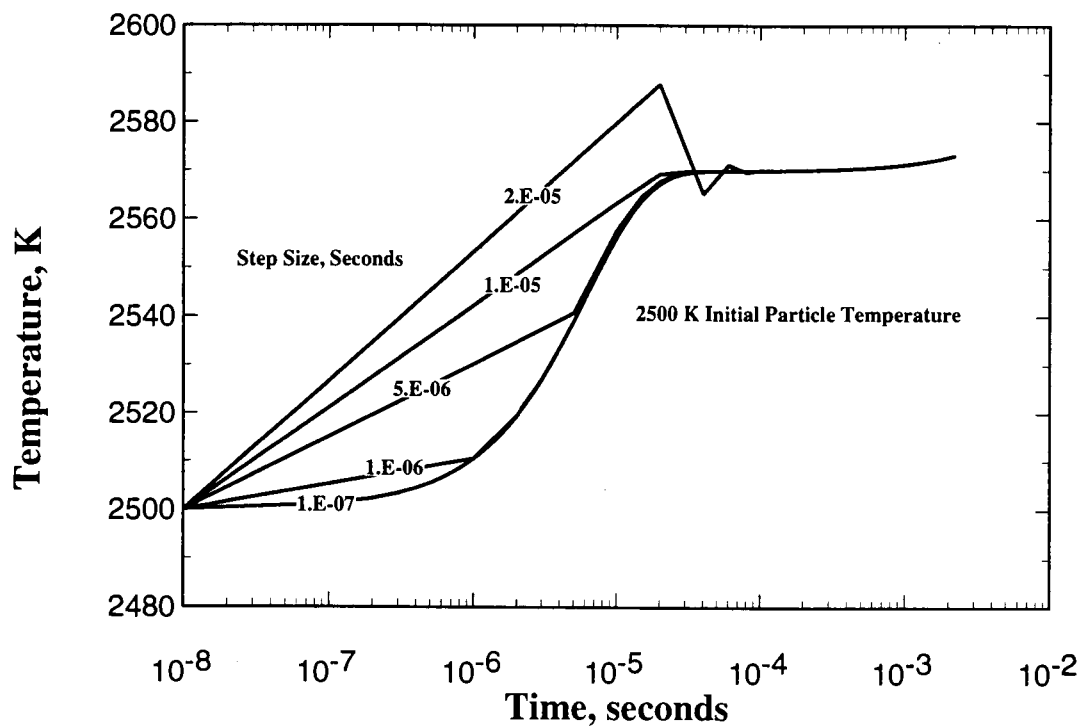


Figure E-1 Stability of the numerical scheme as a function of time step.

The transient behavior is not well captured by the larger time steps, but the final temperature is the same for all time steps shown. Oscillatory behavior does not appear until the time step is increased by two orders of magnitude. Larger step sizes result in instability. The scheme appears to be very stable over this wide range of time steps. For the majority of cases reported in this work, the step size was held constant at 10^{-7} seconds.

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Vita

Robert Hiers was born on December 1, 1961, in Manchester, Tennessee, to Bob and Toni Hiers. He graduated from Tullahoma High School as a National Merit Scholar Finalist in 1980. He attended the University of Tennessee on the Leif J. Sverdrup Scholarship, and worked for Sverdrup Technology, Inc., as a co-op student before graduating with a B. S. degree in Mechanical Engineering in 1985. While working for Sverdrup at the Arnold Engineering Development Center and attending the University of Tennessee Space Institute, he received a M. S. degree in Mechanical Engineering in 1993. He currently resides in Normandy, Tennessee, with his wife, Mary, and their two children, William and Olivia.