NASA TECHNICAL NOTE

NASA TN D-4747

NASA TN D-4747

A SIMPLIFIED EQUILIBRIUM HYDROCARBON-AIR COMBUSTION GAS MODEL FOR USE IN AIR-BREATHING ENGINE CYCLE COMPUTER PROGRAMS

by Vincent R. Mascitti

Langley Research Center
Langley Station, Hampton, Va.

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • SEPTEMBER 1968

NASA TN D-4747

A SIMPLIFIED EQUILIBRIUM HYDROCARBON-AIR COMBUSTION GAS MODEL FOR USE IN AIR-BREATHING ENGINE CYCLE COMPUTER PROGRAMS

By Vincent R. Mascitti

Langley Research Center
Langley Station, Hampton, Va.

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

For sale by the Clearinghouse for Federal Scientific and Technical Information
Springfield, Virginia 22151 – CFSTI price $3.00

A SIMPLIFIED EQUILIBRIUM HYDROCARBON-AIR COMBUSTION GAS MODEL FOR USE IN AIR-BREATHING ENGINE CYCLE COMPUTER PROGRAMS

By Vincent R. Mascitti
Langley Research Center

SUMMARY

This paper presents a simplified hydrocarbon-air combustion gas model, including the effects of dissociation, for convenient use in engine cycle computer programs. The generalized model reduces to the hydrogen-air system as well as to the dissociating-air system. The exclusion of chemical species containing atomic nitrogen allows a considerable simplification of the composition equations. The thermodynamic properties of stoichiometric combustion of the kerosene-air and hydrogen-air systems are computed with the simplified model and compared with those of more comprehensive gas models. In addition, the effect of the neglected chemical species on the performance of an idealized subsonic combustion ramjet is presented. The simplified gas model has been used to define the limiting conditions for solid carbon and ammonia formation for fuel-rich gas mixtures. A computer program listing of the calculation procedure for the simplified gas model is presented.

INTRODUCTION

The current interest in supersonic and hypersonic vehicles has emphasized the need for an accurate yet convenient method of calculation of the thermodynamic properties of combustion gas mixtures. At high temperatures considerable iteration difficulties arise in calculating the chemical composition and thermodynamic properties of combustion gas mixtures, difficulties which stem from the phenomenon of internal energy excitation of the species coupled with chemical dissociation.

In the past, methods such as the method presented in reference 1 have been used to calculate the thermodynamic properties of combustion gases for air-breathing engine cycle computations. The method of reference 1 is based on separate calculations of thermodynamic properties of air and the products of combustion of a stoichiometric fuel-air mixture. It is assumed that the properties of the combustion products for any fuel-air ratio that is less than stoichiometric may be obtained by linear interpolation between the two extreme cases. Results of this method are exact for no dissociation. Application of this method to conditions in which dissociation occurs will only give approximate results. The deviation from an exact calculation is small for turbojet or turbofan calculations since temperatures are relatively low and dissociation is not extensive. However, the high operating temperatures of hypersonic engine cycles may result in extreme dissociation and cause large errors in calculated engine performance.

The method of reference 1 does not allow engine cycle calculations for equivalent ratios above unity. However, at high Mach number flight, the fuel required to cool aerodynamic surfaces and engine components may force engine operation into this region.

In short, the method of reference 1 does not provide a sufficiently general basis for engine cycle calculations under all conditions of current and future interest.

Chemical equilibrium theory which governs dissociation phenomenon has been formulated for many years (for example, ref. 2). However, its application to complex combustion gas mixtures has proved so tedious and complicated as to preclude direct use in engine cycle computer programs. The combustion gas models of references 3 and 4, which serve as a basis of comparison for the simplified gas model presented herein, are elaborate treatments of the hydrogen-air and kerosene-air systems.

The generalized hydrogen-air model of reference 3 assumes 12 chemical species requiring eight independent chemical reactions leading to eight equilibrium expressions. Since the initial proportions of hydrogen and air define four mass balance equations, the mathematical solution (12 equations and 12 unknowns) is demonstrated. The reduction of the system of equations to one equation and one unknown, as recommended in reference 5, is extremely tedious. With the exclusion of the technique of reference 5, solution of this system by a single-level iteration is eliminated. The adoption of a two-level iteration or one of the methods summarized in reference 6 to solve for gas composition has a great effect on the utility of the computation procedure as a subroutine for an engine cycle computer program. Consequently, the most efficient means of representing the thermodynamic properties of these gas models in an engine cycle program is by an elaborate system of fitted curves which sacrifices both computer storage and accuracy.

The purpose of the simplified gas model presented herein is to incorporate the substantial effects of dissociation consistent with convenient use in computerized engine cycle calculations. The proposed gas model is simplified by neglecting the formation of species containing atomic nitrogen. This assumption enables the solution for chemical composition to be obtained with a single-level iteration. Although the original intent of this study was directed toward the hydrogen-air system, it was found that the model could be generalized to any hydrocarbon-air system, as well as to a dissociating-air system, with little additional complexity. The computer program, presented in the appendix, can be readily incorporated as a subroutine in an engine cycle program or used alone to generate

Mollier diagrams. Inputs to the program are the ratio of carbon atoms to hydrogen atoms in the fuel molecule, equivalence ratio, temperature, and pressure. Outputs from the program are the mole fractions of the chemical species assumed, enthalpy, entropy, and molecular weight.

SYMBOLS

A,B	coefficients of iteration functions
D, D_1, D_2, D_3, D_4	initial atomic proportions
F_{net}	net thrust, lbf (N)
f	fuel-air ratio
f_s	stoichiometric fuel-air ratio
g	acceleration due to gravitational field of earth, 32.174 ft/sec^2 (9.807 m/sec^2)
G	Gibbs free energy, Btu/lbm (J/kg)
H	enthalpy, Btu/lbm (J/kg)
I_{sp}	specific impulse, sec
J	mechanical equivalent of heat, 778.20 ft-lbf/Btu (9.991 N-m/J)
K	equilibrium constant in terms of partial pressures; numerical subscripts indicate individual reaction
M	mean molecular weight
n	ratio of hydrogen atoms to carbon atoms in fuel molecule
p	pressure, atm
q	dynamic pressure, lbf/ft^2 (N/m^2)

R	universal gas constant, 1.98588 Btu/mole-^{o}R (8.314 J/mole-^{o}K)
r_{ch}	ratio of carbon atoms to hydrogen atoms in fuel molecule, $1/n$
r_{eq}	equivalence ratio, f/f_s
S	entropy, Btu/lbm-^{o}R (J/kg-^{o}K)
T	temperature, ^{o}R (^{o}K)
V	velocity, ft/sec (m/sec)
w_A	air flow rate, lbm/sec (kg/sec)
X	mole fraction

Subscripts:

∞	free-stream conditions
J	Jth species
j	jet
lim	limiting condition for solid carbon or ammonia formation
s	static conditions
t	stagnation conditions

Superscript:

o	at reference pressure of 1 atmosphere (1.01325×10^5 N/m^2)

DESCRIPTION OF GAS MODEL

The temperatures of interest for air-breathing engine application are assumed to be below 7000^{o} R (3889^{o} K) and the pressures are assumed to be between 0.001 and 100 atm. For these conditions, references 3 and 4 indicate that the formation of nitrogen species, such as N, NH, NH_3, and NO, occurs in negligible amounts and, therefore, has a very small effect on the thermodynamic properties of combustion gas mixtures. The assumption to neglect these species greatly reduces the complexity of the calculation procedure since molecular nitrogen can be considered inert. The results of this assumption on the thermodynamic properties of gas mixtures and on the performance of an idealized ramjet are discussed in a subsequent section.

Figure 1 is a diagram illustrating the chemical species and required chemical reactions considered in this gas model. The figure is divided into regions of temperature and equivalence ratio. Above $T_{cut\text{-}off}$, the gas is considered to be dissociating. $(T_{cut\text{-}off}$ is an arbitrarily defined limit below which dissociation can be considered negligible.) The chemical species assumed for pure air $(r_{eq} = 0)$ are identical to those of reference 3 and include atomic nitrogen species. For the combustion gas model $(r_{eq} > 0)$, the dissociated nitrogen species (N, NH, NH_3, NO) are not included. It is apparent that by excluding the species and reaction containing carbon, the model reduces to the hydrogen-air system.

Below $T_{cut\text{-}off}$, there is no dissociation and combustion is complete. Therefore, the initial proportions of elements are sufficient to define the gas composition. However, for $r_{eq} > 1$, the gas model of reference 4 indicates that CO may form even below $T_{cut\text{-}off}$. As a result, the initial proportions of elements are not sufficient to define the gas composition and one chemical reaction is required.

In this region of fuel-rich operation, solid carbon and ammonia may form. The limiting pressure for the formation of solid carbon depends upon the relative proportions of carbon dioxide CO_2 and carbon monoxide CO, equivalence ratio, and temperature. However, there is a limiting equivalence ratio, for a given hydrocarbon-air system, above which solid carbon can form under any condition.

The formation of ammonia was considered only for the hydrogen-air system since the formation of solid carbon precluded the formation of ammonia for the combustion products of all the hydrocarbon-air systems studied. The limiting pressure for the formation of a given amount of ammonia depends upon the relative proportion of nitrogen N_2 and hydrogen H_2, equivalence ratio, and temperature.

DERIVATION OF GAS MODEL

Overall Stoichiometry and Gas Model Constants

In order to apply the simplified gas model to the combustion of any hydrocarbon fuel, a generalized statement concerning the atomic composition of the fuel is required.

Consider the following stoichiometric reactions:

$$CH + \frac{5}{4} O_2 = CO_2 + \frac{1}{2} H_2O$$

$$CH_2 + \frac{6}{4} O_2 = CO_2 + \frac{2}{2} H_2O$$

$$CH_3 + \frac{7}{4} O_2 = CO_2 + \frac{3}{2} H_2O$$

$$CH_4 + \frac{8}{4} O_2 = CO_2 + \frac{4}{2} H_2O$$

In general terms,

$$CH_n + \frac{n+4}{4} O_2 = CO_2 + \frac{n}{2} H_2O$$

where in a fuel molecule

$$n = \frac{\text{No. atoms H}}{\text{No. atoms C}}$$

Thus, in the general system,

$$\frac{\text{No. moles } CH_n}{\text{No. moles } O_2} = \frac{4r_{eq}}{n + 4}$$

where r_{eq} is the equivalence ratio.

The initial composition of air incorporated in this gas model is the same as that of reference 3; that is, combustion is assumed to have occurred with dry air of the following composition by volume:

O_2	20.9495 percent
N_2	78.0881 percent
Ar	0.9624 percent

The following constants and parameters define, in general terms, the initial atomic proportions of the elements in the gas mixture:

$$D_1 = \frac{\text{No. atoms Ar}}{\text{No. atoms N}} = 0.00616227$$

$$D_2 = \frac{\text{No. atoms N}}{\text{No. atoms O}} = 3.727445$$

$$D_3 = \frac{\text{No. atoms C}}{\text{No. atoms O}} = \frac{2r_{eq}}{n + 4}$$

$$D_4 = \frac{\text{No. atoms H}}{\text{No. atoms O}} = \frac{2nr_{eq}}{n + 4}$$

and a convenient parameter

$$D = 1 + D_2\left(1 + 2D_1\right)$$

Define $r_{ch} = \frac{1}{n}$; then

$$D_3 = \frac{2r_{eq}r_{ch}}{1 + 4r_{ch}}$$

$$D_4 = \frac{2r_{eq}}{1 + 4r_{ch}}$$

For the special system of hydrogen-air combustion,

$$2H_2 + O_2 = 2H_2O$$

$$\frac{\text{No. moles } H_2}{\text{No. moles } O_2} = 2r_{eq}$$

$$r_{ch} = 0 \qquad D_3 = 0 \qquad D_4 = 2r_{eq}$$

The stoichiometric fuel-air ratio is given by

$$f_s = 0.028931\left(\frac{1.008 + 12.01r_{ch}}{1 + 4r_{ch}}\right)$$

It is of value to represent the equilibrium constants for the assumed reactions in a convenient manner. The treatment of chemical equilibria in reference 2 leads to the following equilibrium expression for a general reaction:

$$aA + bB = cC + dD$$

The equilibrium expression is

$$\frac{X_C^c\, X_D^d}{X_A^a\, X_B^b} = p^{-(c+d-a-b)}K$$

where

$$K = \exp\left(-\left[c\,\frac{G_C^o}{RT} + d\,\frac{G_D^o}{RT} - a\,\frac{G_A^o}{RT} - b\,\frac{G_B^o}{RT}\right]\right)$$

Figure 2 shows the variation of $\log_{10} K$ with $1/T$ for the chemical reactions considered in this gas model. The values of Gibbs free energy $\frac{G_J^o}{RT}$ for the species were taken from the data tabulations in references 3 and 4. Figure 2 indicates that the equilibrium constants can be represented as linear functions.

With the initial proportions of the gas mixture elements defined and a convenient representation of the equilibrium constants determined, the governing relations for chemical composition can be formulated. Referring to figure 1 will aid the reader in the following derivations.

Hydrocarbon-Air Gas Model With Dissociation

The following gas model applies to the region $T > T_{cut\text{-}off}$, $r_{eq} > 0$:

Chemical species assumed

H_2O, CO_2, O_2, H_2, N_2, Ar, O, H, CO, OH

Chemical reactions

$2H + O = H_2O$

$2H = H_2$

$2O = O_2$

$O + CO = CO_2$

$H + O = OH$

Mass conservation equations

(1) $\sum_{J=1}^{10} X_J = 1$

(2) $X_A = D_1\left(2X_{N2}\right)$

(3) $2X_{N_2} = D_2\left(2X_{CO_2} + X_{CO} + X_{H_2O} + 2X_{O_2} + X_O + X_{OH}\right)$

(4) $X_{CO_2} + X_{CO} = D_3\left(2X_{CO_2} + X_{CO} + X_{H_2O} + 2X_{O_2} + X_O + X_{OH}\right)$

(5) $X_H + 2X_{H_2} + 2X_{H_2O} + X_{OH} = D_4\left(2X_{CO_2} + X_{CO} + X_{H_2O} + 2X_{O_2} + X_O + X_{OH}\right)$

Equilibrium expressions

(6) $X_{H_2O} = p^2K_1X_OX_H^2$

(7) $X_{H_2} = pK_2X_H^2$

(8) $X_{O_2} = pK_3X_O^2$

(9) $X_{CO_2} = pK_4X_OX_{CO}$

(10) $X_{OH} = pK_5X_OX_H$

Solving for two equations and two unknowns in X_O and X_H gives

$$\alpha = \left(A_{22}X_O^2 + A_{21}X_O + A_{20}\right)X_H^2 + \left(A_{12}X_O^2 + A_{11}X_O + A_{10}\right)X_H + \left(A_{03}X_O^3 + A_{02}X_O^2 + A_{01}X_O + A_{00}\right) = 0$$

$$\beta = \left(B_{22}X_O^2 + B_{21}X_O + B_{20}\right)X_H^2 + \left(B_{12}X_O^2 + B_{11}X_O + B_{10}\right)X_H - \left(B_{03}X_O^3 + B_{02}X_O^2 + B_{01}X_O\right) = 0$$

where

$A_{22} = p^3K_1K_4\left(1 - 2D_3 + D\right)$ $\qquad$ $B_{22} = p^3K_1K_4\left[2\left(1 - 2D_3\right) - D_4\right]$

$A_{21} = p^2\left[K_1(1 + D) + 2K_2K_4\left(1 - 2D_3\right)\right]$ $\qquad$ $B_{21} = p^2\left\{K_1\left[2\left(1 - D_3\right) - D_4\right] + 2K_2K_4\left(1 - 2D_3\right)\right\}$

$A_{20} = 2pK_2\left(1 - D_3\right)$ $\qquad$ $B_{20} = 2pK_2\left(1 - D_3\right)$

$A_{12} = p^2K_4K_5\left(1 - 2D_3 + D\right)$ $\qquad$ $B_{12} = p^2K_4K_5\left(1 - 2D_3 - D_4\right)$

$A_{11} = p\left[K_5(1 + D) + 2K_4\left(1 - 2D_3\right)\right]$ $\qquad$ $B_{11} = p\left[K_5\left(1 - D_3 - D_4\right) + K_4\left(1 - 2D_3\right)\right]$

$A_{10} = 2\left(1 - D_3\right)$ $\qquad$ $B_{10} = 1 - D_3$

$A_{03} = 2Dp^2K_3K_4$ $\qquad$ $B_{03} = 2D_4p^2K_3K_4$

$A_{02} = p\left[2K_3\left(D + D_3\right) + K_4\left(1 - 2D_3 + D\right)\right]$ $\qquad$ $B_{02} = D_4p\left(2K_3 + K_4\right)$

$A_{01} = 1 + D - 2pK_4\left(1 - 2D_3\right)$ $\qquad$ $B_{01} = D_4$

$A_{00} = -2\left(1 - D_3\right)$

Setting D_3 and K_4 equal to zero reduces the system to identically the hydrogen-air system.

The expressions for α and β are satisfied simultaneously by use of the Newton iteration scheme. Newton's iteration scheme for determining X_O and X_H can be written as

$$X_O(L + 1) = X_O(L) - \frac{\alpha\left[X_O(L), X_H(L)\right]}{\frac{d}{dX_O}\left\{\alpha\left[X_O(L), X_H(L)\right]\right\}}$$

where $X_O(L)$ is the Lth approximation of X_O and the derivative of $\alpha\left(X_O, X_H\right)$ with respect to X_O is

$$\frac{d\alpha}{dX_O} = \frac{\partial\alpha}{\partial X_O} - \frac{\partial\alpha}{\partial X_H}\left(\frac{\frac{\partial\beta}{\partial X_O}}{\frac{\partial\beta}{\partial X_H}}\right)$$

With $X_O(L + 1)$ determined, $X_H(L + 1)$ can be calculated by applying the binomial theorem to the expression for β. Although there may be a number of pairs of values $\left(X_O, X_H\right)$ which satisfy $\alpha = 0$, there is only one pair which satisfies the condition $0 \leqq X_J \leqq 1$. The initial value of $X_O(L)$ is taken to be 0 and the iteration scheme is used until X_O is determined to five significant figures.

For $r_{eq} > 1$ the iteration function α is insensitive to changes in X_O. As a result, X_H is used as the iteration variable in this region of computation. Unfortunately, if X_H is assumed, the expression for β is cubic in X_O and an additional iteration is required. For fuel-rich hydrogen-air mixtures, $B_{O3} = 0$, β is quadratic in X_O, and the single-level iteration is maintained. However, for fuel-rich mixtures containing carbon, a two-level iteration is necessary for solution.

Air Gas Model With Dissociation

The following gas model applies to the region $T > T_{cut\text{-}off}$, $r_{eq} = 0$:

Chemical species assumed

O_2, N_2, Ar, O, NO, N

Chemical reactions

$2O = O_2$

$2N = N_2$

$N + O = NO$

Mass conservation equations

(1) $\sum_{J=1}^{6} X_J = 1$

(2) $X_A = D_1\left(2X_{N_2} + X_{NO} + X_N\right)$

(3) $2X_{N_2} + X_{NO} + X_N = D_2\left(2X_{O_2} + X_O + X_{NO}\right)$

Equilibrium expressions

(4) $X_{O2} = pK_3X_O^2$

(5) $X_{N_2} = pK_6X_N^2$

(6) $X_{NO} = pK_7X_OX_N$

Solving for two equations and two unknowns in X_O and X_N yields

$$\alpha = A_{20}X_N^2 + \left(A_{11}X_O + A_{10}\right)X_N + \left(A_{02}X_O^2 + A_{01}X_O + A_{00}\right) = 0$$

$$\beta = B_{20}X_N^2 + \left(B_{11}X_O + B_{10}\right)X_N - \left(B_{02}X_O^2 + B_{01}X_O\right) = 0$$

where

$A_{20} = \left(1 + 2D_1\right)pK_6$ $\qquad$ $B_{20} = 2pK_6$

$A_{11} = \left(1 + D_1\right)pK_7$ $\qquad$ $B_{11} = \left(1 - D_2\right)pK_7$

$A_{10} = 1 + D_1$ $\qquad$ $B_{10} = 1$

$A_{02} = pK_3$ $\qquad$ $B_{02} = 2D_2pK_3$

$A_{01} = 1$ $\qquad$ $B_{01} = D_2$

$A_{00} = -1$

The simultaneous solution of α and β is subject to the same iteration procedure used for the hydrocarbon-air gas model.

Fuel-Rich Gas Model With Solid Carbon Formation

The following gas model applies to the region $T \leqq T_{\text{cut-off}}$, $r_{eq} > 1$:

Chemical species assumed

H_2O, CO_2, H_2, N_2, Ar, CO

Chemical reaction

$H_2 + CO_2 = CO + H_2O$

Mass conservation equations

$$(1) \quad \sum_{J=1}^{6} X_J = 1$$

$$(2) \quad X_A = D_1\left(2X_{N_2}\right)$$

$$(3) \quad 2X_{N_2} = D_2\left(2X_{CO_2} + X_{CO} + X_{H_2O}\right)$$

$$(4) \quad X_{CO_2} + X_{CO} = D_3\left(2X_{CO_2} + X_{CO} + X_{H_2O}\right)$$

$$(5) \quad 2X_{H_2} + 2X_{H_2O} = D_4\left(2X_{CO_2} + X_{CO} + X_{H_2O}\right)$$

Equilibrium expression

$$(6) \quad X_{H_2O}X_{CO} = K_8 X_{H_2} X_{CO_2}$$

Solving for X_{CO} yields

$$AAX_{CO}^2 + BBX_{CO} + CC = 0$$

where

$$AA = \left(1 - K_8\right)\left(D + D_4 + 2D_3 - 1\right)^2$$

$$BB = \left(D + D_4 + 2D_3 - 1\right)\left[2\left(1 - 2D_3\right) + K_8\left(D_4 + 6D_3 - 2\right)\right]$$

$$CC = 2D_3K_8\left(2 - D_4 - 4D_3\right)$$

With the chemical composition in this region defined, the criteria for solid carbon formation can be formulated. Consider the reaction

$CO_2 + C(\text{Solid}) = 2CO$

and equilibrium expression

$$p_{\lim} = K_9 \frac{X_{CO_2}}{X_{CO}^2}$$

If $p > p_{lim}$, solid carbon will form. There is, however, an equivalence ratio for the combustion products of a given hydrocarbon (r_{ch}), where solid carbon can form even in a near vacuum. Consider the following equilibrium expression:

$$p_{lim} X_{CO}^2 = K_9 X_{CO_2}$$

$$\left(p_{lim} \to 0\right) \quad \left(X_{CO_2} \to 0\right)$$

Setting $X_{CO_2} = 0$ in the system for the fuel-rich gas model with solid carbon formation gives

$$r_{eq,lim} = \frac{1 + 4r_{ch}}{2r_{ch}}$$

Nondissociating Gas Model

The following gas model applies to the region $T \leqq T_{cut\text{-}off}$:

Chemical species assumed

H_2O, CO_2, O_2, H_2, N_2, Ar

Mass conservation equations

(1) $\sum_{J=1}^{6} X_J = 1$

(2) $X_{Ar} = D_1\left(2X_{N_2}\right)$

(3) $2X_{N_2} = D_2\left(2X_{CO_2} + X_{H_2O} + 2X_{O_2}\right)$

(4) $X_{CO_2} = D_3\left(2X_{CO_2} + X_{H_2O} + 2X_{O_2}\right)$

(5) $2X_{H_2} + 2X_{H_2O} = D_4\left(2X_{CO_2} + X_{H_2O} + 2X_{O_2}\right)$

In each of the regions $r_{eq} = 0$, $0 < r_{eq} < 1$, and $r_{eq} = 1$, one or more of the species can be eliminated; thus, for $r_{eq} = 0$,

$X_{H_2} = 0$

$X_{CO_2} = 0$

$X_{H_2O} = 0$

X_J = Constants

for $0 < r_{eq} < 1$,

$$X_{H_2} = 0$$

$$X_J = X_J\left(r_{ch}, r_{eq}\right)$$

and for $r_{eq} = 1$,

$$X_{H_2} = 0$$

$$X_{O_2} = 0$$

$$X_J = X_J\left(r_{ch}\right)$$

For the hydrogen-air system $\left(r_{ch} = 0\right)$ with $r_{eq} > 1$,

$$X_{O_2} = 0$$

$$X_{CO_2} = 0$$

$$X_J = X_J\left(r_{eq}\right)$$

With the chemical composition in this region, the condition for the formation of a given amount of ammonia can be determined. Consider the reaction

$$N_2 + 3H_2 = 2NH_3$$

and equilibrium expression

$$p_{lim}^2 = \frac{X_{NH_3}^2}{K_{10} X_{H_2}^3 X_{N_2}} \qquad \left(X_{NH_3} > 0.01,\ p > p_{lim}\right)$$

Thermodynamic Properties of Gas Mixtures

The previous derivations have outlined the solution for gas mixture composition. With the chemical composition defined and a tabulation of the thermodynamic properties of the pure constituents provided, the thermodynamic properties of a gas mixture can be calculated by the following equations (ref. 3):

$$H = \frac{R}{M} \sum_J X_J \frac{H_J^o}{R}$$

$$S = \frac{R}{M} \sum_J X_J \left(\frac{S_J^o}{R} - \ln p - \ln X_J\right)$$

$$M = \sum_J X_J M_J$$

where $\frac{H_J^o}{R}$ and $\frac{S_J^o}{R}$ are the thermodynamic properties of the pure constituents at reference pressure (1 atm). These thermodynamic expressions inherently assume that the pure constituents obey the perfect gas law.

The standard reference state of the elements Ar, N, O, H, C taken from reference 3 are as follows:

Ar as Ar

N as N_2

O as O_2

H as H_2

C as C(Solid)

By definition, the energy content of these elements in their standard reference states ($T = 0^o$ R) is zero. Equations for the computation of fuel enthalpies, consistent with this thermodynamic basis, are presented in reference 4.

A listing of the computer program to calculate the composition and thermodynamic properties of this gas model is presented and discussed in the appendix. Computational time for obtaining the chemical composition and thermodynamic properties with this program has been estimated at 6000 cases/min on the IBM 7094 data processing system at the Langley Research Center.

RESULTS AND DISCUSSION

Comparison of Gas Models

The computer program for the simplified combustion gas model has been used to calculate the thermodynamic properties of the stoichiometric kerosene-air and hydrogen-air systems. The purpose of this calculation is to compare the results of the simplified gas model with the more extensive treatments of references 3 and 4. Since the thermodynamic properties of the pure constituents used in the simplified model were taken from these references, the differences between the results of the simplified model and the reference models are due to the formation of the neglected chemical species N, NH, NH_3, and NO.

Figure 3 is a Mollier diagram for the stoichiometric products of combustion of kerosene with air $\left(r_{ch} = 0.5\right)$. The solid-line curves are values plotted from the tabulated data of reference 4. The dash-line curves are values obtained from the computer program for the simplified model. Unfortunately, the data presented in reference 4 are limited to temperatures below 5000° R (2778° K). Since the formation of species including atomic nitrogen $\left(N, NH, \text{and } NH_3\right)$ is more important at temperatures above 5000° R, the good agreement between gas models is not surprising.

Figure 4 is a Mollier diagram for the stoichiometric products of combustion of hydrogen with air $\left(r_{ch} = 0\right)$. The solid-line curves are values plotted from the tabulated data of reference 3. The dash-line curves are values obtained from the computer program for the simplified model. The thermodynamic properties tabulated in reference 3 cover temperatures as high as 10 000° R (5560° K). The substantial disagreement above 7000° R (3889° K) at low pressures is due to the formation of species containing atomic nitrogen. An interesting result is that the agreement between lines of constant pressure is much better than the agreement between lines of constant temperature. This result is fortunate since, for thermodynamic processes such as isentropic nozzle expansion, temperature is not used directly to calculate performance.

The simultaneous conditions of high temperatures and low pressures, the area of substantial disagreement between the simplified gas model and the reference gas models, are beyond the realm of operation of typical hypersonic engine cycles. For example, for subsonic combustion ramjets, combustion pressures and temperatures are high since the airstream is brought nearly to stagnation conditions before combustion. For supersonic combustion ramjets, combustion pressures and temperatures are low since a large portion of the total air enthalpy remains in the form of kinetic energy. Hence, the conditions of high temperatures and low pressures do not occur simultaneously for engine cycles currently considered feasible for hypersonic flight.

Ramjet Performance

In applying the simplified gas model to hypersonic engine calculations, it is of interest to determine the effect of the use of the simplified gas model on the calculated performance of an idealized subsonic combustion ramjet.

Since the purpose of this calculation is to show the effect of small differences in thermodynamic properties on ramjet performance, the following simplifying assumptions were made:

(1) Free-stream Mach number chosen along a constant dynamic-pressure path ($q = 1500 \text{ lb/ft}^2$ ($718\,200 \text{ N/m}^2$))

(2) Airstream decelerated to stagnation conditions with total pressure recovery degraded to 10 atm (due to internal duct pressure limitations at high Mach numbers)

(3) Completely mixed stoichiometric hydrogen-air combustion

(4) No pressure losses during combustion $\left(p_{t,nozzle} = 10 \text{ atm}\right)$

(5) Enthalpy of injected hydrogen equals zero
Molecular hydrogen is a reference element; thus, $H^{o}_{H_2} = 0$ at $T = 0^{o}$ R.

(6) Combustion gas isentropically expanded to free-stream static conditions by using so-called "shifting equilibrium"

The 1962 Standard Atmosphere (ref. 7) yields free-stream static conditions and with assumption (1) gives the variation of altitude with Mach number shown in figure 5. For steady adiabatic flow, the total energy in the airstream is given by

$$H_{t,air} = H_{\infty,air} + \frac{V_{\infty}^2}{2Jg}$$

For an adiabatic combustion process,

$$H_{t,products} = \frac{H_{t,air} + fH_{t,hydrogen}}{1 + f}$$

With two properties $\left(H_{t,products}\right.$ and $\left.p_{t,nozzle}\right)$ of the combustion gas defined, the Mollier diagram can be entered. Figure 6 is a schematic of a Mollier diagram showing lines of constant pressure for the simplified gas model and model of reference 3. Since the simplified gas model neglects the dissociated nitrogen species, the entropy level is slightly less than that obtained from reference 3. In expanding the combustion gas to free-stream static pressure, the gas enters the region of almost exact agreement between gas models. Consequently, the expansion using the simplified gas model gives a slightly larger value of $\Delta H = H_t - H_s$ than that from reference 3. However, the effect of the difference in ΔH for the two calculations is reduced by the fact that

$$V_j \approx \sqrt{H_t - H_s}$$

The performance parameters are given by the following expressions:

$$\frac{F_{net}}{w_A} = (1 + f)V_j - V_{\infty}$$

$$I_{sp} = \frac{F_{net}}{w_A gf}$$

The variation of specific impulse with Mach number for this idealized ramjet is presented in figure 7. The solid-line curve was calculated by using the thermodynamic properties of reference 3. The dash-line curve was calculated by using the computer program for the simplified gas model. The maximum deviation is 1 percent at a Mach number of 12.

Solid Carbon and Ammonia Formation

The formation of solid carbon extracts useful energy from the combustion gas. If this phenomenon occurs during a nozzle expansion process, the useful energy absorbed in forming solid carbon is not recoverable and a loss in performance results.

The derivation of the nondissociating $\left(T < T_{cut\text{-}off}\right)$ fuel-rich gas model required one chemical reaction in order to include the formation of carbon monoxide CO. The equilibrium expression resulting from the required reaction is independent of pressure. Consequently, the composition of the gas in this region is independent of pressure. This fact simplifies the treatment of solid carbon formation, since the limiting pressure, above which solid carbon can form, is related to temperature and composition only.

The computer program for the simplified gas model indicates the formation of solid carbon by an error statement. When the limiting pressure is exceeded, the error statement is printed, but the program computes the thermodynamic properties as though solid carbon had not formed. When the limiting equivalence ratio is exceeded, the error statement is printed and no calculations are made. The limiting pressure for solid carbon formation is readily extracted from the thermodynamic calculations. Figures 8 to 10 present the variation of limiting pressure with equivalence ratio and temperature for methane-air $\left(r_{ch} = 0.25\right)$, kerosene-air $\left(r_{ch} = 0.5\right)$, and benzene-air $\left(r_{ch} = 1\right)$ combustion products, respectively. For all systems, as

$$r_{eq} \rightarrow r_{eq,lim}, \; p_{lim} \rightarrow 0 \qquad \text{since} \quad X_{CO_2} \rightarrow 0$$

and as

$$r_{eq} \rightarrow 1, \; p_{lim} \rightarrow \infty \qquad \text{since} \quad X_{CO} \rightarrow 0$$

The formation of ammonia is considered only for the hydrogen-air, nondissociating, fuel-rich system. The composition of the gas, under these conditions, depends upon equivalence ratio only. Therefore, the limiting pressure, above which the mole fraction of ammonia is greater than some arbitrary amount, is related to temperature and composition.

The computer program for the simplified gas model indicates the formation of ammonia $\left(X_{NH_3} > 0.01\right)$ by an error statement. When the limiting pressure is exceeded, the error statement is printed, but the program computes the thermodynamic properties as though ammonia had not formed. Figure 11 presents the variation of limiting pressure with equivalence ratio and temperature for hydrogen-air combustion products. For all temperatures, as

$$r_{eq} \rightarrow \infty, \; p_{lim} \rightarrow \infty \qquad \text{since} \quad X_{N_2} \rightarrow 0$$

and as

$$r_{eq} \rightarrow 1, \; p_{lim} \rightarrow \infty \qquad \text{since} \quad X_{H_2} \rightarrow 0$$

CONCLUDING REMARKS

A simplified equilibrium hydrocarbon-air combustion gas model, for use in engine cycle computer programs, has been presented. The generalized gas model includes the effects of dissociation and reduces to the special systems of hydrogen-air combustion products, as well as dissociating air. The associated computer program can be readily incorporated as a subroutine in a general engine cycle computer program or used alone to generate Mollier diagrams.

With the exception of pure air, this gas model neglects the formation of chemical species containing atomic nitrogen; this assumption allows a considerable simplification of the solution for chemical composition. The effect of this assumption on the thermodynamic properties of stoichiometric kerosene-air and hydrogen-air combustion products is presented. The importance of this assumption is shown in terms of the performance of an idealized subsonic combustion ramjet. Good agreement between the simplified model and more comprehensive treatments is obtained in the range of temperatures applicable to hypersonic engine cycles.

The computer program has been used to calculate the limiting pressure for solid carbon and ammonia formation in fuel-rich gas mixtures. The results of this calculation are presented as a function of temperature and equivalence ratio for the combustion products of various hydrocarbon fuels.

Langley Research Center,
National Aeronautics and Space Administration,
Langley Station, Hampton, Va., May 7, 1968,
722-03-00-02-23.

APPENDIX

COMPUTER PROGRAM FOR CALCULATION OF GAS COMPOSITION AND THERMODYNAMIC PROPERTIES OF SIMPLIFIED GAS MODEL

The calculation procedure for determining gas composition and thermodynamic properties for the simplified gas model has been programed for and used with the IBM 7094 data processing system at the Langley Research Center. A printout of the program is presented in this appendix. The program is written in FORTRAN IV language (ref. 8). The symbols used for the program are as follows:

RCH	r_{ch}	X(1)	x_{H_2O}
REQ	r_{eq}	X(2)	x_{CO_2}
TEMP	T	X(3)	x_{O_2}
P	p	X(4)	x_{H_2}
M	M	X(5)	x_{N_2}
H	H	X(6)	x_A
S	S	X(7)	x_O
MT(J)	M_J	X(8)	x_H
TT(I)	T_I	X(9)	x_{CO}
HT(I,J)	H_J^o	X(10)	x_{OH}
ST(I,J)	S_J^o	X(11)	x_{NO}
		X(12)	x_N

Input

The input is read into the IBM 7094 data processing system by the FORTRAN statement

```
    READ (5,100) RCH, REQ, TEMP, P
100 FORMAT (4E 16.8)
```

For example, an input car would be

```
Col.- 1                  17                 23                 49
      +0.00000000E+00    +0.10000000E+01    +0.50000000E+04    +0.10000000E+00
```

APPENDIX

Output

The outputs for this program are the mole fractions of each constituent and the thermodynamic properties of the gas mixture. For example, output for the input example would be as follows:

```
RCH=0.00000000E-38  REQ=0.10000000E+01  TEMP=0.50000000E04R  P=0.100000000E00ATM

       XH2O              XCO2              XO2               XH2
   0.18315569E 00    0.00000000E-38    0.27084661E-01    0.71114589E-01

       XN2               XA                XO                XH
   0.57613321E 00    0.71005768E-02    0.25695777E-01    0.63610586E-01

       XCO               XOH               XNO               XN
   0.00000000E-38    0.46109576E-01    0.00000000E-38    0.00000000E-38

   M=0.21993865E 02  H=0.14316146E 04BTU/LBM  S=0.30918686E 01BTU/LBM-R
```

Built-In Data

The thermodynamic properties of the pure constituents $\left(\frac{H_J^o}{R}, \frac{S_J^o}{R}\right)$ are taken from references 3 and 4 and built in the program as two-dimensional arrays named HT(I,J) and ST(I,J), where I is the index on temperature and J is the index on constituents. The thermodynamic properties are built in for the discrete temperatures given in TT(I). The enthalpy array HT(I,J) is interpolated linearly, whereas the entropy array ST(I,J) is interpolated logarithmically.

Complete Program

The complete program including comments is reproduced in the following pages.

APPENDIX

```
C     THERMODYNAMIC PROPERTIES OF HYDROCARBON-AIR COMBUSTION PRODUCTS
C H2O   CO2    O2    H2    N2    AR    O    H    CO    OH    NO    N
C X(1) X(2) X(3) X(4) X(5) X(6) X(7) X(8) X(9) X(10) X(11) X(12)
      DIMENSION TT(16),MT(12),HT(16,12),ST(16,12),X(12),Y(99),F(99),
     1Z(99),TY(99)
      REAL M,MT,K1,K2,K3,K4,K5,K6,K7,K8,K9,K10
C
C THERMODYNAMIC PROPERTIES OF PURE CONSTITUENTS
C
      DATA(MT(J),J=1,12)/18.016,44.01,32.00,2.016,28.016,
     139.944,16.00,1.008,28.01,17.008,30.008,14.008/
      DATA(TT(I),I=1,16)/0.,200.,400.,600.,800.,1000.,1300.,1600.,2000.,
     12500.,3000.,3500.,4000.,5000.,6000.,7000./
      DATA((HT(I,J),I=1,16),J=1,5)/-51727.,-51100.,-50400.,-49700.,
     1-48900.,-47743.,-46297.,-44939.,-42944.,-40290.,-37449.,-34456.,
     2-31354.,-24889.,-18176.,-11296.,-85117.,-84000.,-83500.,-82801.,
     3-81818.,-80746.,-79007.,-77147.,-74535.,-71116.,-67595.,-63983.,
     4-60312.,-52857.,-44500.,-37000.,0.,698.,1400.,2104.,2826.,3574.,
     54744.,5963.,7639.,9794.,11996.,14241.,16524.,21203.,26021.,30953.,
     60.,751.,1356.,2052.,2755.,3458.,4518.,5588.,7042.,8918.,10867.,
     712886.,14964.,19272.,23744.,28355.,0.,699.,1398.,2099.,2801.,
     83513.,4603.,5743.,7316.,9355.,11456.,13597.,
     913768.,20171.,24629.,29124./
```

APPENDIX

```
 DATA((HT(I,J),I=1,16),J=6,9)/0.,500.,1000.,1500.,2000.,2500.,
13250.,4000.,5000.,6250.,7500.,8750.,10000.,12500.,15000.,17500.,
253425.,54000.,54436.,54900.,55345.,56165.,56801.,57600.,58594.,
359855.,61110.,62356.,63612.,66120.,68640.,71183.,46759.,47300.,
447712.,48380.,48579.,49336.,49977.,50763.,51752.,53008.,54261.,
555503.,56756.,59255.,61758.,64257.,-24639.,-24000.,-23000.,
6-22540.,-21835.,-21116.,-20009.,-18856.,-17261.,-15193.,-13073.,
7-10912.,-8725.,-4295.,0.,3500./
 DATA((HT(I,J),I=1,16),J=10,12)/8424.9,9098.,9750.,10455.,11222.,
111997.,13043.,14130.,15505.,17520.,19508.,21558.,23664.,27996.,
232458.,37024.,19455.,20006.,20567.,21427.,22220.,23091.,24248.,
325445.,26992.,29185.,31341.,33580.,35743.,40220.,44741.,49302.,
4101922.,102000.,102000.,102156.,103312.,104590.,105104.,105933.,
5106908.,108173.,109422.,110663.,111916.,114425.,116946.,119518./
 DATA((ST(I,J),I=1,16),J=1,4)/0.,18.68,21.55,23.157,24.338,25.273,
126.434,27.400,28.505,29.691,30.725,31.6464,32.4745,33.9163,35.14,
236.2003,0.,21.700,24.550,26.20115,27.61677,28.81060,30.32729,
331.61336,33.06955,34.59469,35.87841,36.98959,37.97138,39.63861,
441.0,42.19,0.,21.1538,23.6633,25.0721,26.1033,26.9292,27.9544,
528.7965,29.7306,30.6915,31.4947,32.1868,32.796,33.8396,34.7178,
635.4778,0.,12.5375,14.7172,16.1042,17.1073,17.8829,18.8146,19.55,
720.9638,21.2011,21.9103,22.5326,23.0880,24.0484,24.8623,25.5747/
 DATA((ST(I,J),I=1,16),J=5,9)/0.,19.5245,22.0313,23.4306,24.4362,
```

24

APPENDIX

```
     125.2221,26.1808,26.9656,27.8431,28.7524,29.5175,30.1789,30.758,
     231.74,32.55,33.25,0.,16.11,17.90,18.90,19.61,20.16,20.82,
     321.341,21.899,22.457,22.912,23.298,23.632,24.190,24.646,25.031,0.,
     416.59,18.61,19.662,20.401,15.965,21.632,22.156,22.7177,23.2772,
     523.7344,24.1205,24.4557,25.015,25.474,25.866,0.,11.280,13.08,14.,
     614.787,15.339,15.996,16.514,17.0724,17.6301,18.087,18.4713,18.81,
     719.3622,19.8195,20.2045,0.,20.39,22.80,24.19,25.21,26.007,26.98,
     827.773,28.65,29.59,30.36,31.02,31.61,32.60,33.45,34.15/
      DATA((ST(I,J),I=1,16),J=10,12)/0.,19.643,21.2024,22.4669,23.5156,
     124.300,25.234,25.9813,26.8053,27.6588,28.3836,29.0155,29.5779,
     230.54,31.36,32.06,0.,21.62,24.31,25.75,26.71,27.52,
     328.5805,29.397,30.269,31.250,32.036,32.7121,33.3028,34.3009,
     435.1249,35.8281,0.,15.92,17.71,18.71,19.43,19.979,20.638,21.155,
     521.713,22.272,22.727,23.1126,23.4466,24.0055,24.4654,24.8616/
C
C INPUT
C
 500  READ(5,100)RCH,REQ,TEMP,P
 100  FORMAT(4E16.8)
      WRITE (6,300) RCH,REQ,TEMP,P
 300  FORMAT(10X4HRCH=E15.8,4X4HREQ=E15.8,4X5HTEMP=E15.8,1HR,
     14X2HP=E15.8,3HATM)
      DO 12 J=1,12
```

```
   12 X(J)=0.
C
C GAS MODEL CONSTANTS
C
      D=4.773384
      D1=.00616227
      D2=3.727445
      D3=(2.*REQ*RCH)/(1.+4.*RCH)
      D4=(2.*REQ)/(1.+4.*RCH)
      IF(TEMP.GT.(100.*ALOG10(P)+2800.))GO TO 1.
    7 IF(REQ.EQ.1.)GO TO 2
      IF(REQ.GT.1.)GO TO 3
C
C NON-DISSOCIATING GAS MODEL, REQ.LT.1
C
      X(1)=(2.*D4)/(D4+2.*D)
      X(2)=(4.*D3)/(D4+2.*D)
      X(3)=(2.-4.*D3-D4)/(D4+2.*D)
      X(5)=(2.*D2)/(D4+2.*D)
      X(6)=(4.*D2*D1)/(D4+2.*D)
      GO TO 50
C
C NON-DISSOCIATING GAS MODEL, REQ.EQ.1
```

```
C
    2 X(1)=(2.*(1.-2.*D3))/(D+(1.-2.*D3))
      X(2)=(2.*D3)/(D+(1.-2.*D3))
      X(5)=D2/(D+(1.-2.*D3))
      X(6)=(2.*D2*D1)/(D+(1.-2.*D3))
      GO TO 50
    3 IF (RCH.EQ.0.)GO TO 14
      IF(REQ.GE.((1.+4.*RCH)/(2.*RCH)))GO TO 15
C
C NON-DISSOCIATING GAS MODEL, REQ.GT.1
C
      K8=10.**(1.747-(3415./TEMP))
      K9=10.**(9.272-(16210./TEMP))
      AA=(1.-K8)*(D+D4+2.*D3-1.)**2
      BB=(D-1.+D4+2.*D3)*(2.*(1.-2.*D3)+K8*(D4+6.*D3-2.))
      CC=K8*(2.-D4-4.*D3)*2.*D3
      X(9)=(SQRT(BB**2-4.*AA*CC)-BB)/(2.*AA)
      X(2)=(2.*D3/(D+D4+2.*D3-1.))-X(9)
      X(1)=((1.-2.*D3)*X(2)+(1.-D3)*X(9))/D3
      X(4)=X(1)*X(9)/(K8*X(2))
      X(5)=D2*(2.*X(2)+X(9)+X(1))/2.
      X(6)=2.*D1*X(5)
      PLIM=K9*X(2)/(X(9)**2)
```

```
  200 FORMAT(2X5HPLIM=E16.8)
      IF(P.LT.PLIM)GO TO 50
   15 WRITE (6,600)
  600 FORMAT (10X31H*** SOLID CARBON HAS FORMED ***)
      GO TO 50
C
C NON-DISSOCIATING GAS MODEL, REQ.GT.1, RCH.EQ.0
C
   14 X(1)=(2.*(1.-2.*D3))/(D+D4+2.*D3-1.)
      X(2)=(2.*D3)/(D+D4+2.*D3-1.)
      X(4)=(D4-2.+4.*D3)/(D+D4+2.*D3-1.)
      X(5)=D2/(D+D4+2.*D3-1.)
      X(6)=(2.*D2*D1)/(D+D4+2.*D3-1.)
      K10=10.**((10114./TEMP)-12.089)
      PLIM=.01/(SQRT(K10*X(5)*(X(4)**3)))
      IF(P.LT.PLIM) GO TO 50
      WRITE(6,601)
  601 FORMAT(10X26H*** AMMONIA HAS FORMED ***)
      GO TO 50
C
C DISSOCIATING COMBUSTION GAS MODEL
C
    1 K1=10.**((89877./TEMP)-12.7295)
```

```
  K2=10.**((42387./TEMP)-6.2325)
  K3=10.**((47850./TEMP)-6.9570)
  K5=10.**((41612./TEMP)-5.8720)
  K6=10.**((90047./TEMP)-6.9505)
  K7=10.**((60437./TEMP)-6.2915)
  IF(REQ.EQ.0.)GO TO 4
  IF(RCH.NE.0.) GO TO 5
  K4=0.
  GO TO 6
5 K4=10.**((50173./TEMP)-7.8785)
6 A22=P**3*K1*K4*(1.-2.*D3+D)
  A21=P**2*(K1*(1.+D)+2.*K2*K4*(1.-2.*D3))
  A20=2.*P*K2*(1.-D3)
  A12=P**2*K4*K5*(1.-2.*D3+D)
  A11=P*(K5*(1.+D)+2.*K4*(1.-2.*D3))
  A10=2.*(1.-D3)
  A03=2.*P**2*D*K3*K4
  A02=P*(K4*(1.-2.*D3+D)+2.*K3*(D3+D))
  A01=1.+D-2.*P*K4*(1.-2.*D3)
  A00=2.*(D3-1.)
  B22=P**3*K1*K4*(2.-4.*D3-D4)
  B21=P**2*(K1*(2.-2.*D3-D4)+2.*K2*K4*(1.-2.*D3))
  B20=2.*P*K2*(1.-D3)
```

APPENDIX

```
      B12=P**2*K4*K5*(1.-2.*D3-D4)
      B11=P*(K5*(1.-D3-D4)+K4*(1.-2.*D3))
      B10=1.-D3
      B03=2.*D4*P**2*K3*K4
      B02=D4*P*(2.*K3+K4)
      B01=D4
C
C ITERATION FOR CHEMICAL COMPOSITION
C
   21 Y(1)=(+1.*SQRT((1.+D)**2+16.*D*P*K3)-(1.+D))/(4.*D*P*K3)
      L=1
      IF(REQ.GT.1.)GO TO 25
   16 B=(Y(L)*(Y(L)*B12+B11)+B10)**2+4.*(Y(L)*(Y(L)*B22+B21)+B20)*(Y(L)
     1*(Y(L)*(Y(L)*B03+B02)+B01))
      IF(B.LT.0.)GO TO 20
      Z(L)=(SQRT(B)-1.*(Y(L)*(Y(L)*B12+B11)+B10))/((Y(L)*(Y(L)*B22+B21)
     1+B20)*2.)
      IF((Y(L).LT..00001).AND.(REQ.LE.1.))GO TO 7
      F(L)=Z(L)*(Z(L)*(Y(L)*(Y(L)*A22+A21)+A20)+(Y(L)*(Y(L)*A12+A11)+
     1A10))+(Y(L)*(Y(L)*(Y(L)*A03+A02)+A01)+A00)
      IF((F(L).GT.-.0001).AND.(F(L).LT..0001))GO TO 8
      DELF=(Z(L)**2)*(2.*A22*Y(L)+A21)+Z(L)*(2.*A12*Y(L)+A11)+3.*A03*
     1Y(L)**2+2.*A02*Y(L)+A01-(2.*(Y(L)*(Y(L)*A22+A21)+A20)*Z(L)+(Y(L)
```

```
     2*(Y(L)*A12+A11)+A10))*((Z(L)**2)*(2.*B22*Y(L)+B21)+Z(L)*(2.*B12
     3*Y(L)+B11)-(3.*B03*Y(L)**2+2.*B02*Y(L)+B01))/(2.*(Y(L)*(Y(L)*B22
     4+B21)+B20)*Z(L)+(Y(L)*(Y(L)*B12+B11)+B10))
      Y(L+1)=Y(L)-F(L)/ABS(DELF)
      L=L+1
      GO TO 16
20    Y(L)=.1*Y(L)
      IF((Y(L).LT..00001).AND.(REQ.LE.1.))GO TO 7
      GO TO 16
25    Z(1)=(+1.*SQRT((2.*D4*(1.-D3)+1.+D)**2+16.*P*K2*D4*(1.-D3)*(D4*(1.
     1-D3)+1.+D))-(2.*D4*(1.-D3)+1.+D))/(4.*P*K2*(D4*(1.-D3)+1.+D))
28    B=(B21*Z(L)**2+B11*Z(L)-B01)**2-4.*(B20*Z(L)**2+B10*Z(L))*(B22
     1*Z(L)**2+B12*Z(L)-B02)
      K=1
      TY(K)=(-1.*SQRT(B)-(B21*Z(L)**2+B11*Z(L)-B01))/(2.*(B22*Z(L)**2
     1+B12*Z(L)-B02))
27    DEL=(B22*TY(K)**2+B21*TY(K)+B20)*Z(L)**2+(B12*TY(K)**2+B11*TY(K)
     1+B10)*Z(L)-(B03*TY(K)**3+B02*TY(K)**2+B01*TY(K))
      IF((DEL.LT..00001).AND.(DEL.GT.-.00001)) GO TO 26
      TY(K+1)=TY(K)-DEL/(-3.*B03*TY(K)**2+2.*(B22*Z(L)**2+B12*Z(L)-B02)
     1*TY(K)+(B21*Z(L)**2+B11*Z(L)-B01))
      K=K+1
      GO TO 27
```

```
26 Y(L)=TY(K)
   F(L)=Z(L)*(Z(L)*(Y(L)*(Y(L)*A22+A21)+A20)+(Y(L)*(Y(L)*A12+A11)+
  1A10))+(Y(L)*(Y(L)*(Y(L)*A03+A02)+A01)+A00)
   IF((F(L).LT..0001).AND.(F(L).GT.-.0001))GO TO 8
   IF(Z(L).LT..00001)GO TO 7
   IF(L.EQ.1)GO TO 29
   Z(L+1)=Z(L)-F(L)*(Z(L-1)-Z(L))/(F(L-1)-F(L))
   L=L+1
   GO TO 28
29 Z(2)=.5*Z(1)
   L=2
   GO TO 28
 8 X(7)=Y(L)
   IF(REQ.EQ.0.)GO TO 22
   X(8)=Z(L)
   X(1)=P**2*K1*X(7)*X(8)**2
   X(3)=P*K3*X(7)**2
   X(10)=P*K5*X(7)*X(8)
   X(9)=(D3*(X(1)+2.*X(3)+X(7)+X(10)))/((1.-2.*D3)*P*K4*X(7)+1.-D3)
   X(2)=P*K4*X(7)*X(9)
   X(4)=P*K2*X(8)**2
   X(5)=(D2/2.)*(2.*X(2)+X(1)+2.*X(3)+X(7)+X(9)+X(10))
   X(6)=2.*D1*X(5)
```

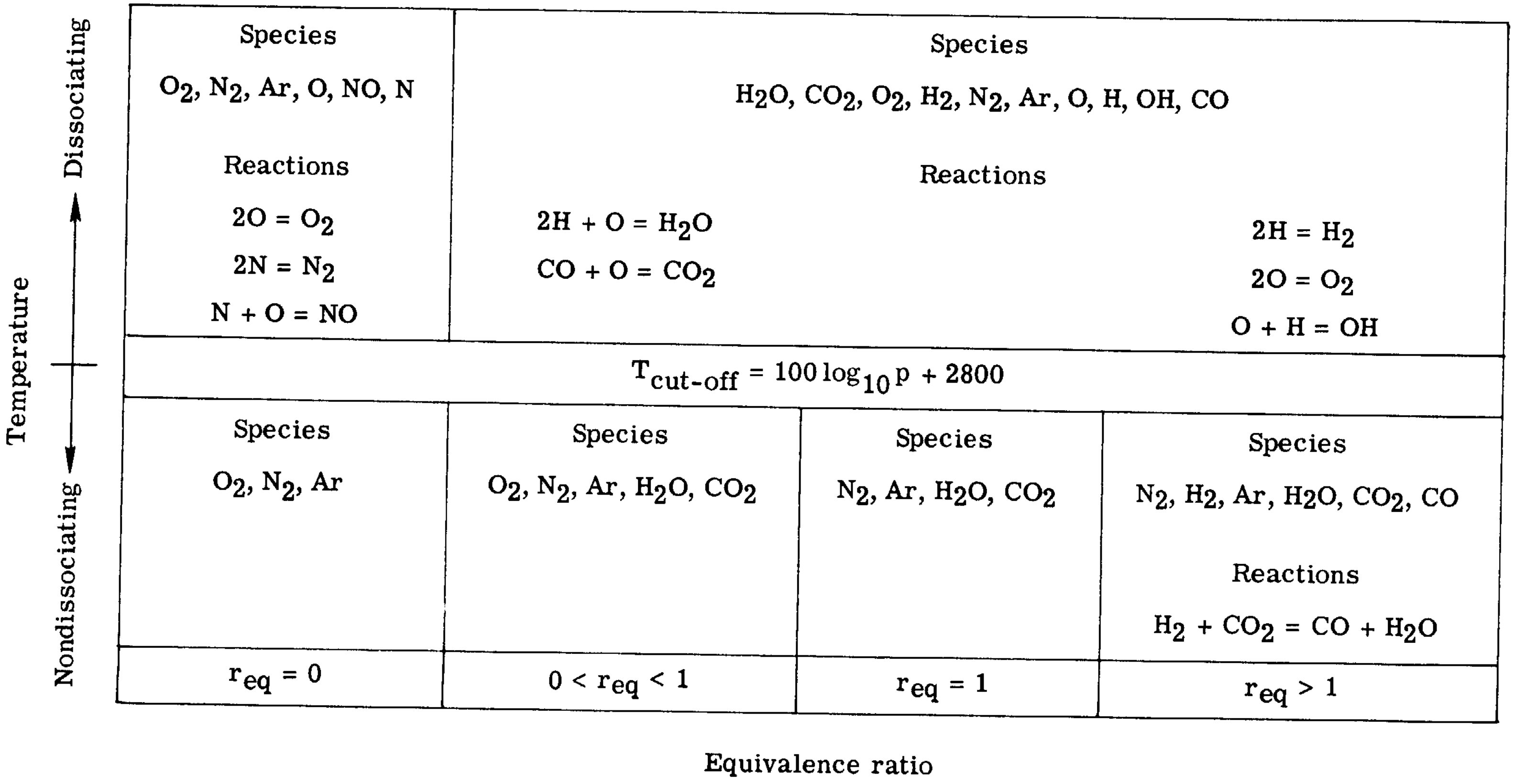
```
      GO TO 50
C
C DISSOCIATING AIR
C
    4 A22=0.
      A21=0.
      A20=P*K6*(1.+2.*D1)
      A12=0.
      A11=P*K7*(1.+D1)
      A10=1.+D1
      A03=0.
      A02=P*K3
      A01=1.
      A00=-1.
      B22=0.
      B21=0.
      B20=2.*P*K6
      B12=0.
      B11=P*K7*(1.-D2)
      B10=1.
      B03=0.
      B02=2.*P*K3*D2
      B01=D2
```

```
      GO TO 21
   22 X(12)=Z(L)
      X(11)=P*K7*X(7)*X(12)
      X(3)=P*K3*X(7)**2
      X(5)=(D2*(2.*X(3)+X(7)+X(11))-X(11)-X(12))/2.
      X(6)=D1*(2.*X(5)+X(11)+X(12))
C
C CALCULATION OF GAS MIXTURE THERMODYNAMIC PROPERTIES
C
   50 DO 9 I=1,16
      IF(TEMP-TT(I))10,10,9
    9 CONTINUE
   10 DELH=(TEMP-TT(I-1))/(TT(I)-TT(I-1))
      DELS=(ALOG(TEMP/TT(I-1)))/(ALOG(TT(I)/TT(I-1)))
      M=0.
      H=0.
      S=0.
      DO 11 J=1,12
      IF(X(J).EQ.0.)GO TO 11
      M=M+X(J)*MT(J)
      H=H+X(J)*(HT(I-1,J)+(HT(I,J)-HT(I-1,J))*DELH)
      S=S+X(J)*(ST(I-1,J)+(ST(I,J)-ST(I-1,J))*DELS-ALOG(P*X(J)))
   11 CONTINUE
```

```
      H=(1.98588/M)*H
      S=(1.98588/M)*S
C
C OUTPUT
      WRITE (6,700)(X(J),J=1,12)
  700 FORMAT(6X4HXH2O,12X4HXCO2,12X3HXO2,13X3HXH2/4E16.8/6X3HXN2,13X3HXA
     1R,14X2HXO,14X2HXH/4E16.8/6X3HXCO,13X3HXOH,13X3HXNO,13X2HXN/4E16.8),
      WRITE(6,400)M,H,S
  400 FORMAT(2X2HM=E15.8,2X2HH=E15.8,7HBTU/LBM,2X2HS=E15.8,9HBTU/LBM-R,
     11//)
      GO TO 500
      END
$DATA
```

REFERENCES

1. Hall, Eldon W.; and Weber, Richard J.: Tables and Charts for Thermodynamic Calculations Involving Air and Fuels Containing Boron, Carbon, Hydrogen, and Oxygen. NACA RM E56B27, 1956.
2. Clarke, J. F.; and McChesney, M.: The Dynamics of Real Gases. Butterworths, 1964.
3. Browne, W. G.; and Warlick, D. L.: Properties of Combustion Gases – System: H_2-Air. R62FPD-366, Advan. Engine Technol. Dep., Gen. Elec. Co., Nov. 1962. (Reprinted Sept. 1964.)
4. Anon.: Properties of Combustion Gases – System: C_nH_{2n}-Air.
   Volume I – Thermodynamic Properties. AGT Develop. Dep., Gen. Elec. Co., c.1955.
   Volume II – Chemical Composition of Equilibrium Mixtures. McGraw-Hill Book Co., Inc., c.1955.
5. Erickson, Wayne D.; Kemper, Jane T.; and Allison, Dennis O.: A Method for Computing Chemical-Equilibrium Compositions of Reacting-Gas Mixtures by Reduction to a Single Iteration Equation. NASA TN D-3488, 1966.
6. Zeleznik, Frank J.; and Gordon, Sanford: An Analytical Investigation of Three General Methods of Calculating Chemical-Equilibrium Compositions. NASA TN D-473, 1960.
7. Anon.: U.S. Standard Atmosphere, 1962. NASA, U.S. Air Force, and U.S. Weather Bur., Dec. 1962.
8. McCracken, Daniel D.: A Guide to FORTRAN Programing. John Wiley & Sons, Inc., c.1961.



Species O_2, N_2, Ar, O, NO, N Reactions $2O = O_2$ $2N = N_2$ $N + O = NO$	Species $H_2O, CO_2, O_2, H_2, N_2, Ar, O, H, OH, CO$ Reactions $2H + O = H_2O$ $CO + O = CO_2$ $2H = H_2$ $2O = O_2$ $O + H = OH$		
$T_{cut\text{-}off} = 100 \log_{10} p + 2800$			
Species O_2, N_2, Ar	Species O_2, N_2, Ar, H_2O, CO_2	Species N_2, Ar, H_2O, CO_2	Species $N_2, H_2, Ar, H_2O, CO_2, CO$ Reactions $H_2 + CO_2 = CO + H_2O$
$r_{eq} = 0$	$0 < r_{eq} < 1$	$r_{eq} = 1$	$r_{eq} > 1$

Figure 1.- Description of gas model.

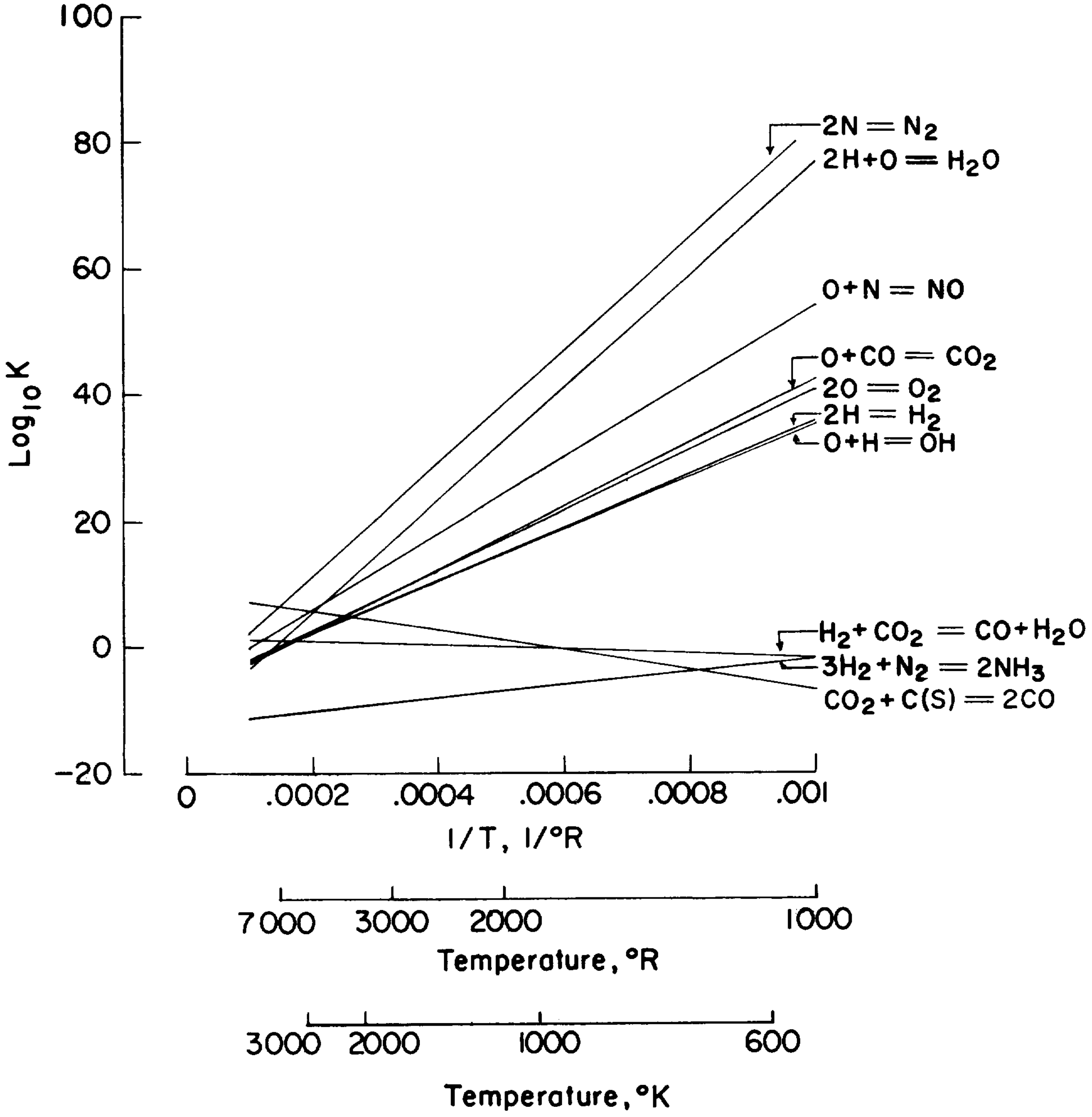


Figure 2.- Variation of equilibrium constants with temperature for gas model reactions.

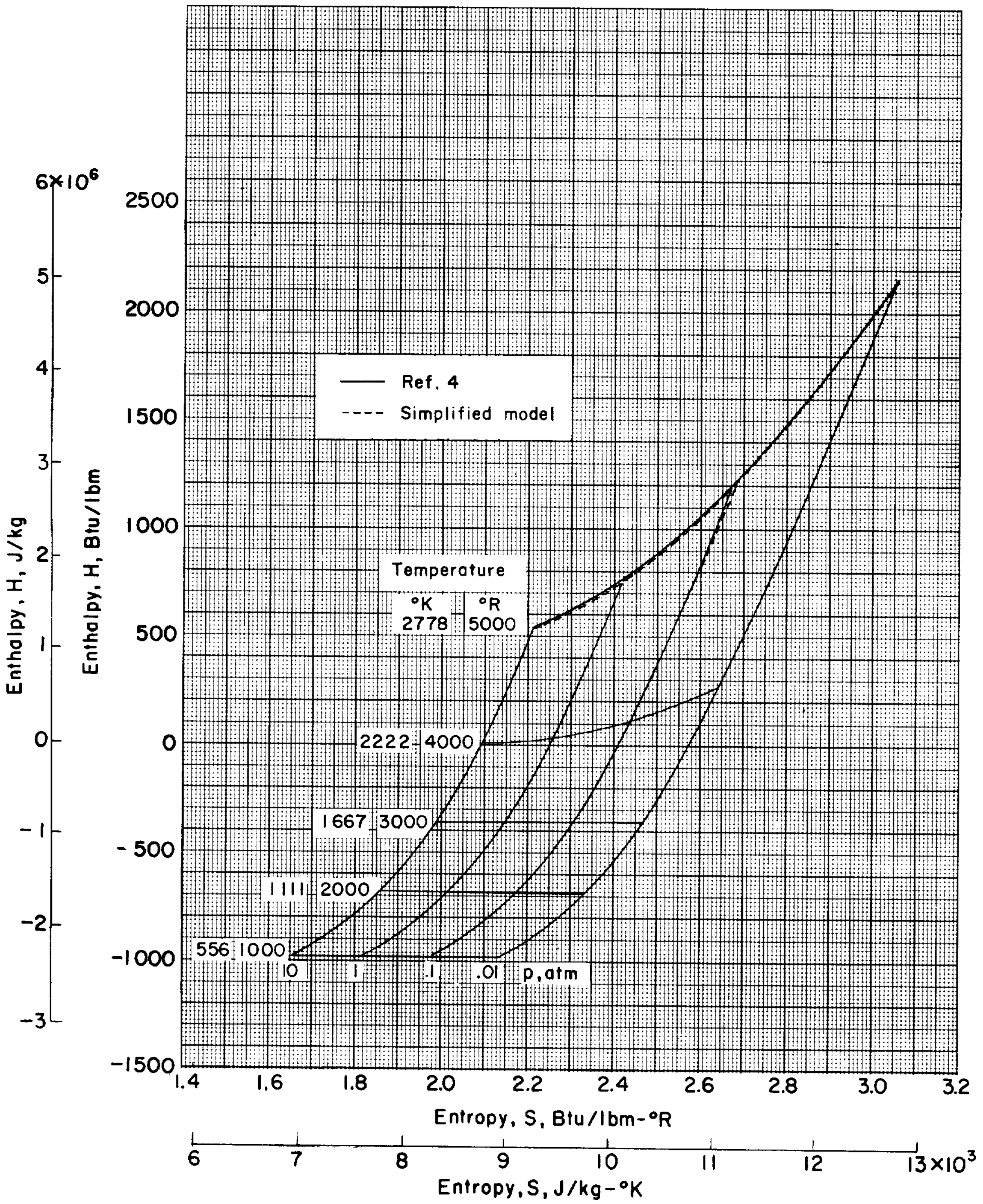


Figure 3.- Mollier diagram for kerosene-air combustion products (r_{ch} = 0.5). r_{eq} = 1.0.

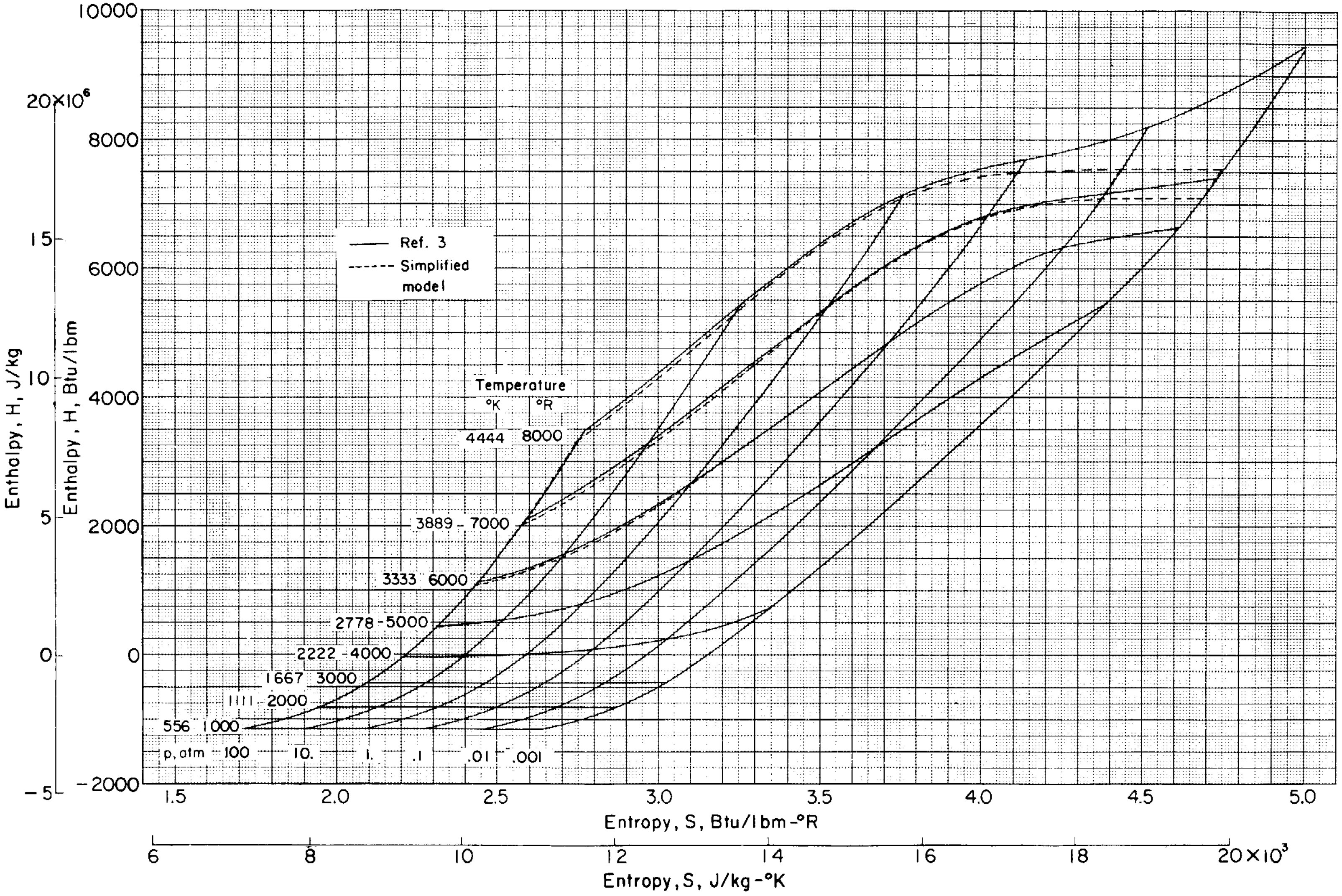


Figure 4.- Mollier diagram for hydrogen-air combustion products $\left(r_{ch} = 0\right)$. $r_{eq} = 1.0$.

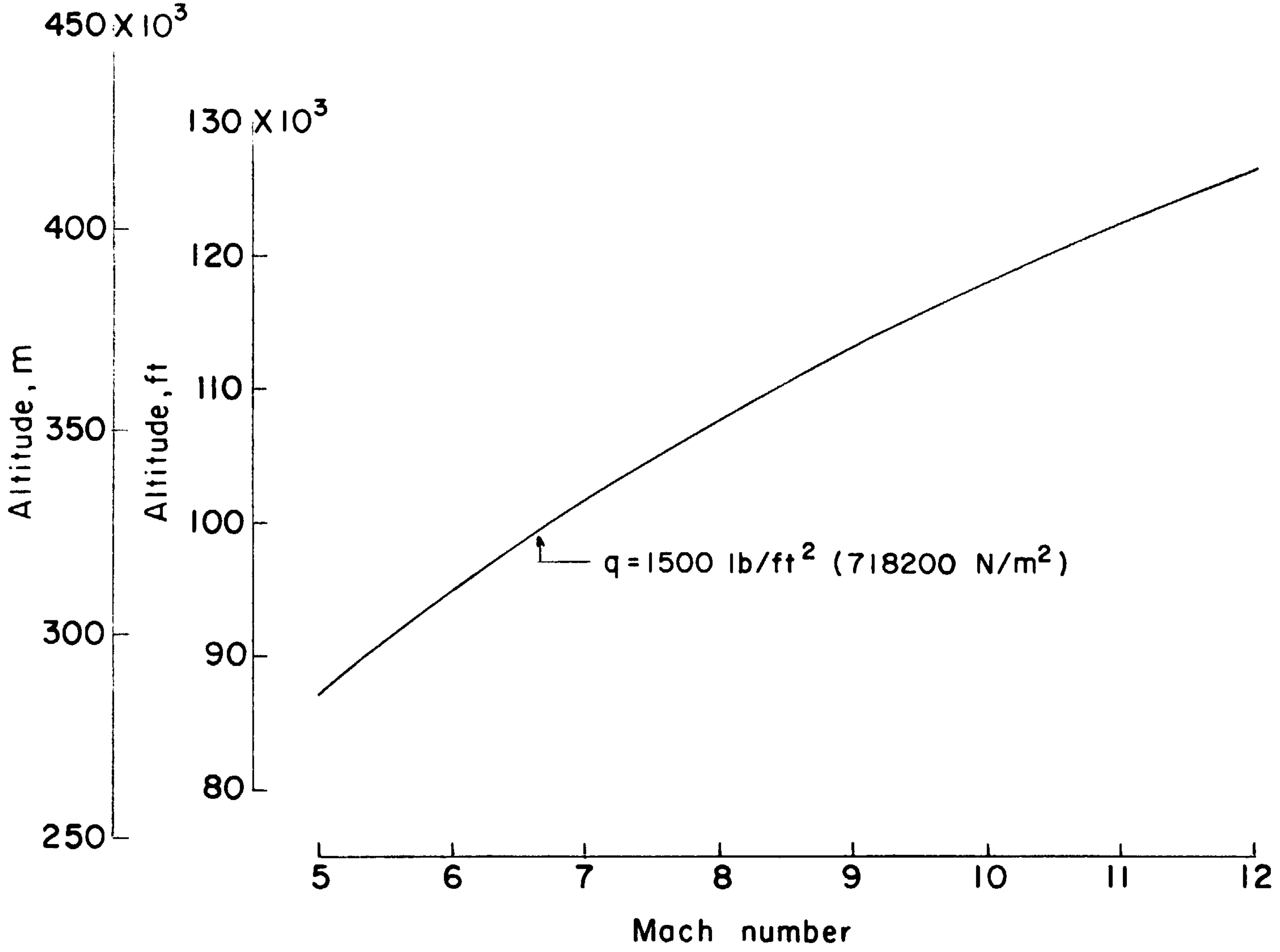


Figure 5.- Assumed flight profile for ramjet performance calculation.

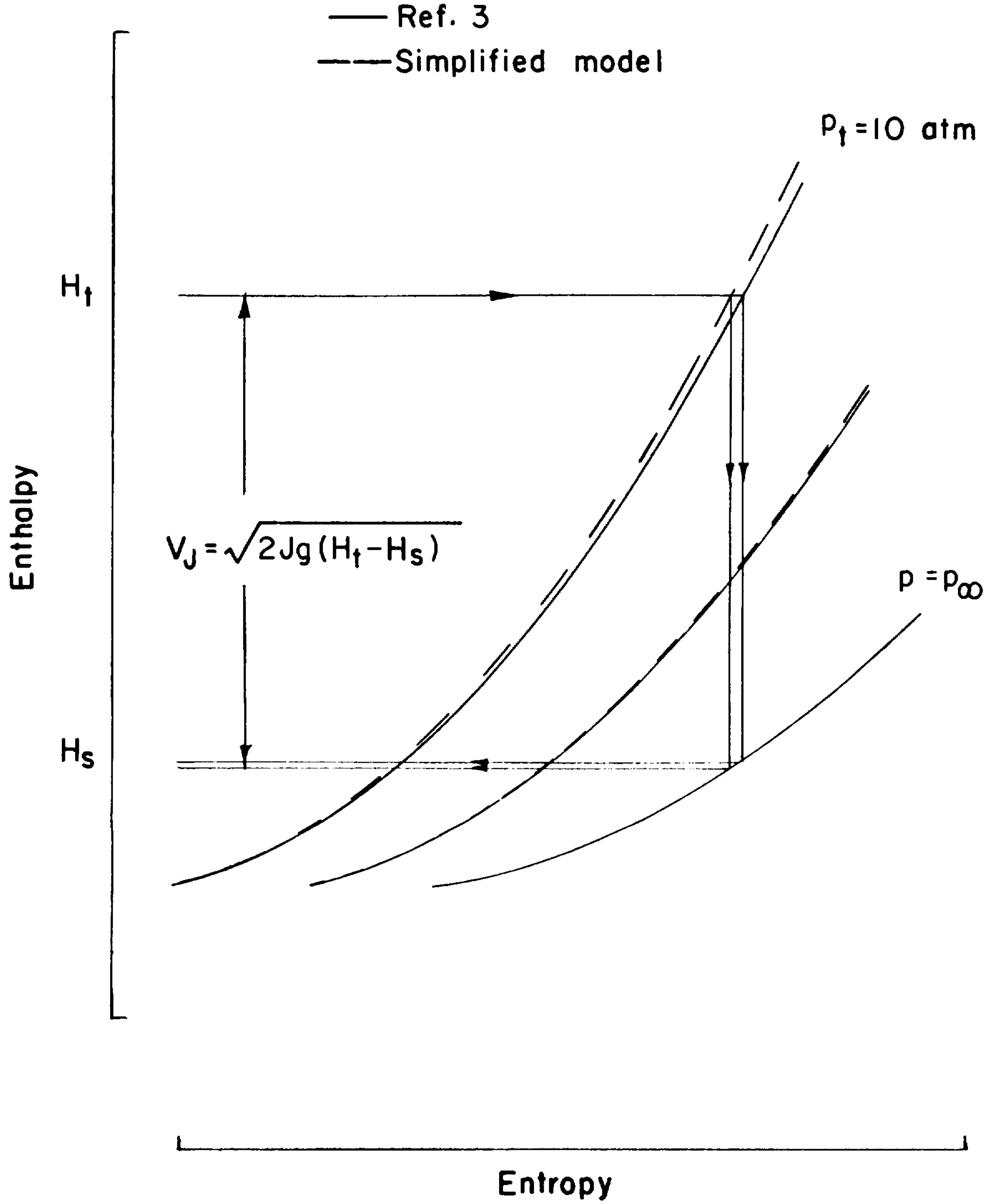


Figure 6.- Isentropic nozzle expansion process.

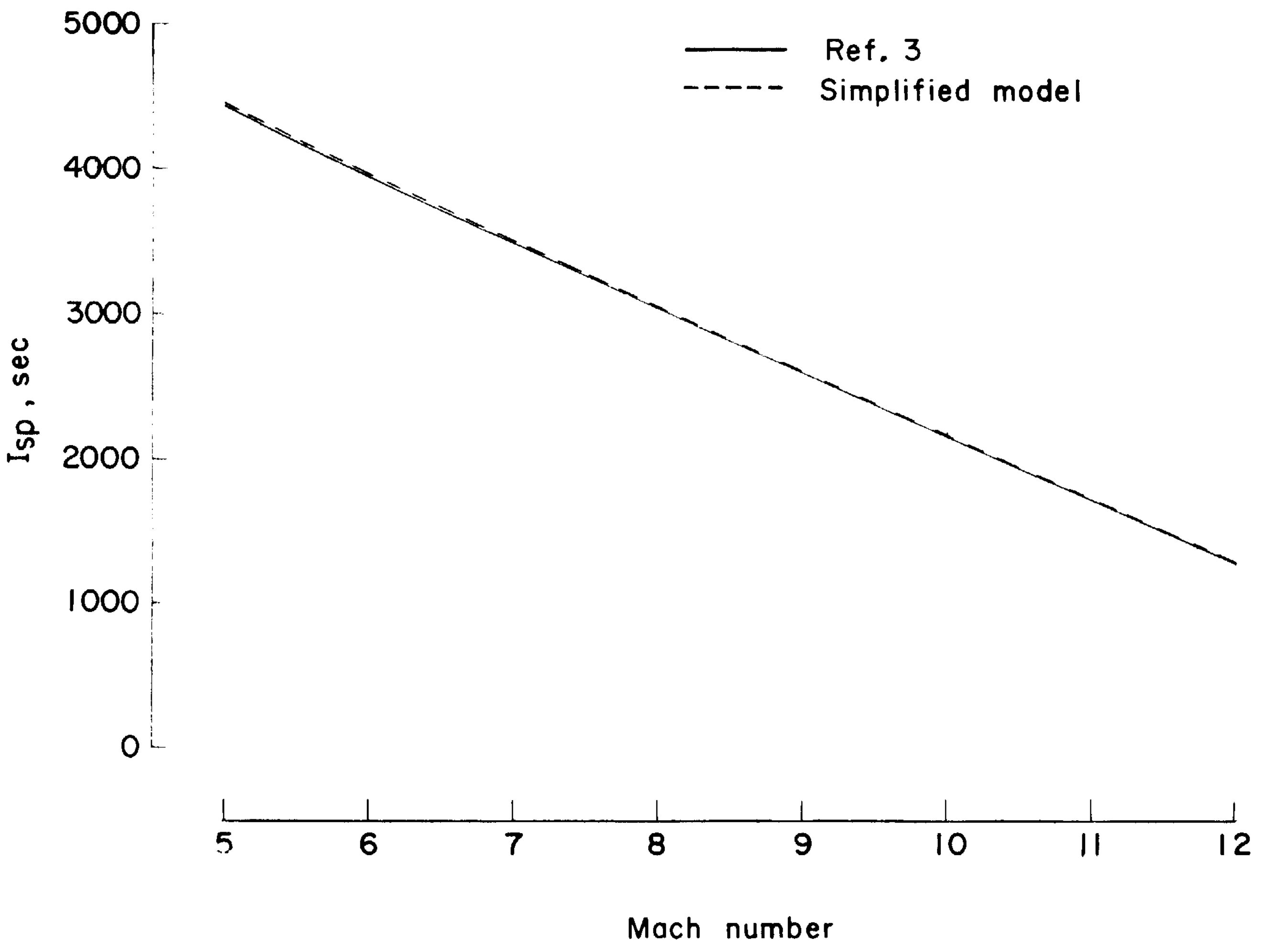


Figure 7.- Effect of gas model on typical ramjet performance. Hydrogen-air combustion; $r_{eq} = 1.0$; $q = 1500$ lbf/ft^2 (718 200 N/m^2); $p_t = 10$ atm; isentropic fully expanded nozzle; 1962 U.S. Standard Atmosphere.

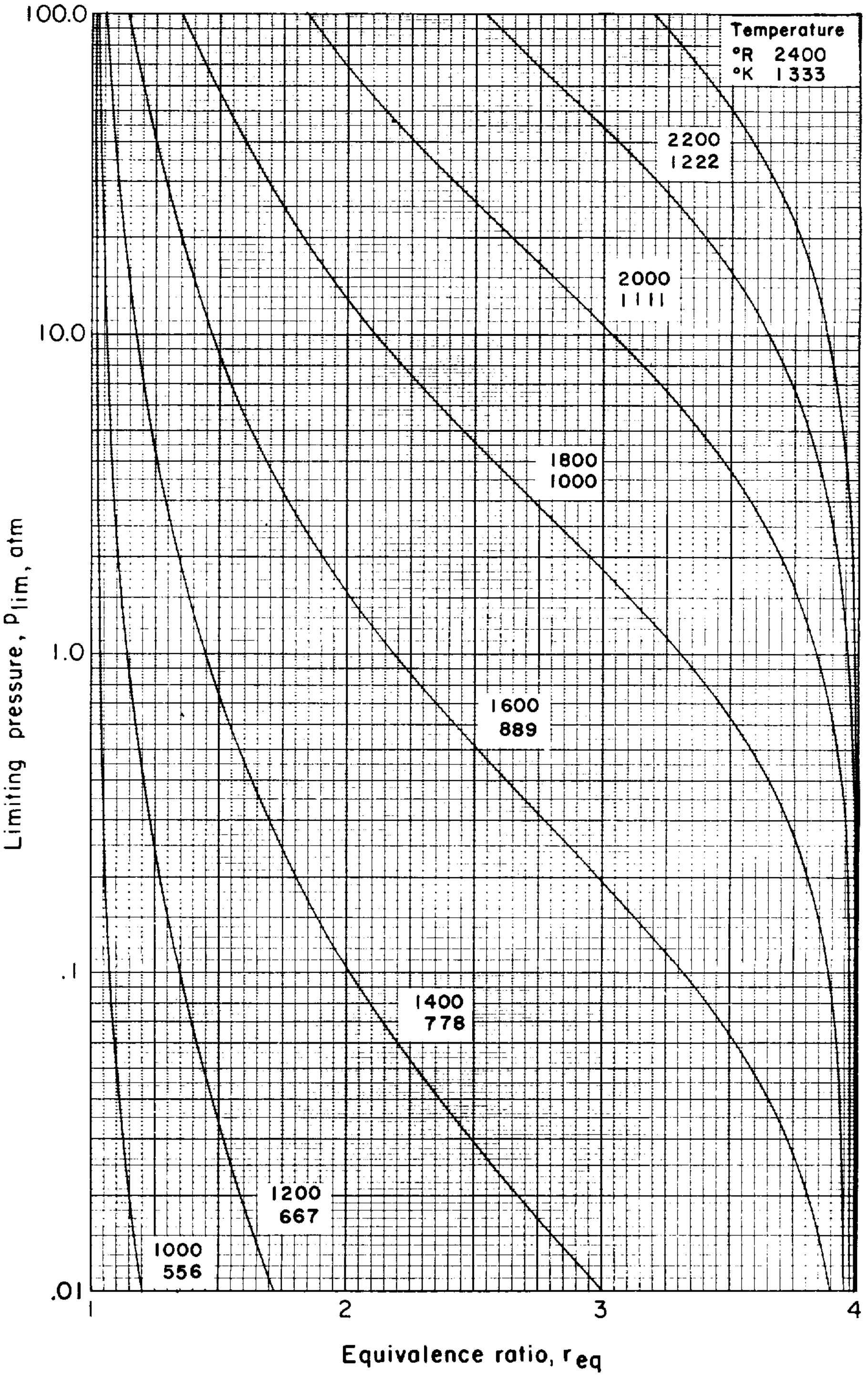


Figure 8.- Limiting pressure for solid carbon formation for methane-air combustion products (r_{ch} = 0.25). $r_{eq,lim}$ = 4.0.

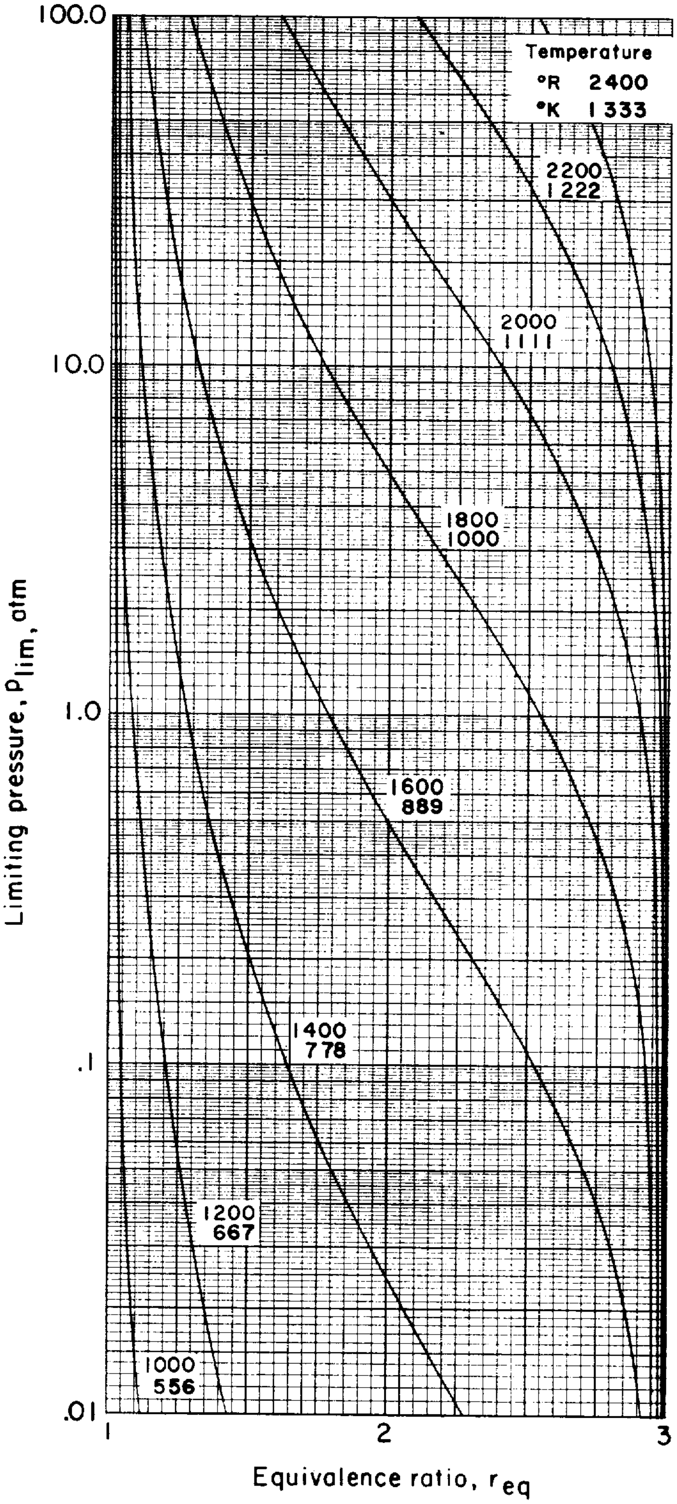


Figure 9.- Limiting pressure for solid carbon formation for kerosene-air combustion products (r_{ch} = 0.5). $r_{eq,lim}$ = 3.0.

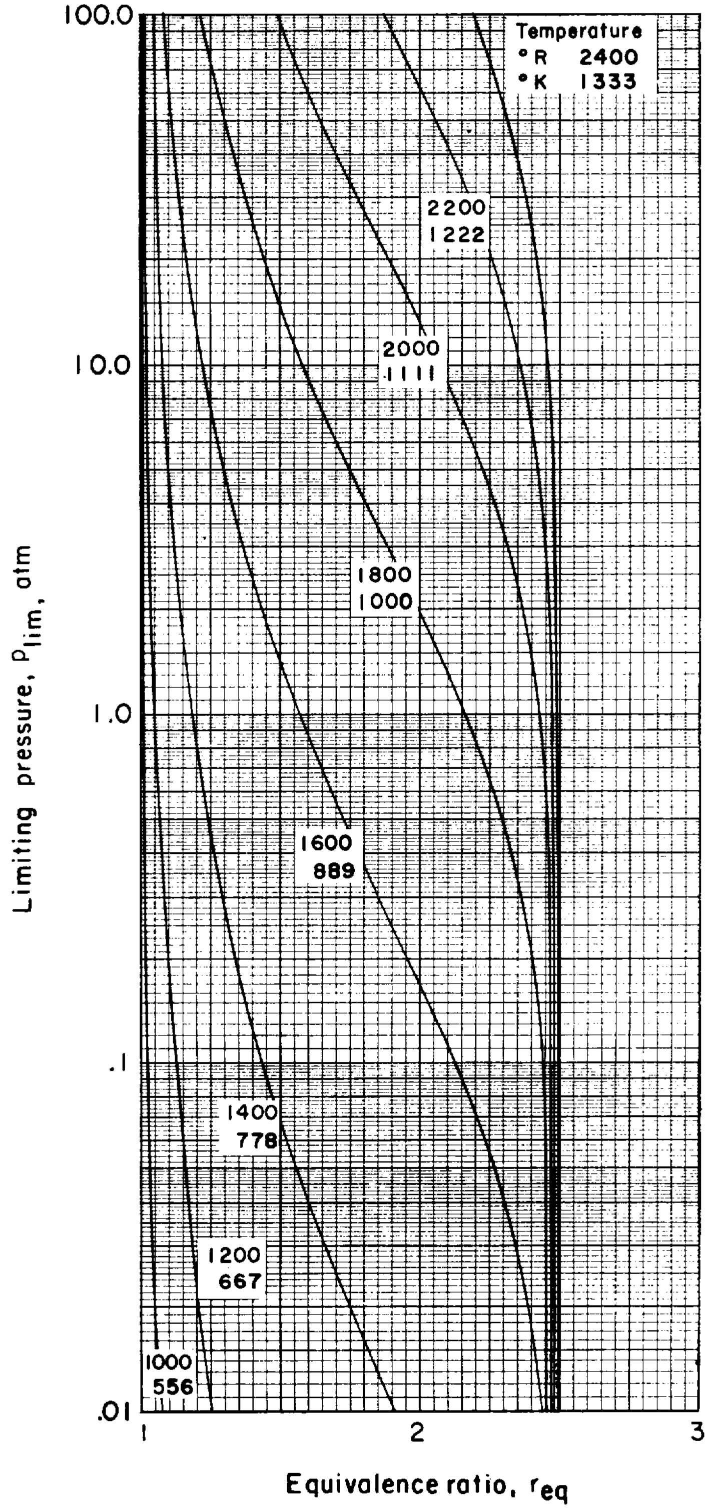


Figure 10.- Limiting pressure for solid carbon formation for benzene-air combustion products $\left(r_{ch} = 1.0\right)$. $r_{eq,lim} = 2.5$.

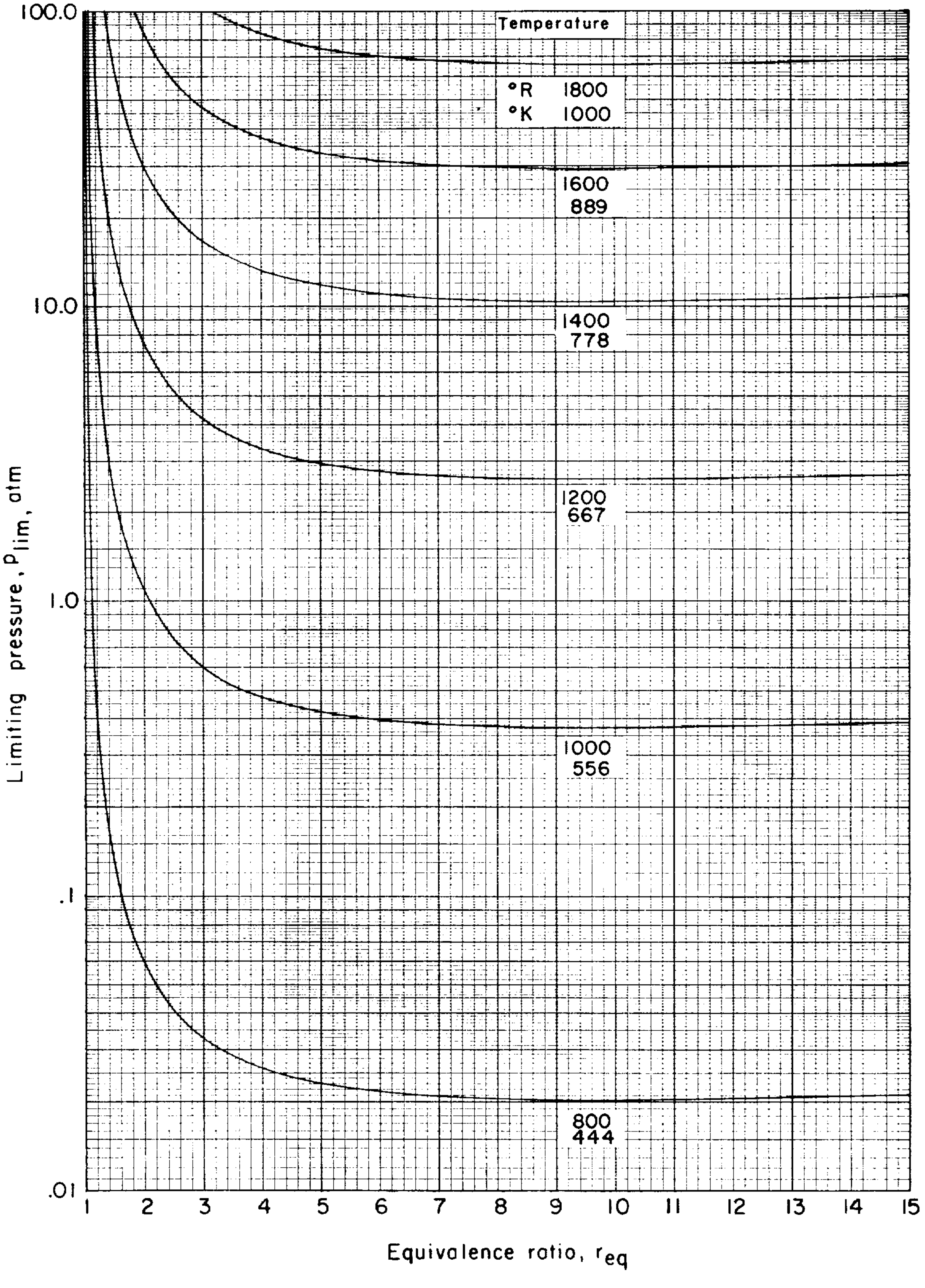


Figure 11.- Limiting pressure for ammonia formation $\left(X_{NH_3} = 0.01\right)$ for hydrogen-air combustion products $\left(r_{ch} = 0\right)$.

NASA-Langley, 1968 —— 28 L-5825