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Analytic Solution for the Equilibrium Composition of a Carbon-Nitrogen-Oxygen Gas Mixture

P. G. CROWELL
Aerothermodynamics Department
Vehicle Engineering Division
Engineering Science Operations
The Aerospace Corporation
El Segundo, Calif. 90245

30 December 1977

Final Report

Prepared for
SPACE AND MISSILE SYSTEMS ORGANIZATION
AIR FORCE SYSTEMS COMMAND
Los Angeles Air Force Station
P.O. Box 92960, Worldway Postal Center
Los Angeles, Calif. 90009



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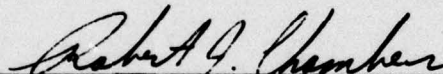
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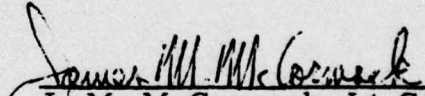
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This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.


R. J. Chambers, Jr., Capt., USAF
Project Officer


J. M. McCormack, Lt. Col., USAF
Chief, Reentry Technology

FOR THE COMMANDER


W. Goldberg, Lt. Col., USAF
Director, Systems Technology

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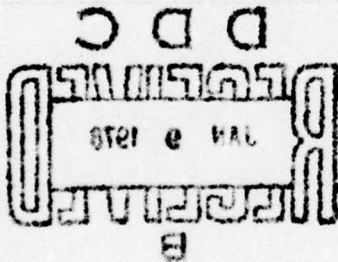
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two-to-three orders of magnitude faster than exact calculation procedures, depending upon the initial guess supplied to the exact calculation.

The analytic solution is particularly suited for use in boundary layer calculations over an ablating carbon surface. It should also find use in planetary entry applications and other fluid dynamic problems where the gas of interest contains carbon, nitrogen, and oxygen species.



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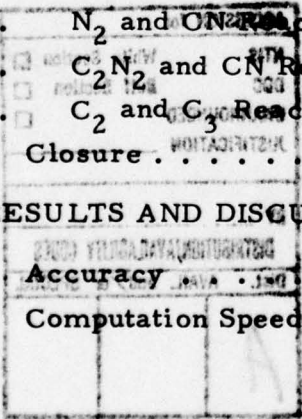
PREFACE

The author would like to express his appreciation to Jovita Jenkins and George Judd of the Information Processing Division for running the NEST Chemistry code to generate the exact solutions used in this report.

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SECTION I

INTRODUCTION

During the past decade, the numerical solution of chemically reacting fluid dynamic flow field problems has received considerable emphasis for a wide variety of applications. The feasibility of such calculations has been made possible by the increase in computation speed achieved by succeeding generations of computers. Despite this, the solution of multidimensional chemically reacting flows imposes severe computational constraints, even for the fastest machines currently available. For rate limited chemistry, the primary difficulty is due to restrictive numerical stability requirements dictated by the reaction rates. Progress in this area is determined by advances in numerical techniques and is not the province of this report.

For equilibrium chemistry, stability requirements are dictated by the fluid dynamics, and the computational penalty arises from the determination of the composition of the gas mixture. That is, solution of the elemental conservation equations yields the element mass fractions. To determine the thermodynamic and transport properties of the gas mixture, the species mass fractions must be known. The determination of the equilibrium composition by species from given element mass fractions is usually carried out by minimizing the Gibb's free energy which involves a time consuming iterative solution. It is the purpose of this report to present a computationally fast, direct, noniterative method for determining the equilibrium composition of a gas mixture for a commonly encountered three-element system (carbon-nitrogen-oxygen).

Direct, noniterative methods have been developed for the equilibrium composition of nitrogen-oxygen systems (i.e., air). References 1, 2, and 3 utilize various levels of approximation and choices of independent variables to obtain the equilibrium properties of air with excellent accuracy. Faster iteration schemes have been developed for other elemental systems (various combinations of H, C, N and O) by algebraically combining a set of equations into a single equation (Refs. 4-6). This approach, while considerably faster than more general methods, is still much slower than a direct, noniterative scheme. Furthermore, it requires substantial algebraic manipulation to obtain the iterative equation and an accurate initial guess to insure convergence. To the author's knowledge, there do not exist any direct, noniterative methods for a carbon-nitrogen-oxygen system. This report provides such a method.

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1. Hansen, C. F., "Approximations for the Thermodynamic and Transport Properties of High Temperature Air," NASA TR R-50, 1959.
 2. Hochstim, A. R., "Approximations to High Temperature Thermodynamics of Air in Closed Form," Kinetics, Equilibria and Performance of High Temperature Systems, Proc. of the 1st Conference, Western States Section, The Combustion Institute, 1959.
 3. Mikhailov, V. V., "Analytical Representation of the Thermodynamic Functions of Dissociating Air," AIAA J., Vol. 1, November 1963, pp. 2689-2696.
 4. Brandmaier, H. E. and J. J. Harnett, "A Brief Survey of Past and Current Methods of Solution for Equilibrium Composition," Kinetics, Equilibria and Performance of High Temperature Systems, Proc. of the 1st Conference, Western States Section, The Combustion Institute, 1959.
 5. Erickson, W. D., J. T. Kemper, and D. O. Allison, "A Method for Computing Chemical Equilibrium Compositions of Reacting-Gas Mixtures by Reduction to a Single Iteration Equation," NASA TN D-3488, 1966.
 6. Mascitti, Vincent R., "A Simplified Equilibrium Hydrocarbon-Air Combustion Gas Model for Use in Air Breathing Engine Cycle Computer Programs," NASA TN D-4747, 1968.

The solution of fluid dynamic problems with equilibrium chemistry generally falls into two different categories, depending on the interest of the investigator. For many applications, the details of the chemistry are of prime importance, particularly with regard to the concentration of certain trace species. In such cases, the specification of the equilibrium composition must be exact, and there is no option but to consider a large number of species and solve the system exactly (using Gibb's free energy minimization technique, for example). On the other hand, there exist many problems in which the main interest is the fluid dynamic quantities, and the chemistry is important only to the extent that it determines the thermodynamic and transport properties of the gas mixture. In this situation, trace species may be ignored since they exert no significant effect on the thermodynamic quantities. Furthermore, moderate errors in the species concentrations may be tolerated since the mixture properties tend to average the errors. This is particularly true for systems in which the elements are adjacent to one another in the periodic table (such as carbon, nitrogen, and oxygen). This report presents an approximate chemistry model suitable for use with this second problem category.

To achieve the desired objectives (simplicity and fast computation time), two assumptions have been made, consistent with the intended usage of the method. That is, neither ionized nor condensed species are considered. Furthermore, species which occur in trace amounts are ignored. The major constraint imposed on the formulation was the requirement that the resulting equations yield analytic solutions. Since analytic solutions do not exist for polynomials of fifth degree and higher, the problem was formulated such that only cubics and quartics are encountered. This was achieved by dividing the problem into carbon-rich and oxygen-rich domains and treating the dominant reactions sequentially rather than simultaneously (i. e., exact).

The choice of independent variables is dependent, to some extent, on the intended usage of the method. Since the partition functions, equilibrium constants and thermodynamic properties for each species are functions of temperature, the temperature must be one of the independent variables. The other independent variable may be pressure or density. For fluid dynamic problems in which the pressure is given (i.e., boundary layer problems) or treated as one of the independent variables, it is the obvious choice as the variable for the equilibrium chemistry calculation. The density is the logical choice of variable in situations where the continuity equation is solved for density (i.e., flow field calculations).

Since the choice of variables exerts a tremendous influence on the complexity of the model, the formulation is divided into two parts depending upon whether pressure or density is used as one of the independent variables. The formulation using pressure and temperature as the variables is the most complex, and is considered first. Following the development of the model, extensive comparisons are made with exact solutions to assess the accuracy of the method.

SECTION II
PRESSURE AND TEMPERATURE AS INDEPENDENT VARIABLES

As discussed previously, the objective of this report is to calculate the equilibrium species mass fractions and mixture properties for a carbon-nitrogen-oxygen system. For general use, an inert monatomic species is included in the formulation. Since the inert species is nonreactive and ionization is ignored, it is characterized solely by its molecular weight. The pressure, temperature and elemental mass fractions are assumed to be specified. By definition, the elemental mass fractions (denoted by a superscript tilde) must sum to unity. That is

$$\tilde{K}_C + \tilde{K}_N + \tilde{K}_O + \tilde{K}_I = 1 \quad (1)$$

where the subscript I denotes the inert species.

The critical assumption of the model is that the problem may be divided into two distinct regimes (denoted as oxygen-rich and carbon-rich) which are essentially uncoupled from one another. This division is based on the observation that carbon will always react preferentially with oxygen to form CO before reacting with nitrogen. Therefore, if sufficient oxygen is present in the system, such that all the carbon is bound up in CO (i. e., oxygen-rich system), then only trace amounts of carbon-nitrogen compounds (CN, C₂N₂) and carbon sublimation species (C₂, C₃) will be present. However, if sufficient carbon is present in the system, such that all the oxygen is bound up in CO (i. e., carbon-rich system), the excess carbon will form carbon sublimation species and carbon-nitrogen species. Therefore, a parameter (denoted as ϵ) defines the two regimes

$$\epsilon \equiv \frac{3}{4} \tilde{K}_O - \tilde{K}_C$$

Oxygen-rich system: $\epsilon \geq 0$ (2)
Carbon-rich system: $\epsilon < 0$

As mentioned, the two regimes are uncoupled from one another and are considered separately below.

A. OXYGEN-RICH SYSTEM: $\epsilon \geq 0$

In view of the above comments, the carbon-nitrogen and carbon sublimation species are ignored. Free monatomic carbon does not exist until CO dissociates. In order to obtain analytic solutions, the dominant reactions must be uncoupled from one another. The CO₂ and O₂ dissociation reactions occur at low to moderate temperatures and are essentially completed before the onset of N₂ and CO dissociation at high temperatures. Therefore, the reactions will be treated sequentially in pairs.

1. CO₂ and O₂ Reactions

The reactions are denoted as



While these reactions are taking place, all nitrogen is presumed to be bound up in N₂. The elemental mass balances yield

$$\begin{aligned} \tilde{K}_C &= \frac{12}{28} K_{\text{CO}} + \frac{12}{44} K_{\text{CO}_2} \\ \tilde{K}_O &= K_O + K_{\text{O}_2} + \frac{16}{28} K_{\text{CO}} + \frac{32}{44} K_{\text{CO}_2} \\ \tilde{K}_N &= K_{\text{N}_2} \\ \tilde{K}_I &= K_I \end{aligned} \tag{4}$$

The molecular weight is given by

$$\frac{1}{M} = \frac{K_{\text{N}_2}}{28} + \frac{K_{\text{O}_2}}{32} + \frac{K_O}{16} + \frac{K_{\text{CO}}}{28} + \frac{K_{\text{CO}_2}}{44} + \frac{K_I}{M_I} \tag{5}$$

The pressure equilibrium constants for the reactions are used to relate the constituent mass fractions of the products and reactants.

$$\begin{aligned}
 K_{\text{CO}_2}^2 &= \alpha_1 M K_{\text{O}_2} K_{\text{CO}}^2 \\
 K_{\text{O}_2} &= \alpha_2 M K_{\text{O}}^2 \\
 \alpha_1 &\equiv \frac{121 P}{1568 K_{P_1}} \\
 \alpha_2 &\equiv \frac{P}{8 K_{P_2}}
 \end{aligned}
 \tag{6}$$

The above system may be solved to obtain the four species mass fractions and molecular weight (M) for given values of the element mass fractions, pressure and temperature. The temperature is required to evaluate the pressure equilibrium constants (K_{P_1} and K_{P_2}). The pressure equilibrium constants are presented in Appendix A.

The solution is discussed in Appendix B and is obtained in terms of a cubic. Although the solution yields values for all the mass fractions of Eq. (4), only the values of CO_2 , O_2 and CO (at low temperatures) are the final values. The mass fraction of atomic oxygen and the molecular weight are only temporary values which are used to obtain these final values. The asymptotic behavior of the above system, for both large and small temperatures, is obtained as

For $T \rightarrow 0$:

$$\begin{aligned}
 K_{\text{CO}} &= 0 \\
 K_{\text{O}} &= 0 \\
 K_{\text{O}_2} &= \tilde{K}_{\text{O}} - \frac{8}{3} \tilde{K}_{\text{C}} \\
 K_{\text{CO}_2} &= \frac{11}{3} \tilde{K}_{\text{C}}
 \end{aligned}
 \tag{7}$$

For $T \rightarrow \infty$:

$$\begin{aligned}K_{O_2} &= 0 \\K_{CO_2} &= 0 \\K_{CO} &= \frac{7}{3} \tilde{K}_C \\K_O &= \tilde{K}_O - \frac{4}{3} \tilde{K}_C\end{aligned}\tag{8}$$

It is apparent from Eq. (7) that the mass fraction of molecular oxygen will be negative for sufficiently low temperatures if $\tilde{K}_O < 3\tilde{K}_C/8$. This indicates that insufficient oxygen exists to tie up all the carbon in CO_2 . In reality, all the oxygen would combine with carbon to form the maximum amount of CO_2 , and the remaining carbon would condense as solid carbon. Thus, even though the system is oxygen-rich with respect to CO at moderate to high temperatures, it is also carbon-rich with respect to CO_2 at low temperatures. However, since this occurs at temperatures below the range of interest of this report, it causes no problem.

As the temperature approaches infinity, the mass fractions for O_2 and CO_2 have the correct behavior. The carbon is all contained in CO, and its mass fraction approaches the maximum possible value. In actuality, at high temperatures, dissociation would take place. The carbon dioxide dissociation reaction is examined in Subsection A-2.

The only remaining limit of interest is the boundary between the oxygen-rich and carbon-rich domains (i. e., $\epsilon = 0$). The above system has the following behavior as the carbon-rich domain is approached.

$\epsilon \rightarrow 0$:

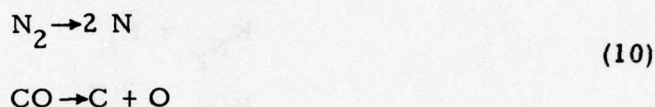
$$\begin{aligned}K_O &= 0 & K_{CO} &= \frac{7}{3} \tilde{K}_C = \frac{7}{4} \tilde{K}_O \\K_{O_2} &= 0 & K_{CO_2} &= 0\end{aligned}\tag{9}$$

Again, it is apparent that O_2 and CO_2 are consistent with the postulated model, namely, that all the oxygen must be contained in CO in the carbon-rich regime. Clearly, at sufficiently low temperatures, this will be incorrect since CO_2 will form to the maximum possible extent and the excess carbon will condense as solid carbon. However, as mentioned earlier this occurs below the temperature regime of interest.

For negative values of ϵ (i.e., carbon-rich), the system yields obviously incorrect values (negative or imaginary), and the mass fractions of O_2 and CO_2 are set equal to zero without solving the cubic.

2. N_2 and CO Reactions

The reactions considered in this section are given by



The nitrogen and carbon monoxide dissociation reactions take place at high enough temperatures such that molecular oxygen and carbon dioxide may be ignored. Then the elemental mass balances, molecular weight and equilibrium relationships are given by

$$\begin{aligned} \tilde{K}_O &= K_O + \frac{16}{28} K_{CO} \\ \tilde{K}_N &= K_N + K_{N_2} \\ \tilde{K}_C &= K_C + \frac{12}{28} K_{CO} \\ \tilde{K}_I &= K_I \\ \frac{1}{M} &= \frac{K_N}{14} + \frac{K_{N_2}}{28} + \frac{K_{CO}}{28} + \frac{K_C}{12} + \frac{K_O}{16} + \frac{K_I}{M_I} \\ K_{CO} &= \alpha_3 M K_C K_O \\ K_{N_2} &= \alpha_4 M K_N^2 \\ \alpha_3 &\equiv \frac{7P}{48 K_{P_3}} & \alpha_4 &\equiv \frac{P}{7 K_{P_4}} \end{aligned} \tag{11}$$

The solution to this system is obtained in terms of a quartic and is detailed in Appendix C. Since the resultant equation is a quartic, more than one solution branch is possible. This is indeed the case, with two solution branches for the oxygen-rich and carbon-rich situations. This is most easily seen from the asymptotic behavior of the quartic as the temperature vanishes (see Appendix C). This yields

$T \rightarrow 0$:

$\epsilon > 0$ (oxygen-rich):

$$K_N = 0$$

$$K_{N_2} = \tilde{K}_N$$

$$K_{CO} = \frac{7}{3} \tilde{K}_C$$

$$K_C = 0$$

$$K_O = \tilde{K}_O - \frac{4}{3} \tilde{K}_C$$

$\epsilon < 0$ (carbon-rich):

$$K_N = 0$$

$$K_{N_2} = \tilde{K}_N$$

$$K_{CO} = \frac{7}{4} \tilde{K}_O$$

$$K_O = 0$$

$$K_C = \tilde{K}_C - \frac{3}{4} \tilde{K}_O$$

(12)

Since the quartic possesses valid solution branches for both the carbon-rich and oxygen-rich case, it must be solved for either case to obtain the carbon monoxide mass fraction.

For the oxygen-rich case, a comparison of Eq. (12) with Eq. (8) shows that the mass fraction of CO has the correct asymptotic behavior. That is, the high temperature limit of Eq. (8) overlaps the low temperature limit of Eq. (12). Thus, the final value for the CO mass fraction (for $\epsilon \geq 0$) is the smaller of the two values obtained from Eqs. (4) and (5) and Eq. (11). For the carbon-rich case, the final value for CO always comes from 11.

The behavior of the system at large temperatures is obtained as

$T \rightarrow \infty$:

$$\begin{aligned}
 K_C &= \tilde{K}_C \\
 K_O &= \tilde{K}_O \\
 K_N &= \tilde{K}_N \\
 K_{N_2} &= 0 \\
 K_{CO} &= 0
 \end{aligned}
 \tag{13}$$

At high temperatures, there is only one valid solution branch for the system. It is apparent from Eqs. (12) and (13) that the molecular and atomic nitrogen mass fractions possess the correct limiting behavior at high and low temperatures. If carbon-nitrogen reactions are ignored, these are the final values for K_N and K_{N_2} . If carbon-nitrogen reactions are included, the final values for the nitrogen mass fraction are obtained from Subsection B-1. This is discussed further in Subsection C.

B. CARBON-RICH SYSTEM: $\epsilon < 0$

It was seen in Subsection A-1 that the O_2 and CO_2 vanished identically as the boundary between the carbon-rich and oxygen-rich domains (i. e., $\epsilon = 0$) was approached. Thus, for negative values of ϵ , the mass fractions of

O_2 and CO_2 may be zeroed and the cubic need not be solved. This yields values for O_2 and CO_2 which are continuous for all values of ϵ .

Since the carbon-nitrogen and carbon sublimation species (as calculated in Subsections B-1 through B-3) do not vanish as ϵ approaches zero, the converse procedure for these species is not possible. In other words, zeroing these species for positive ϵ will yield discontinuous values at $\epsilon = 0$, since the solutions do not yield zero values as the boundary is approached from the carbon-rich side. Therefore, in order to obtain continuous solutions for all ϵ , the carbon-rich equations of this section will be solved for both positive and negative values of ϵ . That is, the carbon-rich equations will also be solved in the oxygen-rich domain. It is emphasized that the values obtained for the carbon-nitrogen and carbon sublimation species (for $\epsilon > 0$) must be quite small since, in reality, they exist in only trace amounts in the oxygen-rich domain. This will be assured by utilizing the mass fraction of CO_2 (a known quantity from Subsection A-1) in the elemental carbon mass balance.

As mentioned in Subsection A-2, the set of Eqs. (11) is also solved for the carbon-rich case to obtain the carbon monoxide and atomic oxygen mass fractions. After obtaining these values, they are then treated as known quantities in the carbon and oxygen elemental mass balances for the remainder of the carbon-rich calculations. If the carbon-nitrogen reactions are ignored, then the values for atomic and molecular nitrogen mass fractions are obtained from Subsection A-2. Generally, however, the dominant carbon-nitrogen reactions are included and are used to obtain the nitrogen mass fraction.

It was noted previously that the formation of solid carbon was possible for the oxygen-rich system at low temperatures where the carbon was bound up in CO_2 instead of CO . For the carbon-rich situation, the formation of solid carbon is possible at much higher temperatures. At sufficiently high temperatures, the excess carbon is contained in the carbon sublimation species (C_2 and C_3). However, as the temperature is lowered these species vanish and the excess carbon condenses out as solid carbon. The temperature at which this occurs is dependent upon the pressure, and sets a lower

limit for the validity of the present model. This lower limit temperature is always high enough so that molecular oxygen and carbon dioxide exist only in trace amounts. This is consistent with zeroing these mass fractions in the carbon-rich domain.

In order to obtain analytic solutions, the C_2 and C_3 reactions must be uncoupled from the carbon-nitrogen reactions. The sequence in which the reactions are considered follows from the observation that at low carbon mass fractions CN is predominant, whereas C_2 and C_3 are predominant for large carbon mass fractions. It is presumed, therefore, that the carbon-nitrogen reactions have first call on the available carbon and will form CN to the maximum possible amount, subject to equilibrium constraints. Following the carbon-nitrogen reactions, the remaining available carbon will be absorbed in C_2 and C_3 .

1. N_2 and CN Reactions

The dominant carbon-nitrogen reaction is represented by the following reactions:



The elemental mass balances, molecular weight and equilibrium relationships are given by

$$\begin{aligned} \tilde{K}_N &= K_N + K_{N_2} + \frac{14}{26} K_{CN} \\ \tilde{K}_C &= K_C + K_{C_2} + \frac{12}{26} K_{CN} + \beta_1 \\ \tilde{K}_I &= K_I \end{aligned} \tag{15 continued}$$

$$\frac{1}{M} = \frac{K_N}{14} + \frac{K_{N_2}}{28} + \frac{K_{CN}}{26} + \frac{K_C}{12} + \frac{K_{C_2}}{24} + \frac{K_I}{M_I} + \beta_2$$

$$K_{N_2} = \alpha_4 M K_N^2$$

$$K_{C_2} = \alpha_5 M K_C^2$$

$$K_{CN} = \alpha_6 M K_C K_N$$

$$\alpha_5 \equiv \frac{P}{6 K_{P_5}}$$

$$\alpha_6 \equiv \frac{13P}{84 K_{P_6}}$$

As indicated, the functions β_1 and β_2 are obtained from the solutions of Subsections A-1 and A-2 and are given by

$$\beta_1 \equiv \frac{12}{28} K_{CO} + \frac{12}{44} K_{CO_2} \tag{16}$$

$$\beta_2 \equiv \frac{K_{CO}}{28} + \frac{K_O}{16} + \frac{K_{O_2}}{32} + \frac{K_{CO_2}}{44}$$

The solution to this system is in terms of a quartic and is contained in Appendix D. The limiting behavior for large and small temperatures is given by

$T \rightarrow 0$:

$$K_C = 0$$

$$K_{C_2} = \tilde{K}_C - \beta_1$$

$$K_N = 0$$

$$\beta_1 = \frac{3}{4} \tilde{K}_O \text{ for } \epsilon < 0$$

$$K_{CN} = 0$$

$$\beta_1 = \tilde{K}_C \text{ for } \epsilon > 0$$

$$K_{N_2} = \tilde{K}_N$$

(17 continued)

$T \rightarrow \infty$:

$$K_{N_2} = 0$$

$$K_{CN} = 0$$

$$K_{C_2} = 0$$

$$K_N = \tilde{K}_N$$

$$K_C = \tilde{K}_C - \beta_1$$

$$\beta_1 = 0$$

It is apparent that at low temperatures, for a carbon-rich system, the excess carbon is absorbed in C_2 instead of condensing as solid carbon. If the system is oxygen-rich, C_2 should vanish with the temperature and it does. The results for nitrogen and cyano (CN) have the correct limiting behavior at both temperature extremes. The final results for the mass fractions of molecular and atomic nitrogen are obtained from this system. The results for CN, C_2 and C are temporary values which are used only to obtain the N_2 result. The value obtained for the CN mass fraction is quite accurate, except in situations where cyanogen (C_2N_2) forms in significant amounts. Therefore, in the following sections the nitrogen bound up in CN is reapportioned between CN and C_2N_2 .

2. C_2N_2 and CN Reactions

Cyanogen will form in moderate amounts close to the temperature boundary where condensed carbon will form. In this subsection, a small correction is applied to the mass fraction of cyano obtained in Subsection B-1. The mass fractions of atomic and molecular nitrogen are known from Subsection B-1. In the interest of simplicity, the molecular weight of Subsection B-1 is also used for this calculation. The reaction of interest is given by



The nitrogen mass balance and the equilibrium relationship are given by

$$\begin{aligned}\tilde{K}_N &= \frac{14}{26} K_{CN} + \frac{28}{52} K_{C_2N_2} + \beta_3 \\ K_{C_2N_2} &= \alpha_7 M K_{CN}^2 \\ \alpha_7 &\equiv \frac{P}{13 K_{P_7}} \\ \beta_3 &\equiv K_N + K_{N_2}\end{aligned}\tag{19}$$

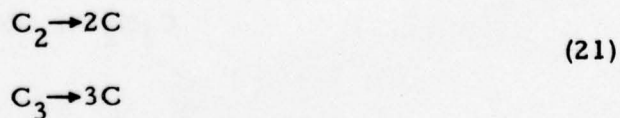
The system yields the following quadratic

$$\left(\frac{7}{13} \alpha_7 M\right) K_{CN}^2 + \frac{7}{13} K_{CN} - \left(\tilde{K}_N - \beta_3\right) = 0\tag{20}$$

Since M is taken from the result of Subsection B-1, this equation may be solved for the CN mass fraction. The cyanogen mass fraction is obtained from the equilibrium relationship. These are the final values for CN and C_2N_2 . Since β_3 approaches \tilde{K}_N at both temperature extremes, it is easily seen that the cyano and cyanogen mass fractions vanish for large and small temperatures.

3. C_2 and C_3 Reactions

In this subsection, the remaining available carbon is apportioned between C , C_2 and C_3 . The pertinent reactions are



The system is determined from the following set of equations:

$$\tilde{K}_C = K_C + K_{C_2} + K_{C_3} + \beta_4$$

$$\tilde{K}_I = K_I$$

$$\frac{1}{M} = \frac{K_C}{12} + \frac{K_{C_2}}{24} + \frac{K_{C_3}}{36} + \frac{K_I}{M_I} + \beta_5$$

(22)

$$K_{C_2} = \alpha_5 M K_C^2$$

$$K_{C_3} = \alpha_8 M^2 K_C^3$$

$$\alpha_8 \equiv \frac{P^2}{48 K_{P_8}}$$

The β functions are known from the preceding calculations and are given by

$$\beta_4 \equiv \frac{12}{28} K_{CO} + \frac{12}{26} K_{CN} + \frac{24}{52} K_{C_2N_2} + \frac{12}{44} K_{CO_2}$$

(23)

$$\beta_5 \equiv \frac{K_{CO}}{28} + \frac{K_{CN}}{26} + \frac{K_{C_2N_2}}{52} + \frac{K_N}{14} + \frac{K_{N_2}}{28} + \frac{K_O}{16} + \frac{K_{CO_2}}{44} + \frac{K_{O_2}}{32}$$

If the carbon-nitrogen reactions are ignored, the mass fractions for CN and C_2N_2 are zeroed in the above expressions for the β functions.

The solution is obtained in terms of a cubic and is presented in Appendix E. The limiting behavior for the system is given by

$T \rightarrow 0:$

$$K_C = 0$$

$$K_{C_2} = 0$$

$$K_{C_3} = \tilde{K}_C - \beta_4$$

$$\beta_4 = \frac{3}{4} \tilde{K}_O: \epsilon < 0$$

$$\beta_4 = \tilde{K}_C: \epsilon \geq 0$$

(24)

$T \rightarrow \infty:$

$$K_C = \tilde{K}_C$$

$$K_{C_2} = 0$$

$$K_{C_3} = 0$$

Thus, at low temperatures, for a carbon-rich system, the excess carbon is contained in C_3 instead of condensing out in the form of solid carbon. For an oxygen-rich system, the C_3 vanishes with the temperature, consistent with the model.

If the quantity $\tilde{K}_C - \beta_4$ is negative, it indicates that all the carbon is bound up in carbon monoxide, carbon dioxide and the carbon nitrogen compounds, and none is available for the formation of C_2 and C_3 . In this case, the mass fractions for C_2 and C_3 are zeroed, and the cubic is not solved.

C. COMPUTATIONAL SEQUENCE

It is important to note that the computational sequence of Subsections A and B is not unique and may be changed to reflect different priorities. For example, the calculation order of these subsections was chosen to insure

continuity at the dividing line between the oxygen-rich and carbon-rich domains. Before discussing this further, the computation sequence is summarized as follows.

For positive ϵ , the mass fractions of O_2 and CO_2 are obtained from Subsection A-1. For negative ϵ , these values are zeroed. For positive ϵ , the CO mass fraction is the smaller of the two values from Subsections A-1 and A-2. For negative ϵ , the CO value comes from Subsection A-2. In the temperature regime of interest (high enough so that condensed carbon is not present) the CO mass fraction will be continuous across the boundary $\epsilon = 0$. If the carbon-nitrogen reactions are ignored, the mass fractions for N and N_2 come from Subsection A-2 for all ϵ . If the reactions are included, the nitrogen values come from Subsection B-1 for all ϵ . The values for CN and C_2N_2 are solved for both positive and negative ϵ from Subsection B-2. The mass fractions of C_2 and C_3 are also solved for all ϵ and are obtained from Subsection B-3. The atomic oxygen and carbon mass fractions are obtained from Eqs. (25).

As mentioned earlier, the equations for the carbon-rich domain are also solved in the oxygen-rich region to insure continuity across the boundary $\epsilon = 0$. If, however, the problem of interest always lies in the oxygen-rich domain, such that the dividing line between oxygen and carbon rich is never crossed, then the carbon-rich calculations would be skipped. The nitrogen mass fractions would then be obtained from Subsection A-2. For example, any fluid dynamics problem with a fixed set of elemental mass fractions (such that $\epsilon > 0$) would fall into this category.

D. MIXTURE PROPERTIES

All the molecular mass fractions were computed in Subsections A and B. Following these calculations, the complete elemental mass balances are used to compute the atomic mass fractions.

$$\begin{aligned}
K_O &= \tilde{K}_O - K_{O_2} - \frac{32}{44} K_{CO_2} - \frac{16}{28} K_{CO} \\
K_C &= \tilde{K}_C - K_{C_2} - K_{C_3} - \frac{12}{44} K_{CO_2} - \frac{12}{28} K_{CO} - \frac{12}{26} K_{CN} - \frac{24}{52} K_{C_2N_2} \\
K_N &= \tilde{K}_N - K_{N_2} - \frac{14}{26} K_{CN} - \frac{28}{52} K_{C_2N_2}
\end{aligned} \tag{25}$$

The final value for the mixture molecular weight is computed from

$$\frac{1}{M} = \sum_i \frac{K_i}{M_i} \tag{26}$$

The mixture gas constant is obtained from

$$R = \frac{R_u}{M} \tag{27}$$

where R_u is the universal gas constant.

The mixture enthalpy is calculated from

$$\frac{H}{RT} = M \sum_i \left(\frac{H}{RT} \right)_i \frac{K_i}{M_i} \tag{28}$$

The enthalpy of each species is obtained from the partition functions of Appendix A. That is

$$\left(\frac{H}{RT} \right)_i = T \frac{d}{dT} (\ln Q_{P_i}) + \left(\frac{E_0}{RT} \right)_i \tag{29}$$

where E_0 is the heat of formation.

The equation of state relates the pressure and density.

$$PM = R_u \rho T \quad (30)$$

Some discussion as to usage is in order. As indicated earlier, one of the independent variables must be temperature because the thermodynamic data for the individual species are specified in terms of temperature. If the energy equation is solved for temperature, then it is immediately available for input into the chemistry calculation. However, the energy equation is usually solved for enthalpy and, thus, the temperature is not known. To obtain the temperature for input into the chemistry subroutine, the enthalpy at a particular mesh point is expanded about the last iterate level, and the resulting Taylor series is solved for temperature.

That is, the enthalpy is specified as

$$H = H(T, P, \tilde{K}_i). \quad (31)$$

At any mesh point in the flow field, this expression may be expanded in a Taylor series about the last iterate (or time) level. If the pressure is assumed to be fixed and does not vary with the iterate level (i. e., boundary layer problem), the expansion is obtained as

$$H^{n+1} = H^n + C_P^n (T^{n+1} - T^n) + \sum_i Z_i^n (\tilde{K}_i^{n+1} - \tilde{K}_i^n)$$

$$C_P \equiv \left(\frac{\partial H}{\partial T} \right)_{P, \tilde{K}_i} \quad (32)$$

$$Z_i \equiv \left(\frac{\partial H}{\partial \tilde{K}_i} \right)_{T, P}$$

The iteration levels are denoted by n for the last iteration and $n+1$ for the current iteration. The enthalpy and elemental mass fractions are available at the current iteration from the energy and elemental conservation equations, and all quantities are known at the last iteration. Therefore, the equation may be solved for temperature at the current iteration and input to the chemistry calculation.

The indicated derivatives (C_P and Z) are evaluated as follows:

$$Z_j = \sum_i H_i \left(\frac{\partial K_i}{\partial \tilde{K}_j} \right)_{T, P} \quad (33)$$

$$C_P = \sum_i \left[H_i \left(\frac{\partial K_i}{\partial T} \right)_{P, \tilde{K}_i} + C_{P_i} K_i \right]$$

The derivatives may be obtained by differentiating the analytic solution. It is important to note that these derivatives may be calculated without resolving the cubics and quartics. Therefore, evaluating these quantities analytically, rather than numerically, will substantially decrease the computation time.

E. CLOSURE

In order to obtain equations which were of fourth order or lower, it was necessary to uncouple the reactions and consider them sequentially. The motivation for determining which reactions to couple and treat independently of the other reactions was discussed above. A considerable effort was made to examine alternate possibilities for increased accuracy and simplicity, several of which are described here.

An attempt was made to consider a single set of equations for the oxygen-rich regime [consisting of Eqs. (3) and (10)] and a single set for the carbon-rich regime [Eqs. (10), (14), (18) and (21)]. In both cases, polynomials of higher than fourth order were encountered. The same difficulty

was encountered when trying to treat the carbon-nitrogen reactions [Eqs. (14) and (18)] simultaneously. An attempt to incorporate the CN reaction of Eq. (14) with the CO and N_2 reaction of Eq. (10) yielded a fifth order polynomial. Therefore, it is felt that the present model is as simplified as possible within the fourth order polynomial constraint imposed on the system.

In several places during the formulation, allusions were made to the possibility of ignoring the carbon-nitrogen reaction. These reactions were included for generality and in the anticipation that they might prove significant for a carbon-nitrogen system. It was found, however, that these reactions exert a negligible effect upon the mixture properties when the system is nearly all carbon and nitrogen with small amounts of oxygen. For a carbon-air system, with a 50 percent carbon mass fraction, it is shown in Section IV that the inclusion of the carbon-nitrogen reactions has only a small influence on the mixture properties (maximum difference of two to three percent). An additional set of comparisons was made for a carbon-nitrogen system with the same conclusion. It is believed, therefore, that the carbon-nitrogen reactions may be ignored with complete generality.

Thus, in its simplest form (ignoring the carbon-nitrogen reaction), the mixture properties of a carbon-nitrogen-oxygen system may be determined by solving two cubics (Subsections A-1 and B-3) and a quartic (Subsection A-2).

It is noted that the formation of nitric oxide (NO) was ignored. Hansen's results (Ref. 1) show that it exerts a negligible influence on the mixture properties of air. Thus, since the nitrogen must compete with carbon for the available oxygen in the carbon-nitrogen-oxygen system, it will be even less significant for this system. However, if the mass fraction of NO were of interest, it could be determined by using the molecular weight and CO mass fraction as calculated by the present formulation and solving the elemental mass balances for nitrogen and oxygen (using K_{CO} as a known quantity) along with the equilibrium relationships for the N_2 , O_2 and NO dissociation reactions.

In the Appendices, an implicit assumption is made that nitrogen was always present in the system (i. e., $\tilde{K}_N \neq 0$). Thus, while the equations are well behaved for zero values of the carbon or oxygen elemental mass fractions, the equations of Appendix C are singular for a zero nitrogen mass fraction. Furthermore, if $\tilde{K}_N = 0$, the CO dissociation reaction is treated by itself and yields a quadratic equation (see Appendix C).

If the carbon elemental mass fraction is zero, the present results reduce to Hansen's (Ref. 3) model (uncoupled O_2 and N_2 dissociation reactions with no nitric oxide). Because of the importance of the nitrogen-oxygen system (which contains air as a special case), a more complete model is treated in Appendix F. It is shown that the N_2 , O_2 and NO reactions can be treated simultaneously and the solution obtained in terms of a quartic.

Some comments concerning round-off errors in the extraction of the roots is in order. Since the α_i coefficients vary by several hundred orders of magnitude over the temperature range of interest (500-10,000^oK), the equations change character at the temperature extremes. The quartics, for example, reduce to quadratics for large and small temperatures. Therefore, extracting the roots from the analytic solution for a quartic introduces some round-off errors in this situation. After obtaining the desired root from the quartic, it was tested to ensure that it did indeed satisfy the equation to within some tight tolerance. At high and low temperatures, it exceeded the tolerance, and the root was recalculated using the asymptotic forms of the equations derived in the Appendices.

Since the analytic solution for a quartic is only marginally more complicated than that for a cubic, the computation time to obtain the four roots is negligible. The decision as to which of the real roots (imaginary roots were ignored) is the desired root is trivial. In all cases, the smallest positive root is the correct value.

SECTION III

DENSITY AND TEMPERATURE AS INDEPENDENT VARIABLES

The analysis of Section II is repeated here with the density replacing the pressure as one of the given variables. An examination of any of the equilibrium relationships shows that the product of pressure and molecular weight always appears in the equation. Thus, for a given value of pressure, the molecular weight remains as an unknown in the equilibrium expression. This couples the elemental mass balances and equilibrium equations to the equation relating molecular weight and species mass fractions. It is this coupling of equations which greatly complicates the algebra required to solve the system.

When the density and temperature are given, the product of pressure and molecular weight is easily evaluated from the equation of state [Eq. (30)]. Therefore, the equilibrium relationships do not contain the molecular weight as an unknown quantity, and the system may be solved for the species mass fractions independently of the molecular weight equation. Since the product of pressure and molecular weight is a known quantity, it is absorbed into a new set of coefficients denoted as $\tilde{\alpha}_i$. These coefficients are simply the α_i of Section II multiplied by the molecular weight; that is

$$\tilde{\alpha}_i = M\alpha_i \quad (34)$$

The partitioning of the problem into carbon-rich and oxygen-rich regimes and the order in which the reactions are considered remains unchanged. As before, the oxygen-rich reactions are considered first.

A. OXYGEN-RICH SYSTEM: $\epsilon \geq 0$

Due to the uncoupling of the elemental mass balance equations and equilibrium expressions from the molecular weight equation, it is possible to treat all the oxygen-rich reactions in one set of equations. That is, the CO

dissociation reaction may be included with the CO_2 and O_2 reactions and the solution obtained in the form of a quartic. However, the negligible increase in accuracy does not warrant replacing the cubic with a quartic. Therefore, the CO dissociation reaction is treated separately, and the analysis exactly parallels that of Subsection II-A.

1. CO_2 and O_2 Reactions

The elemental mass balances are exactly the same as Eqs. (4) and are not repeated here. The equilibrium relationships, with the newly defined $\tilde{\alpha}_i$, are given as

$$\begin{aligned} K_{\text{CO}_2}^2 &= \tilde{\alpha}_1 K_{\text{O}_2} K_{\text{CO}}^2 \\ K_{\text{O}_2} &= \tilde{\alpha}_2 K_{\text{O}}^2 \end{aligned} \quad (35)$$

$$\tilde{\alpha}_1 \equiv \frac{121 \text{ PM}}{1568 K_{\text{P}_1}} \quad \tilde{\alpha}_2 \equiv \frac{\text{PM}}{8 K_{\text{P}_2}}$$

Substitution into the elemental mass balances yields

$$\begin{aligned} AK_{\text{O}}^3 + BK_{\text{O}}^2 + CK_{\text{O}} - \frac{4}{7} \epsilon &= 0 \\ A &\equiv \frac{3}{11} \tilde{\alpha}_2 \sqrt{\tilde{\alpha}_1 \tilde{\alpha}_2} \\ B &\equiv \frac{3}{7} \tilde{\alpha}_2 + \frac{3}{11} \sqrt{\tilde{\alpha}_1 \tilde{\alpha}_2} \\ C &\equiv \frac{3}{7} + \sqrt{\tilde{\alpha}_1 \tilde{\alpha}_2} \left(\frac{8}{11} \tilde{K}_{\text{C}} - \frac{3}{11} \tilde{K}_{\text{O}} \right) \\ K_{\text{CO}} &= \frac{\tilde{K}_{\text{C}}}{\frac{3}{7} + \frac{3}{11} K_{\text{O}} \sqrt{\tilde{\alpha}_1 \tilde{\alpha}_2}} \end{aligned} \quad (36)$$

The limiting behavior of this system is exactly the same as it was for pressure as the independent variable.

2. N₂ and CO Reactions

When the pressure was used as the variable, the N₂ and CO reactions were linked together only through the molecular weight equation. Since the use of density as a variable eliminates the molecular weight, these two reactions are now uncoupled and may be solved separately.

The equilibrium relationships are given by

$$\begin{aligned}K_{\text{CO}} &= \tilde{\alpha}_3 K_{\text{C}} K_{\text{O}} \\K_{\text{N}_2} &= \tilde{\alpha}_4 K_{\text{N}}^2\end{aligned}\tag{37}$$

where the $\tilde{\alpha}_i$ are defined according to Eq. (34).

Substitution into the elemental mass balances of Eq. (11) yields a set of quadratic equations.

$$\begin{aligned}\tilde{\alpha}_4 K_{\text{N}}^2 + K_{\text{N}} - \tilde{K}_{\text{N}} &= 0 \\ \frac{4}{7} \tilde{\alpha}_3 K_{\text{C}}^2 + K_{\text{C}} \left(1 + \frac{4}{7} \tilde{\alpha}_3 \epsilon\right) - \tilde{K}_{\text{C}} &= 0 \\ \frac{3}{7} \tilde{\alpha}_3 K_{\text{O}}^2 + K_{\text{O}} \left(1 - \frac{4}{7} \tilde{\alpha}_3 \epsilon\right) - \tilde{K}_{\text{O}} &= 0\end{aligned}\tag{38}$$

There is only one positive root for K_{N} , and this is the correct value. At low temperatures, the two roots for K_{C} correspond to the two solution branches for the oxygen-rich case ($\epsilon \geq 0$) and the carbon-rich case ($\epsilon < 0$). The oxygen-rich case corresponds to the plus sign in front of the radical in the equation for the roots of a quadratic. The carbon-rich situation corresponds to the minus sign. At high temperatures there is only one positive root for K_{C} , and it is the correct value. The quadratic for K_{O} has similar behavior.

The asymptotic behavior of this system, for large and small temperatures, is identical to Eqs. (12) and (13).

B. CARBON-RICH SYSTEM: $\epsilon < 0$

Again, the carbon-rich analysis exactly parallels that of Subsection II-B with the same elemental mass balances and equilibrium relationships (with the molecular weight absorbed in the $\tilde{\alpha}_1$).

1. N_2 and CN Reactions

The equilibrium relationships are

$$\begin{aligned} K_{N_2} &= \tilde{\alpha}_4 K_N^2 \\ K_{C_2} &= \tilde{\alpha}_5 K_C^2 \\ K_{CN} &= \tilde{\alpha}_6 K_C K_N \end{aligned} \quad (39)$$

Substitution into the elemental mass balances of Eq. (15) yields

$$\begin{aligned} AK_N^4 + BK_N^3 + CK_N^2 + DK_N + \tilde{\alpha}_5 \tilde{K}_N^2 &= 0 \\ A &\equiv \tilde{\alpha}_5 \tilde{\alpha}_4^2 - \frac{42}{169} \tilde{\alpha}_4 \tilde{\alpha}_6^2 \\ B &\equiv 2\tilde{\alpha}_4 \tilde{\alpha}_5 - \frac{42}{169} \tilde{\alpha}_6^2 - \frac{7}{13} \tilde{\alpha}_4 \tilde{\alpha}_6 \\ C &\equiv \frac{42}{169} \tilde{K}_N \tilde{\alpha}_6^2 + \tilde{\alpha}_5 - 2\tilde{\alpha}_4 \tilde{\alpha}_5 \tilde{K}_N + \\ &\quad - \frac{7}{13} \tilde{\alpha}_6 - \frac{49}{169} \tilde{\alpha}_6^2 (\tilde{K}_C - \beta_1) \\ D &\equiv \frac{7}{13} \tilde{\alpha}_6 \tilde{K}_N - 2\tilde{\alpha}_5 \tilde{K}_N \end{aligned} \quad (40)$$

The carbon mass fraction is calculated from the following quadratic:

$$\tilde{\alpha}_5 K_C^2 + K_C \left(1 + \frac{6}{13} \tilde{\alpha}_6 K_N \right) - \left(\tilde{K}_C - \beta_1 \right) = 0 \quad (41)$$

The limiting behavior for large and small temperatures is given by Eq. (17).

2. C₂N₂ and CN Reactions

The purpose of this calculation is simply to reappportion the nitrogen absorbed in CN (in Subsection B-1) between CN and C₂N₂.

Utilizing the nitrogen mass balance and the equilibrium relationship yields

$$K_{C_2N_2} = \tilde{\alpha}_7 K_{CN}^2 \quad (42)$$

$$\left(\frac{7}{13}\tilde{\alpha}_7\right) K_{CN}^2 + \frac{7}{13} K_{CN} - (\tilde{K}_N - \beta_3) = 0$$

The single positive root is the correct value. At the temperature extremes both the CN and C₂N₂ mass fractions vanish.

3. C₂ and C₃ Reactions

The equilibrium expressions are given by

$$K_{C_2} = \tilde{\alpha}_5 K_C^2 \quad (43)$$

$$K_{C_3} = \tilde{\alpha}_8 K_C^3$$

Substitution into the carbon mass balance of Eq. (22) yields the following cubic:

$$\tilde{\alpha}_8 K_C^3 + \tilde{\alpha}_5 K_C^2 + K_C - (\tilde{K}_C - \beta_4) = 0 \quad (44)$$

As before, if $\beta_4 \geq \tilde{K}_C$, all the carbon is tied up in CO and the carbon-nitrogen compounds and is not available to form C₂ or C₃. At low temperature, the excess carbon is contained in C₃.

C. CLOSURE

After the calculations for the molecular mass fractions are completed, the relationships of Subsection II-D are used to calculate the atomic mass fractions and mixture properties.

The computational sequence is exactly the same as for Section II and is again chosen to insure continuity across the boundary $\epsilon = 0$. The calculation sequence is summarized in Subsection II-C, and the same comments concerning alternate computational sequences are applicable here.

Since the physical model treated in Sections II and III is identical, the behavior of the system was not discussed in Section III. It should be emphasized, however, that the results of this section are subject to the same limitations and qualifications as those of Section II. In particular, the same comments apply here concerning the formulation of solid carbon and the advisability of considering carbon-nitrogen reactions.

A comparison of the analysis of this section with that of Section II (as contained in the relevant appendices) makes it obvious that the use of density, instead of pressure, as a variable results in a tremendous reduction in algebraic complexity. The greatest simplification is contained in Subsection A-2 where the quartic of Section II was replaced by two uncoupled quadratic equations. Thus, in its simplest form (ignoring carbon-nitrogen reactions) the formulation using density does not require the solution of any quartics.

It is noted that the elimination of the molecular weight from the determination of the species mass fractions means that the inert species also has no influence on the calculation of the mass fractions. The inert species mass fraction is required only to calculate the molecular weight following the calculation of the other mass fractions.

SECTION IV

RESULTS AND DISCUSSION

In this section, the analytic solution developed in Section II (given pressure and temperature) is compared with exact calculations to determine accuracy and computation speed. The results of Section III (given density and pressure) will yield exactly the same accuracy as those of Section II because the physical model is identical in both cases. The computation speed for given density will be somewhat faster than for given pressure because of the reduced algebraic complexity. The accuracy of the analytic solution is considered first.

A. ACCURACY

There exist two distinct kinds of fluid dynamic problems involving equilibrium chemistry. The first consists of the situation in which the elemental mass fractions are fixed by external circumstances and remain constant with time and throughout the flow field. For this class of problem, a Mollier diagram may be generated, for a fixed set of elemental mass fractions, to provide the properties of the gas mixture over a range of temperature and pressure. Since the elemental mass fractions are known and are independent of the fluid dynamics calculation, the Mollier diagram may be precomputed from an exact equilibrium chemistry code and stored on cards or magnetic tape for use with the fluid dynamic computation. In this manner, the chemistry calculation reduces to a two-dimensional interpolation of the stored data. A commonly encountered problem of this class consists of calculating the flow field about a non-ablating body in a planetary atmosphere (or in a wind tunnel, ballistic range or rocket exhaust).

In the second problem category, the elemental mass fractions vary throughout the flow field and are determined as part of the solution. A common example of this involves the calculation of the boundary layer over an

ablating surface where the ablation process changes the elemental mass fractions. Since the amount of ablation depends on the heat transfer to the surface, it is apparent that the determination of the fluid dynamic and elemental mass fractions is a completely coupled process. It is obviously not possible to provide computer storage for separate Mollier diagrams for each possible set of elemental mass fractions that might be encountered on a problem of this kind. In this case, the equilibrium chemistry calculations must be carried out simultaneously with the fluid dynamic computation.

Thus, while the analytic solution of this report may be used with either category of problem, it apparently will be most useful for those problems with varying mass fractions. In fact, the author's prime motivation in developing this solution was for its use in boundary layer calculations on a carbon surface ablating in air.

The first test case consists of a Mollier diagram for a planetary atmosphere and is typical of the first kind of problem (fixed elemental composition). This case was denoted as a postulated Mars atmosphere in Ref. 7 and consists of 25 percent N_2 , 32 percent Ar and 43 percent CO_2 by volume. The corresponding elemental mass fractions are

$$\begin{aligned}\tilde{K}_C &= 0.1333 \\ \tilde{K}_N &= 0.1808 \\ \tilde{K}_O &= 0.3553 \\ \tilde{K}_I &= 0.3306\end{aligned}\tag{45}$$

This case is oxygen-rich with respect to the formation of both carbon monoxide and carbon dioxide. That is, at low temperatures all the carbon is bound up in CO_2 and, thus, solid carbon will never be present in this mixture.

The results for molecular weight and enthalpy are presented in Figs. 1 and 2 for a range of temperature and pressure. The solid lines are the approximate analytic solution, and the symbols are the exact result from

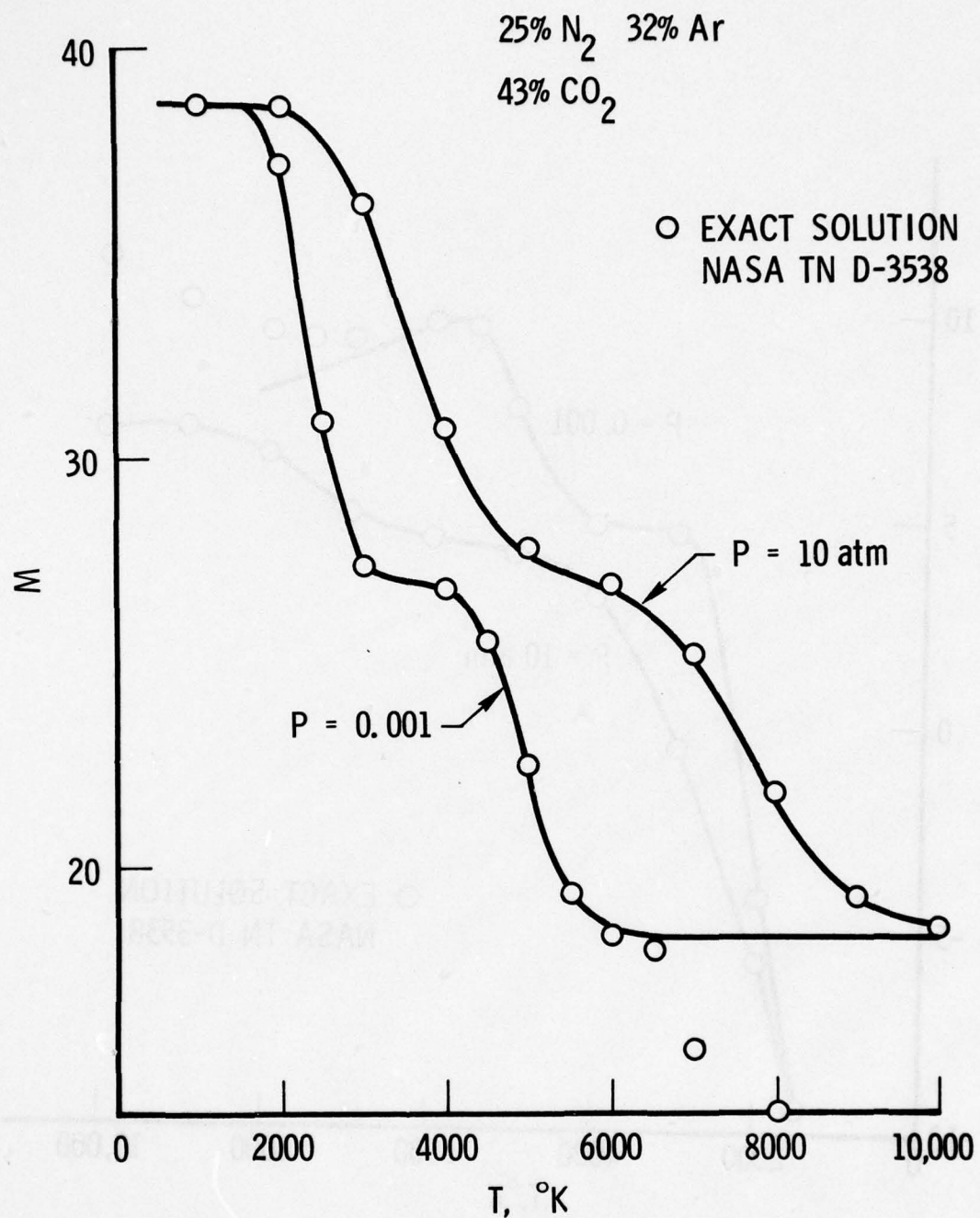


Fig. 1. Molecular Weight Comparison for Planetary Atmosphere

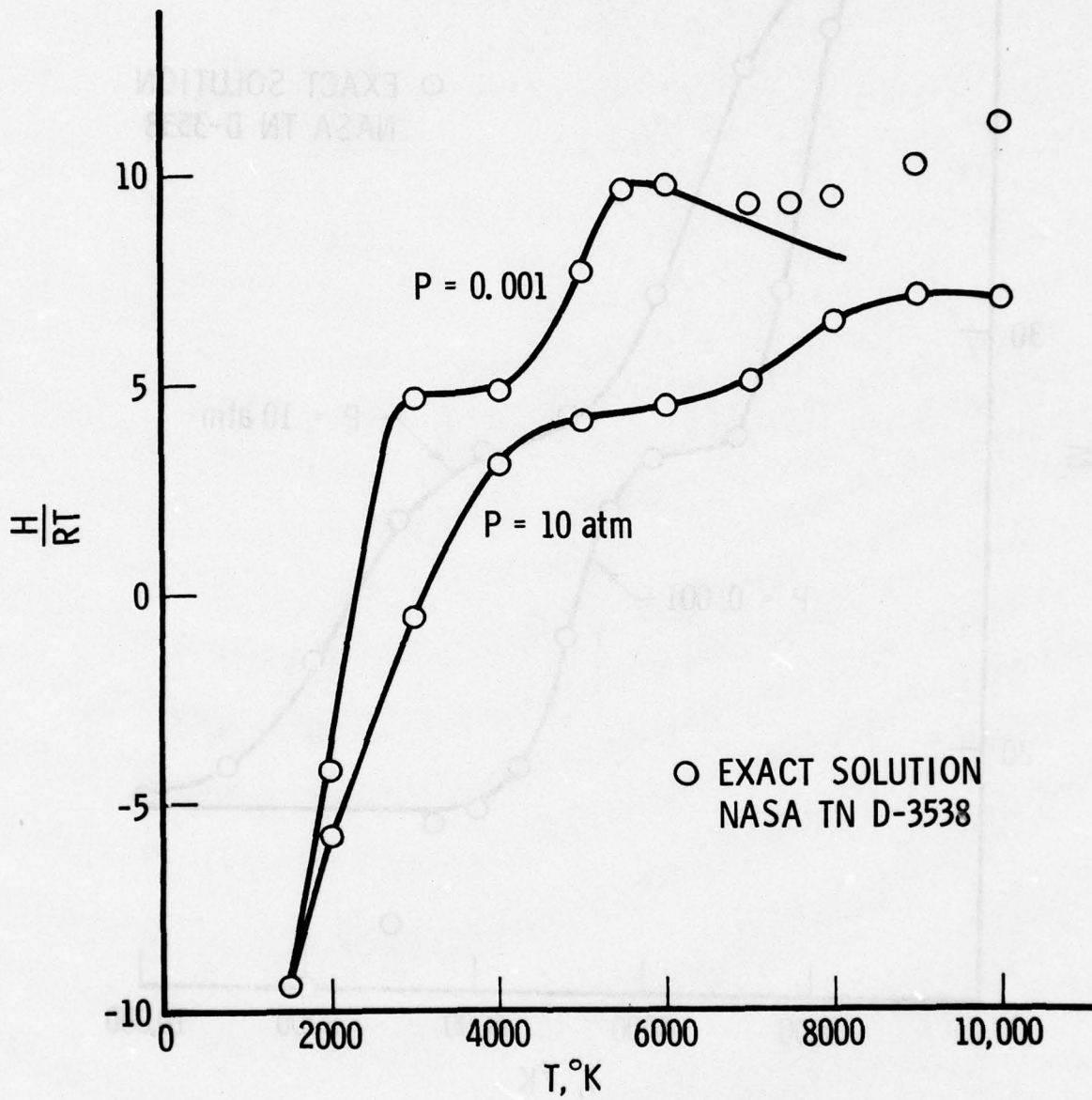


Fig. 2. Enthalpy Comparison for Planetary Atmosphere

Ref. 7. It is apparent that the agreement is excellent, except at low pressure and high temperature where ionization becomes significant. The mass fractions at a pressure of ten atmospheres are compared in Figs. 3a and 3b. The exact calculations for the mass fractions were not presented in Ref. 7 and were obtained from the NEST (Ref. 8) equilibrium chemistry code. Again, the agreement is excellent. The slight error in the mass fractions of molecular oxygen and nitrogen, in the temperature range of 3000-6000°K, is due to the neglect of nitric oxide in the approximate solution.

The remainder of the cases chosen for comparison are pertinent to the second category problem (varying elemental mass fractions) discussed above. The cases are all carbon-air mixtures with varying amounts of carbon. The air was argon free and the volumetric composition was 80 percent molecular nitrogen and 20 percent molecular oxygen. The elemental mass fractions are

$$\begin{aligned}\tilde{K}_N &= \frac{3.5 (1 - \tilde{K}_C)}{4.5} \\ \tilde{K}_O &= \frac{1 - \tilde{K}_C}{4.5} \\ \tilde{K}_I &= 0\end{aligned}\tag{46}$$

The elemental carbon mass fraction is the parameter chosen to characterize the cases and is varied over the range

$$0 \leq \tilde{K}_C \leq 0.50\tag{47}$$

-
7. Allison, D.O., "Calculation of Thermodynamic Properties of Arbitrary Gas Mixture with Modified Vibrational-Rotational Corrections," NASA TN D-3538, 1966.
 8. Turner, E., "The NEST Chemistry Computer Program," The Aerospace Corporation, Report No. TR-0059(6240-20)-1, Vol. I, July 1970.

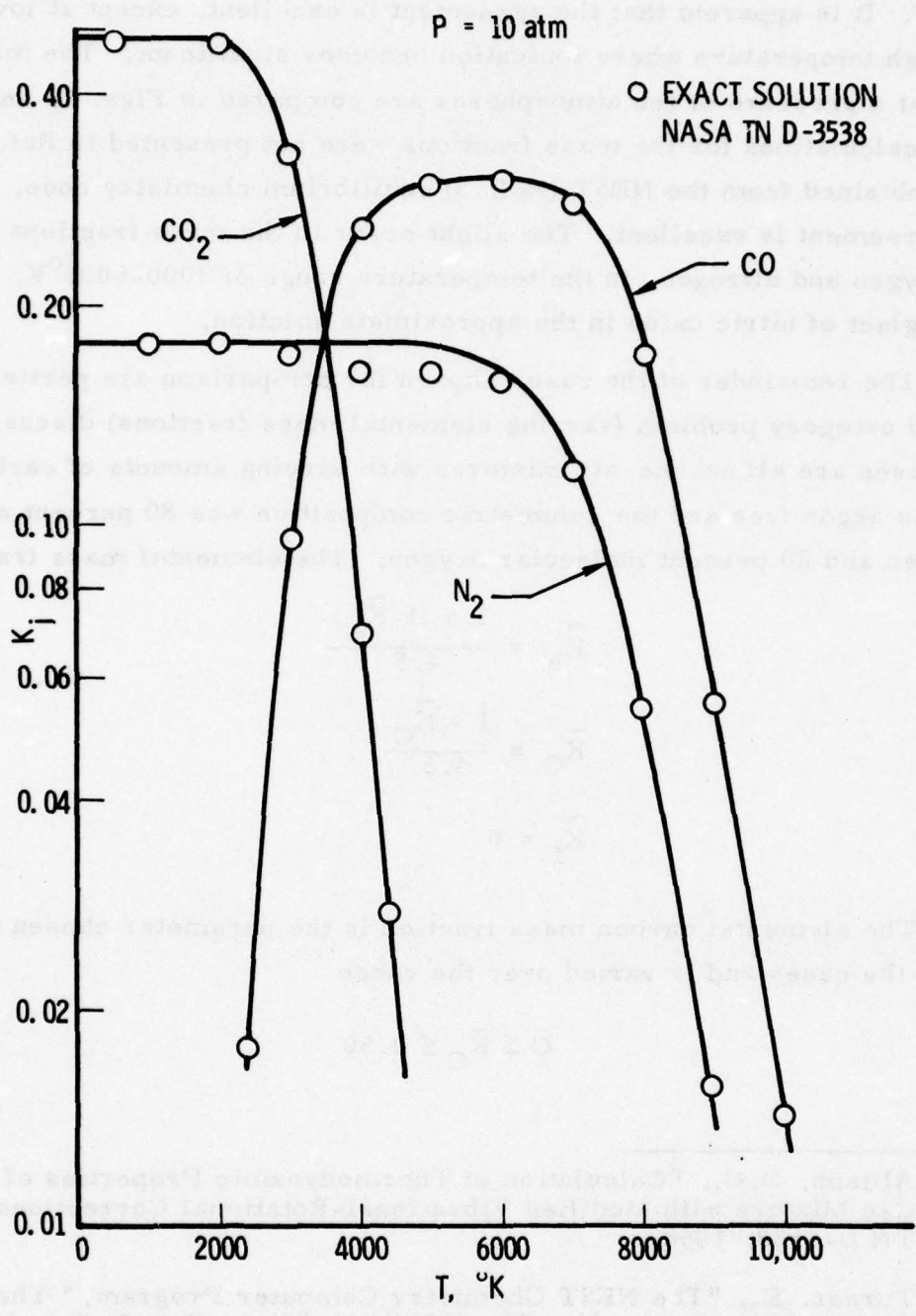


Fig. 3a. Species Mass Fractions for Planetary Atmosphere

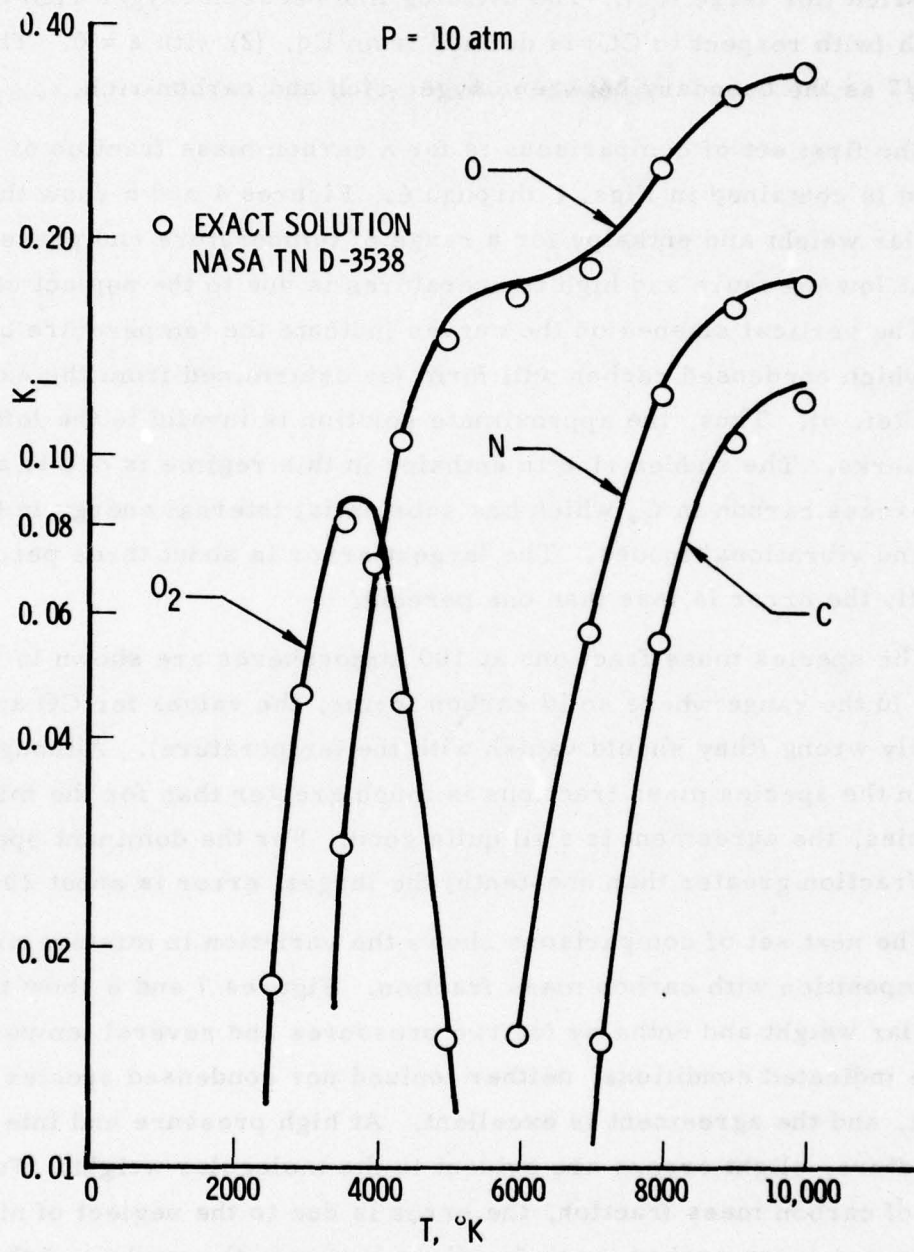


Fig. 3b. Species Mass Fractions for Planetary Atmosphere

This system will range from oxygen rich (for small values of \tilde{K}_C) to carbon-rich (for large \tilde{K}_C). The dividing line between oxygen-rich and carbon-rich (with respect to CO) is defined from Eq. (2) with $\epsilon = 0$. This yields $\tilde{K}_C = 1/7$ as the boundary between oxygen-rich and carbon-rich.

The first set of comparisons is for a carbon mass fraction of 50 percent and is contained in Figs. 4 through 6. Figures 4 and 5 show the mixture molecular weight and enthalpy for a range of temperature and pressure. The error at low pressure and high temperatures is due to the neglect of ionization. The vertical slashes on the curves indicate the temperature boundary below which condensed carbon will form (as determined from the exact solution of Ref. 8). Thus, the approximate solution is invalid to the left of these slash marks. The sudden rise in enthalpy in this regime is due to absorption of the excess carbon in C_3 which has substantial internal energy in the rotational and vibrational modes. The largest error is about three percent, and generally the error is less than one percent.

The species mass fractions at 100 atmospheres are shown in Figs. 6a and 6b. In the range where solid carbon forms, the values for CO and C_3 are obviously wrong (they should vanish with the temperature). Although the error in the species mass fractions is much greater than for the mixture properties, the agreement is still quite good. For the dominant species (mass fraction greater than one-tenth) the largest error is about 20 percent.

The next set of comparisons shows the variation in mixture properties and composition with carbon mass fraction. Figures 7 and 8 show the molecular weight and enthalpy for two pressures and several temperatures. For the indicated conditions, neither ionized nor condensed species are present, and the agreement is excellent. At high pressure and intermediate temperature, slight errors are evident in the molecular weight. For small values of carbon mass fraction, the error is due to the neglect of nitric oxide. The error at large carbon mass fractions is due to the neglect of the heavy molecular weight carbon-nitrogen species C_4N_2 .

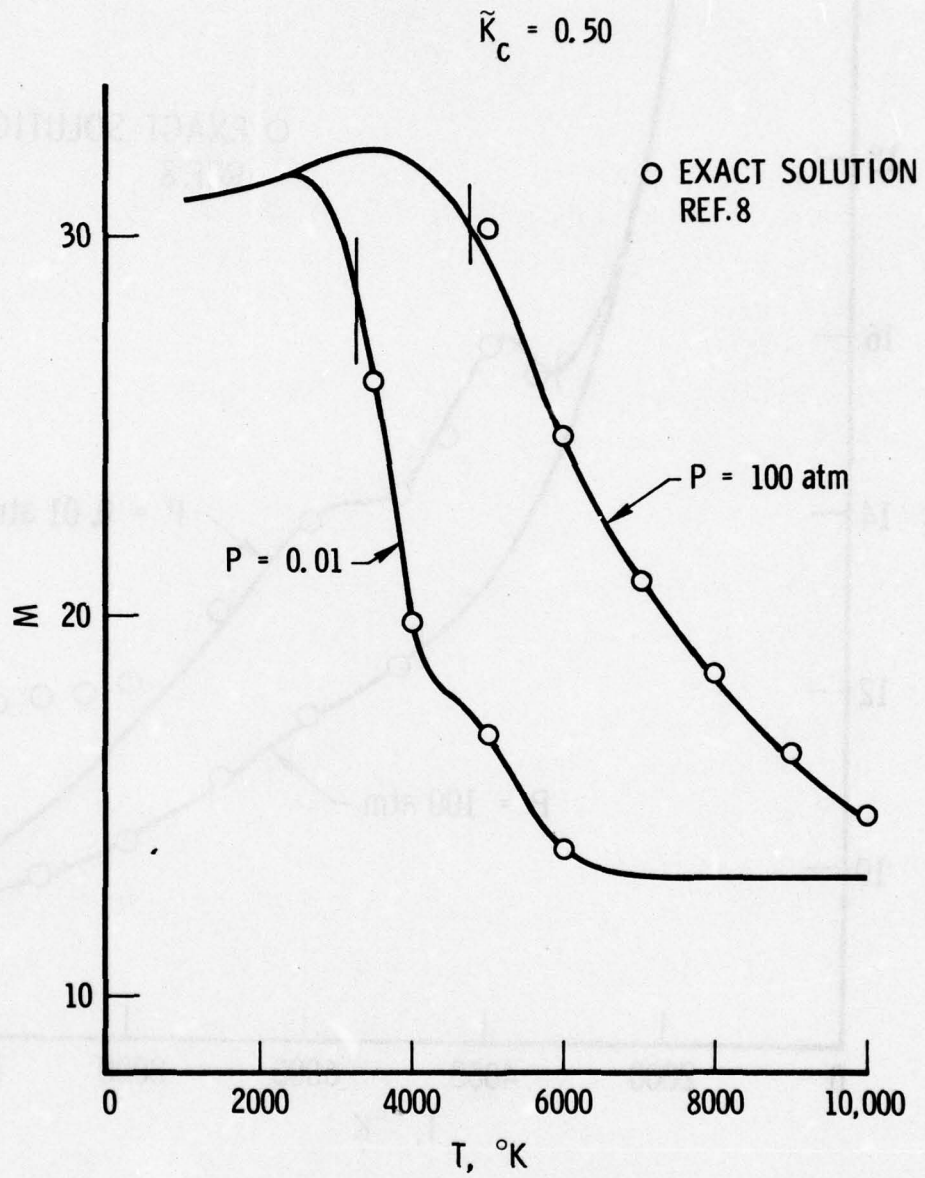


Fig. 4. Molecular Weight Comparison for Carbon-Air Mixture

$$\tilde{K}_C = 0.50$$

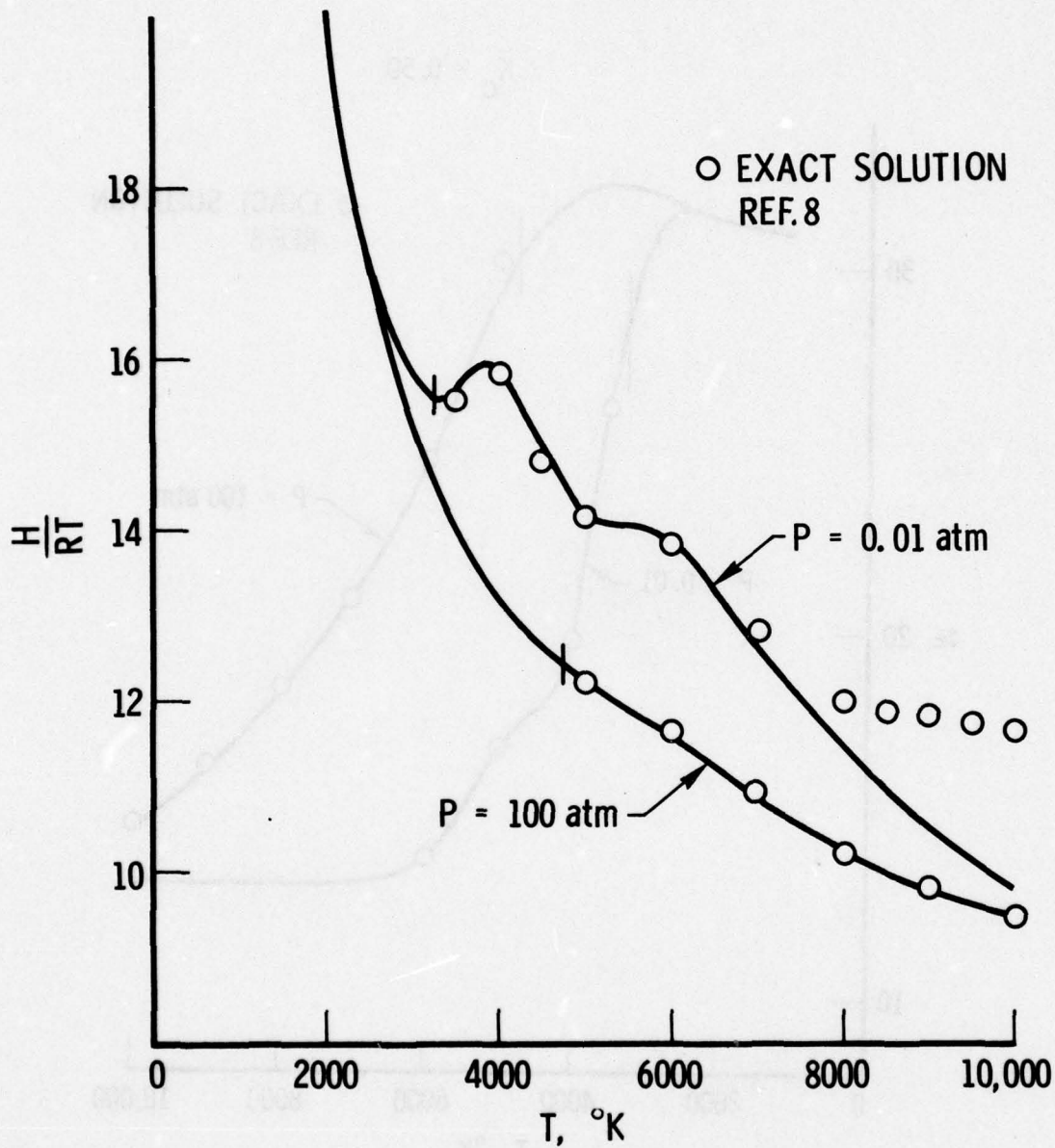


Fig. 5. Enthalpy Comparison for Carbon-Air Mixture

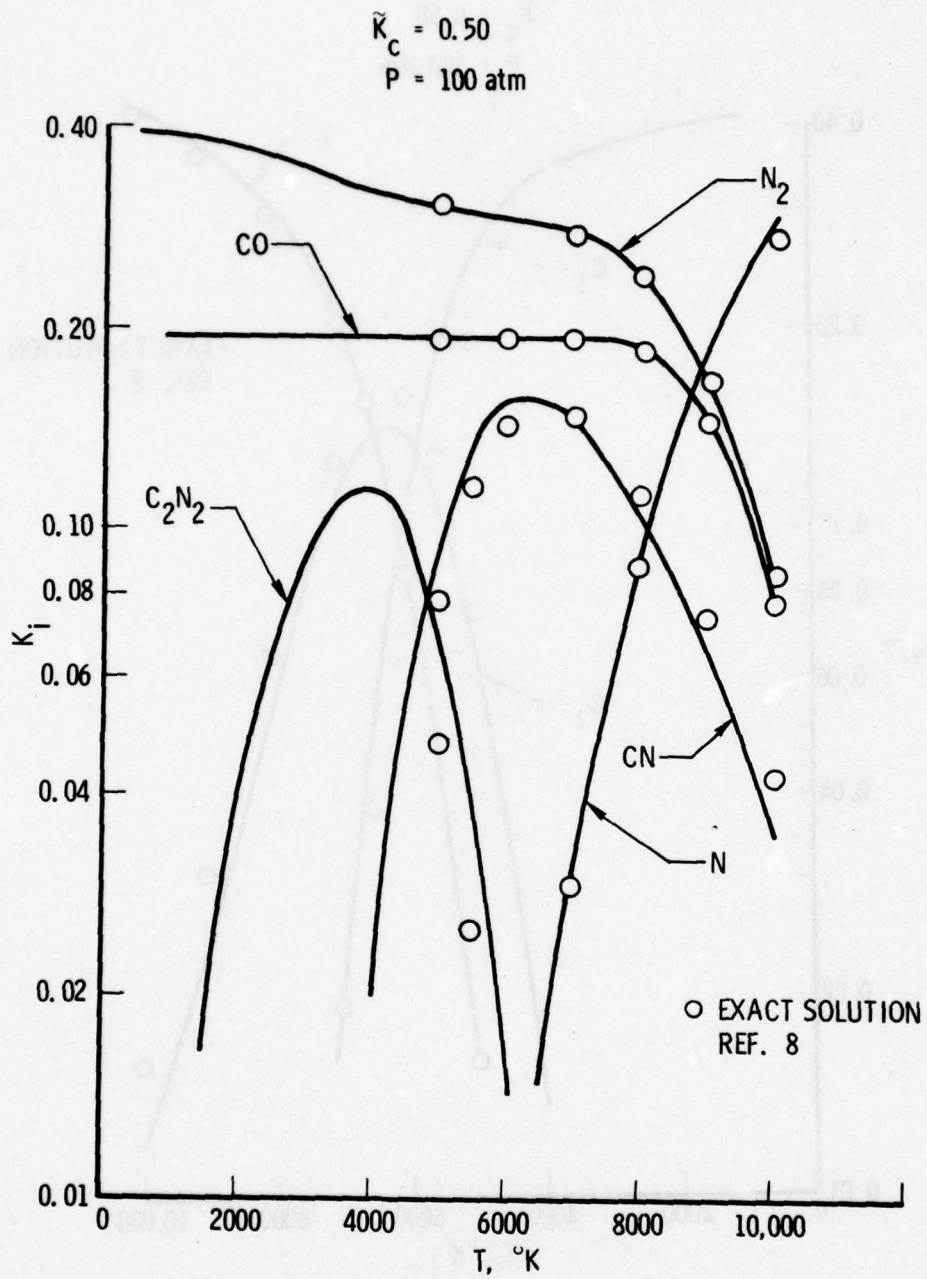


Fig. 6a. Species Mass Fractions for Carbon-Air Mixture

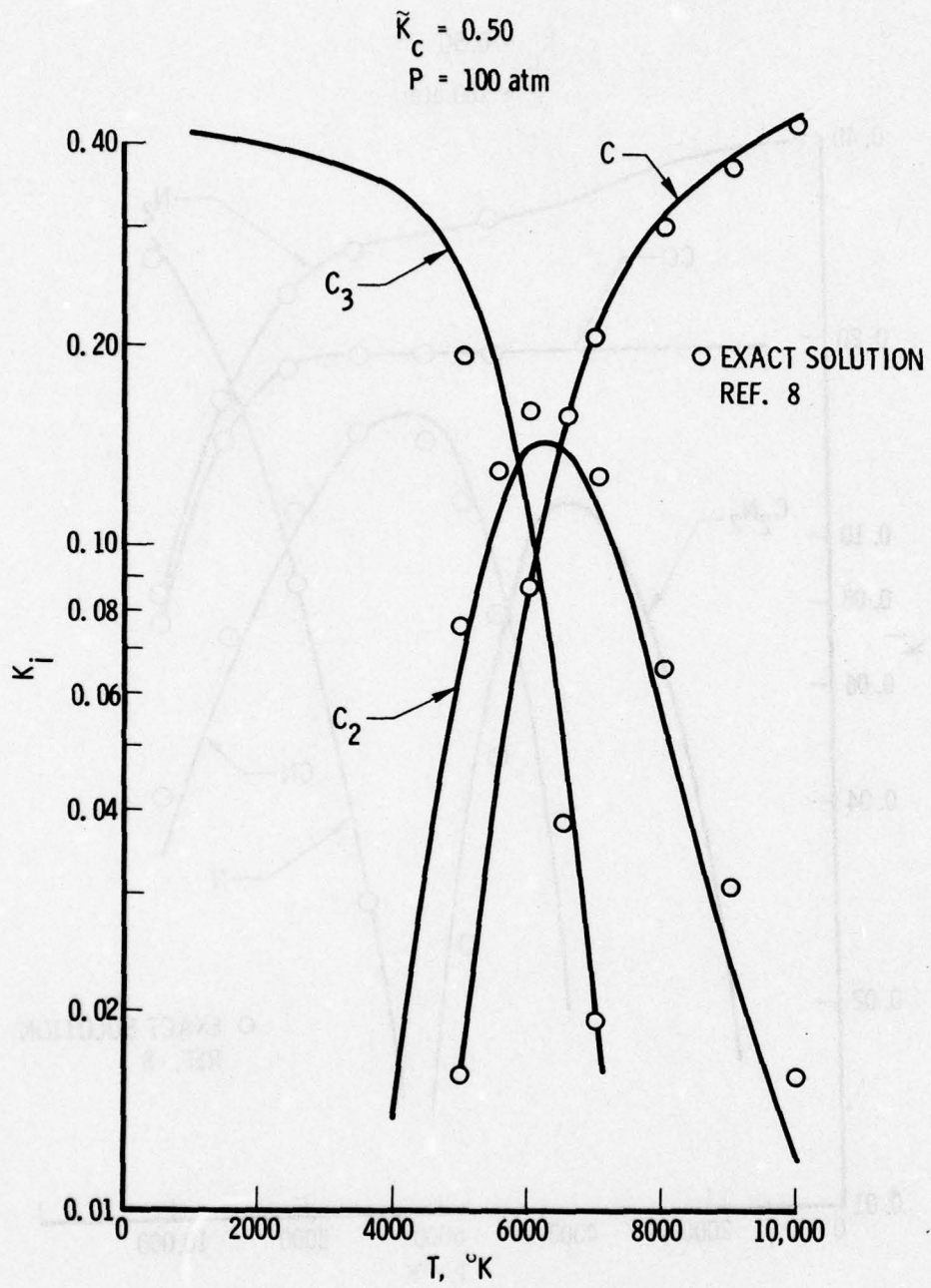


Fig. 6b. Species Mass Fractions for Carbon-Air Mixture

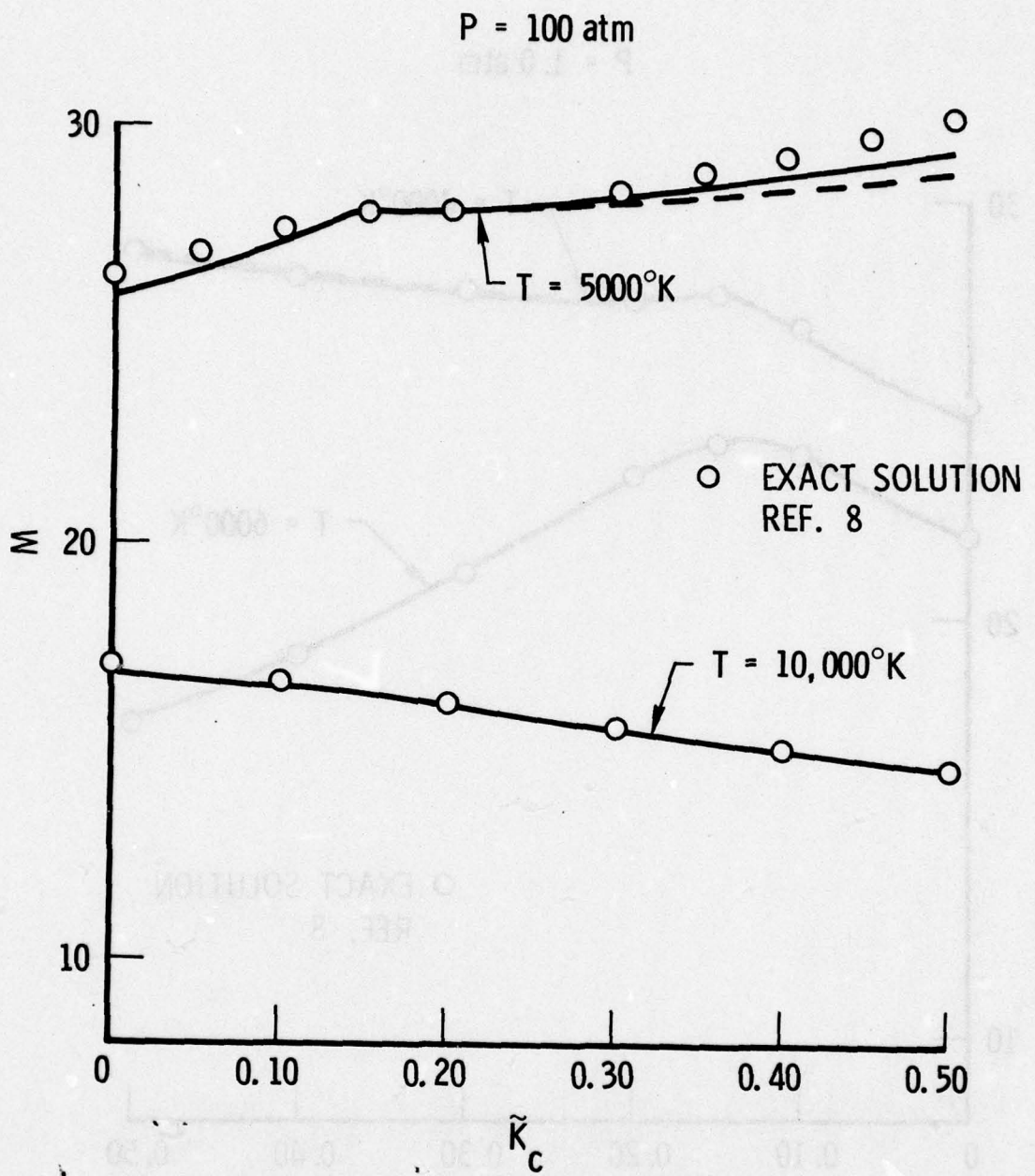


Fig. 7a. Influence of Carbon Mass Fraction on Molecular Weight of a Carbon-Air Mixture

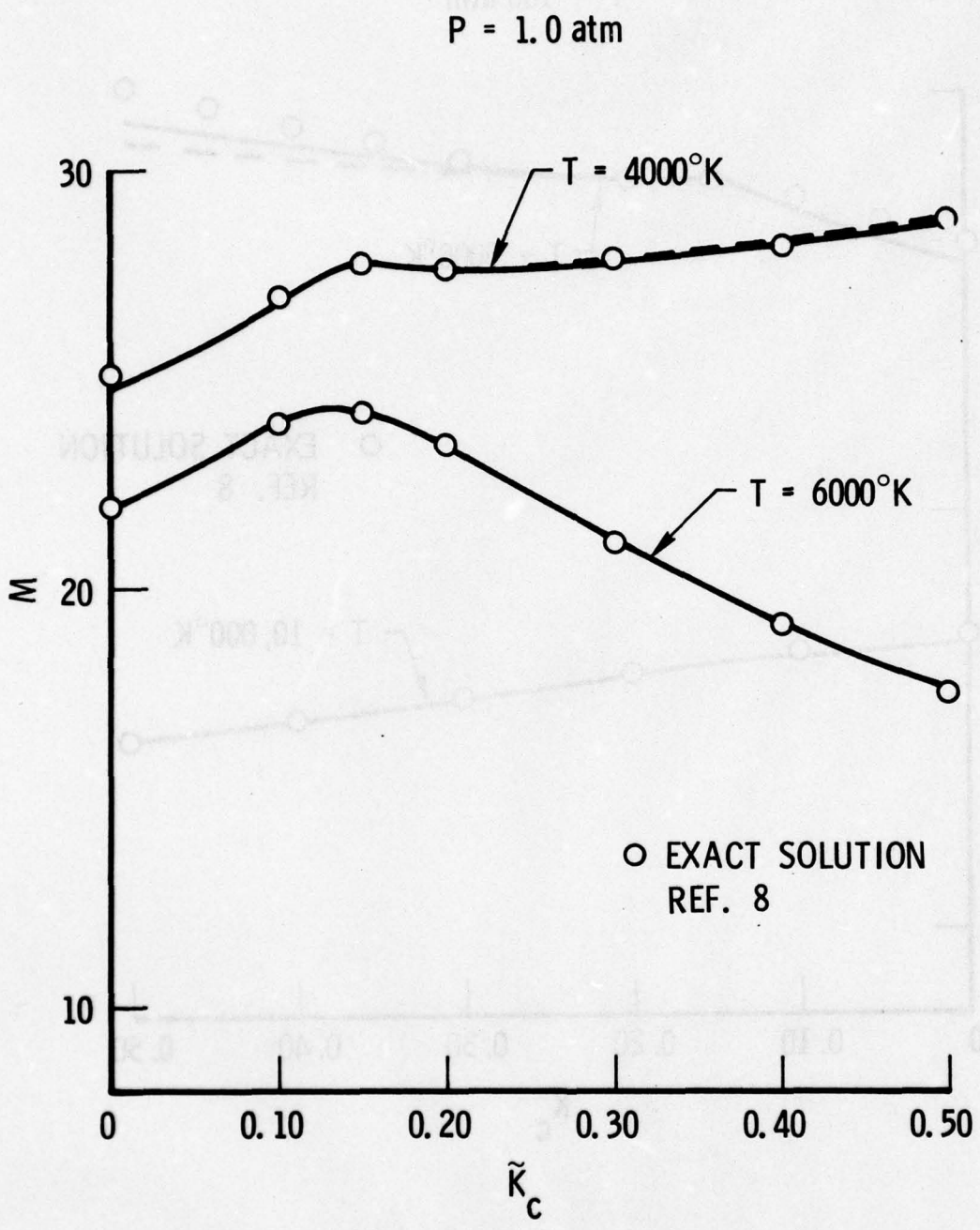


Fig. 7b. Influence of Carbon Mass Fraction on Molecular Weight of a Carbon-Air Mixture

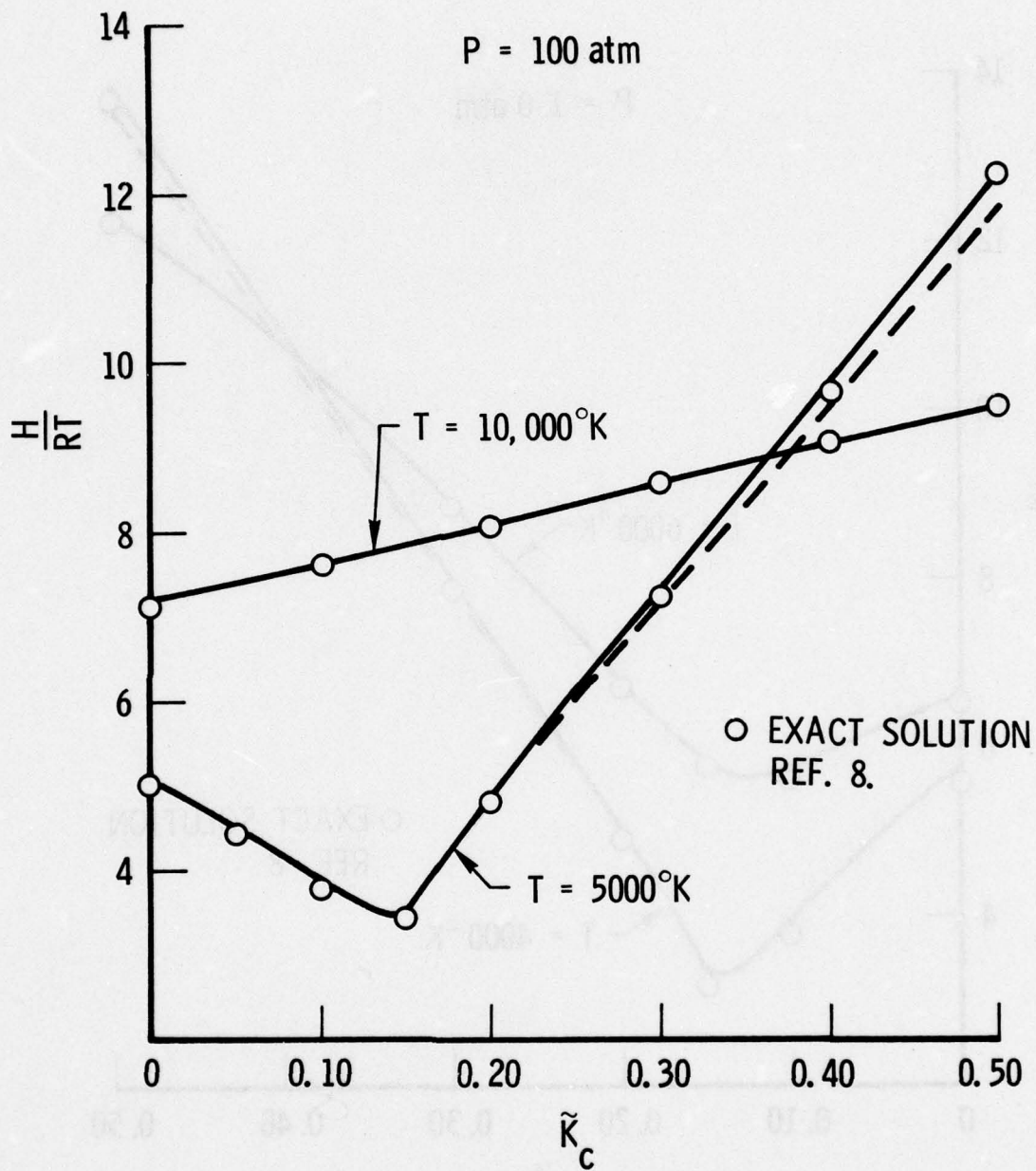


Fig. 8a. Influence of Carbon Mass Fraction on Enthalpy of a Carbon-Air Mixture

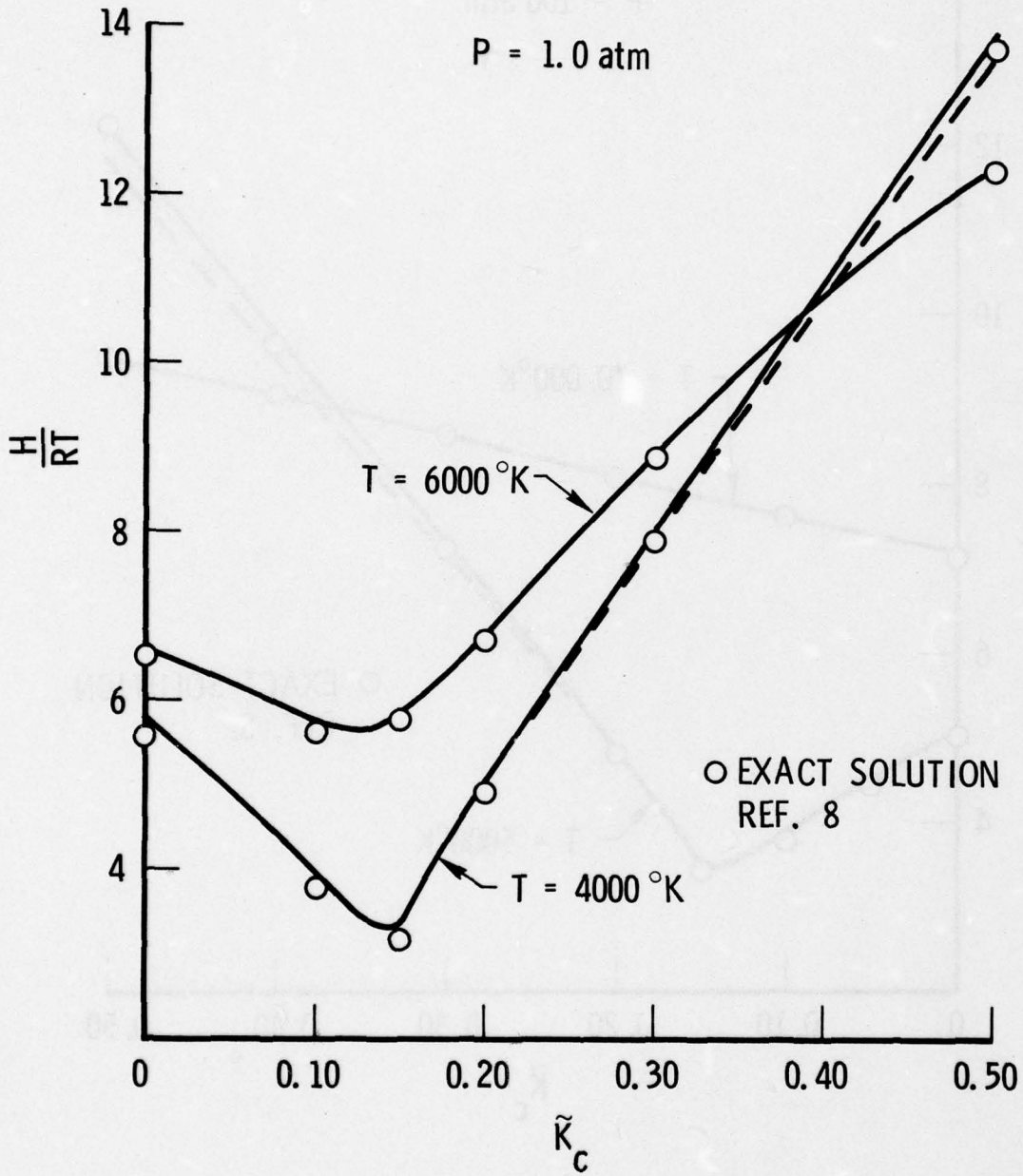


Fig. 8b. Influence of Carbon Mass Fraction on Enthalpy of a Carbon-Air Mixture

The mixture composition is presented in Figs. 9a through 9d for a temperature of 5000°K and pressures of 1.0 and 100.0 atmospheres. Again, the largest error for the dominant species is about 20 percent. The error may be much larger for small species mass fraction (less than one-tenth), but these exert no appreciable influence on the mixture properties.

It is apparent that the errors are smaller for the lower pressure. This is because the assumptions and approximations utilized in the model are inherently more accurate at low pressures. That is, the neglect of nitric oxide and C_4N_2 is an increasingly good approximation as the pressure decreases. The ratio of cyano to cyanogen will increase as the pressure decreases. This improves the accuracy because the calculation for cyano is more accurate than that for cyanogen. Finally, the presumption that the reactions may be uncoupled from one another and treated separately becomes a progressively better approximation as the pressure is lowered.

Figures 9a through 9d demonstrate quite clearly that the partitioning of the problem into two distinct physical regimes (denoted as oxygen- or carbon-rich) is an excellent approximation. It is obvious that the character of the solution changes completely as \tilde{K}_C approaches $1/7$ (the boundary between oxygen- and carbon-rich. As the boundary is approached from small values of \tilde{K}_C , the oxygen is absorbed into CO, and the free oxygen vanishes. As the boundary is approached from large values of \tilde{K}_C , the carbon-nitrogen and carbon sublimation species vanish, and the carbon is bound up in CO. It was also assumed that the carbon sublimation species would vanish faster than the carbon-nitrogen compounds as the oxygen-rich boundary was approached. This is indeed seen to be the case. Finally, it was assumed that CO would always form to the maximum possible extent, subject to the availability of carbon and oxygen. At the boundary between the oxygen- and carbon-rich domains, the formation of CO is unconstrained by the available carbon or oxygen and will reach its maximum value (for a given pressure and temperature). It is apparent from Figs. 9a and 9c that CO does indeed reach its maximum value at $\epsilon = 0$.

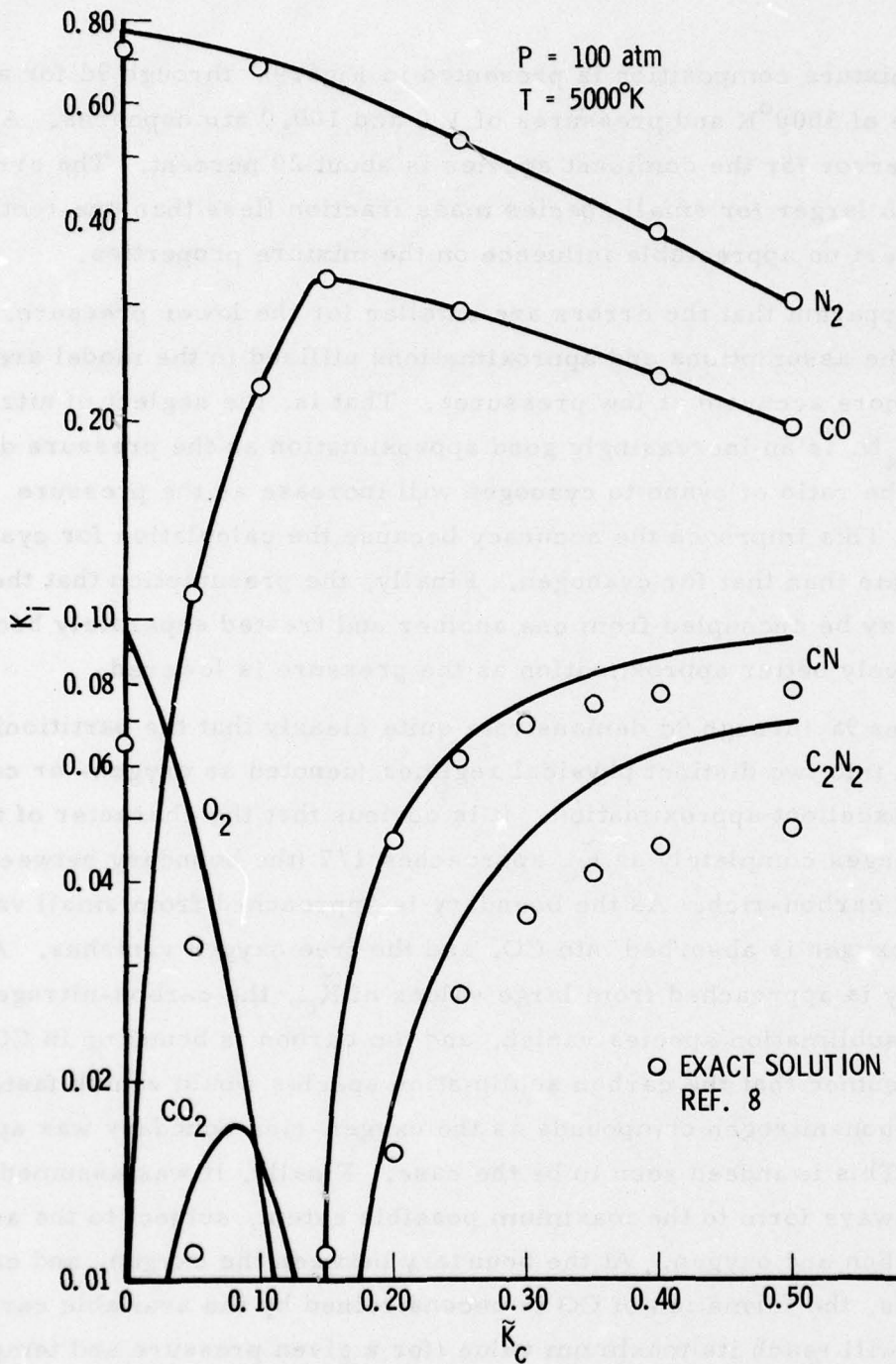


Fig. 9a. Influence of Carbon Mass Fraction on Species Mass Fractions for a Carbon-Air Mixture

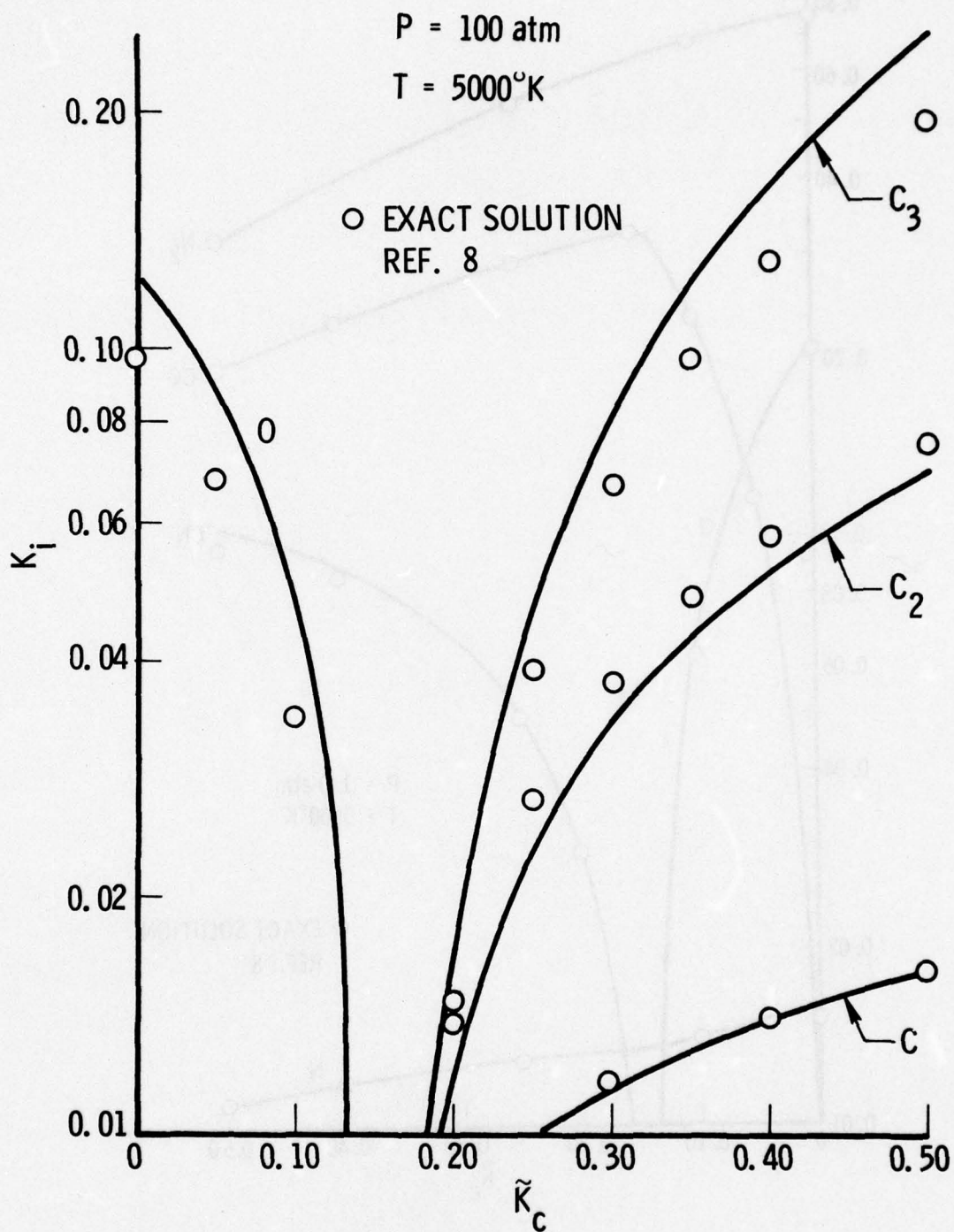


Fig. 9b. Influence of Carbon Mass Fraction on Species Mass Fractions for a Carbon-Air Mixture

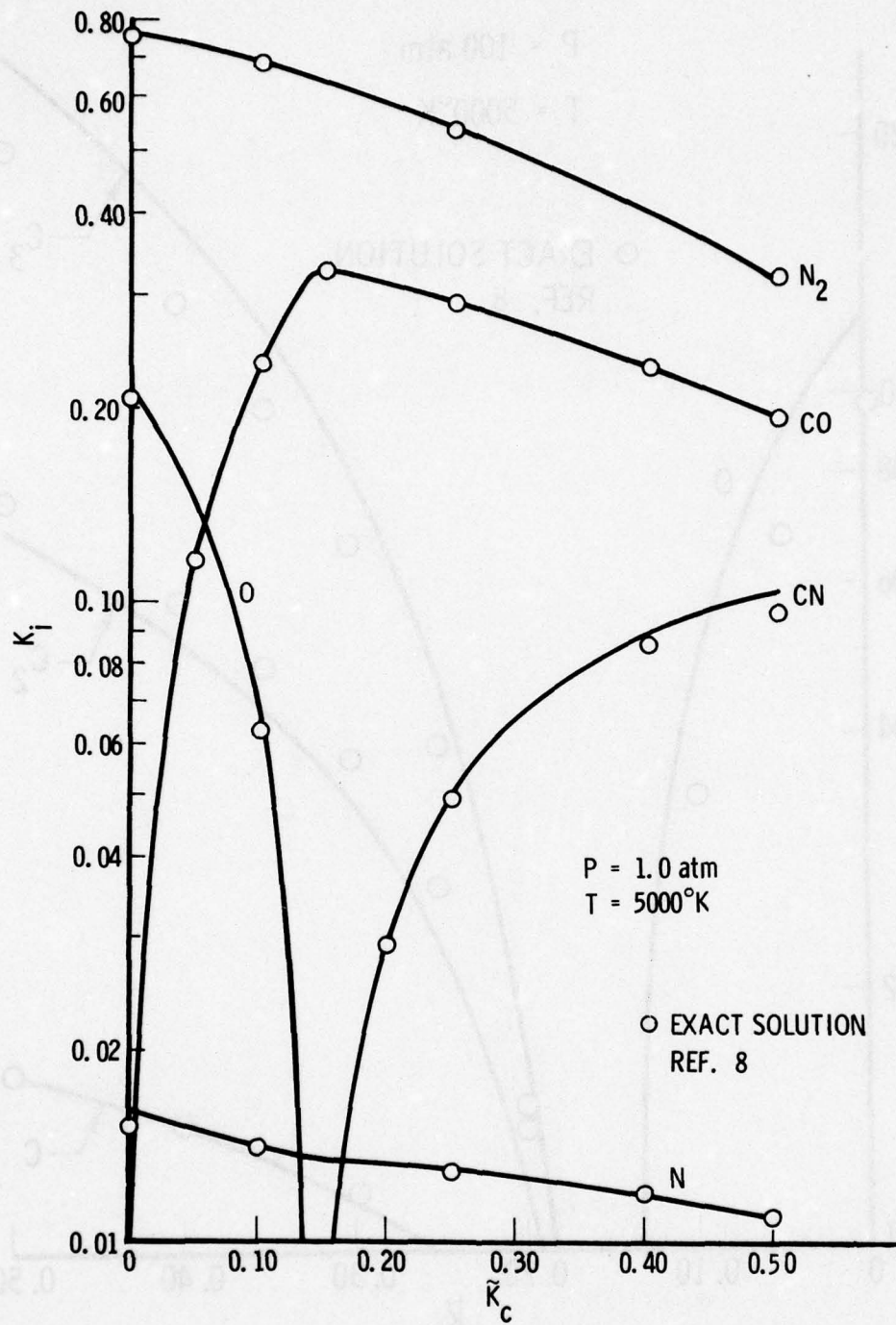


Fig. 9c. Influence of Carbon Mass Fraction on Species Mass Fractions for a Carbon-Air Mixture

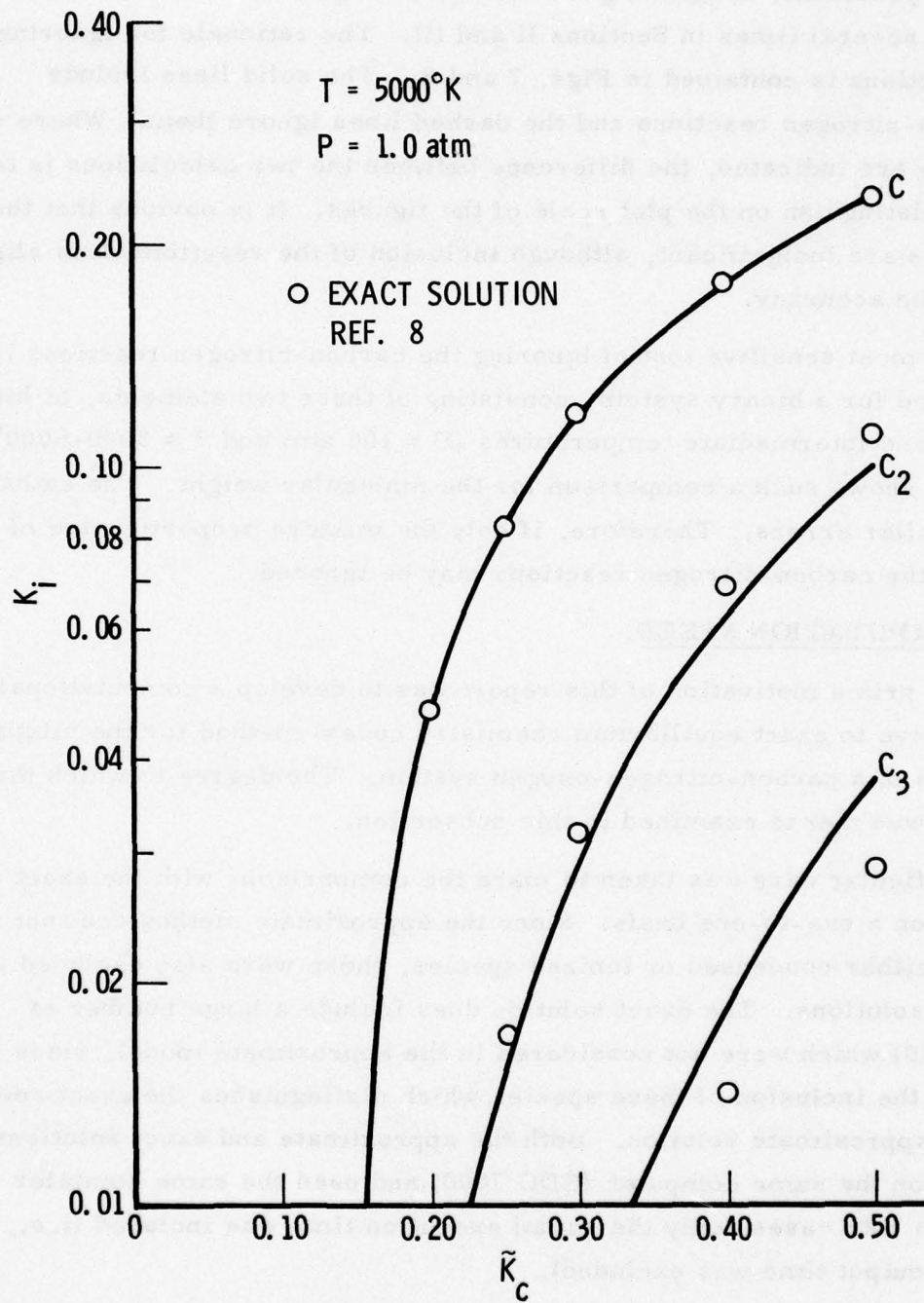


Fig. 9d. Influence of Carbon Mass Fraction on Species Mass Fractions for a Carbon-Air Mixture

The possibility of ignoring the carbon-nitrogen reactions has been alluded to several times in Sections II and III. The rationale for ignoring these reactions is contained in Figs. 7 and 8. The solid lines include the carbon-nitrogen reactions and the dashed lines ignore them. Where only solid lines are indicated, the difference between the two calculations is too small to distinguish on the plot scale of the figures. It is obvious that the differences are insignificant, although inclusion of the reactions does slightly improve the accuracy.

The most sensitive test of ignoring the carbon-nitrogen reactions is encountered for a binary system, consisting of these two elements, at high pressure and intermediate temperatures ($P = 100$ atm and $T = 5000-6000^{\circ}\text{K}$). Figure 10 shows such a comparison for the molecular weight. The enthalpy shows similar errors. Therefore, if only the mixture properties are of interest, the carbon-nitrogen reactions may be ignored.

B. COMPUTATION SPEED

The prime motivation of this report was to develop a computationally fast (relative to exact equilibrium chemistry codes) method for the mixture properties of a carbon-nitrogen-oxygen system. The degree to which this objective was met is examined in this subsection.

Particular care was taken to make the comparisons with the exact solutions on a one-to-one basis. Since the approximate method does not consider either condensed or ionized species, these were also excluded from the exact solutions. The exact solution does include a large number of species (20) which were not considered in the approximate model, since it is precisely the inclusion of these species which distinguishes the exact solution from the approximate solution. Both the approximate and exact solutions were run on the same computer (CDC 7600) and used the same compiler (FTN). In both cases, only the actual execution time was included (i. e., input and output time was excluded).

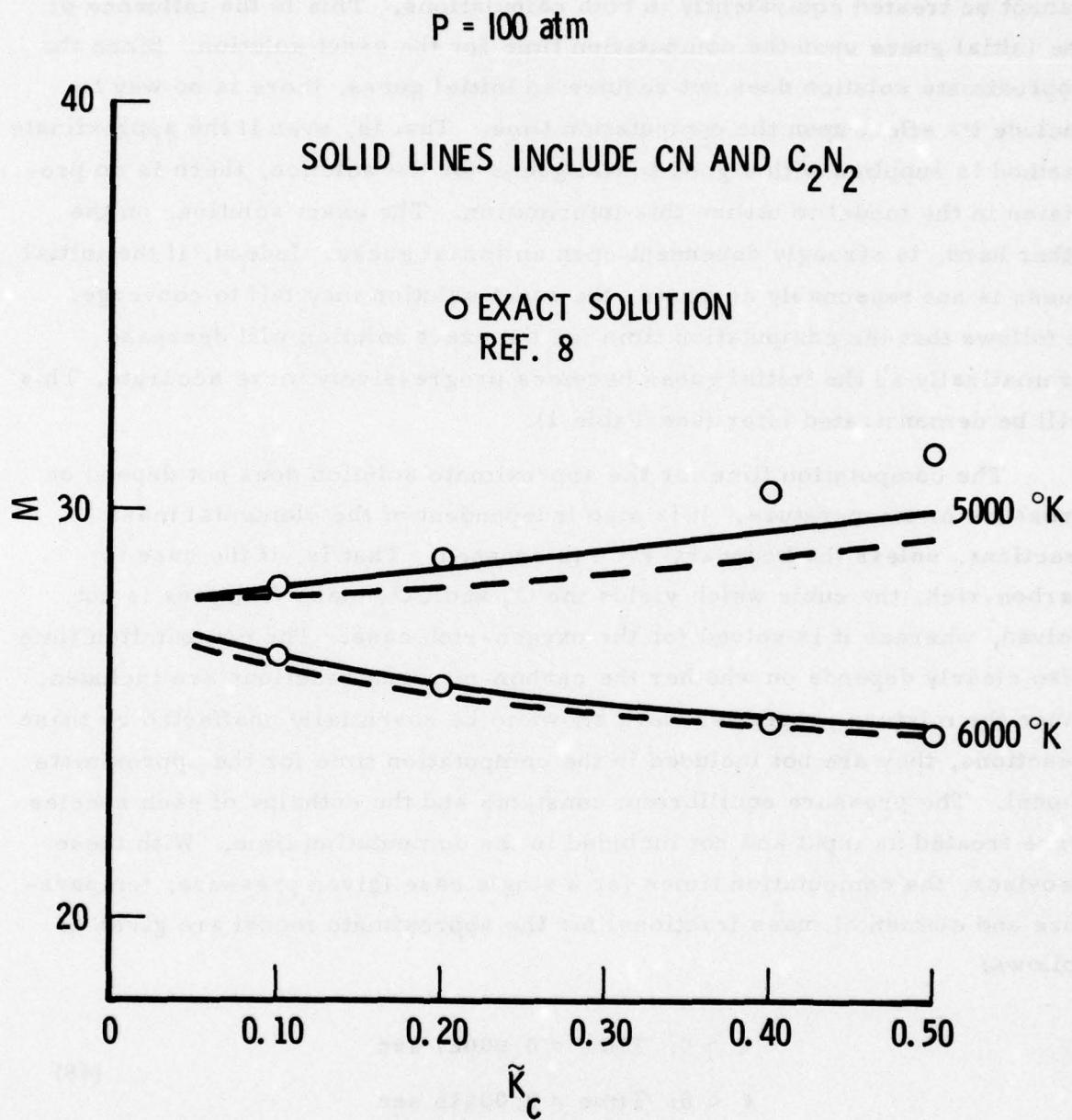


Fig. 10. Influence of Carbon-Nitrogen Reactions on Molecular Weight of a Carbon-Nitrogen Mixture

There is one major difference between the exact and approximate solutions which has a first-order effect on the time comparisons and which cannot be treated equivalently in both calculations. This is the influence of the initial guess upon the computation time for the exact solution. Since the approximate solution does not require an initial guess, there is no way to include its effect upon the computation time. That is, even if the approximate method is supplied with a good initial guess for the solution, there is no provision in the model to utilize this information. The exact solution, on the other hand, is strongly dependent upon an initial guess. Indeed, if the initial guess is not reasonably accurate, the exact solution may fail to converge. It follows that the computation time for the exact solution will decrease dramatically as the initial guess becomes progressively more accurate. This will be demonstrated later (see Table 1).

The computation time for the approximate solution does not depend on pressure or temperature. It is also independent of the elemental mass fractions, unless the boundary $\epsilon = 0$ is crossed. That is, if the case is carbon-rich, the cubic which yields the O_2 and CO_2 mass fractions is not solved, whereas it is solved for the oxygen-rich case. The computation time also clearly depends on whether the carbon-nitrogen reactions are included. Since the mixture properties were shown to be essentially unaffected by these reactions, they are not included in the computation time for the approximate model. The pressure equilibrium constants and the enthalpy of each species were treated as input and not included in the computation time. With these provisos, the computation times for a single case (given pressure, temperature and elemental mass fractions) for the approximate model are given as follows:

$$\begin{aligned} \epsilon > 0: \text{ Time} &= 0.00021 \text{ sec} \\ \epsilon < 0: \text{ Time} &= 0.00016 \text{ sec} \end{aligned} \tag{48}$$

It is emphasized that these computation times are quite conservative, since they were obtained from the development computer code which was not optimized for execution time. If the code is cleaned up, and if only the roots of interest are computed and the FORTRAN coding is optimized, the computation time quoted above could probably be reduced by a factor of two.

The exact calculations were obtained from the NEST (Ref. 8) chemistry code. The computation times were not strongly dependent upon pressure, temperature or elemental mass fractions, and a single condition was chosen for comparative purposes. The comparison is presented for a carbon-air mixture at a pressure of 100 atm and a temperature of 5000°K, with a 50 percent carbon elemental mass fraction.

As discussed above, the major factor influencing the computation time is the accuracy of the initial guess. Therefore, the equilibrium composition for the condition of interest was calculated for various initial guesses. The initial guesses were exact solutions for conditions close to the condition of interest. The computation times for the indicated case are presented in Table 1 as a function of the initial guess.

The first entry in the table uses a preprogrammed initial guess built into the NEST code. The next three entries use initial guesses which are exact solutions for temperatures which differ from 5000°K by varying amounts. These initial guesses have the same carbon mass fraction as the case of interest. As indicated, the computation time is reduced significantly as the initial guess is improved. The last two cases use initial conditions where both the temperature and carbon mass fraction are perturbed about the values for the case of interest. It is seen that a 10 percent change in carbon mass fraction has a significant effect upon the computation time. The initial guesses in the table exhibit the kind of variations encountered during iteration at a boundary layer mesh point. A comparison of the results of Eq. (48) with Table 1 indicates the analytic solution of this report will reduce the computation time by two or three orders of magnitude, depending upon the accuracy of the initial guess available to the exact solution. For typical chemically reacting boundary layer calculations, a reduction in computation time of the order of 500 is a reasonable expectation.

Table 1. Computation Time for Exact Solution of Carbon-Air Gas Mixture

$$P = 100 \text{ atm}$$

$$T = 5000^{\circ}\text{K}$$

$$\tilde{K}_C = 0.50$$

Initial Guess Conditions	Computation Time (sec) for Indicated Case
Not Applicable	0.295
$T = 6000 \quad \tilde{K}_C = 0.50$	0.032
$T = 5500 \quad \tilde{K}_C = 0.50$	0.027
$T = 5100 \quad \tilde{K}_C = 0.50$	0.011
$T = 5500 \quad \tilde{K}_C = 0.45$	0.157
$T = 5100 \quad \tilde{K}_C = 0.45$	0.043

SECTION V
SUMMARY AND CONCLUSIONS

An approximate analytic solution has been developed for the equilibrium composition of a carbon-nitrogen-oxygen gas mixture (including provision for an inert monatomic species). This was accomplished by partitioning the problem into carbon-rich and oxygen-rich domains and then subdividing each domain into high and low temperature regimes. In this manner, the dominant reactions are uncoupled from one another and treated sequentially in pairs. This allows the solution to be expressed in terms of cubics and quartics, both of which possess analytic solutions.

Carbon-nitrogen reactions were included in the formulation and were found to exert a negligible influence on the mixture properties. Ignoring these reactions yields the solution in its simplest form, namely, two cubics and a quartic (for pressure and temperature as independent variables). The solutions are trivial, and there is no ambiguity concerning which is the desired root.

The formulation was carried out for two different sets of independent variables: pressure and temperature, and density and temperature. The use of density as a variable uncoupled the equilibrium relationships from the molecular weight and substantially reduced the algebraic complexity. The uncoupling allowed the solution for the N_2 and CO reactions to be obtained in terms of two uncoupled quadratics instead of the quartic which resulted from the use of pressure as an independent variable. With density as a variable, the solution (ignoring carbon-nitrogen reactions) was obtained in terms of two cubics and two quadratics.

Extensive comparisons were made with exact solutions to determine the accuracy of the approximate solution. The maximum error in mixture properties (molecular weight and enthalpy) was about four percent (ignoring carbon-nitrogen reactions), and generally the error is less than one percent.

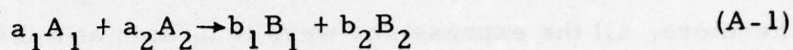
Since the required thermodynamic data (heats of formation, vibrational and rotational constants, etc.) are not known to within five or 10 percent, the difference between the exact and approximate solutions is less than the uncertainty in the input data. In this context, the approximate solution may be regarded as exact.

A detailed examination was made of the computation times for the approximate and exact solutions. It was found that the analytic solution reduces the computation time between two and three orders of magnitude, depending upon the accuracy of the initial guess available to the exact solution. For a boundary layer application, the analytic solution will reduce the computation time required to determine the mixture properties by approximately a factor of 500.

In conclusion, it is believed that the analytic solution of this report represents a significant advance in the ability to handle chemically reacting flows (for a carbon-nitrogen-oxygen-inert system) in a computationally efficient manner, with essentially no loss in accuracy. For fluid dynamics problems of fixed elemental composition, the computation speed is probably competitive with the two-dimensional interpolation required for use with precomputed Mollier diagrams. For this application, the storage requirements for the Mollier diagram may be eliminated. For problems of varying elemental composition, the reduction in calculation time is so great (compared to exact solutions) that the use of the analytic solution essentially eliminates computational constraints imposed by the chemistry.

APPENDIX A
PRESSURE EQUILIBRIUM CONSTANTS

The reactions considered are all of the following form:



where the A_i are the reactants and B_i the products. The pressure equilibrium constant for this reaction is defined in terms of the partial pressures as

$$K_P = \frac{P^{b_1}(B_1) P^{b_2}(B_2)}{P^{a_1}(A_1) P^{a_2}(A_2)} \quad (A-2)$$

The partial pressure of the species A_i is denoted as $P(A_i)$ and is related to the species mass fraction by the following:

$$P(A_i) = MP \frac{K_i}{M_i} \quad (A-3)$$

where P is the pressure and M is the mixture molecular weight.

Substitution of Eq. (A-3) into Eq. (A-2) yields the α_i coefficient which is defined in Section II.

The equilibrium constants are computed from the partition functions as follows:

$$\log K_P = \frac{-\Delta E_0}{RT} + b_1 \log Q_P(B_1) + b_2 \log Q_P(B_2) + \\ - a_1 \log Q_P(A_1) - a_2 \log Q_P(A_2) \quad (A-4)$$

$$\Delta E_0 \equiv b_1 E_0(B_1) + b_2 E_0(B_2) - a_1 E_0(A_1) - a_2 E_0(A_2)$$

where E_0 denotes the heat of formation.

The partition functions are given in Table A-1 for the species of interest. The logarithms are all natural logarithms and the temperatures are in degrees Kelvin. The thermodynamics data was obtained from Refs. 7 and 9. For the diatomic species, the partition functions were simplified by assuming that the rotational and vibrational partition functions for each electronic state are approximately equal to the ground state (Ref. 9). Furthermore, all the expressions were truncated at a level consistent with the temperature range of interest (0-10,000°K).

The values of ΔE_0 are tabulated below for the specific reactions of interest.

K_P	$\frac{\Delta E_0}{R}$ (°K)
1	67190
2	59350
3	128903
4	113228
5	72439
6	87305
7	72763
8	162005
9	75482

9. Horton, T.E., "The Computation of Partition Functions and Thermochemistry Data for Atomic, Ionic, Diatomic and Polyatomic Species," Jet Propulsion Laboratory, TR 32-1425, 1970.

Table A-1. Partition Functions

$$\begin{aligned}
\log Q_P(N) &= 2.5 \log T + 0.30 + \log [4 + 10 \exp(-27660/T)] \\
\log Q_P(O) &= 2.5 \log T + 0.50 + \log [5 + 3 \exp(-229/T) + \exp(-327/T) + 5 \exp(-22830/T)] \\
\log Q_P(C) &= 2.5 \log T + 0.07 + \log [9 + 5 \exp(-14667/T) + \exp(-31147/T)] \\
\log Q_P(O_2) &= 3.5 \log T + 0.12 + \log [3 + 2 \exp(-11341/T) + \exp(-18877/T)] - \log [1 - \exp(-2256/T)] \\
\log Q_P(N_2) &= 3.5 \log T - 0.41 - \log [1 - \exp(-3372/T)] \\
\log Q_P(CN) &= 3.5 \log T + 0.15 + \log [2 + 4 \exp(-13114/T)] - \log [1 - \exp(-2958/T)] \\
\log Q_P(CO) &= 3.5 \log T + 0.32 - \log [1 - \exp(-3103/T)] \\
\log Q_P(C_2) &= 3.5 \log T - 0.54 + \log [1 + 6 \exp(-878/T) + 3 \exp(-8983/T) + 2 \exp(-11896/T) + \\
&\quad + 2 \exp(-14388/T)] - \log [1 - \exp(-2649/T)] \\
\log Q_P(C_3) &= 3.5 \log T + 1.51 - 2 \log [1 - \exp(-719/T)] - \log [1 - \exp(-1870/T)] - \log [1 - \exp(-3165/T)] \\
\log Q_P(C_2N_2) &= 3.5 \log T + 3.04 - 2 \log [1 - \exp(-325/T)] - 2 \log [1 - \exp(-728/T)] \\
&\quad - \log [1 - \exp(-1220/T)] - \log [1 - \exp(-3092/T)] - \log [1 - \exp(-3341/T)] \\
\log Q_P(CO_2) &= 3.5 \log T + 1.90 - 2 \log [1 - \exp(-960/T)] - \log [1 - \exp(-1932/T)] \\
&\quad - \log [1 - \exp(-3380/T)] \\
\log Q_P(NO) &= 3.5 \log T + 0.55 + \log [2 + 2 \exp(-174/T)] - \log [1 - \exp(-2719/T)]
\end{aligned}$$

APPENDIX B
SOLUTION FOR CO₂ AND O₂ REACTIONS

The solution for the equation set of Subsection II-A-1 is presented in this appendix. The following variables are defined:

$$\begin{aligned} X &\equiv MK_{CO} \\ Y &\equiv MK_O \end{aligned} \tag{B-1}$$

Substitution of these variables into Eqs. (4) through (6) yields a cubic in Y

$$\begin{aligned} AY^3 + BY^2 + CY + \frac{16}{7}\epsilon &= 0 \\ \lambda &\equiv \tilde{K}_C + \frac{3}{7}\tilde{K}_N + 12\frac{\tilde{K}_I}{M_I} \\ A &\equiv \frac{\alpha_2}{11}\sqrt{\alpha_1\alpha_2}\left(\tilde{K}_C - \frac{3}{8}\tilde{K}_O - \lambda\right) \\ B &\equiv \frac{\sqrt{\alpha_1\alpha_2}}{11}\left(\tilde{K}_C - \lambda - \epsilon\right) - \frac{\alpha_2}{14}(2\lambda + \epsilon) \\ C &\equiv \frac{32}{11}\sqrt{\alpha_1\alpha_2}\left(\frac{3}{8}\tilde{K}_O - \tilde{K}_C\right) - \frac{1}{7}(\lambda + \epsilon) \end{aligned} \tag{B-2}$$

After the cubic is solved, X is obtained from

$$X = \frac{\tilde{K}_C(Y + \alpha_2 Y^2)}{\frac{4}{7}\epsilon + \frac{3}{11}Y\sqrt{\alpha_1\alpha_2}\left(\tilde{K}_O - \frac{8}{3}\tilde{K}_C\right)} \tag{B-3}$$

The molecular weight is computed from

$$M = \frac{1}{\tilde{K}_O} \left[Y + \alpha_2 Y^2 + \frac{4}{7} X + \frac{8}{11} XY \sqrt{\alpha_1 \alpha_2} \right] \quad (\text{B-4})$$

The mass fractions for CO and O are calculated from Eq. (B-1) and the mass fractions of O₂ and CO₂ from Eq. (6) in Subsection II-A-1.

The asymptotic behavior of the above system, for large and small temperatures, is obtained from a knowledge of the behavior of the α coefficients. That is, as the temperature vanishes, the α coefficients become infinite, and as the temperature becomes infinite, the α coefficients vanish. Therefore, as the temperature becomes infinite, Eq. (B-2) yields

$$T \rightarrow \infty: Y = \frac{16\epsilon}{\lambda + \epsilon} \quad (\text{B-5})$$

As the temperature vanishes, Y vanishes and the cubic and linear terms of Eq. (B-2) become predominant. Therefore, the cubic may be solved to yield

$$T \rightarrow 0: \alpha_2 Y^2 = \frac{32 \left(\tilde{K}_C - \frac{3}{8} \tilde{K}_O \right)}{\tilde{K}_C - \frac{3}{8} \tilde{K}_O - \lambda} \quad (\text{B-6})$$

Substitution of Eqs. (B-6) into (B-3) shows that X also vanishes as the temperature does. Then, using Eqs. (B-5) and (B-6), the asymptotic behavior of Eqs. (7) and (8) is obtained.

As ϵ approaches zero, it is obvious that Y must also vanish and, thus, the behavior of Eq. (9) is obtained.

Some comments about the roots of the cubic are in order. The correct root must lie in the range

$$0 \leq Y \leq \frac{16\epsilon}{\lambda + \epsilon} \quad (\text{B-7})$$

For all the cases considered in this report, there was only one root in the allowable range. Generally, there were two negative roots and one positive root. If, for some case, more than one root lies in the allowable range, the correct root should yield a positive value for X.

APPENDIX C
SOLUTION FOR N₂ AND CO REACTIONS

The solution for the set of Eqs. (11) in Subsection II-A-2 is presented in this appendix. The following variables are defined

$$\begin{aligned} X &\equiv K_O M \\ Y &\equiv K_C M \\ Z &\equiv K_N M \end{aligned} \tag{C-1}$$

The equations may be rearranged to yield a quartic in Z.

$$\begin{aligned} AZ^4 + BZ^3 + CZ^2 + DZ + E &= 0 \\ A &\equiv \alpha_3 \alpha_4^2 (\eta_2 + \eta_4)(\eta_2 + \eta_3) \\ B &\equiv \alpha_3 \alpha_4 [(\eta_1 + \eta_3)(\eta_2 + \eta_4) + (\eta_2 + \eta_3)(\eta_1 + \eta_4)] \\ C &\equiv \alpha_3 (\eta_1 + \eta_3)(\eta_1 + \eta_4) - \frac{7}{48} \alpha_4 (\eta_2 + \eta_3 + \eta_4) + \\ &\quad - \alpha_3 \alpha_4 (2\eta_2 + \eta_3 + \eta_4) \\ D &\equiv -\alpha_3 (2\eta_1 + \eta_3 + \eta_4) - \frac{7}{48} (\eta_1 + \eta_3 + \eta_4) \\ E &\equiv \alpha_3 + \frac{7}{48} \end{aligned} \tag{C-2}$$

The η coefficients are defined by

$$\begin{aligned}\eta_1 &\equiv \frac{1}{14} + \frac{\tilde{K}_I}{\tilde{K}_N M_I} \\ \eta_2 &\equiv \frac{1}{28} + \frac{\tilde{K}_I}{\tilde{K}_N M_I} \\ \eta_3 &\equiv \frac{\tilde{K}_O}{16 \tilde{K}_N} \\ \eta_4 &\equiv \frac{\tilde{K}_C}{12 \tilde{K}_N}\end{aligned}\tag{C-3}$$

After solving the quartic for Z , X and Y are calculated from

$$\begin{aligned}Y &= 12 [1 - Z(\eta_1 + \eta_3) - \alpha_4 Z^2(\eta_2 + \eta_3)] \\ X &= 16 [1 - Z(\eta_1 + \eta_4) - \alpha_4 Z^2(\eta_2 + \eta_4)]\end{aligned}\tag{C-4}$$

The molecular weight is calculated from

$$M = \frac{1}{\tilde{K}_N} (Z + \alpha_4 Z^2)\tag{C-5}$$

Equations (C-1) are used to calculate the mass fractions for atomic oxygen, carbon and nitrogen. The remaining mass fractions are calculated from Eq. (11).

Noting that the α coefficients are infinite for zero temperature and zero for infinite temperature, the asymptotic behavior of the equations is examined. As the temperature vanishes, the even power terms of the quartic are dominant and the equation may be recast as a quadratic. That is, define a variable F as

$$F \equiv \alpha_4 Z^2 \quad (C-6)$$

Substitution of this expression into the quartic yields, for vanishing temperature

$$F^2(\eta_2 + \eta_4)(\eta_2 + \eta_3) - F(2\eta_2 + \eta_3 + \eta_4) + 1 = 0 \quad (C-7)$$

The roots are

$$F = \frac{1}{\eta_2 + \eta_3}; \frac{1}{\eta_2 + \eta_4} \quad (C-8)$$

The first root corresponds to the oxygen-rich case and the second to the carbon-rich case. Substitution of Eq. (C-8) into Eq. (C-4) yields

$\epsilon > 0$ (oxygen-rich):

$$Z = 0$$

$$\alpha_4 Z^2 = \frac{1}{\eta_2 + \eta_3}$$

$$Y = 0$$

$$X = 16 \frac{\eta_3 - \eta_4}{\eta_2 + \eta_3} \quad (C-9 \text{ continued})$$

$\epsilon < 0$ (carbon-rich):

$$Z = 0$$

$$\alpha_4 Z^2 = \frac{1}{\eta_2 + \eta_4}$$

$$X = 0$$

$$Y = 12 \frac{\eta_4 - \eta_3}{\eta_2 + \eta_4}$$

The results of Eq. (12) are easily obtained from Eq. (C-9) for vanishing temperature.

As the temperature approaches infinity, the quartic yields

$$Z = \frac{1}{\eta_1 + \eta_3 + \eta_4} \quad (\text{C-10})$$

This result is used in Eqs. (C-4) and (C-5) to obtain the value of Eq. (13).

The correct root of the quartic lies in the range

$$0 \leq Z \leq \frac{1}{\eta_1 + \eta_3 + \eta_4} \quad (\text{C-11})$$

Since an analytic solution for a quartic exists, there is no difficulty in obtaining the four roots. The analytic solution is only slightly more complex than that of a cubic and requires negligible computation time to obtain the roots. At high temperature, only one root lies in the allowable range. However, at low to moderate temperatures, there are two roots in the allowable range (one for $\epsilon > 0$ and one for $\epsilon < 0$). The correct root is that value which yields positive values for X and Y. For the cases considered in this report, there were generally two positive and two negative roots. When two positive roots are in the allowable range of Eq. (C-11), it is obvious from Eqs. (C-4) that the correct root is the smaller of the two values.

Solution for $\tilde{K}_N = 0$:

It is apparent that the above equations are singular if the nitrogen elemental mass fraction is zero. Thus, for $\tilde{K}_N = 0$, the CO dissociation reaction is considered separately. The solution is obtained in terms of the following quadratic:

$$\begin{aligned}
 AY^2 + BY - \tilde{K}_C &= 0 \\
 A &\equiv \frac{4}{7} \alpha_3 \left(\frac{\tilde{K}_C}{12} + \frac{\tilde{K}_I}{M_I} \right) \\
 B &\equiv \frac{4}{7} \alpha_3 \epsilon + \frac{\tilde{K}_C}{12} + \frac{\tilde{K}_O}{16} + \frac{\tilde{K}_I}{M_I}
 \end{aligned}
 \tag{C-12}$$

At low temperatures, the plus sign is used with the quadratic solution radical for the oxygen-rich branch and the minus sign for the carbon-rich solution. At high temperatures only one positive root exists, and it is the solution.

The molecular weight is calculated from

$$M = \frac{1 - \frac{Y}{12}}{\frac{\tilde{K}_O}{16} + \frac{\tilde{K}_I}{M_I}}
 \tag{C-13}$$

After K_C is calculated from these results, the mass fractions for atomic oxygen and carbon monoxide are easily obtained from the elemental mass balances.

It is noted that the limiting behavior of this system, for large and small temperatures, is exactly that of Eqs. (12) and (13).

APPENDIX D
SOLUTION FOR N₂ AND CN REACTIONS

In this appendix, the solution of Eqs. (15) in Subsection II-B-1 is obtained. Transformed variables are defined as

$$\begin{aligned} Y &\equiv K_C M \\ Z &\equiv K_N M \end{aligned} \tag{D-1}$$

The solution is obtained in terms of a quartic

$$\begin{aligned} AZ^4 + BZ^3 + CZ^2 + DZ + E &= 0 \\ A &\equiv \alpha_5 \alpha_4^2 \eta_4^2 - \frac{42}{169} \alpha_4 \alpha_6^2 \eta_4^2 \\ B &\equiv 2 \alpha_4 \alpha_5 \eta_4 \eta_5 - \frac{42}{169} \eta_1 \eta_4 \alpha_6^2 - \frac{7}{13} \alpha_4 \alpha_6 \eta_4 (2\eta_3 + \eta_1) \\ C &\equiv \alpha_5 \eta_5^2 - 2 \alpha_4 \alpha_5 \eta_4 - \frac{\alpha_4}{24} (\eta_3 + \eta_4) + \\ &\quad + \frac{1176}{169} \alpha_6^2 \eta_4 (\eta_1 - \eta_4) - \frac{7}{13} \alpha_6 (2\eta_3 \eta_4 + \eta_1 \eta_5) \\ D &\equiv \frac{\eta_1}{24} - 2\eta_5 \alpha_5 + \frac{7}{13} \eta_1 \alpha_6 - \frac{\eta_5}{12} \\ E &\equiv \alpha_5 + \frac{1}{24} \end{aligned} \tag{D-2}$$

The η coefficients are defined by

$$\begin{aligned}\eta_1 &\equiv \frac{1}{14} + \frac{\tilde{K}_I}{\tilde{K}_N M_I} + \frac{\beta_2}{\tilde{K}_N} \\ \eta_2 &\equiv \eta_1 - \frac{1}{28} \\ \eta_3 &\equiv \frac{\tilde{K}_C - \beta_1}{24 \tilde{K}_N} \\ \eta_4 &\equiv \eta_2 + \eta_3 \\ \eta_5 &\equiv \eta_1 + \eta_3\end{aligned}\tag{D-3}$$

After the quartic is solved for Z , the following expressions are used to calculate Y and M .

$$\begin{aligned}Y &= \frac{24(1 - \eta_5 Z - \eta_4 \alpha_4 Z^2)}{1 + \frac{168}{13} \eta_4 \alpha_6 Z} \\ M &= \frac{1}{\tilde{K}_N} \left[Z + \alpha_4 Z^2 + \frac{7}{13} \alpha_6 YZ \right]\end{aligned}\tag{D-4}$$

After Eqs. (D-1) are used to obtain the mass fractions of atomic nitrogen and carbon, the remaining mass fractions are obtained from Eqs. (15).

The asymptotic behavior of the system, at low temperatures, is again obtained from the knowledge that the α coefficients become infinite as the temperature vanishes. It is also necessary to know the relative rates at which the α coefficients become infinite. The results of Appendix A are used to obtain the following expression:

$$T \rightarrow 0: \frac{\alpha_6^2}{\alpha_4 \alpha_5} = 0 \quad (\text{D-5})$$

When the substitution $F = \alpha_4 Z^2$ is used, the quartic becomes a quadratic at low temperatures and may be solved directly for F. Both roots of the quadratic are equal and yield

$$F = \frac{1}{\eta_4} \quad (\text{D-6})$$

Thus, in contrast to the results of Appendix C for the N_2 and CO reactions, only one valid solution branch exists at low temperatures.

Using the result for F yields, as the temperature vanishes

$$Y = 0 \quad (\text{D-7})$$

$$\alpha_6 YZ = 0$$

As the temperature becomes infinite, the quartic is linear in Z and yields

$$Z = \frac{1}{\eta_3 + \eta_5} \quad (\text{D-8})$$

With the above expressions, the limiting behavior of Eqs. (17) in Subsection II-B-1 is easily obtained.

As before, the correct root of the quartic lies between the values for the two temperature extremes. That is

$$0 \leq Z \leq \frac{1}{\eta_3 + \eta_5} \quad (\text{D-9})$$

For the cases considered in this report, there were generally two positive roots in the allowable range. Again, the correct root yields a positive value for Y. From Eq. (D-4) it is apparent that the correct root will be the smaller of the two roots in the allowable range.

APPENDIX E
SOLUTION FOR C₂ AND C₃ REACTIONS

The solution of Eqs. (22) in Subsection II-B-3 is obtained in this appendix. The transformed variable is defined by

$$Y \equiv K_C M \quad (E-1)$$

The equations yield the following cubic:

$$\begin{aligned} AY^3 + BY^2 + CY + D &= 0 \\ A &\equiv \alpha_8 \left(\beta_5 + \frac{\tilde{K}_I}{M_I} + \frac{\tilde{K}_C - \beta_4}{36} \right) \\ B &\equiv \alpha_5 \left(\beta_5 + \frac{\tilde{K}_I}{M_I} + \frac{\tilde{K}_C - \beta_4}{24} \right) \\ C &\equiv \beta_5 + \frac{\tilde{K}_I}{M_I} + \frac{\tilde{K}_C - \beta_4}{12} \\ D &\equiv \beta_4 - \tilde{K}_C \end{aligned} \quad (E-2)$$

The molecular weight is obtained from

$$M = \frac{1}{\tilde{K}_C - \beta_4} \left[Y + \alpha_5 Y^2 + \alpha_8 Y^3 \right] \quad (E-3)$$

After solving the above equations for the atomic carbon mass fraction, the mass fractions for C₂ and C₃ are calculated from the equilibrium relationships of Eqs. (22).

The asymptotic behavior as the temperature vanishes is determined from the knowledge that the α coefficients become infinite. The following result is required and may be obtained from the pressure equilibrium constants of Appendix A.

$$T \rightarrow 0: \frac{\alpha_5}{\alpha_8^{2/3}} = 0 \quad (\text{E-4})$$

The cubic yields, for vanishing temperature

$$\alpha_8 Y^3 = \frac{\tilde{K}_C - \beta_4}{\beta_5 + \frac{\tilde{K}_I}{M_I} + \frac{\tilde{K}_C - \beta_4}{36}} \quad (\text{E-5})$$

It is obvious from this result that the mass fraction of C_3 remains finite as the temperature vanishes. To obtain the low temperature limit of Eq. (24), the behavior of β_4 must be known. From the preceding reactions, β_4 has the following behavior:

$$T \rightarrow 0: \beta_4 = \frac{3}{4} \tilde{K}_O \quad (\text{E-6})$$

As the temperature becomes infinite, the cubic yields

$$Y = \frac{-D}{C} \quad (\text{E-7})$$

With these results, the behavior of Eq. (24) is easily obtained.

The only remaining limit of interest occurs for the situation where β_4 approaches \tilde{K}_C . This indicates that all the carbon is contained in CO and the carbon-nitrogen compounds and is not available for the formation of C_2 and C_3 . Thus, for $\beta_4 \geq \tilde{K}_C$, the mass fractions for C_2 and C_3 are zeroed and the cubic is not solved.

The correct root of the cubic lies in the range defined by

$$0 \leq Y \leq \frac{-D}{C} \quad (\text{E-8})$$

At low temperatures there is only one real root, whereas at high temperatures there are three real roots, of which only one lies in the allowable range.

APPENDIX F

NITROGEN-OXYGEN SYSTEM

As mentioned earlier, the analysis of Sections II and III yields an approximate model for the nitrogen-oxygen system if the carbon elemental mass fraction is zero. If pressure is the independent variable, the approximations consist of ignoring the formation of nitric oxide and uncoupling the N_2 and O_2 dissociation reactions. If density is the variable, no approximations are required to uncouple the reactions. Again, nitric oxide is ignored.

These approximations have been used by several investigators to obtain analytic solutions for the mixture properties of air with generally good results. There are, however, situations in which these assumptions begin to influence the results (particularly at high pressures). It is the purpose of this appendix to determine the equilibrium composition of a nitrogen-oxygen system in as general a manner as possible within the constraint of obtaining an analytic solution. As before, this restriction requires the solution to be expressed in terms of a polynomial of fourth order or less. The formulation is first carried out using pressure and temperature as the independent variables. Following this, the problem is reformulated using density and temperature as the independent variables.

1. PRESSURE AND TEMPERATURE AS INDEPENDENT VARIABLES

Hansen (Ref. 1) and Mikhailov (Ref. 3) ignored the formation of nitric oxide and treated the oxygen and nitrogen dissociation reactions sequentially to obtain the properties of air. No provision was made for the inclusion of an inert species. The solution was obtained in the form of quadratic equations. Although Hansen's and Mikhailov's results are specifically for air, they are easily generalized to other nitrogen-oxygen ratios.

The present solution includes nitric oxide, treats all the reactions simultaneously and includes an inert species. To the author's knowledge, the present solution is the most general analytic solution available for a nitrogen-oxygen system. The penalty for this generality is that the solution is obtained in terms of a quartic equation instead of a quadratic. Since Hansen's and Mikhailov's results are quite accurate for most applications, the present solution would be used only at high pressures (greater than 100 atmospheres) or if one were interested in the NO mass fraction.

The elemental mass balances are given by

$$\begin{aligned}\tilde{K}_O &= K_O + K_{O_2} + \frac{16}{30} K_{NO} \\ \tilde{K}_N &= K_N + K_{N_2} + \frac{14}{30} K_{NO} \\ \tilde{K}_I &= K_I\end{aligned}\tag{F-1}$$

The elemental mass fractions (denoted by a superscript tilde) are presumed known and must sum to unity.

The equilibrium relationships are

$$\begin{aligned}K_{O_2} &= \alpha_2 M K_O^2 \\ K_{N_2} &= \alpha_4 M K_N^2 \\ K_{NO} &= \alpha_9 M K_O K_N \\ \alpha_9 &\equiv \frac{15 P}{112 K_{P_9}}\end{aligned}\tag{F-2}$$

The other α coefficients are defined in the main text. The pressure equilibrium constant K_{P_9} is defined for the reaction given by



The molecular weight is given by

$$\frac{1}{M} = \frac{K_{\text{O}}}{16} + \frac{K_{\text{O}_2}}{32} + \frac{K_{\text{N}}}{14} + \frac{K_{\text{N}_2}}{28} + \frac{K_{\text{NO}}}{30} + \frac{K_{\text{I}}}{M_{\text{I}}} \quad (\text{F-4})$$

Transformed variables are defined by

$$\begin{aligned} X &\equiv MK_{\text{O}} \\ Y &\equiv MK_{\text{N}} \end{aligned} \quad (\text{F-5})$$

The above equations may be combined to yield the solution in the form of a quartic.

$$AX^4 + BX^3 + CX^2 + DX + E = 0$$

$$A \equiv \alpha_4 \alpha_2^2 - \frac{56}{225} \alpha_2 \alpha_9^2$$

$$\begin{aligned} B \equiv & 2 \alpha_2 \alpha_4 (1 + \lambda_1) + \frac{56}{225} \alpha_9^2 (\lambda_2 - \lambda_1 - 1) + \\ & - \frac{8}{15} \alpha_2 \alpha_9 (1 + \lambda_1 + \lambda_2) \end{aligned}$$

$$\begin{aligned} C \equiv & \frac{8}{15} \alpha_9 \left[\lambda_2 (\lambda_1 - 1) - (\lambda_1 + 1)^2 \right] + \\ & + \frac{1792}{225} \alpha_9^2 (\lambda_1 - \lambda_2) - \frac{8}{7} \alpha_2 \lambda_1 (1 + \lambda_2) + \\ & - 64 \alpha_2 \alpha_4 \lambda_1 + \alpha_4 (1 + \lambda_1)^2 \end{aligned} \quad (\text{F-6 continued})$$

$$D \equiv \frac{256}{15} \lambda_1 \alpha_9 (1 + \lambda_1 - 2\lambda_2) - 64 \alpha_4 \lambda_1 (1 + \lambda_1) +$$

$$- \frac{8}{7} \lambda_1 (1 + \lambda_1 + \lambda_2)$$

$$E \equiv 256 \lambda_1^2 \left(4\alpha_4 + \frac{1}{7} \right)$$

The λ coefficients are given by

$$\beta \equiv \frac{\tilde{K}_O}{16} + \frac{\tilde{K}_N}{14} + \frac{2 \tilde{K}_I}{M_I}$$

$$\lambda_1 \equiv \frac{\tilde{K}_O}{16\beta} \quad (\text{F-7})$$

$$\lambda_2 \equiv \frac{\tilde{K}_N}{14\beta}$$

After solving the quartic for X, the transformed variable Y and molecular weight are obtained from

$$\alpha_4 Y^2 + Y \left(1 + \lambda_2 + \frac{7}{15} \alpha_9 X \right) + \frac{\tilde{K}_N}{\beta} \left(\frac{X}{16} - 2 \right) = 0 \quad (\text{F-8})$$

$$M = \frac{1}{\beta} \left(2 - \frac{X}{16} - \frac{Y}{14} \right)$$

The limiting behavior, for large and small temperatures, is given by

$$T \rightarrow 0: \alpha_2 X^2 = \frac{2 \tilde{K}_O}{\beta} \quad (\text{F-9})$$

$$T \rightarrow \infty: X = \frac{32 \lambda_1}{1 + \lambda_1 + \lambda_2}$$

From these results, it is easily seen that the mass fraction of nitric oxide vanishes at high and low temperatures. At low temperatures the nitrogen and oxygen are bound up in molecular form and are contained in atomic form at high temperatures.

The solution for X is not monotonic between the temperature extremes. Therefore, an upper bound for X may be defined by using the maximum values for K_O and the molecular weight. The correct root lies in the following range:

$$0 \leq X \leq 2 \frac{\tilde{K}_O}{\beta} \quad (\text{F-10})$$

If more than one positive root lies in the allowable range, the correct value will be the smallest root (i. e., that root which yields a positive value for Y).

2. DENSITY AND TEMPERATURE AS INDEPENDENT VARIABLES

Hochstim (Ref. 2) has obtained the most general solution for this set of independent variables. The solution included nitric oxide and treated the reactions simultaneously. Thus, Hochstim's solution is an exact analog of that obtained above for given pressure and temperature. Since the molecular weight is not required for the determination of the mass fractions (for specified density and temperature), the inert species has no influence on the solution until the molecular weight is calculated.

In the following, the only difference between this analysis and Hochstim's is that here the solution is specified explicitly in terms of a quartic, whereas his solution was presented as two coupled quadratics which were solved iteratively.

The molecular weight in the equilibrium relationships of Eq. (F-2) is absorbed in a new set of $\tilde{\alpha}_i$, given by

$$\begin{aligned}\tilde{\alpha}_2 &= M \alpha_2 \\ \tilde{\alpha}_4 &= M \alpha_4 \\ \tilde{\alpha}_9 &= M \alpha_9\end{aligned}\tag{F-11}$$

The $\tilde{\alpha}_i$ contain the product of pressure and molecular weight. The ideal gas law equates this product to the product of density, temperature and universal gas constant. Since density and temperature are given, the product of pressure and molecular weight is known; therefore, the $\tilde{\alpha}_i$ are known quantities.

Use of the $\tilde{\alpha}_i$ in the equilibrium relationships and substitution into Eqs. (F-1) yields the solution in the form of a quartic.

$$\begin{aligned}AK_O^4 + BK_O^3 + CK_O^2 + DK_O + \tilde{\alpha}_4 \tilde{K}_O^2 &= 0 \\ A \equiv \tilde{\alpha}_4 \tilde{\alpha}_2^2 - \frac{56}{225} \tilde{\alpha}_2 \tilde{\alpha}_9^2 \\ B \equiv 2 \tilde{\alpha}_2 \tilde{\alpha}_4 - \frac{56}{225} \tilde{\alpha}_9^2 - \frac{8}{15} \tilde{\alpha}_2 \tilde{\alpha}_9 \\ C \equiv \tilde{\alpha}_4 - 2 \tilde{\alpha}_2 \tilde{\alpha}_4 \tilde{K}_O + \frac{56}{225} \tilde{\alpha}_9^2 \tilde{K}_O + \\ &\quad - \frac{8}{15} \tilde{\alpha}_9 - \frac{64}{225} \tilde{\alpha}_9^2 \tilde{K}_N \\ D \equiv \frac{8}{15} \tilde{\alpha}_9 \tilde{K}_O - 2 \tilde{\alpha}_4 \tilde{K}_O\end{aligned}\tag{F-12}$$

After the quartic for K_O is solved, the nitrogen mass fraction is obtained from

$$\tilde{\alpha}_4 K_N^2 + K_N \left(1 + \frac{7}{15} \tilde{\alpha}_9 K_O \right) - \tilde{K}_N = 0 \quad (\text{F-13})$$

3. RESULTS

The analytic solution of Subsection F-1 was compared with an exact solution (Ref. 8) for argon free air. The air was composed of 20 percent O_2 and 80 percent N_2 by volume. This corresponds to the following mass fractions:

$$\tilde{K}_O = 0.2222$$

$$\tilde{K}_N = 0.7778$$

The species mass fractions are compared in Fig. F-1, where the solid lines are the solution of Subsection F-1 and the symbols denote the exact solution. The agreement is seen to be excellent.

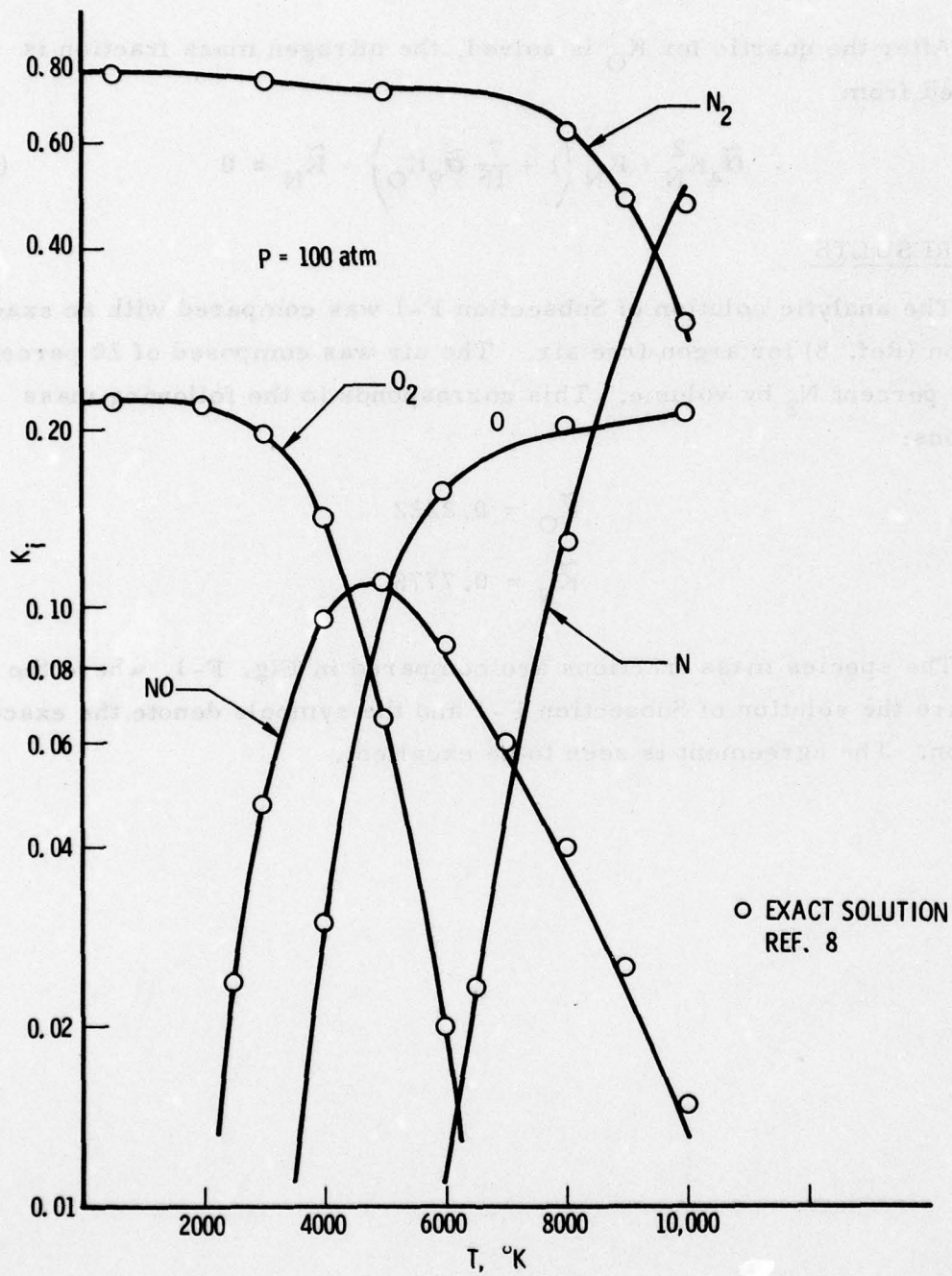


Fig. F-1. Comparison of Species Mass Fractions for Air