Rapid Computation of Chemical Equilibrium Composition: An Application to Hydrocarbon Combustion

A scheme for rapidly computing the chemical equilibrium composition of hydrocarbon combustion products is derived. A set of ten governing equations is reduced to a single equation that is solved by the Newton iteration method. Computation speeds are approximately 80 times faster than the often used free-energy minimization method. The general approach also has application to many other chemical systems.

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SCOPE

The computation of the equilibrium chemical composition of complex reacting mixtures is required for the analysis and design of many engineering systems. Numerous methods for carrying out these computations have been published. Perhaps the most often used algorithms are those that employ the free-energy minimization technique. These are general-purpose algorithms that can be applied to a wide variety of chemical systems. When these general-purpose algorithms are used in analyses that require a very large number of equilibrium chemical composition computations, such as in the application of computational fluid dynamics involving reacting gas mixtures, a large fraction of the total computation time can be due to just determining chemical composition. The objective of this paper is to devise a much more rapid method for computing the equilibrium chemical composition. This is achieved by giving up a degree of generality and reducing the equilibrium and elemental balance equations to a single equation that can be solved by a simple iteration scheme. While the method presented has general application to many chemical systems, this article will deal with a particular system of general interest in combustion. The chemical system is composed of four elements (C, H, O, N) and ten reacting species (H_2O, CO_2, CO, O_2, H_2, N_2, H, O, OH, NO). This study is an extension of the method presented earlier by Erickson et al. (1966) wherein only two elements and six reacting species were considered.

CONCLUSIONS AND SIGNIFICANCE

It has been shown that the elemental balance and equilibrium equations for a rather complex chemical mixture composed of four chemical elements and ten reacting species can be reduced to a single equation that in turn can be solved readily by a simple and rapid iteration scheme. Computation speeds with this method are approximately 80 times faster than the often-used methods based on the free-energy minimization technique. These results were obtained for a chemical system of particular interest in combustion, but application to a wide variety of other chemical mixtures is possible. The proposed rapid method for com-

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puting the equilibrium chemical composition will facilitate the application of computational fluid dynamics techniques to systems involving complex chemically reacting mixtures.

Introduction

Numerous schemes for computing the chemical equilibrium composition of reacting gas mixtures have been developed over the years. One of the earliest schemes was presented by Damköhler and Edse (1943) in which a method of successive approximation was used. That scheme was set up for hand calculation. Some of the earliest general schemes that were developed for application to computers were published by Brinkley (1947), Huff et al. (1951), and White et al. (1958). A review of this early work and subsequent developments, as well as a set of computer programs based on various algorithms for determining the chemical compositions of reacting mixtures, is presented by Smith and Missen (1982).

The available numerical schemes for the most part are based on general-purpose algorithms that can be used to compute the chemical equilibrium composition for a wide variety of chemical systems. This generality is often desired. However, when a very large number of chemical equilibrium composition computations are required for a particular chemical system, it may be desirable to give up a degree of generality in favor of a substantial increase in computational efficiency. The computation time required to determine a single chemical composition using a general algorithm may be quite small, but the application of such an algorithm to a complex flow field computation that involves a coupled set of fluid flow and transport equations requires a very large number of repetitive computations of the chemical composition. For complex flow field computations the time used to determine the chemical equilibrium composition could be a large fraction of the total computation time.

One approach to achieving a more rapid scheme for determining the chemical equilibrium composition for a particular chemical system is to algebraically reduce the number of unknowns in the problem before seeking a numerical solution. Such an approach was given by Erickson et al. (1966) for the specific application to the combustion of hydrogen with air. The scheme included six reacting species—H_2, O_2, H_2O, H, O, and OH—and N_2 was treated as an inert species. The four equilibrium equations and two elemental balance equations were reduced to a single equation of sixth degree involving one unknown. It was shown that the computational speed using the single equation with a Newton iteration scheme was a factor of 100 times faster than one of the general and commonly used algorithms. It was also noted that the reduction to a single equation involved tedious algebra even for a chemical system of intermediate complexity. Since that time, however, computer systems that permit symbolic algebraic manipulation, in particular MACSYMA developed at MIT, have become available; these make it possible to work out the tedious algebra reliably and with little effort.

This paper treats a more general system that has a rather wide application to combustion. The chemical system is composed of ten species that exist in the combustion products resulting from burning hydrocarbons in air/oxygen mixtures. The solution is formulated by specifying the temperature, density, and elemental constraints, and an equation involving one composition variable is developed. A simple iteration scheme and sample results are included. Other chemical systems can also be treated using the approach employed in this paper.

Development of Equations

During the early phases of this study MACSYMA was used extensively to explore various ways to reduce the set of starting equations to a single equation. The use of MACSYMA provided a systematic approach that led to the following scheme. It should be noted, however, that all of the algebraic steps presented for this particular scheme could be carried out by hand with modest effort. The most important consideration was to obtain a final equation and set of auxiliary equations that required the least number of numerical operations.

The following set of equations is developed for determining the equilibrium chemical composition of combustion products composed of ten species. The ten species are assigned indices $i = 1, 2, \ldots, 10$ in the following order: H_2O, CO_2, CO, O_2, H_2, N_2, H, O, OH, and NO. The system temperature and density are to be specified along with relative amounts of the four chemical elements: H, O, C, and N. Starting with an appropriate set of equilibrium and elemental balance equations, the ten equations are reduced to two equations and then to a single equation containing one unknown composition variable.

Equilibrium and elemental balance equations

For a reacting gas mixture containing ten species composed of four chemical elements there are six independent chemical reactions that can be written. The following set of independent reactions is chosen:

$$CO + H_2O = CO_2 + H_2 \qquad [I]$$

$$2CO_2 = 2CO + O_2 \qquad [II]$$

$$H_2 + O_2 = 2OH \qquad [III]$$

$$H_2 = 2H \qquad [IV]$$

$$O_2 = 2O \qquad [V]$$

$$O_2 + N_2 = 2NO \qquad [VI]$$

The corresponding nonlinear equilibrium equations in terms of mole numbers, σ_i, for these six reactions are:

$$K_1 = \sigma_2\sigma_5/\sigma_1\sigma_3 \qquad (1)$$

$$K_2 = \sigma_3^2\sigma_4/\sigma_2^2 \qquad (2)$$

$$K_3 = \sigma_9^2/\sigma_4\sigma_5 \qquad (3)$$

$$K_4 = \sigma_7^2/\sigma_5 \quad (4)$$

$$K_5 = \sigma_8^2/\sigma_4 \quad (5)$$

$$K_6 = \sigma_{10}^2/\sigma_4\sigma_6 \quad (6)$$

and the four linear elemental balance equations are:

$$\sigma_H = 2\sigma_1 + 2\sigma_5 + \sigma_7 + \sigma_9 \quad (7)$$

$$\sigma_O = \sigma_1 + 2\sigma_2 + \sigma_3 + 2\sigma_4 + \sigma_8 + \sigma_9 + \sigma_{10} \quad (8)$$

$$\sigma_N = 2\sigma_6 + \sigma_{10} \quad (9)$$

$$\sigma_C = \sigma_2 + \sigma_3 \quad (10)$$

where the equilibrium constants K_j in terms of mole numbers σ_i are related to the equilibrium constants $K_{p,j}$ in terms of partial pressures for reactions I, III, and VI by

$$K_j = K_{p,j} \quad j = 1, 3, 6 \quad (11)$$

where K_j and $K_{p,j}$ are nondimensional, whereas for reactions II, IV, and V,

$$K_j = K_{p,j}P^o/\rho RT \quad j = 2, 4, 5 \quad (12)$$

where K_j has units of mol/kg and $K_{p,j}$ has units of pressure.

It should be noted that while Eqs. 7–10 comprise an appropriate and complete definition of the elemental balances, it is possible to define the chemical system by specifying only three of the four quantities—σ_C, σ_H, σ_N, and σ_O—and use the identity

$$(12\sigma_C + \sigma_H + 14\sigma_N + 16\sigma_O)/1{,}000 = 1 \quad (13)$$

where the numerical coefficients on σ_C, σ_H, σ_N, and σ_O are the atomic weights of C, H, N, and O, respectively.

Reduction to two-equation set

While there are of course many ways to reduce the set of Eqs. 1–10 to a two-equation set, it was convenient to first introduce a new variable representing the mole ratio of CO to CO_2,

$$\xi = \sigma_3/\sigma_2 \quad (14)$$

and then proceed to eliminate σ_i; $i = 2, 3, \ldots, 10$ by using Eqs. 1–10.

Equations 1–6 can then be written as

$$\sigma_5 = K_1\sigma_1\xi \quad (15)$$

$$\sigma_4 = K_2/\xi^2 \quad (16)$$

$$\sigma_9^2 - K_1K_2K_3\sigma_1/\xi = 0 \quad (17)$$

$$\sigma_7 = (K_4/K_2K_3)^{1/2}\xi\sigma_9 \quad (18)$$

$$\sigma_8 = (K_2K_5)^{1/2}/\xi \quad (19)$$

$$\sigma_{10}^2 - K_2K_6(\sigma_N - \sigma_{10})/2\xi^2 = 0 \quad (20)$$

where Eq. 9 has been used to eliminate σ_6 in Eq. 6 to obtain Eq. 20. In addition, Eqs. 10 and 14 can be combined to give expressions for σ_2 and σ_3 in terms of ξ, so that

$$\sigma_2 = \sigma_C/(\xi + 1) \quad (21)$$

$$\sigma_3 = \xi\sigma_C/(\xi + 1) \quad (22)$$

Now Eqs. 15 and 18 can be used to eliminate σ_5 and σ_7 in Eq. 7 to obtain an expression for σ_9 in terms of σ_1 and ξ,

$$\sigma_9 = [\sigma_H - 2(1 + K_1\xi)\sigma_1]/(K_a\xi + 1) \quad (23)$$

where $K_a = (K_4/K_2K_3)^{1/2}$. When this expression is substituted into Eq. 17 to eliminate σ_9, a quadratic equation in σ_1 is obtained

$$a_2\sigma_1^2 + a_1\sigma_1 + a_0 = 0 \quad (24)$$

where a_m; $m = 0, 1, 2$ are functions of ξ only. The coefficients a_m in Eq. 24 can in turn be expressed as polynomials in ξ, that is

$$a_m = \sum_{n=0}^{3} a_{mn}\xi^n \quad m = 0, 1, 2 \quad (25)$$

where the constant coefficients a_{mn} are given in Table 1.

Equations 16, 19, and 21–23 are used to eliminate σ_4, σ_8, σ_2, σ_3, and σ_9 in Eq. 8 to obtain an expression for σ_{10} in terms of σ_1 and ξ,

$$\sigma_{10} = -[1 - 2(1 + K_1\xi)/(K_a\xi + 1)]\sigma_1 - \sigma_H/(K_a\xi + 1) + \sigma_O - \sigma_C - \sigma_C/(\xi + 1) - 2K_2/\xi^2 - K_b/\xi \quad (26)$$

where $K_b = (K_2K_5)^{1/2}$. This equation is linear in σ_1 and can be expressed in a more compact form as

$$\sigma_{10} = -(f_1\sigma_1 + f_0)/g_0\xi^2 \quad (27)$$

where f_m; $m = 0, 1$ and g_0 are polynomial functions of ξ, that is

$$f_m = \sum_{n=0}^{4} f_{mn}\xi^n \quad m = 0, 1 \quad (28)$$

and

$$g_0 = \sum_{n=0}^{2} g_{0n}\xi^n \quad (29)$$

The constant coefficients in these two equations are listed in Table 2.

Table 1. Constant Coefficients a_{mn} in Eq. 25

n	a_{0n}	a_{1n}	a_{2n}
0	—	$-K_c$	—
1	σ_H^2	$-2(2\sigma_H + K_aK_c)$	4
2	—	$-(4\sigma_HK_1 + K_a^2K_c)$	$8K_1$
3	—	—	$4K_1^2$

Where $K_c = K_1K_2K_3$

Table 2. Constant Coefficients f_{mn} and g_{0n} in Eqs. 28 and 29

n	f_{0n}	f_{1n}	g_{0n}
0	$2K_2$	—	1
1	$2K_2(K_a + 1) + K_b$	—	$K_a + 1$
2	$2\sigma_C + \sigma_H - \sigma_O + (K_a + 1)K_b + 2K_2K_a$	-1	K_a
3	$\sigma_C + \sigma_H - \sigma_O + (2\sigma_C - \sigma_O + K_b)K_a$	$K_a - 2K_1 - 1$	—
4	$(\sigma_C - \sigma_O)K_a$	$K_a - 2K_1$	—

Now it can be seen from Eq. 20 that σ_{10} is a function of ξ only, that is,

$$\sigma_{10} = K_d[(1 + 8\sigma_N\xi^2/K_d)^{1/2} - 1]/4\xi^2 \tag{30}$$

where $K_d = K_2K_6$. Also, Eq. 27 can be rewritten as

$$b_1\sigma_1 + b_0 = 0 \tag{31}$$

wherein

$$b_1 = f_1 \tag{32}$$

and

$$b_0 = f_0 - g_0\sigma_{10}\xi^2 \tag{33}$$

Note that b_1 and b_0 are functions of ξ only. Equations 24 and 31 are two independent equations that are functions of σ_1 and ξ.

Single equation containing ξ

A single equation containing ξ as the only unknown can be obtained by combining Eqs. 24 and 31 to eliminate σ_1, that is

$$F(\xi) = a_2b_0^2 - a_1b_1b_0 + a_0b_1^2 = 0 \tag{34}$$

where a_2, a_1, a_0, b_1, and b_0 are functions of ξ only. This equation can now be solved easily by iteration.

Before proceeding further, it will be helpful to describe a convenient form for introducing the constant quantities σ_C, σ_H, σ_N, and σ_O and also show the limiting equations that apply at low temperature. A convenient scheme for defining the elemental constraints employs the following three parameters: the equivalence ratio ϕ, the mole ratio of hydrogen to carbon in the mixture σ_H/σ_C, and the mole ratio of nitrogen to oxygen in the mixture σ_N/σ_O. The equivalence ratio of the mixture can be expressed as

$$\phi = (\sigma_H/2 + 2\sigma_C)/\sigma_O \tag{35}$$

where the numerator represents the amount of oxygen required for stoichiometric combustion and the denominator represents the total amount of oxygen in the system.

An expression for σ_C/σ_O in terms of ϕ and σ_H/σ_C can be obtained from Eq. 35, that is,

$$\sigma_C/\sigma_O = 2\phi/(4 + \sigma_H/\sigma_C) \tag{36}$$

An expression for σ_O in terms of ϕ, σ_N/σ_O, and σ_H/σ_C can be found by dividing Eq. 13 by σ_O and combining the result with Eq. 36, to obtain

$$\sigma_O = 500/\{8 + 7\sigma_N/\sigma_O + \phi[(12 + \sigma_H/\sigma_C)/(4 + \sigma_H/\sigma_C)]\} \tag{37}$$

The four quantities σ_C, σ_H, σ_N, and σ_O are therefore defined by specifying ϕ, σ_N/σ_O, and σ_H/σ_C.

Low-temperature case

The equations presented in this section so far apply to the general case when all ten species are taken into account. As the temperature decreases the mole numbers σ_i; i = 7, 8, 9, and 10, become small and approach zero at low temperature. As a result, Eq. 23, for $\sigma_9 = 0$, reduces to

$$2(1 + K_1\xi)\sigma_1 - \sigma_H = 0 \tag{38}$$

and Eq. 27, for $\sigma_{10} = 0$, reduces to

$$f_1\sigma_1 + f_0 = 0 \tag{39}$$

where expressions for f_{mn} are taken from Table 2 with $K_a = 0$ because $\sigma_7 = 0$, and $K_b = 0$ because $\sigma_8 = 0$. Combining Eqs. 38 and 39 to eliminate σ_1 results in the quartic equation

$$F(\xi) = \sum_{k=0}^{4} c_k\xi^k \tag{40}$$

where the coefficients c_k are:

$$c_4 = (\sigma_C - \sigma_O)K_1 \tag{40a}$$

$$c_3 = (2\sigma_C - \sigma_O)K_1 + \sigma_H/2 + \sigma_C - \sigma_O \tag{40b}$$

$$c_2 = 2K_1K_2 + (2\sigma_C - \sigma_O) + \sigma_H/2 \tag{40c}$$

$$c_1 = 2K_2(K_1 + 1) \tag{40d}$$

$$c_0 = 2K_2 \tag{40e}$$

for low temperature.

Further simplification at low temperature is possible for the particular cases of fuel-lean ($\phi < 1$), stoichiometric ($\phi = 1$), and fuel-rich ($\phi > 1$) mixtures. Each of these cases is obtained by applying additional constraints.

Low-temperature Fuel-lean Case. This case permits the additional restrictions that $K_2 \ll 1$ and $\xi \ll 1$. These two conditions reduce Eq. 40 to

$$(\sigma_H/2 + 2\sigma_C - \sigma_O)\xi^2 + 2K_2 = 0 \tag{41}$$

which can be rewritten as

$$\xi^2 = \frac{2K_2}{(1 - \phi)\sigma_O} \tag{42}$$

Low-temperature Stoichiometric Case. This case is defined by the condition that $\sigma_O - \sigma_H/2 - 2\sigma_C = 0$, as well as the restric-

tions that $K_2 \ll 1$ and $\xi \ll 1$. It should be noted in this case, in contrast to the fuel-lean case, that the terms containing ξ^3 are not eliminated. Equation 40 in this case reduces to

$$[(2\sigma_C - \sigma_O)K_1 - \sigma_C]\xi^3 + 2K_2 = 0 \quad (43)$$

and can be written as

$$\xi^3 = 2K_2/\{[2(2K_1 - 1)(4 + \sigma_H/\sigma_C)\phi - K_1]\sigma_O\} \quad (44)$$

Low-temperature Fuel-rich Case. This case permits only the additional restriction that $K_2 \ll 1$, since in general ξ is not small. This additional restriction reduces Eq. 40 to

$$(\sigma_C - \sigma_O)K_1\xi^2 + [(2\sigma_C - \sigma_O)K_1 + \sigma_H/2 + \sigma_C - \sigma_O]\xi + \sigma_H/2 + 2\sigma_C - \sigma_O = 0 \quad (45)$$

or

$$(\sigma_C/\sigma_O - 1)K_1\xi^2 + [(2\sigma_C/\sigma_O - 1)K_1 - \sigma_C/\sigma_O + \phi - 1]\xi + (\phi - 1) = 0 \quad (46)$$

Iteration Scheme

There are numerous schemes that could be set up to obtain an iterative solution for ξ based on equations in the previous section. The scheme presented in this section uses Eq. 34 and the simple Newton iteration equation,

$$\xi_{\ell+1} = \xi_\ell - F(\xi_\ell)/F'(\xi_\ell) \quad (47)$$

where $F(\xi_\ell)$ is obtained from Eq. 34 and $F'(\xi_\ell)$ is the derivative of $F(\xi_\ell)$ with respect to ξ_ℓ, that is,

$$F'(\xi) = b_0^2a_2' - b_1b_0a_1' + b_1^2a_0' + (2a_0b_1 - a_1b_0)b_1' + (2a_2b_0 - a_1b_1)b_0' \quad (48)$$

The derivatives a_m' appearing on the righthand side of this equation are

$$a_m' = \sum_{n=1}^{3} na_{mn}\xi^{n-1}; \quad m = 0, 1, 2 \quad (49)$$

and the expressions for b_0' and b_1' can be obtained by using Eqs. 32 and 33 so that

$$b_0' = \sum_{n=1}^{4} nf_{0n}\xi^{n-1} - 2\sigma_N g_0\xi/(1 + 8\sigma_N\xi^2/K_d)^{1/2} - \sigma_{10}\xi^2\sum_{n=1}^{2} ng_{0n}\xi^{n-1} \quad (50)$$

and

$$b_1' = f_1' = \sum_{n=2}^{4} nf_{1n}\xi^{n-1} \quad (51)$$

Now the total computation time τ for any scheme depends on three quantities:

1. The time, τ_o, required to compute the constant terms prior to and outside of the iteration loop, and also the final composition variables σ_i after an acceptable value of ξ is determined.
2. The computation time per iteration, τ_i.
3. The number of iterations, N, required for a specified accuracy, ϵ, and initial estimate, ξ_0.

Various schemes using the equations presented in the previous section were examined by preparing Fortran computer programs to determine the three quantities just noted. The scheme using Eq. 34 was found in general to be superior to the other schemes tried.

Table 3. Iteration Scheme Using Eq. 34

Operation	Parameter	Equation ( ) or Table [ ]
A. Specify	$T, \rho, \phi, \sigma_H/\sigma_C, \sigma_N/\sigma_O, \xi_0, \epsilon$	
B. Compute constants	1. $Kj; j = 1, 2, \ldots, 6$	
	2. a_{mn}, f_{mn}, g_{0n}	[1], [2]
C. Iteration loop	1. a_m, f_m, g_0	(25), (28), (29)
	2. σ_{10}	(30)
	3. b_1, b_0	(32), (33)
	4. $F(\xi), F'(\xi)$	(34), (48)
	5. $\xi_{\ell+1}$	(47)
	6. $\lvert(y_i)_{\ell+1} - (y_i)_\ell\rvert \leq \epsilon$	—
D. Compute final composition	1. $\sigma_i; i = 2, 3, \ldots, 6, 8, 10$	(21), (22), (16), (15), (9), (19), (30)
	2. σ_1	(24)
	3. σ_9	(23)
	4. σ_7	(18)

Table 3 outlines the iteration scheme. The problem is defined by specifying the parameters listed on line A of Table 3. The equilibrium constants K_j listed on line B.1 are computed from temperature-dependent expressions for $K_{p,j}$ and Eqs. 11 and 12. Since there are many ways to represent $K_{p,j}$ with a wide range of accuracy, the time required to compute line B.1 is not included in the computation time. This time required to compute $K_{p,j}$ or the equivalent quantities for any particular representation and accuracy will be the same for any iteration scheme. The time outside the iteration loop, τ_o, is therefore the sum of the times required to compute lines B.2 and D.1 to D.4. The time per iteration, τ_i, is due to lines C.1 to C.6.

Results and Discussion

The implementation of this scheme requires an initial estimate of ξ. One of the requirements is of course that $\xi = \xi_0 > 0$, and another is seen by examining the nature of the function given by Eq. 34 as shown in Figure 1. The shape of the curve shown in Figure 1 is representative of the shape for all test cases examined. Furthermore, the correct solution to Eq. 34 is always the larger of the two roots shown. If the iteration procedure is initiated with $\xi = \xi_0$ in the neighborhood of or less than the smaller root, an incorrect value of ξ can be obtained. This in turn will cause some of the values of σ_i to be negative, which of course is not allowed. In order to avoid this false solution, initial estimates of ξ need to be either greater than the correct value ξ^* or at least greater than the value of ξ at the minimum in $F(\xi)$ between the two roots. Additional comments on the initial estimate of ξ are given in a later section.

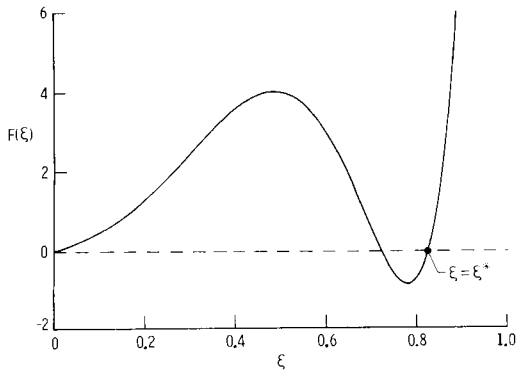

Figure 1. Function $F(\xi)$, Eq. 34, vs. ξ.
$T = 3{,}000$ K; $\rho = 1$ kg/m^3; $\phi = 0.8$; $\sigma_H/\sigma_C = 4$; $\sigma_N/\sigma_O = 79/21$.

Sample results

The chemical composition was computed using the proposed method for a broad range of conditions: $1{,}500 \leq T \leq 5{,}000$ K, $0.05 \leq \rho \leq 20$ kg/m^3, $0.5 \leq \phi \leq 1.5$, $1 \leq \sigma_N/\sigma_O \leq 79/21$, and $1 \leq \sigma_H/\sigma_C \leq 4$. Figure 2 is an example of the results, showing the mole numbers as a function of temperature for the specific case with $\rho = 1$ kg/m^3, $\phi = 0.8$, $\sigma_N/\sigma_O = 79/21$, and $\sigma_H/\sigma_C = 4$.

A series of test cases were run to determine the computation time for a set of initial estimates of ξ: $\xi_0/\xi^* = 1.1$, 1.5, and 2.0; and two levels of accuracy: $\epsilon = 10^{-3}$ and 10^{-4}. The computation times and number of iterations required for the particular case with $T = 3{,}000$ K, $\rho = 1$ kg/m^3, $\phi = 1$, $\sigma_N/\sigma_O = 2$, and $\sigma_H/\sigma_C = 2$ are given in Table 4. These results were obtained on the Control Data Corporation CYBER 170/750 computer at the NASA-Langley Research Center. Note that the computation time outside the iteration loop is $\tau_o = 46$ μs and the time for each iteration is $\tau_i = 42$ μs/iteration. Both τ_o and τ_i are independent of ξ_0/ξ^* and ϵ. The number of iterations N, on the other hand, depends on both ξ_0/ξ^* and ϵ, as shown in Table 4. Over a broad range of conditions explored, the number of iterations required increased by one for each factor-of-ten reduction in ϵ. The number of iterations required for a given accuracy of course increases as ξ_0 departs from the correct equilibrium value of $\xi = \xi^*$. The total computation times for these runs are also shown in Table 4.

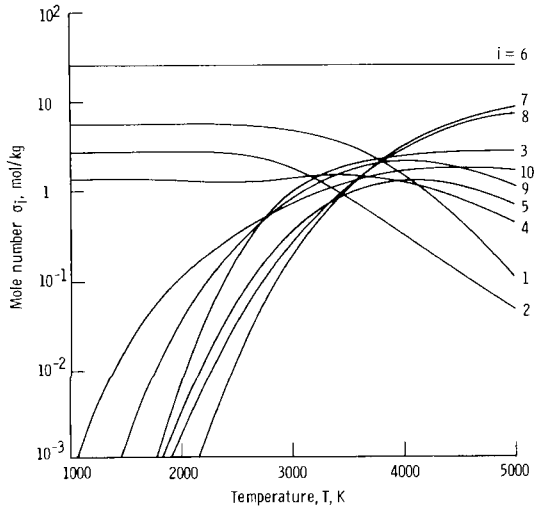

Figure 2. Computed equilibrium composition in terms of mole numbers as a function of temperature.
$\rho = 1$ kg/m^3; $\phi = 0.8$; $\sigma_H/\sigma_C = 4$; $\sigma_N/\sigma_O = 79/21$.

As shown in a later section, it should be possible, by carrying out a set of preliminary calculations in the range of interest, to provide estimates of ξ_0/ξ^* that are in the range of 1.0 to 1.1. If an accuracy of $\epsilon = 10^{-3}$ is used, which is reasonable, the total computation time required to determine the equilibrium chemical composition using the proposed method is therefore no more than 172 μs.

One final note should be made. If the computations include regions of low temperature as well as high temperature, it is desirable to treat the low-temperature region ($T < 1{,}500$ K, say) as a special case by using the fourth-degree expression for ξ given by Eq. 40 or Eqs. 42, 44, or 46, which represent limiting low-temperature cases of Eq. 34. Computer tests have shown that a scheme based on Eq. 40 gives values of $\tau_o = 14$ μs and $\tau_i = 7$ μs. For $\epsilon = 10^{-3}$ and $\xi_0/\xi^* = 1.1$, the number of iterations is $N = 2$ to 3. This gives a total computation time in the range of 28 to 35 μs at low temperature. If Eqs. 42, 44, or 46 are used the total computation time is considerably reduced further.

Comparison with other methods

The computation times given in Table 4 are of course peculiar to a CDC CYBER 170/750 computer. In order to test the performance of the present scheme, two other methods were chosen for comparison and were executed on the same computer system for the same set of conditions. One method is the often-used general free-energy minimization scheme that is based on the method of White et al. (1958). The other scheme is the method of successive approximations suggested by Weinberg (1957) and presented as an algorithm by Strehlow (1984).

The free-energy minimization method requires less time outside the iteration loop, $\tau_o = 16$ μs, as compared to 46 μs for the present method. However, the time per iteration $\tau_i = 1{,}038$ μs is considerably larger than the 42 μs required for the present method. Test runs for the free-energy minimization method were made for $\epsilon = 10^{-3}$ and initial estimates of ξ ranging over $\xi_0/\xi^* = 1.1$, 1.5, and 2.0. In addition to providing an initial estimate of ξ, which of course leads directly to estimates of σ_2 and σ_3 through Eqs. 21 and 22, initial estimates of σ_1, σ_6, and σ_4 were provided by using $\sigma_1 = \sigma_H/2$, $\sigma_6 = \sigma_N/2$, and $\sigma_4 = (\sigma_O - \sigma_1 - 2\sigma_2 - \sigma_3)/2$. In all cases the number of iterations, N, was 13. Since the free-energy minimization method requires the numerical solution of a set of linear simultaneous equations,

Table 4. Computation Times and Number of Iterations for Sample Cases*

τ_o μs	τ_i μs	ϵ	ξ_0/ξ^*	N iterations	$\tau = \tau_o + N\tau_i$ μs
46	42	10^{-3}	1.1	3	172
46	42	10^{-3}	1.5	6	298
46	42	10^{-3}	2.0	9	424
46	42	10^{-4}	1.1	4	214
46	42	10^{-4}	1.5	7	340
46	42	10^{-4}	2.0	10	466

*$T = 3{,}000$ K; $\rho = 1$ kg/m^3; $\phi = 1$; $\sigma_N/\sigma_O = 2$; $\sigma_H/\sigma_C = 2$.

the choice of ξ_0, even a very accurate value, does not strongly affect the number of the iterations. Good initial estimates of a number of the species would be needed to reduce N.

The Weinberg/Strehlow method also requires less time outside the iteration loop, $\tau_o = 28$ μs, as compared to the present method. The time per iteration, $\tau_i = 191$ μs, is much less than the free-energy minimization method but still substantially greater than the present method. It should be noted that the Weinberg/Strehlow scheme uses, within the program, a set of curve-fitted expressions for initial estimates of several composition variables. Furthermore, the number of iterations required by the Weinberg/Strehlow method depends rather strongly on ϕ in the neighborhood of $\phi = 1$. Solutions were obtained with $\epsilon = 10^{-3}$ for $\phi \leqq 0.99$ and required $N = 4$, and for $\phi = 0.999$, $N = 6$. The total time, if $N = 4$, is $\tau = 792$ μs. This is faster than the free-energy minimization scheme but is still four to five times slower than the proposed method.

General characteristics of the solution and initial estimates of ξ

It was mentioned previously that it should be possible to obtain initial estimates of ξ that are in the range of $\xi_0/\xi^* \leqq 1.1$ by carrying out a set of preliminary computations in the range of interest. An attempt has been made to show that it is possible to devise a scheme for choosing a suitable initial estimate of ξ. Computations for ξ using Eq. 34 were made for a broad range of conditions. Then as a guide, the limiting equations that apply at low temperature, that is, Eqs. 42, 44, and 46, were used to identify an approximate relationship between ξ and the various independent parameters that could be used to determine ξ_0.

For the fuel-lean case, that is, for $\phi < 1$, Eq. 42 shows that ξ^2 is proportional to K_2. Furthermore, K_2 is proportional to $K_{p,2}$, and to a good approximation $\log K_{p,2}$ is proportional to $1/T$. This suggests that a plot of $\log \xi$ against $1/T$ for a given set of ρ and σ_O (or σ_N/σ_O, σ_H/σ_C, and ϕ as indicated in Eq. 37) will give a series of nearly straight parallel lines at low temperature for various values of ϕ for $\phi < 1$. Plots of $\log \xi$ against $1/T$ were therefore prepared to cover a range of temperatures, including high temperatures, for a set of values of ϕ with $\rho = 1$ kg/m^3, $\sigma_N/\sigma_O = 2$, and $\sigma_H/\sigma_O = 2$. The range of values of ϕ included not only $\phi < 1$, where Eq. 42 applies at low temperature, but also $\phi = 1$ and $\phi > 1$. The results are shown in Figure 3. In addition to the expected results for $\phi < 1$ at low temperature, it can be seen that an approximately straight-line relationship is also obtained for $\phi = 1$. This is to be expected from Eq. 44, in which ξ^3 is proportional to K_2. It should be noted here that K_2 is a much stronger function of temperature than K_1 so that the influence of K_1 in Eq. 44 is very weak. A comparison between Eq. 42 and Eq. 44 suggests that the slope for the $\phi = 1$ case should be two-thirds of the slope for the $\phi < 1$ cases at low temperature. Figure 3 is in agreement with this. For $\phi > 1$ at low temperature the curves become a set of parallel, nearly straight lines with a much smaller slope. This is due to the fact that $\log K_1$ is proportional to $1/T$ and that the proportionality constant is relatively small. At higher temperatures the curves for $\phi > 1$ tend to merge with the curves for $\phi \leqq 1$. Patterns of curves similar to Figure 3 were obtained for a broad range of conditions.

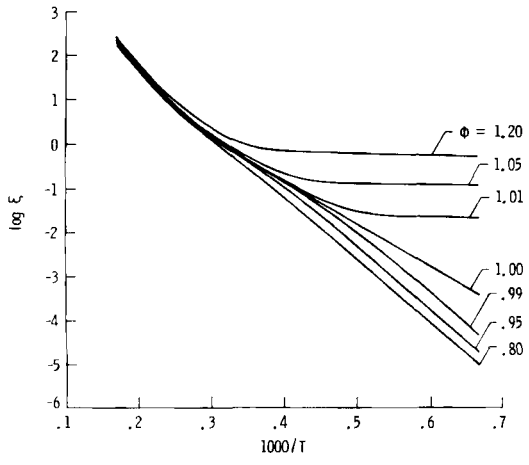

Figure 3. Computed results of $\log \xi$ vs. $1/T$.
$\rho = 1$ kg/m^3; $\sigma_H/\sigma_C = 2$; $\sigma_N/\sigma_O = 2$.

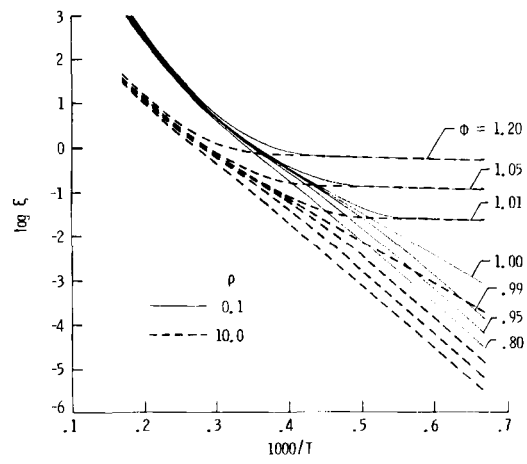

Figure 4. Composite plot of $\log \xi$ vs. $1/T$.
$\sigma_H/\sigma_C = 2$, $\sigma_N/\sigma_O = 2$, for $\rho = 0.1$ and 10 kg/m^3.

Figure 4 is a composite of two sets of curves for $\sigma_N/\sigma_O = 2$ and $\sigma_H/\sigma_C = 2$ with one set computed for $\rho = 0.1$ kg/m^3 and the other for $\rho = 10$ kg/m^3. Note the displacement due to the difference in ρ. For the $\phi \leqq 1$ cases at low temperature this displacement can be explained by noting that K_2 is proportional to $1/\rho$ from Eq. 12, so that $\log \xi$ is proportional to $-\log \rho$. Figure 4 also

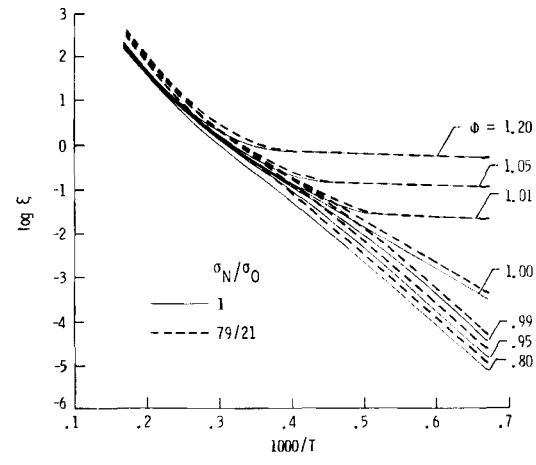

Figure 5. Composite plot of $\log \xi$ against $1/T$.
$\rho = 1$ kg/m^3, $\sigma_H/\sigma_C = 2$, for $\sigma_N/\sigma_O = 1$ and 79/21.

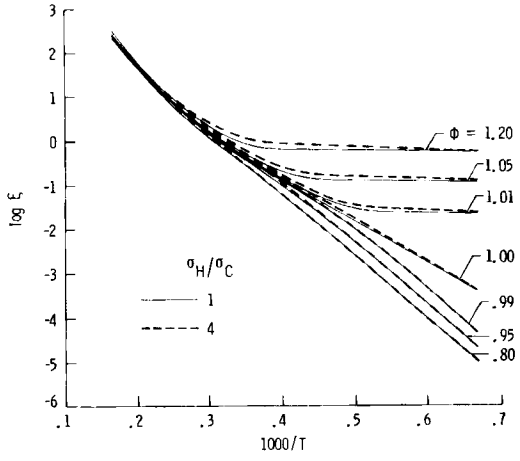

Figure 6. Composite plot of log ξ against $1/T$.
$\rho = 1$ kg/m^3, $\sigma_H/\sigma_O = 2$, for $\sigma_H/\sigma_C = 1$ and 4.

shows that the approximate magnitude of this displacement due to a difference in ρ also extends to higher temperatures. On the other hand, for the $\phi > 1$ cases at low temperature there is no displacement due to ρ because K_1 is independent of ρ, as seen from Eq. 11. At higher temperature the magnitude of the displacement for $\phi > 1$ approaches that for $\phi \leq 1$.

Figure 5 shows the displacement due to a variation of σ_N/σ_O from 1 to 79/21 with fixed values of $\rho = 1$ kg/m^3 and $\sigma_H/\sigma_C = 2$. Again the equations at low temperature can be used as a guide. For cases with $\phi \leq 1$ the displacement due to σ_N/σ_O is proportional to log σ_O for low temperatures according to Eq. 42 or Eq. 44, where σ_O is related to σ_N/σ_O by Eq. 37. The approximate magnitude of this displacement persists to higher temperatures. The low-temperature Eq. 46 suggests no shift due to σ_N/σ_O for $\phi > 1$, which is what is observed in Figure 5. At intermediate and higher temperatures the magnitude of the displacement for $\phi > 1$ approaches that for $\phi \leq 1$.

Figure 6 shows the influence of a variation of σ_H/σ_C from 1 to 4. There appears to be little or no shift for $\phi < 1$, a slight shift for $\phi = 1$ beginning at intermediate temperatures, and a larger shift for $\phi > 1$ as the temperature increases. If the equations for low temperature are again used as a guide, the influence of σ_H/σ_C appears by way of σ_O for $\phi \leq 1$. Equation 37 for σ_O indicates that variations in σ_H/σ_C are strongly masked by the other terms in the equation. The influence of σ_H/σ_C for $\phi > 1$ at low temperature is somewhat obscure but affects ξ in Eq. 46 by way of the term σ_C/σ_O, which is given by Eq. 36.

An examination of Figures 3–6 and the limiting equations at low temperature led to the following approach for devising a scheme for determining a good estimate of ξ_0. Equation 42 for $\phi < 1$ at low temperature is used as a starting point and can be expressed as

$$\log \xi = \tfrac{1}{2} \log [2K_2/(1 - \phi)\sigma_O] \tag{52}$$

The relationship between K_2 and $K_{p,2}$ from Eq. 12 is also used along with the good approximation that

$$\log K_{p,2} = B/T + A \tag{53}$$

where A and B are very nearly constant over a broad temperature range so that Eq. 52 can be written as

$$\log \xi = \tfrac{1}{2}[B/T + A - \log(\rho R T \sigma_O/P^o)] \tag{54}$$

or

$$\log \xi = \frac{B}{2{,}000} [1{,}000/T + \kappa \log(\rho T \sigma_O) + \text{constant}] \tag{55}$$

for a particular ϕ and where $\kappa = -1{,}000/B$. This equation is strictly valid for $\phi < 1$ at low temperature and the value of ξ determined from this equation is the solution to Eq. 34 for $\phi < 1$ at low temperature. Now in order to obtain a value of ξ_0 beyond low temperatures and $\phi < 1$, and include higher temperatures and also $\phi \geq 1$, the following empirical relationship for a particular ϕ is proposed,

$$\log \xi = f[X, \phi] \tag{56}$$

where X is defined as

$$X = 1{,}000/T + \kappa \log (T/1{,}000) + \log [(\rho/\rho_r)^\alpha (\sigma_O/\sigma_{O,r})^\beta] \tag{57}$$

where ρ_r and $\sigma_{O,r}$ represent any convenient reference condition. Note that at low temperature and $\phi < 1$ that $\alpha = \beta = \kappa$ and that log ξ is a simple function of X for a given value of ϕ, as can be seen by looking back at Eq. 55. The numerical value of κ is approximately 0.0340, and α and β are allowed to be functions

Table 5. Tabulated Values of log ξ_r, α, and β for Selected Values of X_r at $\phi = 0.8$, 1.0, and 1.2

	$\phi = 0.8$			$\phi = 1.0$			$\phi = 1.2$		
X_r	log ξ_r	α	β	log ξ_r	α	β	log ξ_r	α	β
0.26	0.9343	0.0343	0.0405	1.0018	0.0341	0.0406	1.0759	0.0338	0.0406
0.28	0.6136	0.0341	0.0403	0.6929	0.0337	0.0404	0.7830	0.0332	0.0404
0.30	0.3181	0.0340	0.0398	0.4139	0.0336	0.0401	0.5286	0.0329	0.0403
0.32	0.0385	0.0340	0.0393	0.1575	0.0335	0.0398	0.3097	0.0325	0.0402
0.34	−0.2326	0.0340	0.0388	−0.0811	0.0335	0.0395	0.1291	0.0320	0.0401
0.36	−0.5022	0.0341	0.0382	−0.3061	0.0334	0.0392	−0.0068	0.0311	0.0397
0.38	−0.7752	0.0341	0.0377	−0.5211	0.0334	0.0390	−0.0943	0.0291	0.0387
0.40	−1.0537	0.0342	0.0372	−0.7291	0.0333	0.0389	−0.1415	0.0250	0.0350
0.42	−1.3373	0.0342	0.0367	−0.9325	0.0333	0.0387	−0.1653	0.0178	0.0269
0.44	−1.6246	0.0343	0.0363	−1.1329	0.0332	0.0386	−0.1791	0.0102	0.0161

of temperature. In addition, Eq. 37 shows how σ_O depends on ϕ, σ_H/σ_C, and σ_N/σ_O.

At the reference condition,

$$X_r(\phi) = 1{,}000/T_r + 0.034 \log (T_r/1{,}000) \qquad (58)$$

The reference conditions chosen are: $\rho = 1$ kg/m^3, $\sigma_H/\sigma_C = 2$, and $\sigma_N/\sigma_O = 2$. At this point it is possible to use the method based on Eq. 34 to compute a set of values of ξ over a range of values of T_r for specific values of ϕ. A table listing values of log ξ_r, where $\xi_r = \xi$ for the reference condition, against $X_r(\phi)$ was then prepared for $\phi = 0.8$, 1.0, and 1.2; this is Table 5.

The coefficient α was determined for $\phi = 0.8$, 1.0, and 1.2 by using the pairs of values of $X_r(\phi)$ and log ξ_r listed in Table 5. Values of ρ different from ρ_r with $\sigma_H/\sigma_C = 2$ and $\sigma_N/\sigma_O = 2$ were used to compute the temperature T at which $\xi = \xi_r$ by using Eq. 34. Values of $\rho = 0.1$ and $\rho = 10$ kg/m^3 were used for each $X_r(\phi)$. The coefficient α was then computed for the condition that $X(\phi)$ based on Eq. 57 was equal to $X_r(\phi)$, that is

$$\alpha = [1{,}000(1/T_r - 1/T) + 0.0340 \log (T_r/T)]/\log (\rho/\rho_r) \qquad (59)$$

The computed values α are listed in Table 5 and show only a slight dependence on temperature for $\phi \leq 1$. For $\phi > 1$ the magnitude of α is about the same as for $\phi \leq 1$ for the smaller values of X_r, that is, at higher temperatures, but decreases for the larger values of X_r, corresponding to lower temperatures. This simply indicates, as does Eq. 46, that ξ is not a function of ρ for $\phi > 1$ at low temperature.

The values of β were determined in a similar fashion, but by selecting a set of values of σ_O different from $\sigma_{O,r}$. Now since most practical applications utilize a constant fuel type, the ratio σ_H/σ_C was set equal to $(\sigma_H/\sigma_C)_r$. Values of $\sigma_N/\sigma_O = 79/21$, 3, and 1, with $\rho = 1$ kg/m^3 and $\sigma_H/\sigma_C = 2$ were used. The coefficient β was computed by again using Eq. 59 but with α replaced by β and ρ/ρ_r by $\sigma_O/\sigma_{O,r}$. The values of β are listed in Table 5 and are weakly dependent on temperature for $\phi \leq 1$ and approach zero for $\phi > 1$ at the larger values of X_r.

The quantities in Table 5 have been used to compute ξ_0 for a range of conditions for $\sigma_H/\sigma_C = 2$: $2{,}500 \leq T \leq 3{,}500$ K, $0.1 \leq \rho \leq 10$ kg/m^3, $1 \leq \sigma_N/\sigma_O \leq 79/21$, and $\phi = 0.8$, 1.0, and 1.2. The values of $\xi_0 (= \xi_r)$ were obtained by using a linear interpolation of log ξ_r with respect to X_r. In most cases ξ_0 was within 1% of ξ^* and in all cases within 1.5%. If a different fuel type is to be considered, a similar table could easily be prepared for the appropriate value of σ_H/σ_C. It should be noted that Table 5 is included only to indicate that it is possible to obtain a suitable value of ξ_0.

Notation

A = constant, Eq. 53
B = constant, Eq. 53
a_m = coefficients that are functions of ξ, Eq. 24
a_{mn} = constant coefficients, Eq. 25
b_m = coefficients that are functions of ξ, Eq. 31
c_k = constant coefficients, Eq. 40
f_m = coefficients that are functions of ξ, Eq. 27
f_{mn} = constant coefficients, Eq. 28
g_0 = coefficient that is a function of ξ in denominator of Eq. 27
g_{0n} = constant coefficients, Eq. 29
K_j = equilibrium constant in terms of mole numbers for reaction j
$K_{p,j}$ = equilibrium constant in terms of partial pressures for reaction j
$K_a = (K_4/K_2K_3)^{1/2}$, $K_b = (K_2K_5)^{1/2}$, $K_c = K_1K_2K_3$, $K_d = K_2K_6$
N = number of iterations
P^o = standard state pressure
R = universal gas constant
T = absolute temperature
X = function, Eq. 57
y_i = mole fraction $y_i = \sigma_i/\Sigma_{i=1}^{10} \sigma_i$

Greek letters

α = temperature-dependent coefficient, Eq. 57
β = temperature-dependent coefficient, Eq. 57
ϵ = accuracy, $\epsilon = |(y_i)_{\ell+1} - (y_i)_\ell|$, for each chemical species
κ = constant, Eq. 55
ξ = mol CO/mol CO_2, Eq. 14
ρ = mass density of mixture
σ_i = mole number of species i, mol of species i/kg mixture
σ_H, σ_O, σ_N, σ_C = mole numbers of elements H, O, N, C
τ = total computation time
τ_i = computation time per iteration
τ_o = computation time outside iteration loop
ϕ = equivalence ratio, Eq. 35

Subscripts

i = chemical species index
j = chemical reaction index
k = degree of ξ, Eq. 40
ℓ = number of iteration steps
m = degree of σ_1, Eqs. 24, 27, 31
n = degree of ξ, Eqs. 25, 28, 29
r = reference condition

Superscripts

$'$ = differentiation with respect to ξ
$*$ = equilibrium solution

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