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COMPUTER MODELING OF COAL GASIFICATION REACTORS

Quarterly Technical Progress Report

For the Period July 1, 1977 - September 30, 1977

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ABSTRACT

This report presents a summary of the work accomplished during the ninth quarter of a three year study conducted for the U.S. Energy Research and Development Administration, under Contract No. E(49-18)-1770, to develop and apply computer codes representing the performance of fluidized bed and entrained flow coal gasification reactors.

SECTION 1

OBJECTIVE AND SCOPE OF WORK

The purpose of this three year program is to develop and apply general computer models that will expedite the development and aid in the optimization and scale-up of reactors for coal gasification. Initial applications will be to fluidized bed gasification processes; subsequently both entrained flow reactors and fast fluidized beds will be examined.

During the first year (Year 1), work will be initiated on the fluidized bed model in the areas of multiphase fluid flow without chemical reactions, and chemical reactions without fluid flow. The models, developed to represent these aspects of gasification processes, will be combined in the second year (Year 2) of the program into a numerical model of a time-dependent field description of fluidized bed flows in two space dimensions. Calculations will be performed with the prototype code during Years 1 and 2 to verify the accuracy of the formulations employed. In Year 2, these calculations should provide some preliminary results relevant to coal gasification.

During Year 2, a computer model for entrained flow gasifiers will be formulated and the coal chemistry defined; this model will provide a field description of entrained flows in two and three spatial dimensions. Nonreactive flow calculations will be performed for entrained flow processes by the end of Year 2.

In the third year (Year 3) of the program, application of the fluidized bed computer model to specify gasifier processes will be extended and a model which includes three-dimensional effects developed. Also, during this third year the coal chemistry defined in Year 2 will be combined with the entrained flow computer model and some calculations of such gasifier configurations performed.

SECTION II

SUMMARY OF PROGRESS TO DATE

This was the first quarter in the third year of research to develop and apply computer codes, based upon continuum theories of multiphase flows, to the performance of fluidized bed and entrained flow coal gasification reactors.

The research on the fluidized bed computer code included the modification of the code to treat axisymmetric geometries. Test calculations were performed and studies were initiated to calculate the relative behavior of planar and axisymmetric bubble evolution. Analytical and numerical formulations of fluidized bed chemistry and hydrodynamics were examined, for the purposes of extending and improving the fluidized bed model. Specific numerical calculations of solids convection, with application to the synthane gasifier, were performed as part of a continuing investigation of jet and bubble formation at the distributor plate.

The work on the entrained flow computer model involved the extension of this code to treat flows in three spatial dimensions. Subroutines in the new code were tested and calculations were initiated to simulate the gas dynamics and solid particle flows in a combustion stage of a two stage gasifier configuration. The formulation of a kinetics model for pulverized coal particles was continued. A model study of the relative influences of oxidation and gasification reactions upon mass loss from a carbon particle was completed.

SECTION III

DETAILED DESCRIPTION OF TECHNICAL PROGRESS

3.1 TASK 00: MANAGEMENT, DOCUMENTATION AND CONSULTING

This reporting period has been typified by a rather large number of technical visits for the purpose of coordination and liaison of the Systems, Science and Software (S^3) modeling activity with developmental programs in coal conversion research.

A prime interest in this coordination is the accumulation of information on other theoretical and experimental studies for comparison with the computer models. To this end, S^3 staff members visited the Massachusetts Institute of Technology on July 11 to meet with Dr. S. Tung and discuss the subjects of fluidized bed combustion and fluidization of large particles. Previous meetings and conversations with the staff at the Institute of Gas Technology, together with this MIT visit, provided some insight into the need for predictive models for high pressure fluidization and fluidization of beds with large particles. Meetings and discussions of cold flow visualization studies for fluidized beds were held at City College, New York, on September 14 and at the Pittsburgh Energy Research Center on September 27; Professor Joseph Yerushalmi participated in both of these meetings. Experimental studies in gas dynamics and chemistry relative to entrained flows was reviewed in meetings with Foster Wheeler and Combustion Engineering staffs on September 14 and 15, respectively. Both organizations will provide reports of experimental results from their flow visualization studies of entrained flow gasifiers. Continued liaison with the Phillips Petroleum Company at Bartlesville and Homer City (the BIGAS pilot plant) was maintained via telephone conversations.

Dr. Blake attended the Symposium on Instrumentation and Control for Fossil Demonstration Plants in Chicago on July 13-15.

Professor Joseph Yerushalmi visited S^3 on August 23 and reviewed the experimental studies of high velocity fluidization and jet penetration in fluidized beds.

Professor C. Y. Wen of West Virginia University consulted at S^3 in July and September, reviewing experimental data and theoretical models for coal conversion in fluidized bed environments. The data base for devolatilization was examined. He presented, on September 1, a summary of the progress at West Virginia University in the development of a homogeneous reactor model for steam-osygen gasification. This modeling activity is being funded as a subcontract to S^3 and will provide a simple hydrodynamic model for the study of coal kinetics and transport formulations.

In July and August, Professor Julius Siekmann of the Technische Hochschule, Darmstadt, visited La Jolla and consulted with S^3 staff members on the subjects of fluidization and the relationship between bed rheology and bubble characteristics.

Professor Paul Libby of the University of California at San Diego continued his theoretical studies of carbon particle oxidation and gasification. His analytical and numerical results have provided a theoretical understanding of kinetics and transport influences upon control of the rate carbon mass loss.

The technical activities and the progress on the present S^3 project were reviewed with Dr. Leonard Naphtali at ERDA on August 2 and were presented formally to a group of ERDA program managers on September 26. A presentation on this computer model development was made at the Morgantown Energy Research Center on August 1.

3.2 TASK 01: FLUIDIZED BED COAL GASIFICATION MODEL

The incorporation of chemistry and transport into the fluidized bed computer model was continued. A version of that code was developed to treat fluidized bed flows with axisymmetric geometry. This numerical model should have particular application to jet and bubble formation at discrete orifices in fluidized bed distributor plates. The code has been utilized in test calculations to investigate the numerical methodology and it, further, is being used to study the relative characteristics of jet and bubble formation in planar and axisymmetric orifice flows. These calculations are being compared with experimental data and theoretical models; preliminary comparisons indicated good qualitative and quantitative agreement.

Theoretical studies were continued on the subjects of bed rheology, compressibility, particle size affects and heterogeneous reaction rate control. These investigations will eventually provide formulations which will be incorporated into the numerical model. The influence of bed rheology, e.g., the response of the fluidized particles to deformation, is important in relating the numerical model to experimental data on bed expansion and bubble formation. At the present time, we use a Newtonian representation for the stress-deformation behavior of the solid phase, which appears to be quite satisfactory in describing experimental observations for a range of flow conditions. However, the influence of particle-particle interlocking upon bed expansion and bubble formation is only partially treated by such a model. We are studying alternative formulations and investigating experimental data to determine the applicability of different models for the solid phase rheology. The influence of compressible gas behavior upon fluidized bed flows was investigated through the formulation of transport and constitutive relationships relfecting density variations in the gas phase. With the use of a density weighted spatial averaging procedure these relationships have been developed in a formal manner analogous to those for incompressible fluidized bed flows. A theoretical formulation describing particle size affects upon transport in fluidized beds was continued; the theoretical model represents the motion of "bins" of particles which move relative to the average fluidized bed flow. This average fluidized bed is composed of the "bins" of particles which, in the model description, provide the averaged particle size, determining the mechanical interactions of the particle and gas flows for the average bed. Finally, a study of transport and kinetics phenomena upon reaction rate control for carbon particles was completed. In this study, a detailed boundary layer model, for stagnation point flow, was used to examine homogeneous chemistry, diffusion and convective transport and heterogeneous chemistry upon carbon mass loss in an oxidizing environment; the gas phase composition included oxygen carbon monoxide and carbon dioxide. Regimes of diffusion and kinetic control for both carbon-oxygen and dioxide heterogeneous reactions were considered. A major conclusion was that for sufficiently high temperatures the latter heterogeneous reaction, in a kinetically controlled regime, could be important in the combustion of carbon. This mechanism of carbon loss, which has been invoked by other investigators (c.f., Avedesian and Davidson [1973]; Kurylko and Essenhigh [1972]) was also found to be significant in our theoretical studies of carbon particle oxidation in the entrained flow regime.

A study of possible simplifications in the theory and numerical methodology for the fluidized bed model was initiated. We are particularly interested in examining alternative formulations for reacting three dimensional flows.

The fluidized bed code was used in a continuing study of distributor plate flows simulating the synthane gasifier. These calculations represented air at pressures of 1 and 40 atmospheres as well as steam, at 40 atmospheres and 1273°K. The low pressure calculations for air fluidization were compared with flow visualization tests at the Pittsburgh Energy Research Center and were found to be in good qualitative and quantitative agreement. Further, correlations used by PERC on jet penetration were quantitatively consistent with the calculated jet penetration for both 1 and 40 atmosphere air flows. Based upon the S^3 theoretical studies and numerical calculations it was concluded that air at 40 atmospheres and ambient temperatures is equivalent, as a fluidizing medium, to steam at 40 atmospheres and 1273°K. Since steam is the dominant species in the synthane distributor plate flow, this suggests that the high temperature synthane fluidization can be simulated by air at 40 atmospheres. This calculational effort is continuing and, in particular, the influence of bed height effects on bubble formation is being investigated.

3.3 TASK 02: ENTRAINED FLOW COAL GASIFICATION MODEL

The entrained flow computer model is based upon a finite element/finite difference formulation to provide a transient representation of compressible, turbulent gas-solid particle dynamics. In the previous year of this project (Year II) this model was developed to treat flows in two spatial dimensions. During this quarter the computer code was modified and extended to represent time dependent entrained processes in three spatial dimensions. This extension was facilitated by the finite element character of the numerical model, which permits a flexible geometrical description of the complicated internal flow geometries in three dimensions for only a slightly greater computational and labor effort than is needed for a two-dimensional description. The finite element treatment of space and reactor geometry was originally adopted because it provides the only practical numerical methodology for the accurate multidimensional description of the wide assortment of internal configurations (converging-diverging channels, interconnecting spools, nozzles, etc.) that are present in a typical entrained flow gasifier. This requirement is even more important in the treatment of the three dimensional effects present in swirling flow regions near coal or char injection for combustion and/or gasification. Further, the transient character of the code is necessary to insure that stationary flows which typically occur in entrained, swirling processes can be accurately predicted. Coincidentally, the three dimensional code can also be operated in a two-dimensional axisymmetric mode, for the treatment of such axisymmetric flows.

The many subroutines of this three dimensional entrained flow code have been tested. A calculation of three dimensional swirling flow has been formulated. The finite element grid was defined and boundary and initial conditions were chosen; the calculation will be performed during the next quarter. This test problem simulates a cold flow model of the combustion stage in the design of the Foster Wheeler two stage gasifier [McCallister, 1977]; velocity field measurements from McCallister [1977] will be compared with the calculated velocity profiles.

The study of devolatilization of pulverized coal/char was continued. There are three major aspects to the theoretical definition of pyrolysis which can have important quantitative influences upon the numerical model of entrained flow gasifiers. First there is the definition of individual species evolution and total volatiles yield. Recent studies by Campbell and Stephens [1976] and Howard and his coworkers [Suuberg, et al., 1977; Anthony and Howard, 1976; Anthony, et al., 1975] provide a basis for a kinetics description of the individual species yield. We have chosen a description, suggested by Howard, based upon a distribution of activation energies [c.f., Suuberg, et al., 1977] which appears to provide a good representation of species and total volatile yield for Montana Lignite. In essence, each species evolution is assumed to be related to one or more reactions and the corresponding activation energies; the total of these reactions provides a relationship between total volatile yield and a "continuous" distribution of the activation energies. The behavior of Pittsburgh Seam bituminous is qualitatively different [Howard, 1977; Bush, et al., 1977] in that each species evolution seems to be related to a "continuous" distribution of activation energies for that species. However, a similar methodology should be useful in describing the individual species and total yield. Secondly, there is the influence of gas composition and, in particular, H_2, upon the evolution of gaseous species and total volatile yield during high temperature pyrolysis. It is not clear, for example, whether the increase in CH_4 yield with the increase of H_2 partial pressure is best explained by the concept of active sites [Johnson, 1974,1977] or by the dominance of hydropyrolysis over cracking reactions [Howard, 1977; Bush, et al., 1977]. However, the overall kinetic description of this CH_4 production is important to the theoretical model. A simple description of hydropyrolysis is being explored within the context of existing data and theoretical formulations. Finally, the geometrical and physical evolution of the coal/char particle during devolatilization determines the mass, momentum and energy exchange between the particles and the gas. The swelling, shrinking, etc. of particles is very dependent upon the coal type and the ambient conditions during devolatilization. While some mechanistic concepts are available [c.f., Lewellen, 1975], in general this evolution is not understood and we do not expect to provide a very complete representation of the process.

The kinetics and transport models for the heterogeneous reactions associated with combustion and gasification have been essentially selected based upon earlier representations [Blake, et al., 1977]. However, we have continued to examine on a fundamental, albeit ideal, basis the influences of heterogeneous and homogeneous reactions and convective transport upon carbon loss for a spherical particle in a stagnant ambient environment; of particular interest is the importance of the carbon-carbon dioxide reaction relative to the carbon-oxygen reactions for a range of particle sizes and ambient gas compositions. Further, the radial convection of gaseous species upon the reaction rate control was examined. It is interesting to note that for expected partial pressures of CO_2 and O_2 and for representative particle sizes, the kinetically controlled $C-CO_2$ reaction can, compared to the diffusion controlled $C-O_2$ reactions, contribute a significant fraction to the total rate of carbon loss. This implies that for some regimes the $C-CO_2$ reaction is important in the overall process of carbon combustion [c.f., Avedesian and Davidson, 1973; Kurylko and Essenhigh, 1972]. A discussion of this model effort is presented in the Appendix.

SECTION 4

CONCLUSIONS

In summary, we note the following aspects of our modeling effort.

- The fluidized bed computer model has been extended to represent axisymmetric geometries.
- The entrained flow computer model has been extended to represent axisymmetric and three dimensional geometries.

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APPENDIX

A THEORETICAL STUDY OF BURNING CARBON PARTICLES*

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*This model development is authored by Professor P. A. Libby, University of California at San Diego.

1. INTRODUCTION

We consider the burning of carbon particles in a hot, quiescent, oxidizing atmosphere. There is an extensive literature related to this subject; Ubhayaker and Williams [1976], recently noted: "The oxidation of carbon has been one of the most widely studied topics in the field of combustion. ..." Inter alia they provide an extensive review of this literature as does Blake [1977]. Despite the considerable efforts implied by this extensive literature, there appears to remain considerable disagreement on points of essential concern for the burning of carbon under conditions of interest in entrained flows. Our purpose here is to carry out a theoretical analysis in an attempt to allay some of these concerns.

Two mechanisms for the heterogeneous oxidation of carbon are generally considered. One involves the direct mechanism, $C + \frac{1}{2} O_2 \rightarrow CO$; this appears to be the widely preferred chemical step, but it is interesting that in a recent paper Avedesian and Davidson [1973], investigate and appear to endorse the second, long-standing mechanism involving $C + CO_2 \rightarrow 2CO$. The rates for both of these reactions are known, although as noted by Ubhayakar and Williams [1976], that for the direct oxidation is in doubt above 2000°K; these rates seem to indicate that the first mechanism is far more effective and thus the dominant one. However, the second mechanism can be imagined to be of significance if the oxygen concentration at surface of the particle becomes low, either because of a low oxygen concentration in the surrounding ambient or because of depletion of the oxygen by heterogeneous and homogeneous reactions near the particle. In this case the second reaction, although inefficient, may still be significant. In fact, Avedesian and Davidson [1973], invoke a flame sheet model apparently due to Spalding [1951,1955] to account for the behavior of carbon particles; in this model oxygen from the surrounding ambient diffuses to a reaction surface or flame sheet displaced from the particle and combines with carbon monoxide diffusing from the particle to form carbon dioxide which in turn diffuses to the particle and participates in the second heterogeneous reaction. The implication from this consideration is that under some conditions, in particular low oxidant concentration in the surrounding ambient, the indirect oxidation mechanism may be significant.

From this discussion of alternative mechanisms of heterogeneous reaction, we can infer the important role played by homogeneous reactions in determining the behavior of burning carbon particles. In the limiting case of no homogeneous reactions, so called frozen flow, there appears little doubt that the direct oxidation of carbon leading to the single product, carbon monoxide, is the dominant mechanism and that the oxygen concentration at the surface of the particle is determined by competition between diffusion from the surrounding ambient and consumption of oxygen at the surface of the particle.

In the other limiting case, in which there prevails gas phase chemical equilibrium, the situation is more complex. At low particle temperatures it appears that the carbon monoxide resulting from the direct carbon oxidation will be consumed by oxygen diffusing to the surface so that the apparent product of the heterogeneous reaction is carbon dioxide. Clearly, the amount of oxygen available at the particle surface for heterogeneous reaction is diminished by the homogeneous reaction of carbon monoxide and oxygen. In addition, the energetic balance at the particle surface is likewise altered. If, on the contrary, the particle temperature is sufficiently high and the pressure and gas phase temperatures are such that carbon monoxide and oxygen are unlikely to coexist, the model of Spalding [1951,1955] with a flame sheet removed from the surface would appear to be operative.

The range of pressures and temperatures under which the limiting cases of frozen and equilibrium chemistry apply can only be determined by examination of the case of finite chemical kinetics. In the situation of concern here this involves the rate of oxidation of carbon monoxide. Under the relatively low temperatures of interest to us it would appear that a partial equilibrium between atomic and molecular oxygen can be assumed so that a fictitious mechanism of gas phase reaction, $CO + \frac{1}{2} O_2 \rightleftarrows CO_2$, can be considered.

Another point of essential concern related to the burning of carbon particles in entrained flows and cloaked in disagreement involves the non-uniformity of temperature within the particle as it burns. Dobner [1976] indicates that temperature differences between the particle center and surfaces of 300-400°F can be expected under conditions of interest. Other sources indicate considerably smaller temperature differences. Ubhayakar and Williams [1976] assume in their theoretical analysis a uniform particle temperature as does Blake [1977]. In this situation and in view of the sensitivity of the heterogeneous reactions to small differences in surface temperature (activation temperatures are on the order of $2(10^4)$°K) it seems worthwhile to estimate the effects of non-uniformity in particle temperature on particle behavior.

Our treatment is organized as follows: we first consider a quasi-steady flow about a spherical particle with a specified surface temperature and under various conditions of composition and temperature in the surrounding ambient. In doing so we attempt to clarify the various chemical phenomena involved in the burning of carbon under conditions of interest in entrained flows. The second part of our study relates to the unsteady thermal response and mass loss of a particle which is initially cold and which is injected into a hot, oxidizing ambient. We consider the two cases of uniform temperature within the particle and of variable temperature as described by an approximate solution to the spherical Stefan problem. Throughout our considerations we invoke assumptions which, while physically satisfactory, permit the analysis to be carried forth with a minimum of numerical treatment. Suggestions for more accurate analysis are given as appropriate.

2. THE FLUID MECHANICS AND CHEMISTRY

The flow is assumed to be spherically symmetric, implying that particle motion is neglected. In addition, the flow field is assumed to involve a succession of steady states with unsteadiness in the entire system confined to the thermal response and mass loss of the particle. The equation of momentum conservation yields the pressure distribution within the flow and is inessential since aerothemochemically the pressure may be considered uniform.

2.1 THE CONSERVATION EQUATIONS

Steady state mass balance leads to

$$d/dr\ (\rho r^2 v_r) = 0 \tag{1}$$

which yields

$$\rho r^2 v_r = (\rho v_r) r^2 \Big|_{r=r_p} = m\ r_p^2 \tag{2}$$

where m is the mass flux from the particle and r_p is the particle radius.

We consider next species and element conservation, follow our previous analysis [Libby, 1977] and deal with the species

$$\begin{aligned} O_2 &\rightarrow Y_1 \\ CO_2 &\rightarrow Y_2 \\ CO &\rightarrow Y_3 \\ N_2 &\rightarrow Y_4 \end{aligned} \tag{3}$$

where Y_i is the mass fraction of species i. Associated with these species are the three element mass fractions

$$O_2 \rightarrow \tilde{Y}_1 = Y_1 + \mu_{12}Y_2 + \mu_{13}Y_3$$

$$C \rightarrow \tilde{Y}_2 = \mu_{22}Y_2 + \mu_{23}Y_3 \qquad (4)$$

$$N_2 \rightarrow \tilde{Y}_3 = Y_4 = 1 - \tilde{Y}_1 - \tilde{Y}_2$$

where μ_{ij} is the number of grams of element i in a gram of species j.

Elements are conserved so that we have

$$m\, r_p^2\, d/dr(\tilde{Y}_i) = d/dr\ (\rho D\, r^2 d/dr(\tilde{Y}_i)),\ i = 1,2 \qquad (5)$$

In Equation (5) we have invoked the first of several simplifying assumptions, namely that a single diffusion coefficient can be identified and considered to describe adequately the diffusional properties of the mixture. This assumption is justified by the relatively narrow range of molecular weights for the species involved and by the consequent simplification of the analysis.

We make the further approximation which significantly simplifies the analysis, namely that $\rho D = (\rho D)_\infty = \mu_\infty$, where the subscript ∞ denotes conditions remote from the particle. This assumption implies that variation of the diffusion coefficient in the form of ρD is neglected and that the Schmidt number is unity. The present analysis can be readily extended so as to incorporate a more realistic description of the transport properties but numerical analysis is then indicated.

The solution of Equation (5) with primative and obvious boundary conditions at $r = r_p, \infty$ is

$$\tilde{Y}_i = ((\tilde{Y}_{i\infty} - \tilde{Y}_{ip})\, e^{-K/\xi} + (\tilde{Y}_{ip} - \tilde{Y}_{i\infty}\, e^{-K}))/(1-e^{-K}) \qquad (6)$$

where

$$K = m\, r_p/\mu_\infty \ ,$$

and

$$\xi = r/r_p$$

and where the subscript p denotes conditions on the surface of the particles.

The concentration of the element mass fractions at the surface of the particle must be eliminated in order to make Equation (6) useful. Conservation of elements at the surface leads to the conditions

$$\begin{aligned} d/d\xi\ (\tilde{Y}_1) &= K\ \tilde{Y}_1 \\ d/d\xi\ (\tilde{Y}_2) &= -K\ (1 - \tilde{Y}_2) \end{aligned} \qquad (7)$$

which apply at $\xi = 1$. If Equations (7) are used to eliminate $\tilde{Y}_{ip}$ in Equation (6), we find a result useful for further developments, namely

$$\begin{aligned} \tilde{Y}_{1p} &= \tilde{Y}_{1\infty}\ e^{-K} \\ \tilde{Y}_{2p} &= 1 - (1 - \tilde{Y}_{2\infty})\ e^{-K} \end{aligned} \qquad (8)$$

Throughout this study we assume $\tilde{Y}_{2\infty} = \mu_{22} Y_{2\infty}$, i.e., that no carbon monoxide is present in the surrounding ambient. We include $Y_{2\infty}$ as a parameter in our analysis in order to examine the behavior of particles in oxygen depleted regions of an entrained flow. We shall assume that the mass fraction of nitrogen is conserved and that there is no carbon dioxide present initially; thus the sum of $Y_{1\infty}$ and $Y_{2\infty}$ is taken constant.

If Equations (8) are substituted into Equation (6), we have explicit equations for the distribution of the elements involving the independent variable ξ and the mass flux parameter K. To make further progress we must be more specific about the chemistry of the system.

2.2 THE GAS PHASE CHEMISTRY

As a preliminary to further consideration of the chemistry, it is important to recognize that, if at a point within the flow, the two element mass fractions, $\tilde{Y}_i$, i = 1,2, are known, one additional species mass fraction is required to specify completely the composition. We shall take the mass fraction of oxygen to be the preferred species whose determination will do so. Thus, from Equations (4) we have

$$Y_2 = (\mu_{23}\ (\tilde{Y}_1 - Y_1) - \mu_{13}\ \tilde{Y}_2)/(\mu_{12}\mu_{23} - \mu_{22}\mu_{13}) \qquad (9)$$

$$Y_3 = (\mu_{12}\ \tilde{Y}_2 - \mu_{22}\ (\tilde{Y}_1 - Y_1))/(\mu_{12}\mu_{23} - \mu_{22}\mu_{13}) \qquad (10)$$

The means for determining the distribution of oxygen, i.e., of $Y_1(\xi)$, depends on the rates of the homogeneous reactions; if they are sufficiently slow so that the assumption of frozen flow is appropriate, then no gas phase reactions occur and the solution for Y_1 is given by Equation (6) with all $\tilde{Y}_i$'s replaced by Y_i. The boundary condition applicable to the oxygen concentration at the surface of the particle involves the heterogeneous reactions and will be discussed later. For convenience we rewrite Equation (6) for Y_1 and have

$$Y_1 = ((Y_{1\infty} - Y_{1P})e^{-K/\xi} + (Y_{1P} - Y_{1\infty}e^{-K}))/(1 - e^{-K}) \qquad (11)$$

The other limiting case of homogeneous reaction refers to chemical equilibrium. The condition describing the equilibrium for the CO_2 - CO - O_2 system leads to the algebraic equation

$$K_e = ((\tilde{Y}_1 - Y_1) - \tilde{\mu}\tilde{Y}_2)/(Y_1^{1/2}(\hat{\mu}\tilde{Y}_2 - \tilde{Y}_1 + Y_1)) \qquad (12)$$

where $\hat{\mu} = \mu_{12}/\mu_{22}$, $\tilde{\mu} = \mu_{13}/\mu_{23}$, $K_e = K_e(T,p)$ is a given function of the indicated variables, namely $K_e = K_p\ p^{1/2}(W_2W^{1/2}/W_1^{1/2}W_3)$ when $K_p = K_p(T)$ is the equilibrium constant for partial pressures. If Equation (12) is applied at the surface of the particle where $T = T_p$ with a known pressure, p, and if Equations (8) are substituted therein, it becomes a nonlinear algebraic equation of the form $F(K, Y_{1p}) = 0$. Again, the equations are closed by consideration of the heterogeneous reactions.

In the pressure and temperature ranges of interest in the present study, i.e., $10^3 \leq T_p \leq 3\ (10^3)°K$, $0.1 < p < 10$ atmospheres, $K_e >> 1$ so that two alternative approximations arise. If the rate of mass loss and the level of oxygen concentration in the surrounding ambient are such that there is significant oxygen at the surface of the particle, the solution to Equation (12) can be approximated by

$$\hat{\mu}\tilde{Y}_{2p} - \tilde{Y}_{1p} + Y_{1p} = 0$$

or

$$Y_{1p} = \tilde{Y}_{1\infty}\ e^{-K} - \hat{\mu}(1 - (1 - \mu_{22}Y_{2\infty})\ e^{-K}) \qquad (13)$$

The concentration of the second reactant is from Equation (9)

$$Y_{2p} = \tilde{Y}_{2p}/\mu_{22} = (1 - (1 - \mu_{22}Y_{2\infty})e^{-K})/\mu_{22} \qquad (14)$$

This approximation corresponds to a flame sheet contiguous with the surface of the particle. In this sheet the carbon monoxide created by the heterogeneous reaction is consumed by some of the oxygen diffusing toward the particle. The limit of validity of the approximation is found to be given only loosely by $Y_{1p} \sim 0$.

When $Y_{1p} << 1$, i.e., when the oxygen at the surface of the particle is nearly depleted, the alternative approximation to the solution to Equation (12) applies and we take $Y_{1p} = 0$. Only the second heterogeneous reaction can be effective in this case with Equation (9) yielding

$$Y_{2p} = (\tilde{Y}_{1p} - \tilde{\mu}\tilde{Y}_{2p})(\mu_{22} (\hat{\mu} - \tilde{\mu}))$$

or

$$Y_{2p} = (\tilde{Y}_{1\infty} \; e^{-K} - \tilde{\mu}(1 - (1 - \mu_{22}Y_{2\infty})e^{-K}))/(\mu_{22}(\hat{\mu}-\tilde{\mu})) \quad (15)$$

With $Y_{1p} = 0$, the requirement that $Y_{3p} \geq 0$ leads to a sharp lower limit on the value of K for which this approximation applies; we find the requirement

$$a \equiv \hat{\mu} - (\tilde{Y}_{1\infty} + \hat{\mu}(1 - \mu_{22}Y_{2\infty}))e^{-K} \geq 0 \qquad (16)$$

Equation (16) defines a lower bound on K for this model to be applicable.* Finally, we note that the location of the flame surface is given by the requirement that both the oxygen and the carbon monoxide vanish there; the result is

$$\xi_f = - K/\ell n \; (\hat{\mu}/(Y_{1\infty} + \hat{\mu} \; (1 - \mu_{22}Y_{2\infty}))) \qquad (17)$$

Note that at the lower limit of the validity of this model, $\xi_f = 1$, i.e., the flame is contigous with the surface of the particle.

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*We show later that the transition from one limiting approximation to the other occurs in the neighborhood of $a = 0$.

The most accurate description of the oxygen concentration in the flow involves considering the finite oxidation of carbon monoxide. In this case we must treat explicitly the conservation equation for the species oxygen. In non-dimensional form we have

$$\frac{d}{d\xi} Y_1 = \frac{d}{d\xi}\left(\xi^2 \frac{d}{d\xi} Y_1\right) + \frac{\dot{w} r_p^2}{\mu_\infty} \xi^2 \qquad (18)$$

where $\dot{w}$ is the rate of production of oxygen, e.g., in gm/cm^3 sec. The oxidation of carbon monoxide is strongly catalyzed by the presence of water vapor; since we do not explicitly account for water vapor in our calcualtion, we implicitly incorporate its presence in the reaction rate and further idealize the reaction mechanism by assuming

$$(w\ r_p^2/\mu_\infty) = -\ (\rho_\infty^{3/2}\ r_p^2\ K_3 W_1^{1/2}/\mu_\infty W_3)(\rho/\rho_\infty)^{3/2} e^{-(T_{a3}/T)}$$

$$Y_1^{1/2} Y_3\ (1 - K_e^{-1}\ (Y_2/Y_1^{1/2} Y_3)) \qquad (19)$$

where K_3 is a rate constant with the units of (cm$^{3/2}$/mol$^{1/2}$sec) and K_e is the non-dimensional equilibrium constant introduced in Equation (12).*

If Equation (19) is substituted into Equation (18) and Equations (9) and (10) are used to eliminate Y_2 and Y_3, there will result a single equation in $Y_1(\xi)$ involving the known distributions of the element mass fractions, $\tilde{Y}_i(\xi)$. Also involved, however, will be the temperature so that the energy equation is required to complete the formulation. Consistent with our earlier assumptions of simplified transport properties, the energy equation in terms of the static enthalpy is identical with the conservation equations for the element mass fraction. Accordingly, we can deduce from Equation (6)

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*The rate constant K3 depends on the water concentration.

that the distribution of static enthalpy is

$$h = ((h_\infty - h_p)\ e^{-K/\xi} + (h_p - h_\infty e^{-K}))/(1-e^{-K}) \tag{20}$$

where h_∞ and h_p are the mixture enthalpies remote from the particle and at the particle surface, respectively. The former is assumed to be known and the latter must be determined as part of the solution of Equation (17).

2.3 THE HETEROGENEOUS REACTIONS

We now turn to the heterogeneous reactions, adopt the description of the two mechanisms and their associated rate constants given by Blake [1977], and take

$$R_1 = (K_1 p W_p / W_1)\ Y_{1p}\ e^{-(T_{a1}/T_p)} \tag{21}$$

$$R_2 = (K_2 p W_p / W_2)\ Y_{2p}\ e^{-(T_{a2}/T_p)} \tag{22}$$

where K_1, K_2, T_{a1} and T_{a2} are known constants and where the units are such as to yield the R_i's in units of mass flux of carbon, e.g., of gm/cms sec.

If the reasonable approximation is made that the molecular weight ratios appearing in R_1 and R_2 may be taken to be constants, and if $W_p \simeq W_1$, Equations (21) and (22) may be combined to yield the following convenient form for the mass loss parameter

$$K = A(p\ r_p,\ T_p,\ T_\infty)\ Y_{1p} + B(p\ r_p,\ T_p,\ T_\infty)\ Y_{2p} \tag{23}$$

where the functions A and B are clearly implied by comparison with Equations (21) and (22).* If the values of Y_{1p} and Y_{2p} corresponding to the various cases of chemical behavior in the gas phase are substituted into Equation (23), it becomes a transcendental equation for the mass loss parameter K.

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*We take K_1 = 8710 gm/cm^2 sec, K_2 = 247 gm/cm^2 sec, T_{a1} = 18000°K and T_{2a} = 21060°K; if μ_∞ is estimated to be associated with air of 1500°K, we find $A = 1650\ (pr_p)e^{-T_{a1}/T_p}$,

$$B = 34.8\ (pr_p)\ e^{-T_{a2}/T_p}$$ where (pr_p) is in

atmos-microns. If μ_∞ is taken to be proportional to T_∞, corrections to these values for $T_\infty \neq 1500°K$ can be readily made.

3. CALCULATIONS FOR THE RATE OF MASS LOSS

We now apply the analysis in the previous section to the determination of the mass loss under conditions of interest in entrained flows according to the various cases of gas phase chemical behavior.

We shall treat one temperature in the surrounding ambient, namely $T_\infty = 1500°K$. Within the present approximations as to the transport properties T_∞ enters in the simple cases of gas phase chemical behavior only via μ_∞ and thus changes in T_∞ can be interpreted as an alteration of the product $p\ r_p$; in the case of finite chemical reaction rate T_∞ enters more directly. We consider a range of values of the product $p\ r_p$, namely from 1 to 10^4 in atmos-microns and a range of temperatures at the surface of the particle, T_p, from 1000 to 3000°K. Finally, we assume various values for the oxygen concentration in the surrounding ambient, $Y_{1\infty}$, with associated values for the carbon dioxide concentrations.

3.1 FROZEN FLOW

To analyze the case of frozen gas phase we must eliminate Y_{1p} from Equation (11). Conservation of the species oxygen at the surface of the particle implies

$$W_1 R_1 / W_c = - \frac{1}{2} \left(m\ Y_{1p} - \rho D (dY_1/dr) \right)_{r=r_p} \qquad (24)$$

where W_c is the molecular weight of carbon. If we employ Equation (11) and our previous assumption regarding the diffusion coefficient and relate R_1 to A, we find

$$Y_{1p} = \dot{\mu} Y_{1\infty} K\ e^{-K} / (A\ (1 - e^{-K}) + \dot{\mu} K) \qquad (25)$$

where $\dot{\mu} = 2W_c/W_1 = \tilde{\mu}^{-1}$. If the rate of mass loss is small so that $K << 1$, Equation (25) becomes

$$Y_{1p} = \dot{\mu} Y_{1\infty} (1 - K)/(A + \dot{\mu}) \tag{26}$$

A further useful result can be derived from Equation (26); if carbon dioxide is not present in the surrounding ambient, then in the case of frozen flow under consideration there is no carbon dioxide present anywhere in the flow and only the first heterogeneous reaction is operative. In this situation from Equation (23) we see that $K = A\ Y_{1p}$ and thus find that Equation (26) yields an explicit expression for the rate of mass loss, namely

$$K \cong A\ Y_{1\infty}/(1 + A(Y_{1\infty} + \tilde{\mu})) \tag{27}$$

This result resembles previous expressions for the mass loss of particles in an oxidizing atmosphere (c.f., Blake [1977]) but differs in some respects; more importantly, we appreciate from the development leading to Equation (27) the variety of assumptions restricting its generality.

Equation (27) contains the two limiting cases of kinetically and diffusion controlled surface reactions; the assumption that $K << 1$ implies that the numerator must be small compared to unity. If, in addition, the second term in the denominator is also small, then we have

$$K \cong A\ Y_{1\infty} \tag{28}$$

which corresponds to the kinetically controlled limit. The opposite limit arises if the second term in the denominator dominates, e.g., $A\ Y_{1\infty} << 1$ but $A\tilde{\mu} >> 1$, then

$$K \cong Y_{1\infty}/(Y_{1\infty} + \tilde{\mu}) \tag{29}$$

This corresponds to the diffusion controlled limit for which the kinetics of the surface reaction are irrelevant.

We return now to the more general case; Equation (26) is one of three equations required for the description of the general frozen flow situation. The second is Equation (9) applied at the surface of the particle and yields the concentration of carbon dioxide at that surface. The third is Equation (23). If Equation (26) and the second equation specialized for $K << 1$ are substituted into Equation (23), an explicit equation for the mass loss parameter is obtained, namely

$$\begin{aligned} K \cong &((A\dot{\mu}\ Y_{1\infty}/(A + \dot{\mu})) + (B/(\mu_{22}(\hat{\mu}-\tilde{\mu})))((\tilde{Y}_{1\infty} - (\dot{\mu}Y_{1\infty}/ \\ &(A + \dot{\mu}))) - \tilde{\mu}\mu_{22}Y_{2\infty}))/(1 + (A\dot{\mu}\ Y_{1\infty}/(A + \dot{\mu})) \\ &+ (B/(\mu_{22}(\hat{\mu}-\tilde{\mu})))(\tilde{Y}_{1\infty} - (\dot{\mu}Y_{1\infty}/(A+\dot{\mu})) + \tilde{\mu}\ (1 - \mu_{22}Y_{2\infty}))) \end{aligned} \tag{30}$$

This cluttered equation reduces properly to the operative special cases; if the second heterogeneous reaction is neglected by setting $B = 0$, Equation (30) reduces to Equation (27) as it should. Also if $Y_{2\infty} = 0$ and $\tilde{Y}_{1\infty} = Y_{1\infty}$, then again this same reduction is achieved.

Despite the clutter it is possible to identify the kinetically controlled and diffusion controlled limits given by Equation (30). If the second and third terms in the denominator are negligible compared to unity, the mass loss rate is given by the numerator alone; this is the former limit. At the other, more interesting, limit Equation (30) can be rewritten in the convenient, approximate form

$$K = (\tilde{Y}_{1\infty} - \tilde{\mu}\ \mu_{22}Y_{2\infty})/(\tilde{Y}_{1\infty} + \tilde{\mu}(1 - \mu_{22}Y_{2\infty})) \tag{31}$$

The rate of mass loss for various concentrations of oxygen and carbon dioxide in the surrounding ambient can be readily determined from this equation.

To show illustrative results given by Equation (30), treated fully, we present in Figures 1a-1e the variation of the mass loss parameter with the surface temperature of the particle for five values of the product $p\ r_p$ and for three pairs of concentrations, $Y_{1\infty}$ and $Y_{2\infty}$*. The principal implications from these calculations can be established by consideration of Figure 1a. We see that the highest rate of mass loss occurs with the highest concentration of oxygen in the surrounding ambient; in this situation the second heterogeneous reaction is inoperative. When $Y_{1\infty} = Y_{2\infty} = 0.1$, the mass loss rate is less than in the previous circumstance. For this case we show the predicted distribution of K when the second heterogeneous reaction is arbitrarily turned off, i.e., $B = 0$; we see that at the higher temperatures the second reaction does contribute roughly 20 percent of the total rate of mass loss. Finally, with no oxygen present in the surrounding ambient so that only the second reaction is operative we see that the mass loss is only significant at higher temperatures, above 2000°K, but as the diffusion limit is approached becomes roughly one-third that with only oxygen in the surrounding ambient.

The effect of reduced values of the product $p\ r_p$ seen from a comparison of Figures 1a and 1e with Figure 1a, for example, is to shift the particle temperature at which a given rate of mass loss is obtained to higher values. Thus, for example, at $T_{p2} = 3000°K$ the diffusion limit is well established if $p\ r_p = 10^2$ atmos-microns, only suggested if $p\ r_p = 10$ and far from established if $p\ r_p = 1$. Furthermore, we see that at this latter value of the product the second heterogeneous reaction is less significant; in fact with no oxygen present in the surrounding ambient there is no significant mass loss even at $T_p = 3000°K$.

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*Note the change in scale in Figure 1e.

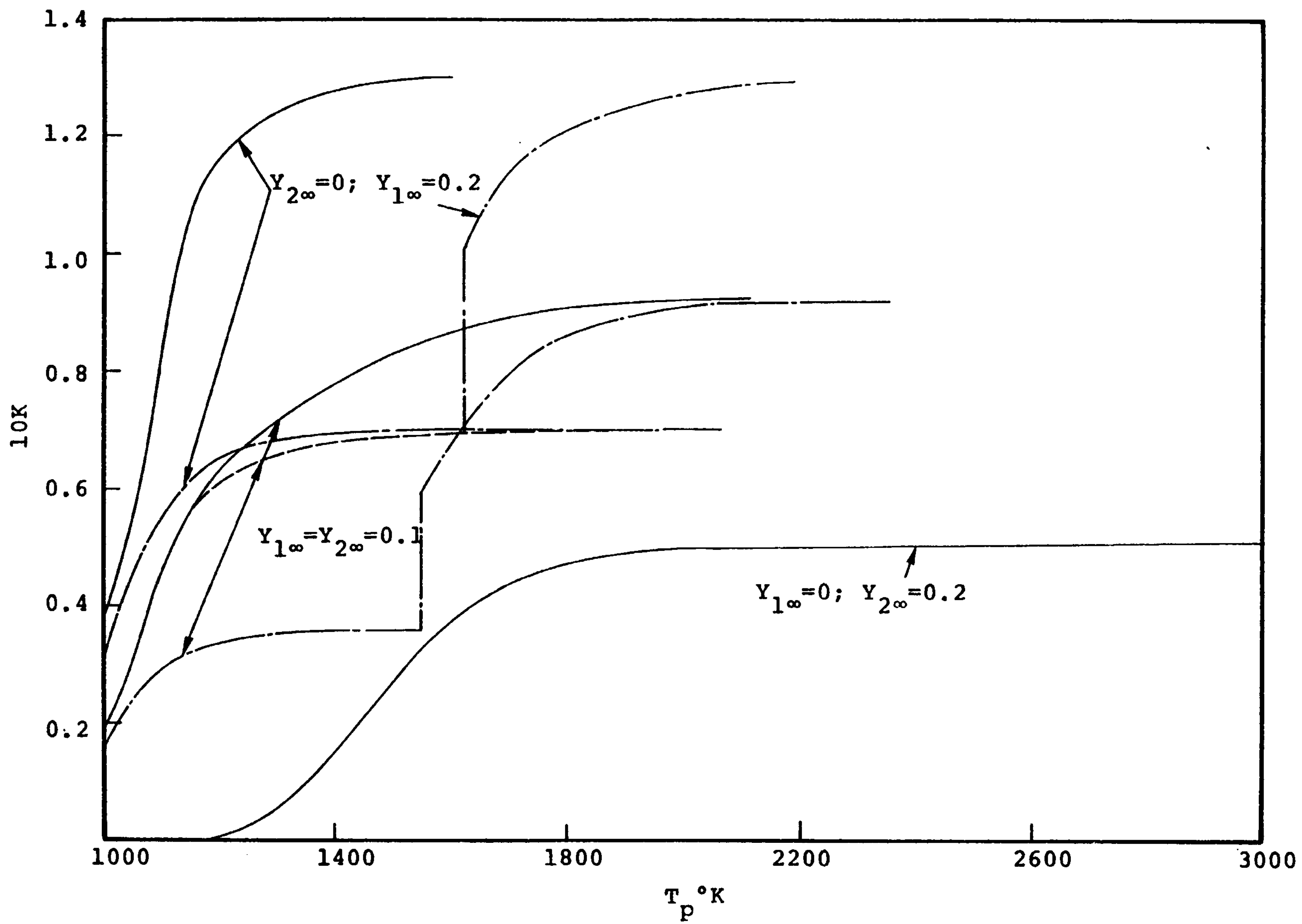

Figure 1a. Variation of mass loss parameter with particle temperature $p\ r_p = 10^4$ atmos-microns. —— Frozen flow with both heterogeneous reactions; --- Frozen flow with only direct oxidation reaction; -·- Equilibrium.

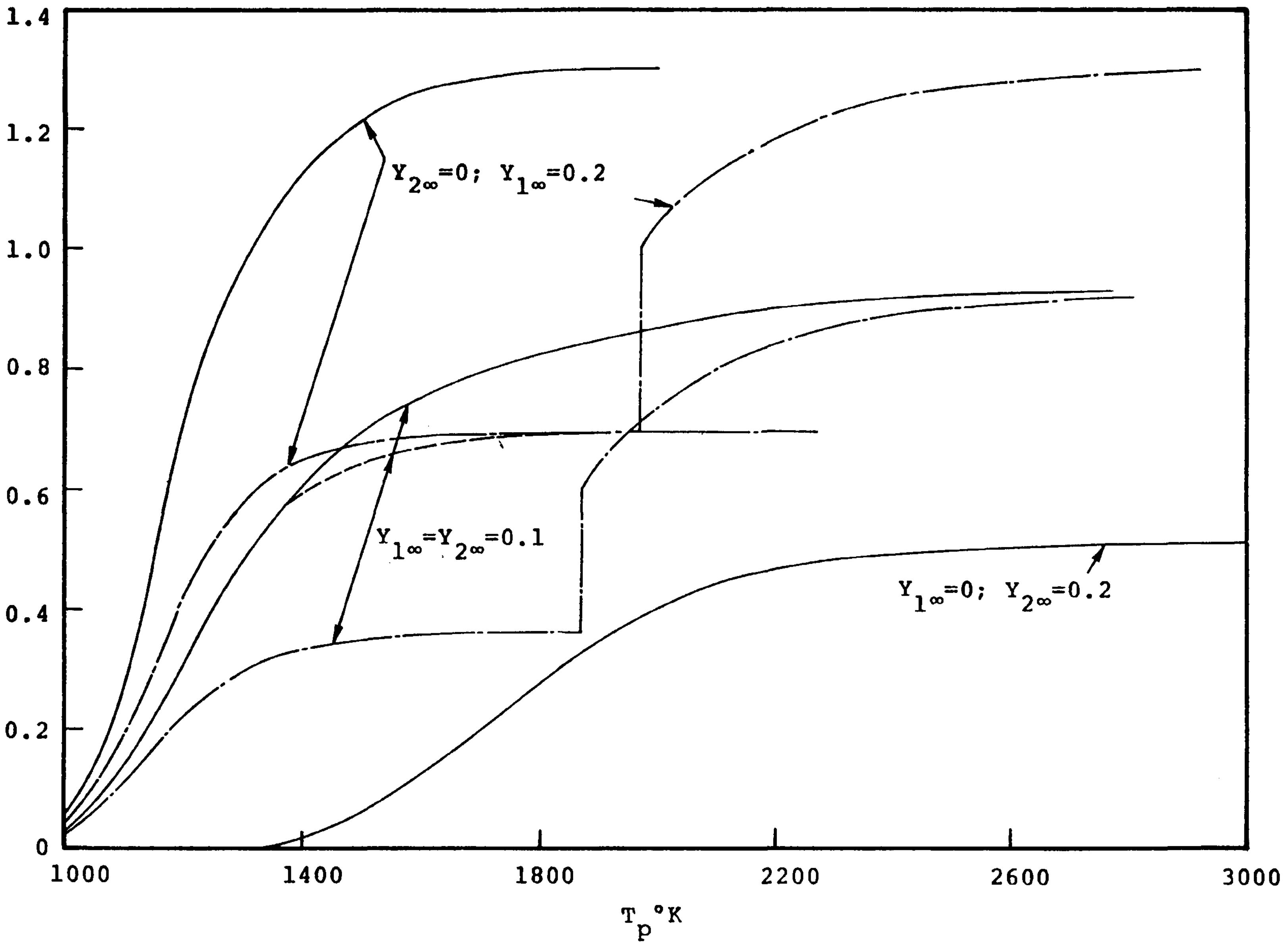

Figure 1b. Variation of mass loss parameter with particle temperature $p\ r_p = 10^3$ atmos-microns. — Frozen flow with both heterogeneous reactions; --- Frozen flow with only direct oxidation reaction; -·- Equilibrium.

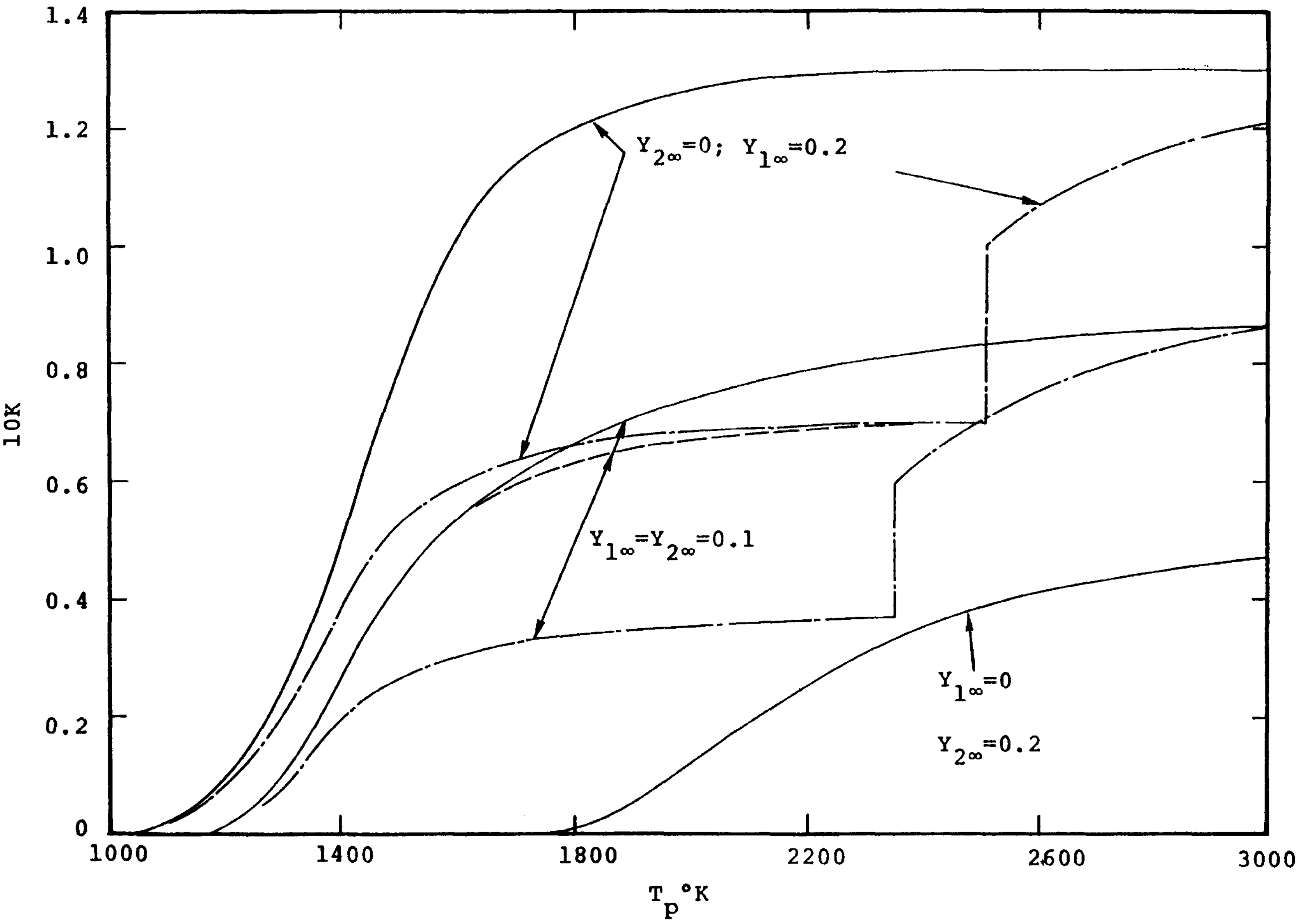

Figure 1c. Variation of mass loss parameter with particle temperature p $r_p = 10^2$ atmos-microns. — Frozen flow with both heterogeneous reactions; --- Frozen flow with only direct oxidation reaction; -·- Equilibrium.

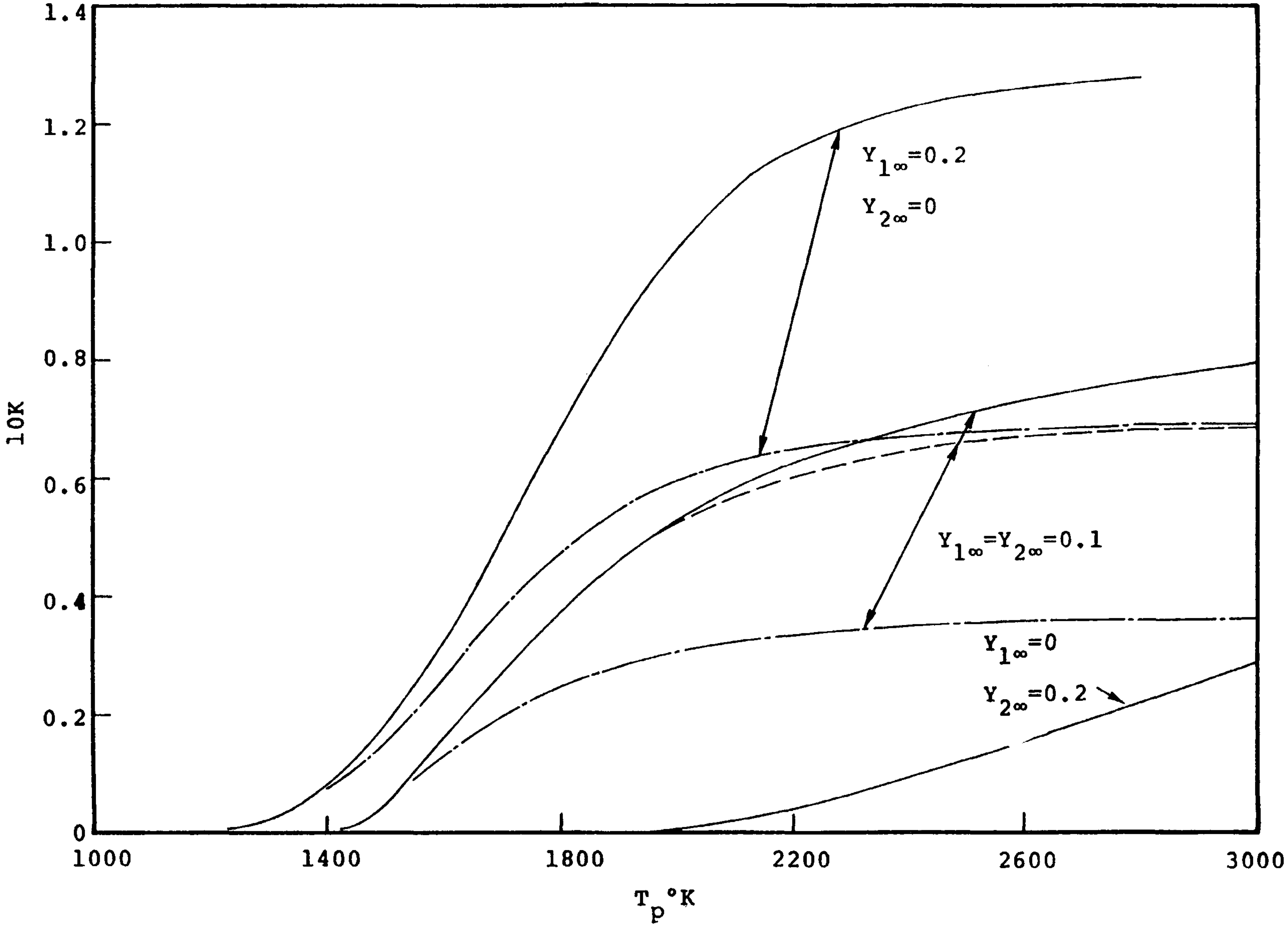

Figure 1d. Variation of mass loss parameter with particle temperature $p\ r_p = 10$ atmos-microns. — Frozen flow with both heterogeneous reactions; --- Frozen flow with only direct oxidation reactions; -·- Equilibrium.

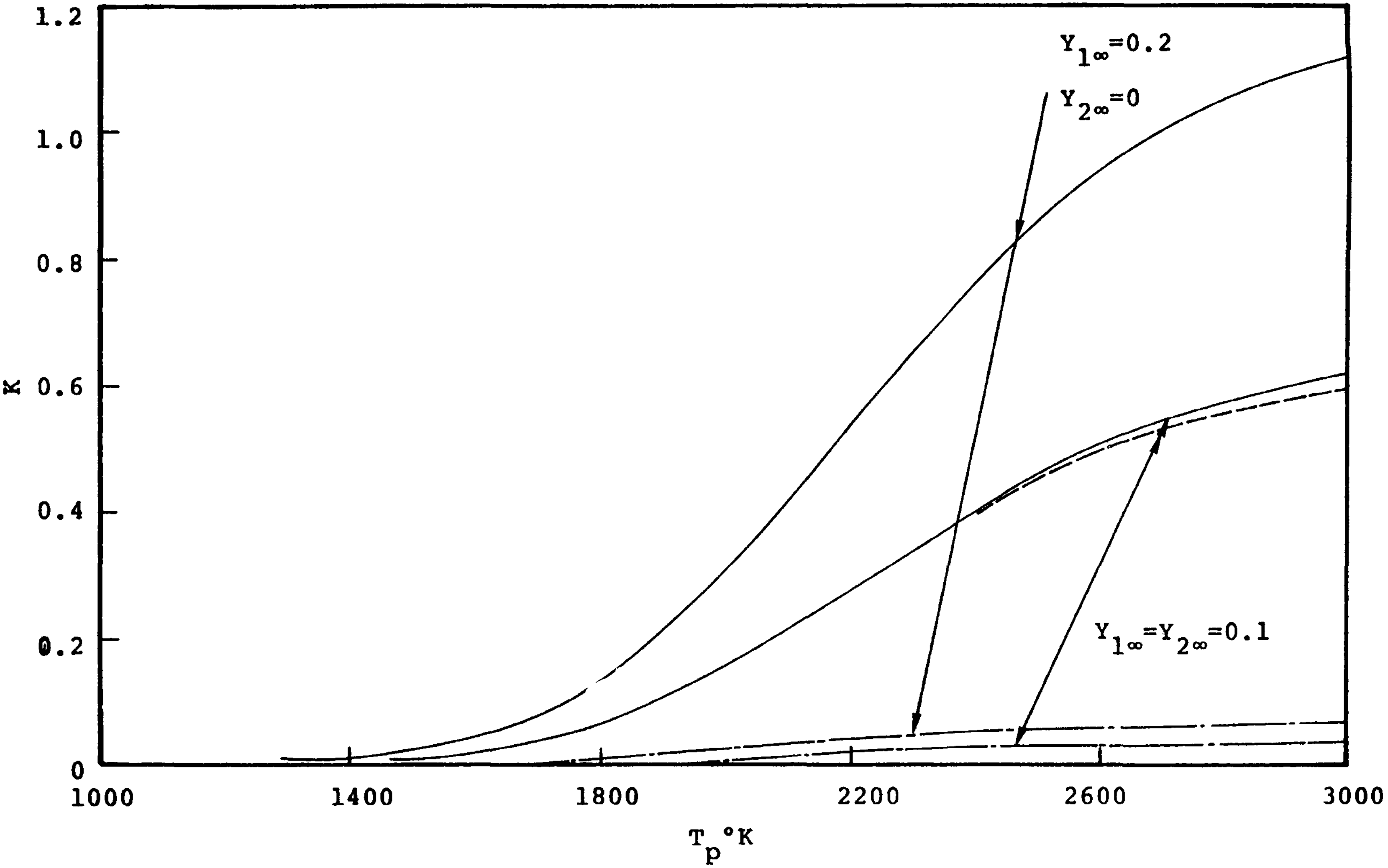

Figure 1e. Variation of mass loss parameter with particle temperature $p\ r_p = 1$ atmos-microns. — Frozen flow with both heterogeneous reactions; --- Frozen flow with only direct oxidation reactions; -·- Equilibrium.

3.2 EQUILIBRIUM CHEMICAL BEHAVIOR

As indicated in the previous section the case of chemical equilibrium in the gas phase is more complex. The exact calculation for this case and the several approximations thereto are conveniently discussed in terms of Equations (12) and (23) considered as two equations for K and Y_{1p} with p, r_p, T_p, Y_1 and Y_2 specified. Note that in the exact calculation individual values for the pressure and particle radius are required whereas in the approximate calculations only the product of the two appears.

Equations (12) and (23) are conveniently written as

$$K_e\, Y_{1p}^{1/2}\, (\hat{\mu}(1 - (1 - \mu_{22}Y_{2\infty})e^{-K}) - (Y_{1\infty}e^{-K} - Y_{1p}))$$

$$= (\tilde{Y}_{1\infty}e^{-K} - Y_{1p}) - \tilde{\mu}(1 - (1 - \mu_{22}Y_{2\infty})e^{-K}) \qquad (32)$$

$$K = A\, Y_{1p} + B((\tilde{Y}_{1\infty}e^{-K} - Y_{1p}) - \tilde{\mu}(1 - (1 - \mu_{22}Y_{2\infty})e^{-K}))/\bar{\mu} \qquad (33)$$

where $\bar{\mu} \equiv \mu_{22}\, (\hat{\mu} - \tilde{\mu})$. In principal these two equations can be solved numerically for K and Y_{1p}. However, the essential elements of interest to us can be extracted by consideration of an intermediate approximation and of the two limiting approximations associated with the flame sheet contiguous with, or remote from, the surface of the particle.

For the case corresponding to $Y_{3p} = 0$, $Y_{1p} = \tilde{Y}_{1p} - \tilde{\mu}\, \tilde{Y}_{2p}$, we have from Equation (32) the results given earlier by Equations (13) and (14) so that Equation (33) becomes

$$K = A\, (\tilde{Y}_1\, e^{-K} - \hat{\mu}(1 - (1 - \mu_{22}Y_{2\infty})e^{-K}))$$

$$+ B(\hat{\mu} - \tilde{\mu})\, (1 - (1 - \mu_{22}Y_{2\infty})e^{-K})/\bar{\mu} \qquad (34)$$

We can again achieve a more illuminating form by assuming $K << 1$; we then obtain

$$K = (A\ Y_{1\infty} + B(\hat{\mu}-\tilde{\mu})\mu_{22}Y_{2\infty})/(1 + A(Y_{1\infty} + \hat{\mu})$$

$$- B(\hat{\mu}-\tilde{\mu})(1 - \mu_{22}Y_{2\infty})) \qquad (35)$$

This may be subjected to the further approximations associated with the kinetically controlled and diffusion controlled limits; for the former we have

$$K \cong A\ Y_{1\infty} + B\ (\hat{\mu}-\tilde{\mu})\ \mu_{22}Y_{2\infty} \qquad (36)$$

while for the latter

$$K \cong (A\ Y_{1\infty} + B(\hat{\mu}-\tilde{\mu})\ \mu_{22}Y_{2\infty})/(A\ (Y_{1\infty} + \hat{\mu})$$

$$- B(\hat{\mu}-\tilde{\mu})\ (1 - \mu_{22}Y_{2\infty}) \qquad (37)$$

If the second heterogeneous reaction is neglected by setting $B = 0$, we obtain a much simpler result from Equation (37). Note that there are limitations on the validity of this equation suggested by the negative sign in the denominator; these are associated with the assumption of the flame sheet contiguous with the surface of the particle.

For the other limiting solution to equilibrium behavior, we have $Y_{1p} = 0$ so that Equation (29) gives

$$K = B(\tilde{Y}_1\ e^{-K} - \tilde{\mu}(1 - (1 - \mu_{22}\ Y_{2\infty})e^{-K})/\bar{\mu} \qquad (38)$$

For $K << 1$ this yields

$$K = B(\tilde{Y}_{1\infty} - \tilde{\mu}\ \mu_{22}Y_{2\infty})/(\bar{\mu} + B(\tilde{Y}_{1\infty} + \tilde{\mu}(1 - \mu_{22}Y_{2\infty}))) \qquad (39)$$

Since there is a lower limit to the validity of this calculation, the kinetically controlled limit is of no interest;

however, in the diffusion limit we find from Equation (35) that

$$K \underset{=}{\sim} (Y_{1\infty} - \bar{\mu}\, \mu_{22}\, Y_{2\infty})/(\tilde{Y}_{1\infty} + \tilde{\mu}(1 - \mu_{22}Y_{2\infty}) \qquad (40)$$

Comparison of this result with its counterpart for frozen flow, i.e., with Equation (31), yields the interesting and useful result that the mass loss in the diffusion limit for both frozen flow and for equilibrium flow with the indirect mechanism for the heterogeneous oxidation of carbon incorporated is the same.

An intermediate approximation is needed to bridge the two limiting approximations corresponding to $Y_{1p} \sim 0$, $Y_{3p} \sim 0$. To develop such an approximation we focus on Equation (32) and consider the left side. By consideration of the definition of the quantity a from Equation (16) we see that the left side involves the product $Y_{1p}^{1/2}(a + Y_{1p})$. Moreover, Equation (17) which determines the location of the flame sheet via ξ_f indicates that $a \sim 0$ as the flame sheet approaches the surface of the particle. In this case the requirement that $Y_{1p} \gtrsim 0$ implies that Equation (32) is satisfied for $K_e >> 1$ by $Y_{1p}^{1/2} \underset{-}{\sim} 0$ and that $K > K_{cr}$ where $a(K_{cr}) = 0$. On the contrary, if $K < K_{cr}$, $a < 0$ and Equation (32) with $K_e >> 1$ is satisfied by $Y_{1p} = -a$. These considerations are simply alternative and supplementary to those leading to the two limiting cases already treated but introduce the intermediate case at hand.

It is illuminating to consider the following model problem:

$$x\ (3\xi + x^2) = 2\varepsilon,\ x > 0 \qquad (41)$$

If an exact identification with Equation (32) is desired, let $x = Y_{1p}^{1/2}$; $\varepsilon = 1/2\ (Y_{1\infty}e^{-K_{cr}} - \tilde{\mu}\ (1 - (1 - \mu_{22}Y_{2\infty})e^{-K_{cr}})/K_e$,

$0 < \varepsilon << 1$; and $\xi = (\hat{\mu}/3)\ \partial B/\partial T_p|_{T_p = T_{pcr}} (T_p - T_{pcr})$. Note that in this identification Equation (33) implicitly determines the temperature of the particle at which the transition between the two limiting approximations occurs; we have for $K = K_{cr}$ from Equations (16) and (33) with $Y_{1p} \simeq 0$

$$K_{cr}/B = \tilde{Y}_{1\infty}(\hat{\mu}-\bar{\mu})/(\hat{Y}_{1\infty} + \hat{\mu}(1 - \mu_{22}Y_{2\infty}) \tag{42}$$

All quantities on the right side are known as is K_{cr}, so that Equation (42) determines T_{pcr}.

The requirements that $x > 0$ and that the desired limits are recovered as $\xi \sim \pm \infty$ restrict the roots in our model problem. Thus, we find

$$x=(\varepsilon+(\xi^3+\varepsilon^2)^{1/2})^{1/3}-(|\varepsilon-(\xi^3+\varepsilon^2)^{1/2}|)^{1/3},\quad \xi^3+\varepsilon^2>0$$

$$=2(-\xi)^{1/2}\cos\phi,\quad \xi^3+\varepsilon^2<0 \tag{43}$$

where $\phi = (1/3)\tan^{-1}((-(\xi^3 + \varepsilon^2))^{1/2}/\varepsilon)$. Note that for $\xi^3 + \varepsilon^2 > 0$ and $\varepsilon \sim 0$, $x \sim 0$ whereas for $\xi^3 + \varepsilon^2 < 0$ and $\varepsilon \sim 0$, $\theta \sim \pi/6$ and $x \sim (-3\xi)^{1/2}$, i.e., the desired asymptotic behavior is obtained.

In Figure 2 we show the variation of the solutions $x(\xi;\varepsilon)$ for several values of ε including $\varepsilon = 0$. It is seen that for $\varepsilon > 0$ there is a smooth transition into the limits. The range of ξ over which the bridging takes place is of practical interest since it suggests the temperature range for the transition between the two limiting equilibrium cases.

To demonstrate the practical implications from our model problem consider the following cases: $\tilde{Y}_{1\infty} = 0.2$, $\tilde{Y}_{2\infty} = 0$, $p = 1$ atmos., $r_p = 10^2$ microns. In this case we find $K_{cr} = 0.072$, $T_{pcr} = 2510°K$, and $\varepsilon = 10^{-3}$. If we take a value of $Y_{1p} = 10^{-4}$ to be sufficiently small so that the

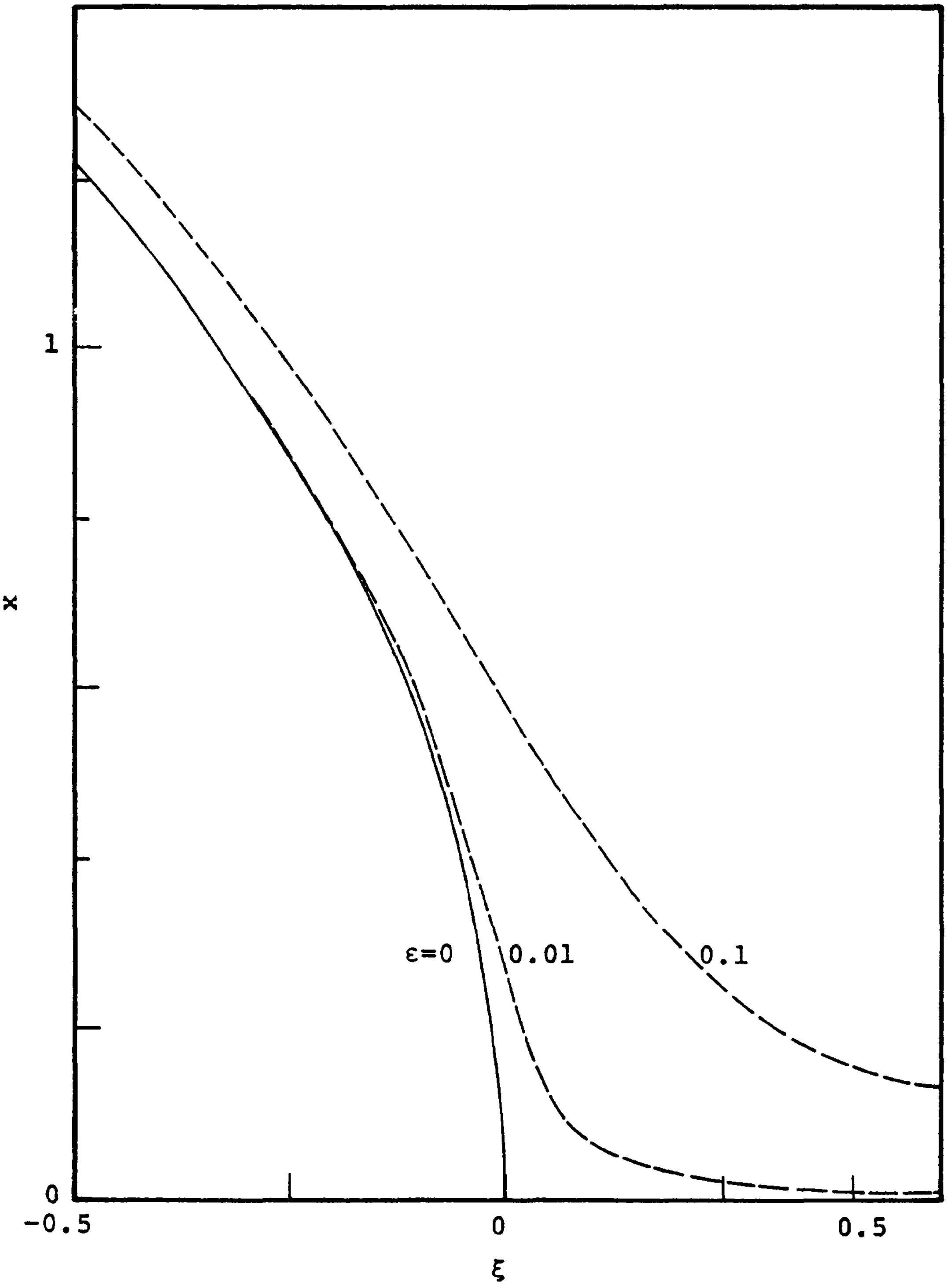

Figure 2. Variation of root of model equation.

limiting case associated with $Y_{1p} = 0$ acceptably approximated, we find that the range of T_p for which the intermediate approximation is operative is $\pm$ 100°K. This range is reduced as the pressure p is increased, if the temperature T_{pcr} is smaller because of increased oxygen concentrations in the surrounding ambient and of increase in $p\ r_p$, and if more tolerance for the approximation to $Y_{1p} = 0$ is accepted, i.e., if $Y_{1p} = 10^{-3}$ is considered acceptably small. This result suggests that for many purposes and, under most conditions of interest in this study, the detailed variation of the mass loss parameter K with T_p according to this intermediate approximation can be ignored and a discontinuity in $K(T_p)$ at $T_p = T_{pcr}$ can be introduced to bridge the two limiting cases.

In Figures 1a-1e we showed the results of the distribution of mass loss parameter with particle temperature T_p for the same products $p\ r_p$ and compositions in the surrounding ambient or considered in frozen flow. For purposes of exposition consider the results for $\tilde{Y}_{1\infty} = 0.2$, $\tilde{Y}_{2\infty} = 0$ shown in the mass loss with equilibrium behavior in the gas phase is less than with frozen flow. The physical explanation for this result resides in the interception of some of the oxygen diffusing to the particle by the carbon monoxide diffusing from the particle and thereby making it unavailable for heterogeneous reaction. Furthermore, note that under equilibrium conditions the mass loss due to the direct oxidation reaction becomes diffusion limited and, therefore, remains essentially constant until the particle temperature becomes sufficiently high for the second heterogeneous reaction to become effective. Finally, we see displayed graphically the earlier result that the diffusion limits for equilibrium and frozen gas phase behavior are identical.

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