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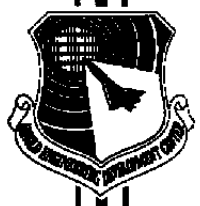

Algorithmic Calculation of Complex Gas Mixtures Equilibrium Composition

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13 ABSTRACT (Maximum 200 words)

A simple numerical algorithm is presented for the computation of the equilibrium composition of complex gas mixtures based upon the equilibrium constant approach. The algorithm uses a little-known form of the quadratic root extraction formula to solve for the equilibrium composition using a successive substitution with iteration to convergence technique. Experience with the algorithm for various complex gas mixtures has revealed excellent stability/convergence properties. Its application in computational fluid dynamics codes as a subroutine is straightforward.

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PREFACE

The work reported herein was conducted at Arnold Engineering Development Center (AEDC), Air Force Systems Command (AFSC). The work was accomplished by Sverdrup Technology, Inc., AEDC Group, operating contractor for the propulsion test facilities at AEDC, AFSC, Arnold Air Force Base, Tennessee, under Project DC12EW. The Air Force project manager was K. Zysk. The project manager for Sverdrup Technology was H. T. Bentley, III. The mansucript was submitted for publication on May 22, 1992.

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1.0 INTRODUCTION

Calculation of the equilibrium chemical composition of complex gas mixtures has received much attention over the years. Several textbooks (Refs. 1-6) and technical reports/papers (Refs. 7-10) present the necessary fundamentals. There are basically two approaches toward computation of the equilibrium composition for a complex gas mixture:

1. Equilibrium constant formulation,

2. Free-energy minimization formulation.

Most modern-day multipurpose chemical equilibrium computer programs (Refs. 11-14) use the free-energy minimization procedure. These programs generally employ a Newton-Raphson iteration procedure to solve a set of simultaneous nonlinear algebraic equations with various "practical" enhancements (such as restrictions on sizes of allowable corrections during an iteration cycle) to avoid numerical difficulties. The resulting solution minimizes the Gibbs free energy of the mixture subject to the constraint of conservation of elements. A linear equation solver/matrix inversion routine must be invoked at each iteration cycle; this results in most of the computer time required for a converged solution being spent to perform the requisite numeric matrix operations.

For solution of complex chemical equilibrium compositions as a subroutine in a computational fluid dynamics code (say an unsteady Navier-Stokes flow-field solver), a stable, fast numerical algorithm which does not require matrix-type numerical operations is needed. This becomes especially critical when it is realized that the equilibrium composition must be calculated at every grid point (which may number in the thousands) over numerous time cycles (which may also number in the thousands). For this reason, many past applications have used approximate approaches for computing complex mixture equilibrium composition, the work by Mascitti (Ref. 15) being an excellent example of a simplified equilibrium hydrocarbon-air combustion model specifically created for use in air-breathing engine cycle computer programs. Other examples include the chemically reacting boundary-layer programs by Blottner (Refs. 16-17) which contain the capability for chemical equilibrium ablation products at an ablating surface.

The various programs by Spalding and associates (Refs. 18-21) for analysis of hydrogen-air combustion under various flow conditions embody a significant advance in the numerical calculation of complex equilibrium composition mixtures. They utilize a little-known form of the quadratic root extraction formula to develop an iterative algorithm for solving the hydrogen-air equilibrium composition problem based upon the equilibrium constant formulation without recourse to matrix techniques. This approach meets the desired criteria

delineated above for application to computational fluid dynamics codes, and provides the basis for the current work which formalizes an algorithmic technique that is computationally fast, absolutely stable, and simple to program for general gas mixtures. Details of the requisite quadratic root extraction formula are presented in Appendix A.

2.0 APPROACH

Calculation of the equilibrium composition of complex gas mixtures using the equilibrium constant formulation generally entails the following five steps (see Chap. V, Sec. 5 in the book by Vincenti and Kruger, Ref. 4):

1. Specify an independent set of chemical reactions containing all the chemical species of interest for the gas mixture.

2. Apply the law of mass action individually to each of the chemical reactions from Step 1.

3. Supplement the equations from Step 2 by equations expressing the conservation of atomic nuclei and the fact of zero net electronic charge if ionization is present.

4. Combine the equations resulting from Steps 2 and 3 to form a set of simultaneous nonlinear algebraic equations, the number of equations being equal to the number of chemical species in the gas mixture.

5. For a specified pressure, temperature, and initial composition, solve the equations from Step 4 to yield the gas mixture equilibrium composition.

It is only in Step 5 that the actual numerical solution algorithm becomes important. However, the manner in which the governing equations are posed in Step 4 is critical to the selection and application of this solution algorithm.

As discussed in Section 1.0, the present work is concerned with a fast, absolutely stable numerical algorithm for solving the equilibrium composition problem without recourse to matrix techniques. This approach will be illustrated through application to two complex gas mixtures:

1. High-temperature ionized air,

2. Hydrocarbon-air products of combustion.

Sufficient detail will be included to allow application of the algorithm to other mixtures.

3.0 APPLICATION EXAMPLES

3.1 HIGH-TEMPERATURE IONIZED AIR

Following Ref. 4, ionized air at temperatures up to about 8,000 K may be regarded as composed of seven chemical species: O_2, O, N_2, N, NO, $NO+$, and $e-$. The equilibrium of the resulting mixture can be taken to be controlled by the following four independent chemical reactions, identified by the letter r:

$$\begin{aligned} r = 1&: O_2 \rightleftharpoons 2O \\ 2&: N_2 \rightleftharpoons 2N \\ 3&: NO \rightleftharpoons N + O \\ 4&: NO \rightleftharpoons NO^+ + e^- \end{aligned}$$

Application of the law of mass action to these four reactions yields the conditions for equilibrium of the mixture as

$$r = 1: \frac{X_O^2}{X_{O_2}} = \frac{1}{\varrho} K_{C_1} \tag{1}$$

$$2: \frac{X_N^2}{X_{N_2}} = \frac{1}{\varrho} K_{C_2} \tag{2}$$

$$3: \frac{X_N X_O}{X_{NO}} = \frac{1}{\varrho} K_{C_3} \tag{3}$$

$$4: \frac{X_{NO^+} X_{e^-}}{X_{NO}} = \frac{1}{\varrho} K_{C_4} \tag{4}$$

where X_i denotes the number of moles of the species i per unit mass of the mixture, ϱ denotes the density of the mixture, and K_{c_r} is the equilibrium constant for the reaction r based on concentration. These equations, which are four equations in seven unknowns, must be supplemented by three additional equations expressing the atomic conservation of oxygen and nitrogen nuclei as well as the fact of zero net electronic charge. These are, in terms of the X mole-mass ratios:

$$2X_{O_2} + X_O + X_{NO} + X_{NO^+} = 2X_{O_2}^* \tag{5}$$

$$2X_{N_2} + X_N + X_{NO} + X_{NO^+} = 2X^*_{N_2} \tag{6}$$

$$X_{NO^+} - X_{e^-} = 0 \tag{7}$$

where $X_{O_2}^*$ and $X_{N_2}^*$ are the O_2 and N_2 compositions at low temperature where the mixture is totally O_2 and N_2. Values for X_{O_2} and X_{N_2} that are a good approximation to real air are

$$X^*_{O_2} = 0.00733 \frac{\text{mole}}{\text{gram} - \text{mixture}}$$

$$X^*_{N_2} = 0.0273 \frac{\text{mole}}{\text{gram} - \text{mixture}}$$

as given in Ref. 4. With the pressure p and temperature T of the mixture specified, the mixture density ϱ is given from the thermal equation of state for the gas mixture

$$\varrho = \frac{p}{\sum_i X_i RT} \tag{8}$$

where R is the universal gas constant and the summation is over the gaseous species of the mixture.

Substitution of Eqs. (1), (2), and (3) allows Eqs. (5) and (6) to be written as

$$\left[\frac{2\varrho}{K_{C_1}}\right] X_O^2 + \left[1 + \frac{\varrho X_N}{K_{C_3}}\right] X_O + \left[-2X^*_{O_2} + X_{NO^+}\right] = 0 \tag{9}$$

$$\left[\frac{2\varrho}{K_{C_2}}\right] X_N^2 + \left[1 + \frac{\varrho X_O}{K_{C_3}}\right] X_N + \left[-2X^*_{N_2} + X_{NO^+}\right] = 0 \tag{10}$$

which are of the proper form for application of the quadratic root extraction discussed in Appendix A. Note that Eqs. (9) and (10) result in A, B, and C coefficients which satisfy the necessary criteria discussed in the Appendix; i.e., A and B are both positive and C is negative (it is physically impossible for X_{NO^+} to be larger in magnitude than X_{O_2} or X_{N_2}). A pseudo-coding of a suitable algorithm for numerical solution of these equations is presented in List 1. Note that the algorithm is very simple (successive substitution with iteration to convergence). The computational philosophy embodied in the algorithm is detailed in four steps:

1. Solve first for the atomic species compositions from the quadratic equations which result through substitution of the law of mass action equations into the

conservation of atomic nuclei equations. Use the quadratic root extraction formula of Appendix A.

2. Next, solve for the diatomic species compositions by substitution of the atomic species compositions from Step 1 into the law of mass action equations.

3. Finally, update the density of the gas mixture based upon the thermal equation of state.

4. Iterate to convergence on all species compositions.

Also illustrated in the algorithm pseudo-coding of List 1 is the necessary specification of the initial composition, as well as the curve fit form of the equilibrium constants taken from Ref. 4 for the four chemical reactions in question.

Practical application of this algorithm reveals convergence within three to five iteration cycles using reasonable initial guesses for the species mole-mass ratios and gas density. For poor initial guesses (zero values for the mole-mass ratios and gas density based on the low-temperature $O_2 - N_2$ air mixture), convergence is obtained in from four to eight iteration cycles.

3.2 HYDROCARBON-AIR PRODUCTS OF COMBUSTION

Many combustion problems require the knowledge of the equilibrium composition of a complex hydrocarbon-air mixture which may contain water vapor and various oxides. For the present example the hydrocarbon-air mixture will be taken to be composed of the following thirteen chemical species: C, H, N, O, O_2, N_2, H_2, OH, H_2O, CO, CO_2, NO, and NO_2. The equilibrium of the resulting mixture can be taken to be controlled by the following nine independent chemical reactions, identified by the letter r:

$$r = 1: O_2 = O + O$$

$$2: N_2 = N + N$$

$$3: H_2 = H + H$$

$$4: OH = O + H$$

$$5: H_2O = H + H + O$$

$$6: CO = C + O$$

$$7: CO_2 = C + O + O$$

$$8: NO = N + O$$

$$9: NO_2 = N + O + O$$

Applying the law of mass action to these eight reactions yields the conditions for equilibrium of the mixture as

$$r = 1: \quad \frac{X_O^2}{X_{O_2}} = \frac{1}{\varrho} K_{C_1} \tag{11}$$

$$2: \quad \frac{X_N^2}{X_{N_2}} = \frac{1}{\varrho} K_{C_2} \tag{12}$$

$$3: \quad \frac{X_H^2}{X_{H_2}} = \frac{1}{\varrho} K_{C_3} \tag{13}$$

$$4: \quad \frac{X_O X_H}{X_{OH}} = \frac{1}{\varrho} K_{C_4} \tag{14}$$

$$5: \quad \frac{X_H^2 X_O}{X_{H_2O}} = \frac{1}{\varrho^2} K_{C_5} \tag{15}$$

$$6: \quad \frac{X_C X_O}{X_{CO}} = \frac{1}{\varrho} K_{C_6} \tag{16}$$

$$7: \quad \frac{X_C X_O^2}{X_{CO_2}} = \frac{1}{\varrho^2} K_{C_7} \tag{17}$$

$$8: \quad \frac{X_N X_O}{X_{NO}} = \frac{1}{\varrho} K_{C_8} \tag{18}$$

$$9: \quad \frac{X_N X_O^2}{X_{NO_2}} = \frac{1}{\varrho^2} K_{C_9} \tag{19}$$

where X_i denotes the number of moles of the species i per unit mass of the mixture, ϱ denotes the density of the mixture, and K_{c_r} is the equilibrium constant for the reaction r based on concentration. These equations, which are nine equations in thirteen unknowns, must be supplemented by four additional equations expressing the atomic conservation of oxygen, nitrogen, hydrogen, and carbon nuclei. These are, in terms of the X mole-mass ratios:

$$2X_{O_2} + X_O + X_{H_2O} + X_{OH} + X_{NO} + 2X_{NO_2} + 2X_{CO_2} + X_{CO} = X_O^* \tag{20}$$

$$2X_{N_2} + X_N + X_{NO} + X_{NO_2} = X_N^* \tag{21}$$

$$2X_{H_2} + X_H + 2X_{H_2O} + X_{OH} = X_H^* \tag{22}$$

$$X_C + X_{CO_2} + X_{CO} = X_C^* \tag{23}$$

where X_O^*, X_N^*, X_H^*, and X_C^* represent the initial elemental composition of the mixture.

At this point exactly the same computational philosophy discussed earlier relative to the ionized air example is followed, namely substitution of the law of mass action equations into the four conservation of atomic nuclei equations to yield three quadratic equations for the atomic oxygen O, atomic nitrogen N, and atomic hydrogen H mole-mass ratios, and a single equation for the atomic carbon C mole-mass ratio. These three quadratic equations are solved using the quadratic root extraction formula of Appendix A with the results substituted into the law of mass action equations to yield the diatomic H_2, O_2, N_2, OH, NO, and triatomic H_2O, CO_2, NO_2 mole-mass ratios. A pseudo-coding of this algorithm is given in List 2; note the similarity with the ionized air algorithm of List 1. Iterative convergence of this algorithm to the final mixture composition can be significantly enhanced by:

1. Performing an inner iteration within the overall iteration process for some specified number of cycles (typically five) on the four conservation of atomic nuclei equations.

2. Extrapolating the atomic oxygen O mole-mass ratio based upon the two most recent iterations.

These two "practical" considerations are embodied in the algorithm formulation.

Application of the present successive substitution algorithm to numerous hydrocarbon-air product of combustion mixtures for various fuels (e.g., methane, hydrogen, kerosene, and JP-4) reveals convergence within three to five iterations using reasonable initial guesses for the species mole-mass ratios and gas density. For poor initial guesses (zero values for the mole-mass ratios and gas density based on the low-temperature $O_2 - N_2$ air mixture only), convergence is obtained in from four to eight iteration cycles. The algorithm has been exercised over a wide range of fuel-air ratios (fuel lean to stoichiometric to fuel rich) with no degradation in performance. In general, it has proven to be highly reliable and robust, mainly because of the desirable numerical properties of the quadratic root extraction formula of Appendix A.

4.0 ALGORITHM VALIDATION

To validate the presently proposed algorithm for application to complex gas mixtures equilibrium compositions, calculations have been performed for two hydrocarbon-air mixtures using (1) the hydrocarbon-air iterative successive substitution algorithm of List 2, (2) the free-energy minimization procedure of NASA SP-273 (Ref. 13) involving matrix inversion, and (3) the equilibrium constant approach of AEDC-TR-71-256 (Ref. 14) involving linearization of the governing conservation equations in conjunction with Newton-Raphson iteration. All three approaches utilized exactly the same set of thermochemical properties, namely the JANNAF (Joint Army, Navy, NASA, Air Force) data curve fits from Ref. 13. Hence, any differences observed upon comparison of results from the three totally different methods can be directly attributed to numerics and/or precision in performing the actual calculations.

Mixture	Pressure, atm	Temperature, K	Theoretical Air, percent
Methane/Air	1.0	1,000.0	110.0
Propane/Air	50.0	2,500.0	100.0

As shown in Table 1 for the methane/air mixture, the present successive substitution hydrocarbon-air products of combustion algorithm yields results in perfect agreement with the other two methods. Only four iterations were required for convergence of the present algorithm with an initial guess of zero for all species mole-mass ratios and the mixture density initialized at the low-temperature $O_2 - N_2$ air value. Table 2 presents corresponding results for the propane/air mixture; note that the disagreement between any of the three methods for any species is in the fifth decimal digit. For this propane/air case, five iterations were

required for convergence of the present algorithm using initial guesses as described above for the methane/air mixture.

As an additional validation, the presently proposed algorithm was used to calculate the adiabatic flame temperature and resulting chemical composition for a gaseous rocket combustion chamber application; specifically:

Fuel: 75-percent ethylene and 25-percent nitrogen (by volume)

Oxidizer: Oxygen

Oxidizer/Fuel Ratio: 2.14

Chamber Pressure: 6.8 atm

using the hydrocarbon-air iterative successive substitution algorithm and the free-energy minimization procedure of NASA SP-273 involving matrix inversion. Both approaches used exactly the same thirteen chemical species and same set of thermochemical properties, namely the JANNAF data curve fits from Ref. 13. Hence, any differences observed upon comparison of results from the two totally different methods can be directly attributed to numerics and/or precision in performing the actual calculations.

Table 3 shows the present hydrocarbon-air products of combustion algorithm yields results in perfect agreement with the NASA SP-273 chamber calculation procedure. For a given value of the adiabatic flame temperature, three to four iterations were required for convergence of the present algorithm using the species mole-mass ratios from the previous adiabatic flame temperature calculation as the initial guess. Six iterations on the adiabatic flame temperature were required for adiabatic flame convergence starting from an initial guess of 3,000 K. Nine iterations in the NASA SP-273 chamber calculation procedure were required for adiabatic flame convergence.

The above results clearly show that the presently proposed interactive successive substitution algorithm does, indeed, converge rapidly to the correct solution for complex hydrocarbon mixtures, even with poor initial guesses to start the iteration process. Better initial guesses significantly increase the rate of iterative convergence as discussed previously.

Execution timing studies of the presently proposed iterative successive substitution algorithm given in List 2 relative to the NASA SP-273 algorithm reveal the following comparison:

Algorithm	Relative Time for One Iteration
Present Successive Substitution Algorithm	1.0
NASA SP-273	13.2

for the gaseous rocket combustion chamber application discussed earlier. Both algorithms used the exact same number of chemical species (namely thirteen), and the relative time for one iteration was determined via system time calls at the start and finish of each iteration cycle. Only the time spent in actually performing the equilibrium composition numerics was included; no input/output or thermodynamic property calculations were contained in the timing. Thus, the presently proposed algorithm is over an order of magnitude faster than the NASA SP-273 algorithm (which requires matrix inversion) for this thirteen-species case.

For application of the present successive substitution algorithm in computational fluid dynamic codes, a simple, easy-to-use curve-fit format for the equilibrium constant K_c is desired. Appendix B presents an Arrhenius-type curve fit (Ref. 4, pp. 214-215) to the JANNAF data curve fit from Ref. 13. As shown in Appendix B, the Arrhenius-type curve fit is an excellent approximation to the JANNAF data curve fit for all chemical species/reactions considered. When they are applied to the present algorithm validation cases of Tables 1 and 2, the Arrhenius-type curve fit results are in essentially identical agreement with the JANNAF data curve fit values from Tables 1 and 2 as shown in Table 4. Hence, the equilibrium constant curve fit coefficients given in Table B-1 are recommended for general use where many evaluations of the equilibrium constant K_c must be performed, as in a computational fluid dynamics code at numerous grid points over numerous time steps.

5.0 CONCLUDING REMARKS

A simple numerical algorithm has been developed for the computation of the equilibrium composition of complex gas mixtures based upon application of the equilibrium constant approach. The algorithm utilizes a little-known form of the quadratic root extraction formula to solve for the gas mixture equilibrium composition using a successive substitution with iteration to convergence technique. Experience with the algorithm for various complex gas mixtures (ionized air and hydrocarbon products of combustion) has revealed excellent stability and convergence properties. Its application for arbitrary gas mixtures in computational fluid dynamics codes as an economical, easy-to-use subroutine is straightforward.

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List 1. Algorithm Pseudo-Coding for High-Temperature Ionized Air

Equilibrium Composition of High Temperature Ionized Air Chemical Species: O, O2, N, N2, NO, NO+, e-		
Chemical Reactions:		r
	O2 = O + O	1
	N2 = N + N	2
	NO = N + O	3
	NO = NO+ + e-	4

```
{Low Temperature Mole-Mass Ratio Composition of O2 - N2 Air}

        XSTAR [ O2 ] = 0.00733
        XSTAR [ N2 ] = 0.0273

{Calculate Equilibrium Constants For Each Of The Four Chemical Reactions}

        KC [ 1 ] = 1200.0 * EXP( -59500.0 / T ) / SQRT( T )
        KC [ 2 ] = 18.0 * EXP( -113000.0 / T )
        KC [ 3 ] = 4.0 * EXP( -75500.0 / T )
        KC [ 4 ] = 14.4E-10 * T * SQRT( T ) * EXP( -107000.0 / T )

{Repeat Iterative Solution Procedure For Mole-Mass Ratios Until Converged}

BEGIN REPEAT UNTIL CONVERGED ON ALL X [ I ] FOR ALL SPECIES

    {Solve Conservation of Atomic Element Equations}

    A = 2.0 * RHO / KC [ 1 ]
    B = 1.0 + RHO * X [ N ] / KC [ 3 ]
    C = -2.0 * XSTAR [ O2 ] + X [ NO+ ]
    X [ O ] = -2.0 * C / ( B + SQRT( B * B - 4.0 * A * C ) )

    A = 2.0 * RHO / KC [ 2 ]
    B = 1.0 + RHO * X [ O ] / KC [ 3 ]
    C = -2.0 * XSTAR [ N2 ] + X [ NO+ ]
    X [ N ] = -2.0 * C / ( B + SQRT( B * B - 4.0 * A * C ) )

    {Solve Law Of Mass action Algebraic Equations}

    X [ O2 ] = RHO * X [ O ] * X [ O ] / KC [ 1 ]

    X [ N2 ] = RHO * X [ N ] * X [ N ] / KC [ 2 ]

    X [ NO ] = RHO * X [ N ] * X [ O ] / KC [ 3 ]

    X [ NO+ ] = SQRT( KC [ 4 ] * X [ NO ] / RHO )

    { Apply Conservation of Electronic Charge }

    X [ e- ] = X [ NO+ ]

    {Calculate Density Of Gas Mixture Using The Thermal Equation of State}

    SUM = 0.0
    BEGIN DO LOOP FOR I = 1 TO NUMBER OF GASEOUS SPECIES
        SUM = SUM + X [ I ]
    END DO LOOP FOR I = 1 TO NUMBER OF GASEOUS SPECIES
    RHO = P / ( SUM * R * T )

    {Insert Suitable Logic For Testing Convergence of Iteration Process Here}

END REPEAT UNTIL CONVERGED ON ALL X [ I ] FOR ALL SPECIES

{ End of Algorithm }
```

List 2. Algorithm Pseudo-Coding for Hydrocarbon-Air Products of Combustion

Equilibrium Composition For C-H-N-O Mixtures
Hydrocarbon - Air Products of Combustion
Chemical Species: C, H, N, O, O2, N2, H2, OH, H2O, CO, CO2, NO, NO2

Chemical Reactions:	r
O2 = O + O	1
N2 = N + N	2
H2 = H + H	3
OH = O + H	4
H2O = H + H + O	5
CO = C + O	6
CO2 = C + O + O	7
NO = N + O	8
NO2 = N + O + O	9

```
(Repeat Iterative Solution Procedure For Mole-Mass Ratios Until Converged)
BEGIN REPEAT UNTIL CONVERGED ON ALL X ( I ) FOR ALL SPECIES
    (Solve Conservation Of Atomic Element Equations)
    BEGIN DO LOOP FOR J = 1 TO NUMBER OF INNER ITERATIONS
      A = 2.0 * RHO * ( 1.0 / KC [ 1 ]
        + RHO * ( X [ C ] / KC [ 7 ] + X [ N ] / KC [ 9 ] ) )
      B = 1.0 +  RHO * ( X [ H ] / KC [ 4 ] + X [ C ] / KC [ 6 ]
        + X [ N ] / KC [ 8 ] + RHO * X [ H ] * X [ H ] / KC [ 5 ] )
      C = -XSTAR [ O ]
      XOO = XO
      XO = X [ O ]
      X [ O ] = -2.0 * C / ( B + SQRT( B * B - 4.0 * A * C ) )
      CAPFF= CAPF
      CAPF = XO - X [ O ]
      IF ( ( J > 2 ) AND ( CAPF <> CAPFF ) ) THEN
        EXTRAPOLATE = XO - CAPF * ( XO - XOO ) / ( CAPF - CAPFF )
        IF ( EXTRAPOLATE > 0.0 ) THEN X [ O ] = EXTRAPOLATE
      END IF THEN

      A = 2.0 * RHO/ KC [ 2 ]
      B = 1.0 + RHO * X [ O ] * ( 1.0 / KC [ 8 ] + RHO * X [ O ] / KC [ 9 ] )
      C = -XSTAR [ N ]
      X [ N ] = -2.0 * C / ( B + SQRT( B * B - 4.0 * A * C ) )

      A = 2.0 * RHO * ( 1.0 / KC [ 3 ] + RHO * X [ O ] / KC [ 5 ] )
      B = 1.0 + RHO * X [ O ] / KC [ 4 ]
      C = -XSTAR [ H ]
      X [ H ] = -2.0 * C / ( B + SQRT( B * B - 4.0 * A * C ) )

      X [ C ] = XSTAR [ C ] / ( 1.0 + RHO * X [ O ] * ( 1.0 / EQKC [ 6 ]
              + RHO * X [ O ] / KC [ 7 ] ) )

    END DO LOOP FOR J = 1 TO NUMBER OF INNER ITERATIONS

    (Solve Law of Mass Action Algebraic Equations)

    X [ O2 ] = RHO * X [ O ] * X [ O ] / KC [ 1 ]
    X [ N2 ] = RHO * X [ N ] * X [ N ] / KC [ 2 ]
    X [ H2 ] = RHO * X [ H ] * X [ H ] / KC [ 3 ]
    X [ OH ] = RHO * X [ O ] * X [ H ] / KC [ 4 ]
    X [ H2O ] = RHO * RHO * X [ H ] * X [ H ] * X [ O ] / KC [ 5 ]
    X [ CO ] = RHO * X [ C ] * X [ O ] / KC [ 6 ]
    X [ CO2 ] = RHO * RHO * X [ C ] * X [ O ] * X [ O ] / KC [ 7 ]
    X [ NO ] = RHO * X [ N ] * X [ O ] / KC [ 8 ]
    X [ NO2 ] = RHO * RHO * X [ N ] * X [ O ] * X [ O ] / KC [ 9 ]

    (Calculate Density Of Gas Mixture Using The Thermal Equation of State)

    SUM = 0.0
    BEGIN DO LOOP FOR I = 1 TO NUMBER OF GASEOUS SPECIES
      SUM = SUM + X [ I ]
    END DO LOOP FOR I = 1 TO NUMBER OF GASEOUS SPECIES
    RHO = P / ( SUM * R * T )

    (Insert Suitable Logic For Testing COnvergence of Iteration Process Here)
END REPEAT UNTIL CONVERGED OF ALL X [ I ] FOR ALL SPECIES
(End Of Algorithm)
```

Table 1. Equilibrium Composition of Methane/Air Mixture*

Species (Mass Fraction)	Successive Substitution Algorithm	NASA SP-273 (Ref. 13)	AEDC-TR-71-256 (Ref. 14)
O_2	0.02010	0.02010	0.02010
H_2O	0.11320	0.11320	0.11320
N_2	0.72841	0.72841	0.72841
NO	0.00001	0.00001	0.00001
CO_2	0.13827	0.13827	0.13827
C, O, H_2 H, OH, N, NO_2, CO	< 0.00001	< 0.00001	< 0.00001

* Pressure = 1 atm
Temperature = 1,000 K
110-percent Theoretical Air
Air Taken to be 21-percent O_2 and 79-percent N_2 by Volume

Table 2. Equilibrium Composition of Propane/Air Mixture*

Species (Mass Fraction)	Successive Substitution Algorithm	NASA SP-273 (Ref. 13)	AEDC-TR-71-256 (Ref. 14)
O_2	0.00402	0.00404	0.00402
O	0.00007	0.00007	0.00007
H_2	0.00015	0.00015	0.00015
H_2O	0.09638	0.09640	0.09638
OH	0.00148	0.00143	0.00148
N_2	0.71932	0.71931	0.71933
NO	0.00319	0.00320	0.00319
CO_2	0.16622	0.16624	0.16621
CO	0.00916	0.00915	0.00916
C, H, N, NO_2	< 0.00001	< 0.00001	< 0.00001

* Pressure = 50 atm
Temperature = 2,500 K
100-percent Theoretical Air
Air Taken to be 21-percent O_2 and 79-percent N_2 by Volume

Table 3. Adiabatic Flame Temperature Composition for a Gaseous Rocket Combustor*

	Successive Substitution Algorithm	NASA SP-273 (Ref. 13)
Adiabatic Flame Temperature (K)	3431.9	3431.9
Species (Mole Fraction)		
H	0.0518	0.0518
O	0.0339	0.0339
O_2	0.0463	0.0463
N_2	0.0602	0.0602
H_2	0.0726	0.0726
OH	0.0819	0.0820
H_2O	0.2519	0.2519
CO	0.2727	0.2726
CO_2	0.1186	0.1187
NO	0.0101	0.0101
C, N, NO_2	< 0.0001	< 0.0001

* Pressure = 6.8 atm
Oxidizer/Fuel Ratio = 2.14
Fuel: 75-percent Ethylene and 25-percent Nitrogen (by Volume)
Oxidizer: Oxygen

Table 4. Influence of Equilibrium Constant on Equilibrium Composition Using Successive Substitution Algorithm

Species (Mass Fraction)	Methane/Air Mixture*		Propane/Air Mixture+	
	JANNAF Data K_c	Appendix B K_c	JANNAF Data K_c	Appendix B K_c
O_2	0.02010	0.02010	0.00402	0.00402
O	< 0.00001	< 0.00001	0.00007	0.00007
H_2	< 0.00001	< 0.00001	0.00015	0.00015
H_2O	0.11320	0.11320	0.09638	0.09639
OH	< 0.00001	< 0.00001	0.00148	0.00147
N_2	0.72841	0.72841	0.71932	0.71932
NO	0.00001	0.00001	0.00319	0.00319
CO_2	0.13827	0.13827	0.16622	0.16623
CO	< 0.00001	< 0.00001	0.00916	0.00915
C, H, N, NO_2	< 0.00001	< 0.00001	<0.00001	< 0.00001

* Pressure = 1 atm
Temperature = 1,000 K
110-percent Theoretical Air
Air Taken to be 21-percent O_2 and 79-percent N_2 by Volume

+ Pressure = 50 atm
Temperature = 2,500 K
100-percent Theoretical Air
Air Taken to be 21-percent O_2 and 79-percent N_2 by Volume

APPENDIX A

QUADRATIC ROOT EXTRACTION FORMULA

The two real roots of a quadratic equation

$$AX^2 + BX + C = 0$$

are well known to be

$$X = \frac{-B \pm \sqrt{B^2 - 4AC}}{2A}$$

What is not so well known is that these two real roots are also given by*

$$X = \frac{-2C}{B \pm \sqrt{B^2 - 4AC}}$$

which has many desirable advantages for numerical applications. If it is physically known that both A and B are greater than zero (i.e., positive) and that C is less than zero (i.e., negative), then the positive root of the equation (which is the root of interest in most physical applications) is given by

$$X = \frac{-2C}{B + \sqrt{B^2 - 4AC}}$$

without any danger of numerical precision problems caused by subtraction error. Further observe that this form reduces to the correct positive root in the limit of either the A or B coefficient approaching zero.

*AIAA Aerospace Design Engineers Guide, Revised and Enlarged, January 1987, pp. 1-3.

APPENDIX B

EQUILIBRIUM CONSTANT CURVE FIT

Vincenti and Kruger (Ref. 4, p. 168 and pp. 214–215) recommend an Arrhenius-type curve fit for the equilibrium constant K_c, specifically

$$K_c = A\ T^B \exp(C/T) \tag{B-1}$$

where A, B, and C are curve fit constants to be determined in a least-squares sense from the equilibrium constant versus temperature data for a given chemical reaction. Table B-1 provides the A, B, and C curve fit constants for the nine chemical reactions of present interest based upon the JANNAF data curve fit given in Ref. 13. In fitting the JANNAF data of Ref. 13, the fits were performed over a low (300-1,000 K) and high (1,000-5,000 K) temperature range for each reaction using a constrained least-squares curve fit which forced continuity of the fit value at the low-high temperature match point, namely 1,000 K. All calculations were performed using double precision arithmetic (16 digits) with all JANNAF data input from Ref. 13 also performed in double precision.

Table B-2 presents the standard error of estimate for each reaction's curve fit in terms of LN (K_c) where

$$LN(K_c) = LN(A) + B\ LN(T) + C/T \tag{B-2}$$

from Eq. (B-1). Note that the standard error of estimate is of the order 0.01 to 0.001 for values of LN (K_c) in the range -10 to -600, which clearly shows the high accuracy of the Arrhenius-type curve fit relative to the equilibrium constant data.

Figures B-1, B-2, and B-3 illustrate graphically the behavior of the equilibrium constant data for each reaction when plotted in terms of Eq. (B-2) variables, namely LN (K_c) versus 1/T. Figure B-1 shows that the $H_2 = H + H$ and $OH = O + H$ reactions have nearly the same equilibrium constant variation with temperature; similarly, for the $H_2O = H + H + O$ and $NO_2 = N + O + O$ reactions on Fig. B-2.

For high-temperature air, the pioneering work by Wray (Ref. 22) performed in 1961 provided the equilibrium constant curve fits for the reactions

$$O_2 \rightleftharpoons 2O$$

$$N_2 \rightleftharpoons 2N$$

$$NO \rightleftharpoons N + O$$

which are used in the present Fig. 1 algorithm pseudo-coding for high-temperature ionized air. Figure B-4 shows a comparison of the Wray curve fits relative to the present JANNAF curve fits over the high-temperature range from 2,500 to 5,000 K. Agreement is essentially exact over this temperature range.

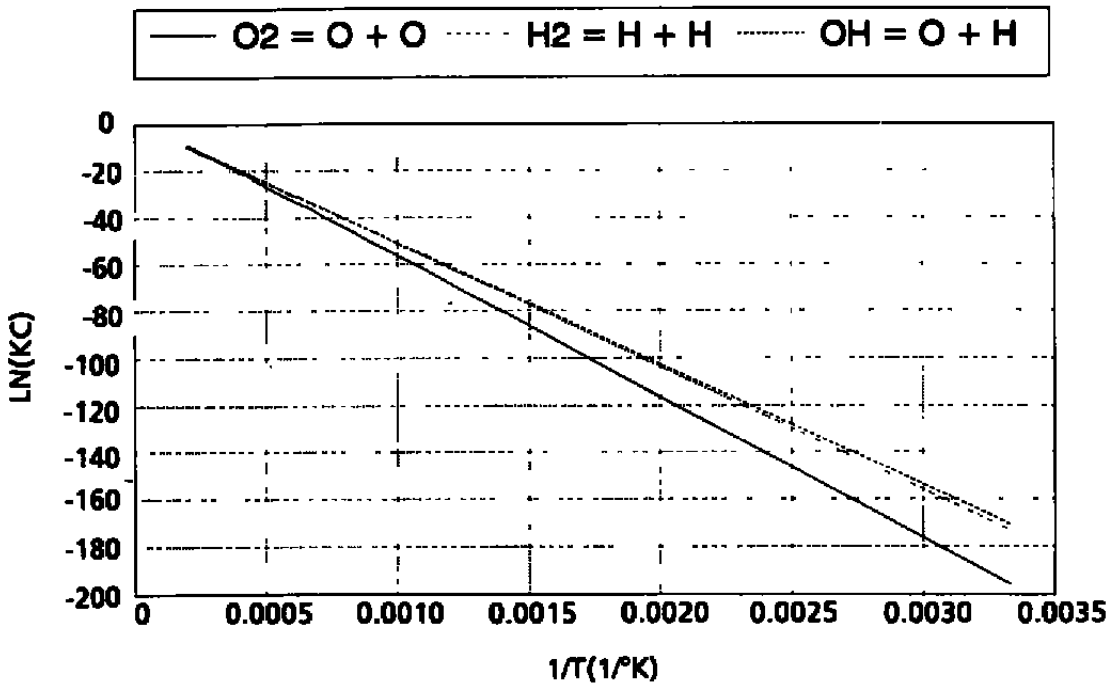

Figure B-1. Chemical equilibrium constant variation with temperature, O_2, H_2, and OH.

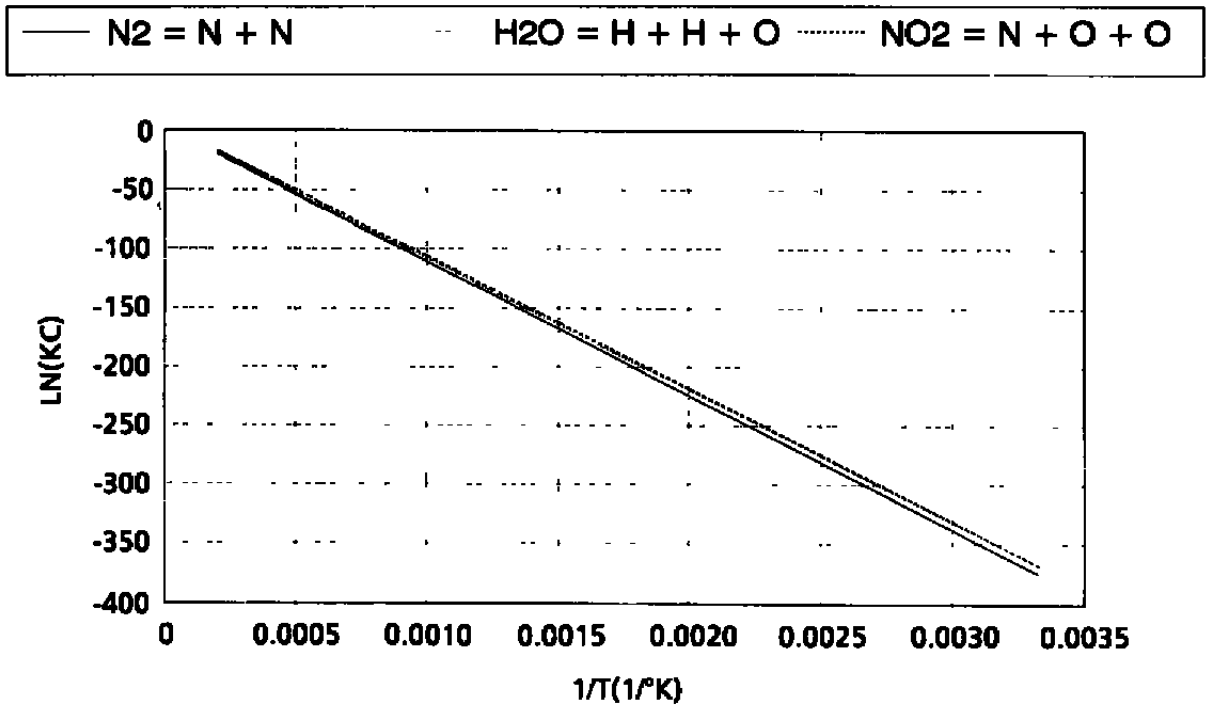

Figure B-2. Chemical equilibrium constant variation with temperature, N_2, H_2O, and NO_2.

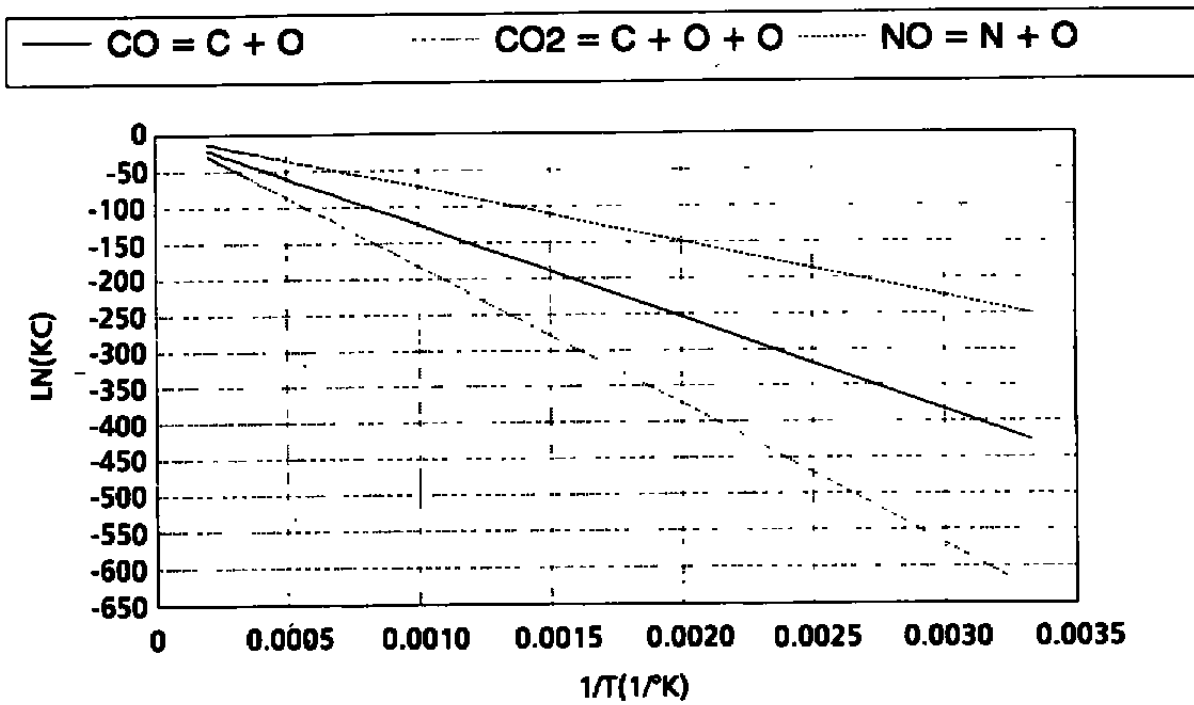

Figure B-3. Chemical equilibrium constant variation with temperature, CO, CO_2, and NO.

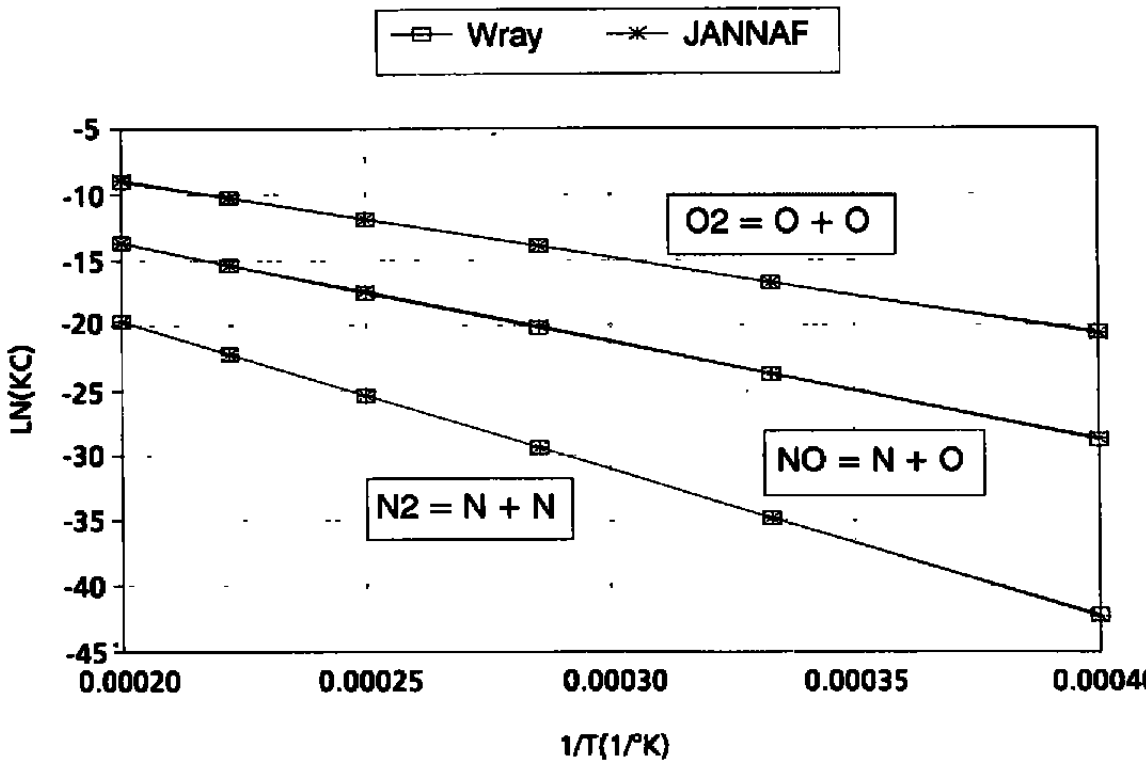

Figure B-4. Comparison of Wray and JANNAF chemical equilibrium constant curve fit variation with temperature.

Table B-1. Equilibrium Constant Curve Fit Coefficients*

r	Range	A	B	C
1	L	4.062702994580318	0.2502842621822995	−59606.12559562957
	H	3047.358840886025	−0.5810944837674182	−60483.34670079666
2	L	1.368670697255243	0.3649632776333878	−113312.4168571282
	H	290.6847098177596	−0.307468905987193	−114025.8191245152
3	L	0.09447126526609221	0.4675387830430657	−52005.88558611053
	H	21.6209968596366	−0.1991760350848257	−52833.50726295615
4	L	0.03927314917445225	0.4790269258033703	−51064.14698292007
	H	9.437740626012161	−0.1982331074650644	−51867.73124463861
5	L	0.003362325850839724	1.169921035885374	−110586.4571538467
	H	13843.73806527046	−0.724239179515325	−112732.7725377666
6	L	2.802867695064791	0.3794166065314485	−129073.3747337088
	H	633.4027082089172	−0.3045586535585327	−129769.1043600149
7	L	30136.53402335615	−0.02686298150640948	−192979.4188364627
	H	16648911484.32225	−1.701127984990677	−194636.1231254872
8	L	0.6117641964723212	0.2857408752663698	−75604.48446764979
	H	127.867751455553	−0.3883093860925471	−76290.71512510274
9	L	217.6601569189995	0.1482325072416944	−112264.619822127
	H	12708271.17655437	−1.246715227962329	−113603.4909203498

* $K_c = A(T^B) \exp(C/T)$

L: Low-Temperature Range (300–1,000 K)

H: High Temperature Range (1,000–5,000 K)

r Chemical Reaction

1 $O_2 = O + O$

2 $N_2 = N + N$

3 $H_2 = H + H$

4 $OH = O + H$

5 $H_2O = H + H + O$

6 $CO = C + O$

7 $CO_2 = C + O + O$

8 $NO = N + O$

9 $NO_2 = N + O + O$

Table B-2. Equilibrium Constant Curve Fit Statistics*

r	Range	Standard Error of Estimate in $LN(K_c)$	Maximum $LN(K_c)$	Minimum $LN(K_c)$
1	L	0.008446705	−195.8516	−56.47537
	H	0.008945615	−56.47537	−9.038786
2	L	0.004053238	−375.3098	−110.4775
	H	0.004279492	−110.4775	−19.75358
3	L	0.0008926589	−173.0451	−51.1357
	H	0.01417387	−51.1357	−9.214879
4	L	0.001472959	−170.7178	−50.99236
	H	0.0103901	−50.99236	−9.833852
5	L	0.009161721	−367.6373	−108.2001
	H	0.02416324	−108.2001	−19.21817
6	L	0.005646218	−427.0459	−125.4218
	H	0.002992297	−125.4218	−22.09832
7	L	0.02045509	−633.0897	−182.8515
	H	0.007943118	−182.8515	−29.88921
8	L	0.006034852	−250.8724	−74.12206
	H	0.003529303	−74.12206	−13.71652
9	L	0.01920225	−367.9731	−105.8577
	H	0.004792126	−105.8577	−16.98331

* $LN(K_c) = LN(A) + B\ LN(T) + C/T$
L: Low-Temperature Range (300–1,000 K)
Maximum at 300 K and Minimum at 1,000 K

H: High-Temperature Range (1,000–5,000 K)
Maximum at 1,000 K and Minimum at 5,000 K

r Chemical Reaction
1 $O_2 = O + O$
2 $N_2 = N + N$
3 $H_2 = H + H$
4 $OH = O + H$
5 $H_2O = H + H + O$
6 $CO = C + O$
7 $CO_2 = C + O + O$
8 $NO = N + O$
9 $NO_2 = N + O + O$

Definition of Standard Error of Estimate (S):

$$S = \sqrt{\frac{\sum_{i=1}^{N} (y_i^{fit} - y_i^{data})^2}{N - F}}$$

N = Total Number of Data Points
F = Total Number of Functions in Curve Fit