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THE THERMODYNAMICS OF COMBUSTION GASES: GENERAL CONSIDERATIONS

BY STUART R. BRINKLEY, JR., AND BERNARD LEWIS

United States Department of the Interior— April 1952

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CONTENTS

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I. INTRODUCTION AND SUMMARY

For a theoretical description of power plants that derive their energy from the combustion of a fuel, it is necessary to solve, to an appropriate degree of precision, a hydrodynamic problem that requires for its solution a knowledge of the thermodynamic properties of the working fluid composed of the products of the combustion reaction. It is usually a good approximation to assume that the properties of the combustion gas are determined by the conditions of thermal equilibrium, and it is thus possible to employ the methods of classical thermodynamics for their computation. The thermodynamic properties of fuel gases also are of considerable importance, as they form the basis for the design of appropriate means for their effective utilization. The specification of the operating conditions to produce a gas for use as an intermediate in a chemical process, such as the synthesis of liquid fuels, may be based upon a study of the variation of the composition of the synthesis gas with changes in the various process variables.

Although there exist a large number of important scientific and technical applications of the data that can be obtained from the systematic determination of the thermodynamic properties of combustion gases, such application has been greatly handicapped by the extremely tedious and time-consuming computational methods required. The development of large-scale automatic computational equipment makes feasible the initiation of a systematic program for the determination of the thermodynamic properties of combustion gases and for the application of such data to specific problems of scientific and technical importance.

As a part of its program of basic research in flame and combustion phenomena, the Explosives and Physical Sciences Division of the Bureau of Mines is engaged in such a program. The present communication is designed to introduce a series of reports presenting the results of this program.

There has long existed a need for systematic and economical methods for the calculation of the thermodynamic properties of systems of many constituents, and this need is emphasized by the application of automatic computational equipment. In the present report, we wish to assemble the methods that have been employed in this laboratory and that have been shown to be particularly well-adapted to routine application.

Consideration of the thermodynamics of combustion gases is introduced by a discussion of the stoichiometry of multicomponent systems and of applications of the phase rule to such systems. This formal treatment serves to introduce the notation that will be employed consistently throughout the remainder of the report, and it establishes the conditions for equilibrium in multicomponent systems in a mathematical form that is particularly appropriate for computational procedures.

Two methods are described for the calculation of the equilibrium composition of systems of many constituents. These methods are employed in the formulation of several specific computational programs for the calculation of the equilibrium composition of systems composed of compounds of carbon, hydrogen, oxygen, and nitrogen.

Throughout this report, we assume that the ideal gas law provides an adequate equation of state for the gaseous phase. However, it is shown that the methods for the calculation of equilibrium composition are easily generalized to take account of gas imperfections, and that this generalization does not affect in any important respect the detailed computational programs already formulated. The necessary general relations are summarized. They can be applied to specific forms of the equation of state without difficulty.

The calculation of the thermodynamic properties of the equilibrium mixture is straightforward after the composition of the mixture is known. We summarize briefly the well-known thermodynamic relations that are employed for this purpose.

We conclude with a description of a massive generalized table of the equilibrium composition and thermodynamic properties at equilibrium of the four-component system containing compounds of carbon, hydrogen, oxygen, and nitrogen. The table will list the composition and thermodynamic properties over an extended range of temperature and pressure, and it will include all possible combinations of the four elements, the spacing of calculated points being small enough to permit accurate interpolation. The table will be the result of about half a million individual computations, and its construction utilizes the computational methods described in this report.

II. ACKNOWLEDGMENTS

The numerical calculations by means of which the generalized table, referred to above, is being constructed were performed on the Electronic Numerical Integrator and Calculator (the ENIAC) at the Ballistic Research Laboratory, Aberdeen Proving Ground, Md. This calculator was made available for this program by the Office of the Chief of Ordnance, Department of the Army. The authors are greatly indebted to L. S. Diderick, of the Ballistic Research Laboratory, for his interest and continued cooperation. They wish to record their appreciation of the labors on this project of all of the members of the ENIAC staff. The assistance of John V. Holberton and Helen Mark in preparing the programs for the ENIAC is gratefully acknowledged.

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III. STOICHIOMETRY AND APPLICATION OF THE PHASE RULE

The composition and the thermodynamic properties of a mixture at equilibrium are independent of the path by which equilibrium is attained. From the point of view of thermodynamics, the molecular form in which the different elements are initially introduced to the system is therefore irrelevant, and it suffices to specify the gross composition of the system in terms of the elements contained by it. As the composition of the system at equilibrium is most appropriately expressed in terms of intensive quantities (mole fractions), the results are independent of the total size of the system, which may be taken to be any convenient value. Therefore, if the number of different elements in the system is m, it is sufficient for a unique description of the system to specify the number of gram atoms of m-1 elements relative to an arbitrary amount of the m-th element, i.e., to specify values of the quantities $(X^{(k)}/X^{(m)})$ $k = 1, 2, \ldots m-1$, where

$$Q_k = (X^{(k)}/X^{(m)})\, Q_m, \tag{3.1}$$

and Q_k and Q_m are the number of gram atoms of the k-th and m-th elements, respectively, available to the system. Alternatively, one may specify m-1 different linearly independent combinations of these ratios R_{km}. We note that it is not always necessary to specify as many as m-1 different quantities.

Description of Carbon, Hydrogen, Oxygen, Nitrogen Systems

A large number of different sets of parameters can be employed for the description of the gross composition of any given system. In this section, we introduce certain parameters that are particularly convenient for the description of systems composed of compounds of carbon, hydrogen, oxygen, and nitrogen, and we deduce several relations that will be employed later. Alternative descriptions may be transposed into the language of this section by obvious algebraic procedures.

For a discussion of the thermodynamics of combustion gases, it is convenient for the description of the gross composition of the system to employ the parameters,

$$\begin{aligned} A &= Q_N/(4Q_C + Q_H + Q_N), \\ B &= Q_H/(4Q_C + Q_H), \\ C &= 2Q_O/(4Q_C + Q_H + 2Q_O), \end{aligned} \tag{3.2}$$

where Q_C, Q_H, Q_O, Q_N are the number of the gram atoms of carbon, hydrogen, oxygen, and nitrogen, respectively, available to the system. Quantity C is a measure of the amount of oxygen actually available to the system relative to that required for conversion of all of the carbon to carbon dioxide and all of the hydrogen to steam. At this stoichiometric point $C = 1/2$. Rich fuel-oxidant systems are characterized by $C < 1/2$ and lean systems by $C > 1/2$.

It will be shown that for the characterization of rich fuel-oxidant systems consisting of a gas mixture in heterogeneous equilibrium with solid carbon, it is sometimes convenient to describe the relative hydrogen, oxygen, and nitrogen content by means of parameters that are independent of the amount of carbon. For this purpose, an appropriate set of parameters consists of

$$\begin{aligned} B &= Q_H/(4Q_C + Q_H) \\ D &= Q_N/(Q_H + 2Q_O + Q_N) \\ E &= 2Q_O/(Q_H + 2Q_O). \end{aligned} \tag{3.3}$$

We note the sets (3.2) and (3.3) are not independent, but that

$$\begin{aligned} D &= \frac{A(1-C)}{(1-A)\,[B(1-C) + C] + A(1-C)} \\ E &= \frac{C}{B(1-C) + C.} \end{aligned} \tag{3.4}$$

Equations (3.2) or (3.3) determine the amounts available to the system of three of the elements relative to the amount available of the fourth. If oxygen is selected as the reference element, then

$$
\begin{aligned}
(C/O) &= \frac{Q_C}{Q_O} = \frac{(1-B)(1-C)}{2C} = \frac{(1-B)(1-E)}{2BE}, \\
(H/O) &= \frac{Q_H}{Q_O} = \frac{2B(1-C)}{C} = \frac{2(1-E)}{E}, \qquad (3.5) \\
(N/O) &= \frac{Q_N}{Q_O} = \frac{2A(1-C)}{C(1-A)} = \frac{2D}{E(1-D)}
\end{aligned}
$$

For the characterization of fuel-air systems, it is convenient to employ the parameters A, B, and C as defined by equations (3.2) to describe the relative concentrations of carbon, hydrogen, oxygen, and nitrogen of the fuel alone without regard to the constituents of air. These fuel parameters may be distinguished from their more general counterparts by a superscript f. Then, if the fuel-air ratio is determined by the general parameter C, taking account of the total available oxygen, it is easy to show that

$$
\begin{aligned}
(C/O) &= \frac{b(1-B^f)(1-C)(1-C^f) + c(C-C^f)}{2bC(1-C^f) + 2c(C-C^f)}, \\
(H/O) &= \frac{4bB^f(1-C)(1-C^f)}{2bC(1-C^f) + 2c(C-C^f)}, \\
(N/O) &= \frac{4bA^f(1-C)(1-C^f)/(1-A^f) + 2a(C-C^f)}{2bC(1-C^f) + 2c(C-C^f)}, \qquad (3.6) \\
(A/O) &= \frac{d(C-C^f)}{2bC(1-C^f) + 2c(C-C^f)},
\end{aligned}
$$

where A^f, B^f, C^f are measures of the fuel composition, C is the measure of the total amount of available oxygen in fuel and air, and where $a = 0.780881$, $b = 0.209495$, $c = 0.000300$, and $d = 0.009324$. The composition by volume of dry air has been taken to be

Oxygen, 20.9495%	Carbon dioxide, 0.0300%
Nitrogen, 78.0881%	Rare gases (Argon), 0.9324%

If the fuel is a hydrocarbon, $A^f = C^f = 0$, and equations (3.6) reduce to

$$
(C/O) = \frac{b(1-B^f)(1-C) + cC}{2C(b+c)},
$$

$$(H/O) = \frac{4bB^f(1-C)}{2C\,(b + c)}, \tag{3.7}$$

$$(N/O) = \frac{a}{b + c},\ (A/O) = \frac{d}{2\,(b + c)}$$

The Components

In a system containing many constituents, it is possible to select certain constituents that are sufficient for the complete thermodynamic description of the composition. By this it is meant that if the system is conceived to consist of the selected constituents only, its gross composition (in terms of the amounts of each chemical element present) is completely defined. The constituents thus sufficient to describe the composition are called the components of the system. An analytical criterion has been published[3/] for the choice of the components. In terms of this criterion, the conditions for equilibrium may be written in a form that has a high degree of symmetry and is particularly well-adapted for formulating a computational method for the calculation of the equilibrium composition.

The number of constituents of any system depends upon the accuracy with which it is desired to describe its composition. The constituents to be considered must be chosen a priori, and this choice usually will imply the neglect of certain equilibria that may be expected to exert a negligible effect on the composition of the system at equilibrium.

Consider a closed system containing s different substances, which are assumed to be in chemical equilibrium. The molecular formula of the i-th substance may be represented by

$$Y^{(i)} = X^{(1)}_{\alpha i1} \ldots X^{(k)}_{\alpha ik} \ldots X^{(m)}_{\alpha im}, \tag{3.8}$$

$i = 1, 2, \ldots s$, where $X^{(k)}$ is the symbol of the k-th element, α_{ik} is the subscript (which may be zero) to this symbol in the formula to the i-th substance, and m is the total number of elements represented in the system. For every i, the array of subscripts α_{ik}, $k = 1, 2, \ldots, m$, may be said to define a vector

$$y_i = (\alpha_{i1}, \ldots, \alpha_{ik}, \ldots, \alpha_{im}), \tag{3.9}$$

which may be called the formula vector of substance i. If the rank of the matrix of the vector elements α_{ik} is c, it follows from a well-known theorem of algebra that there are c linearly independent vectors, and if $c \leqslant s$ there are (s-c) linearly dependent vectors, which may be expressed as linear combinations of the independent vectors. It may be assumed that the independent vectors are designated by the values 1, 2, . . . , c of their index. Then the dependent vectors may be expressed as linear combinations of the form

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[3/] Brinkley, S. R., Jr., Note on the Conditions of Equilibrium for Systems of Many Constituents: Jour. Chem. Phys., vol. 14, 1946, pp. 563-64.

$$\sum_{j=1}^{c} \nu_{ij}\, y_j = y_i, \tag{3.10}$$

$i = c + 1, c + 2, \ldots, s$. To equation (3.10) there correspond (s-c) conceivable chemical reactions

$$\sum_{j=1}^{c} \nu_{ij}\, Y^{(j)} = Y^{(i)}, \tag{3.11}$$

resulting in the formation, from the c substances with linearly independent formula vectors, of the (s-c) substances with linearly dependent formula vectors. It follows that the specification of c substances such that their formula vectors are linearly independent is sufficient for a description of the composition of the system. Therefore, the number of components of the system equals the rank c of the matrix of the subscripts to the symbols of the elements in the formulas of the substances comprising the system. The number of components is usually, but not necessarily, equal to the number of different elements in the system. It may be noted that the choice of independent vectors is not, in general, unique and that, in consequence, the choice of c substances as components and the expression of the remaining (s-c) substances as products of reactions involving only the chosen components is usually not unique. However, for the heterogeneous case, consisting of a gas mixture in equilibrium with a solid phase composed of a single constituent, these criteria can be satisfied only by the selection of that constituent as a component.

This discussion has demonstrated the possibility of a choice of components, which make it possible to express each of the dependent constituents as products of reactions involving components only. Our computational procedure for the determination of the equilibrium composition is based upon the possibility of writing down for the case of interest the reactions that are expressed by equations (3.11). In many cases it is possible to write these reactions immediately by intuition. In some cases it may be necessary to formulate the reactions of equations (3.11) by applying to the system under consideration the steps indicated by equations (3.8) to (3.10).

If the number of moles of the j-th component contained in the hypothetical system consisting of components only is denoted by q_j, it is evident that

$$\sum_{j=1}^{c} \alpha_{jk}\, q_j = Q_k, \tag{3.12}$$

$k = 1, 2, \ldots m$. We shall assume henceforth that the number of components c is equal to the number of different elements m. Introducing the ratios defined by equation (3.1), we obtain

$$\sum_{j=1}^{c} \alpha_{jk}\, q_j - (X^{(k)}/X^{(m)})\, Q_m = 0. \tag{3.13}$$

For the systems to be considered in this report, it is convenient to assume that

$$\sum_j{}' \; q_j = 1, \tag{3.14}$$

where the operator $\sum_j{}'$ denotes a summation over the gaseous components only. Equations (3.13) and (3.14) constitute c+1 linear nonhomogeneous equations in the quantities Q_m and q_j, $j = 1, 2, \ldots c$, and they may be employed to express the q_j in terms of the ratios $(X^{(k)}/X^{(m)})$ and thus in terms of the parameters employed for the description of the system. Equation (3.14) is equivalent to an assumption as to the total size of the system, the weight M_0 of the gaseous phase being given by

$$M_0 = \sum_j{}' \; q_j \, M_j, \tag{3.15}$$

where M_j is the molecular weight of the j-th component. We shall call the constants q_j, determined by means of equations (3.13) and (3.14), the normalized stoichiometric constants.

Conditions for Equilibrium

The discussion of equilibrium in systems of many constituents assumes a particularly simple and symmetrical form in terms of the definitions that have been introduced. We consider the general case where the s substances are distributed among π coexisting phases. The conservation of mass in the system as a whole requires that

$$\sum_{k=1}^{\pi} \left\{ \sum_{j=1}^{c} n_j^{(k)} M_j + \sum_{i=c+1}^{s} n_i^{(k)} M_i \right\} = \sum_{j=1}^{c} q_j \, M_j, \tag{3.16}$$

where $n_i^{(k)}$ and $n_j^{(k)}$ are the number of moles in the k-th phase of the i-th and j-th substances, respectively, and M_i and M_j are the corresponding weights of 1 mole. As mass is conserved by each of reactions (3.11), one may substitute

$$M_i = \sum_{j=1}^{c} \nu_{ij} \, M_j \tag{3.17}$$

into equation (3.16). On equating the coefficients of M_j, there are obtained

$$\sum_{k=1}^{\pi} \left\{ n_j^{(k)} + \sum_{i=c+1}^{s} \nu_{ij} \, n_i^{(k)} \right\} = q_j, \tag{3.18}$$

$j = 1, 2, \ldots c$.

The derivation by means of the method employed by Gibbs,[4] subject to the constraints of equations (3.18), of the conditions for equilibrium is straightforward, and it is unnecessary to reproduce it here. The usual conditions for thermal and mechanical equilibrium are obtained, and the conditions for chemical equilibrium take the form,

$$\mu_j^{(k)} = \lambda_j, \tag{3.19}$$

$$\mu_i^{(k)} = \sum_{j=1}^{c} \nu_{ij} \lambda_j, \tag{3.20}$$

$k = 1, 2, \ldots \pi$; $j = 1, 2, \ldots c$; $i = c + 1, c + 2, \ldots s$, where $\mu_i^{(k)}$ and $\mu_j^{(k)}$ are the chemical potentials in the k-th phase of the i-th and j-th substances, respectively, the λ_j are constants that may be eliminated from equations (3.19) and (3.20), and where it has been assumed for simplicity that each substance of the system is included in every phase. If a particular component is excluded a priori from some phase, the corresponding member of equations (3.19) disappears as being without meaning, and similar considerations obtain if a particular dependent constituent is excluded a priori from some phase.

Together with equation (3.18), equations (3.19) and (3.20) provide, by reason of their symmetry, the simplest basis for calculating the concentrations at equilibrium of the several constituents of the system. In particular, if the substances are limited to a single phase, the equations become

$$n_j + \sum_{i=c+1}^{s} \nu_{ij} n_i = q_j, \tag{3.21}$$

$$\mu_i - \sum_{j=1}^{c} \nu_{ij} \mu_j = 0, \tag{3.22}$$

$j = 1, 2, \ldots c$, $i = c + 1, \ldots s$, for equilibrium at constant temperature and pressure. Equations (3.21) and (3.22) are also applicable to systems composed of a gas phase in equilibrium with a single pure solid phase, as in this case it is not necessary to retain explicitly the index label of the phase.

The chemical potential of the k-th constituent of a gas mixture can be expressed as[5]

$$\mu_k = \overset{o}{\mu}_k (T) + RT \log p_k^{*} \tag{3.23}$$

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[4] Collected Works of J. Willard Gibbs: Longmans, Green & Co., New York and London, 1928, vol. 1, pp. 63-82.

[5] See, for example, Guggenheim, E. A., Modern Thermodynamics by the Methods of Willard Gibbs: Methuen & Co., Ltd., London, 1933, p. 72.

where p_k^* is the fugacity of the k-th constituent in the mixture and μ_k^o (T), the chemical potential of the k-th constituent in the standard state of unit fugacity, is a function of the temperature, T, only. The chemical potential of a constituent, say the m-th, existing as a pure solid phase, can be written as a function of temperature only,

$$\mu_m = \mu_m^o (T), \tag{3.24}$$

for the range of pressures to be considered in this report. Equations (3.22) can be written

$$\log p_i^* - \sum_j^{'} \nu_{ij} \log p_j^* = \log K_i, \tag{3.25}$$

where

$$RT \log K_i = \sum_{j=1}^{c} \nu_{ij} \mu_j^o - \mu_i^o \tag{3.26}$$

K_i, the thermodynamic equilibrium constant of the reaction (3.11) for the formation of the i-th dependent constituent from the components, is a function of the temperature only. Equations (3.25) are valid both for homogeneous gas mixtures and for heterogeneous systems composed of a gas mixture in equilibrium with a single pure solid phase, the summation being over gaseous components only.

Degrees of Freedom of Carbon, Hydrogen, Oxygen, Nitrogen Systems

The phase rule of Gibbs can be obtained directly from Equations (3.18), (3.19), and (3.20).[6] It can be expressed in the form

$$f = c + 2 - \pi,$$

where f is the number of degrees of freedom possessed by a system of c components and π phases that depends on two state variables.

The four-component system containing carbon, hydrogen, oxygen, and nitrogen consists of two regions. There is a region of low oxygen: carbon ratio in which the system is heterogeneous, consisting of a gas phase in equilibrium with solid carbon. If the oxygen:carbon ratio exceeds a critical value (which depends on the temperature, pressure, and composition), the system is homogeneous, consisting of a single gas phase.

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[6] Brinkley, S. R., Jr., Work cited in footnote 3.

According to the phase rule, the homogeneous portion of the four-component system possesses five degrees of freedom, and the heterogeneous portion four degrees of freedom. The state is uniquely determined by the specification of two state variables, for which purpose either the temperature and pressure or the temperature and volume are commonly selected. The thermodynamic requirements for the description of the homogeneous portion of the system are completed by the specification of three parameters defining its gross composition. The specification of only two parameters defining gross composition is necessary in the case of the heterogeneous portion of the system.

As equations (3.25) are independent of the amount of solid phase actually contained by the system, it is convenient to define the relative amounts of hydrogen, oxygen, and nitrogen available to the system. For this purpose, parameters D and E of equations (3.3) are appropriate, and the specification of D and E together with two state variables is sufficient thermodynamically for the complete description of the system. The number of gram atoms of carbon present in the gas phase of the system at equilibrium (as carbon monoxide, carbon dioxide, methane, etc.) is easily computed after the equilibrium composition is known. If this quantity is denoted by Q_c', we may calculate

$$B_1 = Q_H/(4Q_c' + Q_H). \tag{3.27}$$

As Q_c' is a function of the composition at equilibrium, the ratio defined by equation (3.27) is an implicitly defined function of the state (say the temperature and pressure) and of the relative hydrogen, oxygen, and nitrogen compositions. This functional relationship is expressed by

$$B_1 = B_1 (D, E, p, T), \tag{3.28}$$

where p is the pressure. Equation (3.28) defines a surface in the space with coordinates B, D, and E that may be termed the carbon boundary surface. This surface represents the limiting conditions under which a gas phase can exist in equilibrium with solid carbon.

If the relative gross composition of a particular mixture of the four elements is specified by values of the three quantities B, D, and E, as defined by equations (3.3), and if $B < B_1$ for a given temperature and pressure, then the mixture at equilibrium consists of a gas phase whose composition is uniquely determined by the values of D and E in equilibrium with $Q_c - Q_c'$ gram atoms of carbon, where

$$Q_c - Q_c' = \left(\frac{1-E}{E}\right)\left(\frac{B_{11} - B}{B_1 B}\right) Q_o. \tag{3.29}$$

As the ratios D and E can be expressed as functions of A, B, and C by means of equations (3.4)

$$D = D(A, B, C),$$

$$E = E(B, C),$$

it follows that the functional relation, equation (3.28), defining the carbon boundary surface, can be converted to the form,

$$B_1 = B_1 (A, C, p, T), \tag{3.30}$$

and inverted to the form

$$C_1 = C_1 (A, B, p, T) \tag{3.31}$$

by suitable numerical procedures. Here C_1 is the critical value of C for the carbon boundary surface, the heterogeneous portion of the system corresponding to the region $C < C_1$. The representation, equation (3.28), is the natural one to employ for investigations within the heterogeneous portion of the system, and the representation, equation (3.31), is the more convenient one to employ for the description of the extent of the homogeneous region. We shall show in a later section that it is possible to determine the relation (3.31) by direct calculation for given values of A, B, p, and T, as an alternative procedure to the series of interpolations required to obtain the representation (3.31) from the representation (3.28).

If $C \geqslant C_1$ (A, B, p, T), the system consists of an homogeneous gas phase with five degrees of freedom. The complete description of the system therefore requires the specification of two state variables and three parameters describing the gross composition of the system, the set A, B, C of equations (3.2) being a particularly convenient set for the consideration of combustion gases.

IV. CALCULATION OF THE EQUILIBRIUM COMPOSITION

The composition of a system at chemical equilibrium is easily calculated where there is only a single reaction (one dependent constituent) to be considered. In this case, the concentration of each constituent can be related to a single variable, "the degree of reaction," and the solution of the mass action equation is straightforward. Difficulties are encountered if this method is extended to a consideration of two simultaneous equilibria; and when the number of such simultaneous equilibria becomes large, the ordinary methods become very laborious. In a recent publication,7/ a systematic procedure for calculating the equilibrium composition of a system of many constituents was presented. This method presents a simple rule for formulating the work program of such calculations, with the result that very little time is required for setting up a particular problem. The systematic nature of the procedure makes the method well adapted to computation by modern automatic computational equipment. In the publication cited, the method was

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7/ Brinkley, S. R., Jr., Calculation of the Equilibrium Composition of Systems of Many Constituents: Jour. Chem. Phys., vol. 15, 1947, pp. 107-110.

developed for systems of a very general nature. In subsequent communications,[8,9,10] application of the method was restricted to the calculation of the equilibrium composition of mixtures consisting of a single homogeneous gas phase or of a gas phase in equilibrium with a single pure solid phase, and it was assumed that the gas phase is adequately described by the ideal gas equation of state. By taking advantage of these restrictions, it was possible to formulate a computational method applicable to these particular cases, which is substantially simpler and more systematic than the more general method. In addition, it was possible to formulate a special method, applicable in restricted cases, that has the advantage of converging considerably more rapidly than the more systematic general method.

In order that the present discussion may be self contained, we repeat portions of the development of the basic equations that have been published elsewhere.

The General Method

The formal methods of the preceding section have resulted in a statement of the conditions for equilibrium in a form that is particularly well suited to serve as a basis for the computation of the equilibrium composition. We shall henceforth limit consideration to the cases of a homogeneous gaseous system or of a heterogeneous system composed of a gas mixture in equilibrium with a single, pure, solid phase.

The conservation of each element was shown to require that

$$n_j + \sum_{i=c+1}^{s} \nu_{ij} n_i = q_j, \tag{4.1}$$

$j = 1, 2, \ldots c$, where n_i and n_j are the number of moles of the i-th dependent constituent and j-th component, respectively, in the equilibrium mixture containing M_0 grams of gas, q_j is the number of moles of the j-th component in the hypothetical mixture containing components only and where ν_{ij} is the coefficient to the symbol of the j-th component in the equation for the formation of the i-th dependent constituent (involving only components as reactants). The constants q_j are normalized in accord with the relation,

$$\sum_j q_j = 1, \tag{4.2}$$

8/ Kandiner, H. J., and Brinkley, S. R., Jr., Calculation of Complex Equilibrium Relations: Ind. Eng. Chem., vol. 42, May 1950, pp. 850-855.

9/ Brinkley, S. R., Jr., and Smith, R. W., Jr., Calculation of the Equilibrium Composition of Systems of Many Constituents: Proc. Scientific Computation Forum 1948, International Business Machines Corp., New York, 1950, pp. 77-82.

10/ Brinkley, S. R., Jr., and Smith, R. W., Jr., Calculation of the Equilibrium Composition of Homogeneous Multicomponent Systems: Proc. Seminar on Scientific Computation 1949, International Business Machines Corp., New York, 1950, pp. 58-63.

where the operator $\sum_j'$ denotes a summation over gaseous components only, and this normalization implies that the weight of the gas phase M_0 is assigned the arbitrarily assumed value given by equation (3.15).

The conditions for chemical equilibrium, given in equations (3.25), can be put in the form,

$$K_i = p_i^* \pi_j' (p_j^*)^{-\nu_{ij}}, \tag{4.3}$$

$i = c+1, \ldots s$, where p_i^* and p_j^* are the fugacities of the i-th dependent constituent and j-th component, respectively, K_i is the thermodynamic equilibrium constant, a function of the temperature only that is defined by equation (3.26), of the reaction for the formation of the i-th dependent constituent, and where the operator π_j' denotes that the repeated product is to be taken over gaseous components only. The equilibrium constant K_i is most easily obtained by the relation,

$$K_i = Kf_i \pi_{j=1}^{c} (Kf_j)^{-\nu_{ij}}, \tag{4.4}$$

where Kf_i and Kf_j are the equilibrium constants for the formation of the i-th dependent constituent and j-th component, respectively, from the elements.

For each gaseous component we employ equations (4.1) in the form

$$x_j + \sum_{i=c+1}^{s} \nu_{ij} x_i = q_j/n, \tag{4.5}$$

where x_i and x_j are the mole fractions in the equilibrium mixture of the i-th dependent constituent and the j-th gaseous component, respectively, and n is the total number of moles of gas in the equilibrium mixture corresponding to the normalized constants q_j. In view of equation (4.2)

$$\sum_j' x_j + \sum_{i=c+1}^{8} \nu_i x_i = 1/n, \tag{4.6}$$

where

$$\nu_i = \sum_j' \nu_{ij}.$$

The mole fractions of the gaseous constituents are subject to the identity relation

$$\sum_j' x_j + \sum_{i=c+1}^{s} x_i = 1.$$

Therefore, equation (4.6) becomes

$$1/n = 1 + \sum_{i=c+1}^{s} (\nu_i - 1)\, x_i,$$

and equations (4.5) may be written

$$x_j = q_j - \sum_{i=c+1}^{s} [\nu_{ij} - q_j (\nu_i - 1)]\, x_i, \qquad (4.7)$$

there being a member of the set (4.7) for each gaseous component.

If an activity coefficient f_k of the k-th gaseous constituent is defined by the relations

$$p_k^* = x_k f_k p, \qquad (4.8)$$

$$\text{Lim}\ (p \rightarrow 0)\ f_k = 1,$$

equations (4.3) can be written in the form

$$x_i = k_i \pi'_j x_j^{\nu_{ij}} \qquad (4.9)$$

$i = c + 1, \ldots s$, where the k_i are functions of temperature and pressure given by

$$k_i = K_i p^{\nu_i - 1} \Gamma_i, \qquad (4.10)$$

$$\Gamma_i = f_i^{-1} \pi'_j f_j^{\nu_{ij}},$$

in which the Γ_i are in general functions of the temperature and pressure. In this section we shall assume that the gas mixture is ideal and therefore that $\Gamma_i = 1$ for every i. In a later section we shall consider the evaluation of the Γ_i for imperfect gas mixtures.

The computation of the equilibrium composition requires the simultaneous solution of equations (4.7) and (4.9. If $x_i \ll x_j$ for all i and j, the solution may be carried out by a simple iteration method. 11/ An approximate set of values is chosen for the x_j. (In the absence of any criteria for the choice of the initial set, one may take $x_j = q_j$.) Equations (4.9) are employed in the computation of corresponding values of the x_i. These, in turn, are employed with equations (4.7) for the determination of an improved set of values for the x_j. This iterative process is continued until the difference between successive approximations to the x_j is less than the desired precision of the computation.

11/ Scarborough, J. B., Numerical Mathematical Analysis: Johns Hopkins Press, Baltimore, Md., 1930, pp. 191-195.

The convergence of this simple iteration method is very slow for larger relative values of the x_i, and when the x_i and x_j are of the same order of magnitude, this method may not converge at all for any choice of components. A more powerful computational procedure is provided by the Newton-Raphson method.[12/] Equations (4.7) may be written in the form

$$F_j = 0 \tag{4.11}$$

for each gaseous component, where

$$F_j = q_j G - x_j - \sum_{i=c+1}^{s} \nu_{ij} x_i,$$

$$G = 1 + \sum_{i=c+1}^{s} (\nu_i - 1) x_i.$$

We seek the solution of equations (4.11) subject to equations (4.9). If the functions F_j are expanded in Taylor series about an approximate set of values of the variables x_j with neglect of terms involving derivatives of second and higher orders, there results a set of linear equations that can be compactly represented in the notation of matrices by

$$\left[A_{jj'}^{(r)}\right] \left[h_j^{(r)}\right] = \left[F_j^{(r)}\right], \tag{4.12}$$

where the r-th and (r + 1)-th approximations to the composition are related by

$$x_j^{(r+1)} = x_j^{(r)} (1 + h_j^{(r)}), \tag{4.13}$$

and where the elements of the matrix are given by

$$A_{jj'} = U_{jj'} - q_j V_{j'} \tag{4.14}$$

where

$$U_{jj'} = x_j \delta_{jj'} + \sum_{i=c+1}^{s} \nu_{ij} \nu_{ij} x_i,$$

$$V_{j'} = \sum_{i=c+1}^{s} \nu_{ij'} (\nu_i - 1) x_i,$$

and where $U_{jj'} = U_{j'j}$. The superscript r indicates that the designated quantity is to be evaluated with the r-th approximation to the composition of the system, and $\delta_{jj'}$ is the Kronecker delta.

[12/] Scarborough, J. B., Work cited in footnote 11, pp. 178 and 187.

Criteria for the choice of components that results in the most rapid convergence of the iteration process can be developed from the remainders to the two-term Taylor series expansions of functions F_j. However, the resulting expressions are too cumbersome for practical utility, and in practice the convergence will be found to be satisfactory if the components are selected so as to minimize the quantities k_i, $i = c + 1, \ldots, s$.

A Special Method

An alternative computational procedure is very useful in certain special cases. We employ equations (4.1),

$$n_j + \sum_{i=c+1}^{s} \nu_{ij} n_i = q_j, \tag{4.1}$$

and write equations (4.9) in the form

$$\begin{aligned} n_i &= k_i'(n)\, \pi_j'\, n_j^{\nu_{ij}}, \\ k_i'(n) &= k_i\, n^{1-\nu_i}, \end{aligned} \tag{4.15}$$

$i = c + 1, \ldots s$, by means of the substitution $n_k = x_k n$. In view of equations (4.1) and (4.2), the total number of moles of gas n is given by

$$n = 1 + \sum_{i=c+1}^{s} (1 - \nu_i)\, n_i. \tag{4.16}$$

We define a variable μ by

$$\mu = \pi_j'\, n_j^{\eta_j}, \tag{4.17}$$

and rewrite equations (4.15) in the form

$$\begin{aligned} n_i &= k_i'(n)\, \mu^{\xi_i}\, \pi_j'\, n_j^{\sigma_{ij}}, \\ \sigma_{ij} &= \nu_{ij} - \xi_i \eta_j, \end{aligned} \tag{4.18}$$

$i = c+1, \ldots s$. We endeavor to choose the η_j, so that for each i there exists only a single value of j, say j', for which σ_{ij} does not vanish, and so that for some value of j, say j^*, σ_{ij^*} vanishes for every value of i. If this can be done, equations (4.18) reduce to expressions of the form

$$n_i = k_i'(n)\mu^{\xi_i}\, n_{j'}^{\sigma_{ij'}}, \tag{4.19}$$

$i = c + 1, \ldots s$, $j' = j^*$.

Introduction of the variable μ leads immediately to a separation of variables in the set of equations composed of equations (4.19) and those of equations (4.1), for which $\neq j^*$ when mass action expressions of the form (4.19) can be obtained with

$$\mu = n_{j*}^{\eta_{j*}} \tag{4.20}$$

Then η_{j*} is the lowest common divisor of those coefficients ν_{ij*} that are nonzero and $\sigma_{ij} = \nu_{ij}$ for $j \neq j^*$. By substitution of equations (4.19) into equations (4.1), we obtain

$$n_j + \sum_{i(j)} \nu_{ij} k_i'(n) \mu^{\xi_i} n_j^{\nu_{ij}} - q_j = 0 \tag{4.21}$$

for $j \neq j^*$, which can, at least in principle, be solved for n_j by ordinary algebraic methods for given values of n and μ. If equations (4.19) and (4.20) are then employed, a solution can be found in the form

$$n_j = n_j (n, \mu),$$

$$n_i = n_i (n, \mu),$$

$j = 1, 2, \ldots c;\ i = c + 1, \ldots s.$

The values of n and μ leading to an exact solution of the equilibrium conditions must satisfy equation (4.16) and the member of equations (4.1) for which $j = j^*$. These can be written in the form

$$F(\mu) = 0, \quad F(n) = 0, \tag{4.22}$$

$$F(\mu) = q_{j*} - n_{j*} - \sum_{i=c+1}^{s} \nu_{ij*} n_i,$$

$$F(n) = n - 1 + \sum_{i=c+1}^{s} (\nu_i - 1) n_i.$$

If the functions F (μ) and F (n) are expanded in Taylor series about approximate values of n and μ with neglect of terms involving second and higher derivatives, there result a pair of linear equations,

$$\begin{bmatrix} A_{11}^{(r)} & A_{12}^{(r)} \\ A_{21}^{(r)} & A_{22}^{(r)} \end{bmatrix} \begin{bmatrix} h(\mu)^{(r)} \\ h(n)^{(r)} \end{bmatrix} = \begin{bmatrix} F(\mu)^{(r)} \\ F(n)^{(r)} \end{bmatrix}, \tag{4.23}$$

where the r-th and (r+1)-th approximation to μ and n are related by

$$\mu^{(r+1)} = \mu^{(r)} \left[1 + h(\mu)^{(r)} \right],$$
$$n^{(r+1)} = n^{(r)} \left[1 + h(n)^{(r)} \right], \tag{4.24}$$

and where the coefficients are given by

$$A_{11} = n_{j*} L + \sum_{i=c+1}^{s} \nu_{ij*} \xi_i n_i + \sum_{i=c+1}^{s} \nu_{ij*} \nu_{ij(i)} U_{j(i)} n_i,$$

$$A_{12} = \sum_{i=c+1}^{s} \nu_{ij*} (1 - \nu_i) n_i + \sum_{i=c+1}^{s} \nu_{ij*} \nu_{ij(i)} V_{j(i)} n_i,$$

$$A_{21} = n_j^* M + \sum_{i=c+1}^{s} (1 - \nu_i) \xi_i n_i + \sum_{i=c+1}^{s} (1 - \nu_i) \nu_{ij(i)} U_{j(i)} r_i, \tag{4.25}$$

$$A_{22} = -n + \sum_{i=c+1}^{s} (1 - \nu_i)^2 n_i + \sum_{i=c+1}^{s} (1 - \nu_i) \nu_{ij(i)} V_{j(i)} n_i,$$

where j(i) is the value of j, for which σ_{ij} does not vanish for a given i, and where

$$L = 1/\eta_j, \; M = 0,$$

$$U_j = -\left[\sum_{i(j)} \nu_{ij} \xi_i n_i \right] \left[n_j + \sum_{i(j)} (\nu_{ij})^2 n_i \right]^{-1},$$
$$V_j = -\left[\sum_{i(j)} \nu_{ij} (1 - \nu_i) n_i \right] \left[n_j + \sum_{i(j)} (\nu_{ij})^2 n_i \right]^{-1} \tag{4.26}$$

The superscript r indicates that the designated quantity is to be evaluated with the r-th approximation to the composition of the system.

Introduction of the variable μ also leads to a separation of variables in the set of equations composed of equations (4.19) and those of equations (4.1), for which $j \neq j^*$ when mass action expressions of the form (4.19) can be obtained with

$$\mu = n_{j'}{}^{\eta_{j'}} n_{j*}, \tag{4.27}$$

$j' \neq j^*$. Then $\xi_i = \nu_{ij*}$, $\sigma_{ij} = \nu_{ij}$ for $j \neq j'$, j^*, and $\sigma_{ij'} = \nu_{ij'} - \nu_{ij*} \eta_{j'}$. The stoichiometric conditions for $j \neq j^*$ can then be put into a form analogous to equations (4.21)

$$n_j + \sum_{i(j)} \nu_{ij} k_i'(n)\mu^{\xi_i} n_j^{\nu_{ij}} - q_j = 0, \; j \neq j',$$

$$n_{j'} - \eta_{j'} \mu \, n_{j'}^{-\eta_{j'}} + \sum_{i(j')} \sigma_{ij'} k_i'(n)\mu^{\xi_i} n_j^{\sigma_{ij'}} - q_{j'} + \eta_{j'} q_{j*} = 0, \tag{4.28}$$

which can, at least in principle, be solved for n_j, $j \neq j^*$, by ordinary algebraic methods for given values of n and μ. If equations (4.19) and (4.27) are then employed, a solution can be found in the form

$$n_j = n_j(n, \mu),$$

$$n_i = n_i(n, \mu),$$

$j = 1, 2, \ldots c; \; i = c + 1, \ldots s.$

The values of n and μ leading to an exact solution of the equilibrium conditions must satisfy equations (4.22). The application of the Newton-Raphson method to obtain an improved pair of values of n and μ requires the solution of equations (4.23) and the application of equations (4.24). The coefficients of equations (4.23) are given by equations (4.25) but with

$$L = 1 - \eta_{j'} U_{j'} \qquad , M = - \eta_{j'} V_{j'}$$

$$U_j = - \left[\sum_{i(j)} \nu_{ij} \xi_i n_i \right] \left[n_j + \sum_{i(j)} (\nu_{ij})^2 n_i \right]^{-1}, \; j \neq j',$$

$$U_{j'} = \left[\eta_{j'} n_{j*} - \sum_{i(j')} \sigma_{ij'} \xi_i n_i \right] \left[n_{j'} + \eta_{j'}^2 n_{j*} + \sum_{i(j')} (\sigma_{ij'})^2 n_i \right]^{-1}, \tag{4.29}$$

$$V_j = - \left[\sum_{i(j)} \nu_{ij} (1 - \nu_i) n_i \right] \left[n_j + \sum_{i(j)} (\nu_{ij})^2 n_i \right]^{-1}, \; j \neq j',$$

$$V_{j'} = - \left[\sum_{i(j)} \sigma_{ij'} (1 - \nu_i) n_i \right] \left[n_{j'} + \eta_j^2 n_{j*} + \sum_{i(j')} (\sigma_{ij})^2 n_i \right]^{-1},$$

replacing equations (4.26).

The special method converges considerably more rapidly than the general method and can be advantageously employed for computations where it is applicable. It has the disadvantage, however, that the computation program for a single iteration is longer and less systematic than for the general method. The final results are easily expressed in terms of mole fractions by the application of the relation

$$x_k = n_k/n. \tag{4.30}$$

Modifications for Computation at a Specified Density

Many of the applications of thermodynamics to combustion processes are such that it is natural to specify the state by means of the variables temperature and pressure. The methods for the calculation of the equilibrium composition that have been described assume that the temperature and pressure have been explicitly specified, i.e., that the equation of state is of the form

$$p/\rho = nRT\,\varphi(p,T)/M_o,$$

where n is the number of moles of gas contained in M_o grams of gas, ρ is the density, and $\varphi(p,T)$ is explicit in the pressure and temperature and unity for the ideal gas.

In certain applications, as in those of internal ballistics, it is more natural to specify the state by means of the variables temperature and density (or volume). For these cases the equation of state may be assumed to be of the form

$$p/\rho = nRT\,\psi(\rho,T)/M_o,$$

where $\Psi(\rho,T)$ is explicit in the density and temperature and unity for the ideal gas. The methods for the calculation of the equilibrium composition at a specified density are analogous for those at a specified pressure, but they differ in certain details.

The conditions for equilibrium, equations (4.3), can be advantageously written in the form,

$$n_i = k_i' \pi_j' n_j^{\nu_{ij}}, \tag{4.31}$$

$i = c+1, \ldots s$, where the k_i' are functions of temperature and density given by

$$\begin{aligned} k_i' &= K_i\,(RT\rho/M_o)^{\nu_i - 1}\,\Gamma_i', \\ \Gamma_i' &= [\psi(\rho,T)]^{\nu_i - 1} f_i^{-1} \pi_j' f_j^{\nu_{ij}}, \end{aligned} \tag{4.32}$$

in which the Γ_i' are in general functions of the temperature and density and are unity for every i if the gas mixture is ideal. In a formal way, equations (4.31) and (4.32) can be obtained from the analogous expressions, equations (4.9) and (4.10), employed in the general method above by replacing x_i and x_j by n_i and n_j, respectively, and by replacing k_i by k_i'. We note that the k_i' of equations (4.15) and (4.31) are identical, although they are evaluated in different ways.

Equations (4.31) determine the concentrations of the dependent constituents for assumed values of the concentrations of the components. In order that these calculations lead to an exact calculation of the equilibrium composition, it is necessary that the results satisfy the stoichiometric conditions, equations (4.1), which we write in the form

$$F_j' = 0, \tag{4.33}$$

where

$$F'_j = q_j - n_j - \sum_{i=c+1}^{s} \nu_{ij} n_i.$$

In a formal way, equations (4.33) can be obtained from the analogous expressions, equations (4.11) by replacing x_i and x_j by n_i and n_j, respectively, and by setting G = 1.

The application of the Newton-Raphson method to the improvement of an approximate set of values of the concentrations of the components requires the solution of equations analogous to equations (4.12),

$$\begin{bmatrix} A'^{(r)}_{jj'} \end{bmatrix} \begin{bmatrix} h'^{(r)}_{j'} \end{bmatrix} = \begin{bmatrix} F'^{(r)}_{j} \end{bmatrix}, \tag{4.34}$$

where the r-th and the (r+1)-th approximations to the composition are related by

$$n_j^{(r+1)} = n_j^{(r)} (1 + h'^{(r)}), \tag{4.35}$$

and where the elements of the matrix are given by

$$A'_{jj'} = n_j \delta_{jj'} + \sum_{i=c+1}^{s} \nu_{ij} \nu_{ij'} n_i. \tag{4.36}$$

In a formal way, equations (4.34), (4.35), and (4.36) can be obtained from the analogous expressions, equations (4.12), (4.13), and (4.14), respectively, by replacing x_i and x_j by n_i and n_j, respectively, and by setting $V_j = 0$ for all j.

It is evident that the general method for computations at specified density is similar in outline with the previously described general method for computations at specified pressure, and that a particular computational program for the former case can easily be derived in a formal way from the equivalent program for the latter case. The total number of moles n contained in M_0 grams of gas mixture can be calculated with equation (4.16).

The alternative computational method, which we have called the special method, is easily applied without substantial modification to calculations at specified density. We again employ the stoichiometric conditions as expressed by equations (4.1) and the equilibrium conditions as expressed by equations (4.15). The constants k'_i appearing in the equilibrium conditions are to be calculated by equations (4.32), and for specified temperature and density they are independent of the total number of moles n. Consequently, it is possible to seek a solution of the form

$$n_j = n_j(\mu)$$
$$n_i = n_i(\mu)$$

j = 1, 2, . . . c; i = c+1, . . . s, for those cases where the introduction of a variable u results in a separation of variables.

The value of μ leading to an exact solution of the equilibrium conditions must satisfy the condition,

$$F(\mu) = 0 \tag{4.37}$$

where $F(\mu)$ is defined by equations (4.22). The application of the Newton-Raphson method to obtain an improved value of μ requires the application of the relation

$$\mu^{(r+1)} = \mu^{(r)} \; [1 + h(\mu)^{(r)}] \tag{4.38}$$

where

$$h(\mu)^{(r)} = F(\mu)^{(r)} / A_{11}^{(r)} \tag{4.39}$$

and where A_{11} has been defined as one of equations (4.25). Equations (4.37), (4.38), and (4.39) are obtained from the analogous expressions, equations (4.23), (4.24), and (4.25), respectively, by retaining only those terms of significance in the latter equations after setting $F(n) = 0, h(n) = 0$.

Calculation of the Equilibrium Composition of Imperfect Gas Mixtures

In the previous discussion it has been assumed that the gas mixture can be described adequately by the ideal gas equation of state. At the temperatures of interest in the consideration of combustion gases this assumption is adequate for most purposes. However, for combustion processes occurring at high pressures, as in closed bombs or in gun barrels, the ideal gas equation of state is no longer adequate, and it is necessary to consider the effects of gas imperfection on the calculation of the equilibrium composition. In the present section, we indicate the modifications to the previously described computation methods that are necessary to take account of gas imperfections, and we assemble the relations required for this purpose. A comprehensive discussion of the evaluation of the thermodynamic properties of mixtures of real gases, with derivations of the necessary relations, has been given by Beattie.[13]

For calculations that are carried out at a specified pressure, the mass action constant k_i is related to the thermodynamic equilibrium constant K_i by equation (4.10),

$$k_i = K_i \, p^{\nu_i - 1} \, \Gamma_i,$$

where

$$\Gamma_i = f_i^{-1} \pi'_j \, f_j^{\nu_{ij}}, \tag{4.40}$$

and where the activity coefficient of the k-th constituent is the ratio of the fugacity to the partial pressure of the k-th constituent in the gas mixture

$$f_k = p_k^* / x_k P,$$

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[13] Beattie, J. A., The Computation of the Thermodynamic Properties of Real Gases and Mixtures of Real Gases: Chem. Rev., vol. 44, February 1949, pp. 141-192.

tending to the unity as the pressure tends to zero. In the general case of the non-ideal gas, the Γ_i are functions of temperature, pressure, and composition.

If the equation of state is explicit in the pressure and of the form

$$\frac{p}{\rho} = \frac{nRT}{M_o}\,\varphi(p,T), \tag{4.41}$$

where $\varphi(p,T)$ is generally a function of the composition as well as of the temperature and pressure, the activity coefficient of the k-th constituent of the gas mixture is given by

$$\log f_k = \int_o^p \left[\varphi - 1 + n\frac{\partial\varphi}{\partial n_k}\right]\frac{dp}{p}. \tag{4.42}$$

This expression can be evaluated explicitly for a particular equation of state and employed to determine the activity coefficients of the constituents of the mixture as functions of temperature, pressure, and, in general, composition. Equation (4.40) can then be employed to evaluate the functions Γ_i that determine the effect of gas imperfection on the mass action constants k_i.

If the activity coefficients are functions of the composition of the system, the Γ_i must be evaluated with each successive approximation to the composition. The Γ_i are relatively insensitive to the composition, and, consequently, it is unnecessary to modify the computation procedure by means of which a particular approximation to the composition is determined by the one preceding it.

Lewis and Randall[14/] have proposed as a basis for an approximate thermodynamic treatment of imperfect gas mixtures the rule

$$p_k^* = x_k\, P_k^*(p), \tag{4.43}$$

where $P_k^*(p)$ is the fugacity of k-th constituent as a pure gas at the temperature and total pressure of the mixture. If the k-th constituent obeys the gas law

$$pV = n_k RT\,\varphi_k(p,T), \tag{4.44}$$

where φ_k is a function of pressure and temperature only and V is the volume occupied by n_k moles at temperature T and pressure p, the Lewis and Randall rule results in the expression

$$\log f_k = \int_o^p [\varphi_k - 1]\,\frac{dp}{p}, \tag{4.45}$$

for the activity coefficient of the k-th constituent. Where applicable, equation (4.45) is more convenient than the exact form, equation (4.42), as it is independent of the composition of the mixture. The range of validity of the approximate expression for a particular application may be determined by comparison between results obtained from equations (4.42) and (4.45) with an explicit form of the equation of state.

14/ Lewis, G. N., and Randall, M., Thermodynamics: McGraw-Hill Book Co., Inc., New York, 1923, pp. 225-227.

For calculations at a specified density, the equation of state may be assumed to be of the form

$$\frac{p}{\rho} = \frac{nRT}{M_o} \psi(\rho,T), \tag{4.46}$$

where $\psi(\rho,T)$ is generally a function of composition as well as of temperature and density. The mass action constants k_i' for this case have been related to the corresponding thermodynamic equilibrium constants by the expressions

$$k_i' = K_i \left(\frac{RT\rho}{M_o}\right)^{\nu_i - 1} \Gamma_i',$$

with

$$\Gamma_i' = [\psi(\rho,T)]^{\nu_i - 1} f_i^{-1} \pi_j' f_j^{\nu_{ij}} = g_i^{-1} \pi_j' g_j^{\nu_{ij}} \tag{4.47}$$

where we have introduced an alternative activity coefficient,

$$g_k = f_k \psi(\rho,T). \tag{4.48}$$

The activity coefficient g_k of the k-th constituent of the mixture is given by the general thermodynamic relation

$$\log g_k = \int_o^\rho \left[\psi - 1 + n\frac{\partial\psi}{\partial n_k}\right] \frac{d\rho}{\rho}. \tag{4.49}$$

This expression can be evaluated explicitly for a particular equation of state and employed to determine the activity coefficients of the constituents of the mixture as functions of temperature, density, and, in general, composition. Equations (4.47) can then be employed to evaluate the functions Γ_i' that determine the effect of gas imperfection on the mass action constants k_i'.

If the activity coefficients are functions of the composition of the system, the Γ_i' must be evaluated with each successive approximation to the composition. The Γ_i' are relatively insensitive to the composition, and it is unnecessary to modify the computation procedure by means of which a particular approximation to the composition is determined by the one preceding it.

As a basis for the approximate thermodynamic treatment of gas mixtures, Gibbs 15/ has proposed that the pressure of a mixture of gases be assumed to be equal to the sum of the pressures of the different gases as existing each by itself at the same temperature and with the same value of its chemical potential. If the k-th constituent obeys the gas law

$$pv_k = RT\ \psi_k(T, v_k), \tag{4.50}$$

where v_k is the molar volume of the k-th constituent, then the assumption of Gibbs has been shown by Beattie 16/ to lead to the approximate relation

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15/ Gibbs, J. W., Collected Works: Longmans, Green & Co., New York, 1906, vol. I, pp. 155-158.

16/ Beattie, J. A., Work cited in footnote 13.

$$\log g_k = \int_0^{\rho} \left[\psi_k - 1 + n_k \frac{\partial \psi_k}{\partial n_k}\right] \frac{d\rho}{\rho} \tag{4.51}$$

for the activity coefficient of the k-th constituent. This expression is not in general independent of the composition of the mixture. It may, however, lead to simpler expressions than those derived from the general relation, equation (4.49). The range of validity of the approximate expression for a particular application may be determined by comparison between results obtained from equations (4.49) and (4.51) with an explicit form of the equation of state.

V. COMPUTATION PROGRAMS FOR CARBON-HYDROGEN-OXYGEN-NITROGEN SYSTEMS

A large number of the fuel-oxidant systems of scientific and technical interest yield on combustion a mixture of products composed of compounds of carbon, hydrogen, oxygen, and nitrogen. Because of the importance of such systems, we give explicitly in this section the relations obtained by the application of the general methods of the preceding section. These computational programs will also serve to illustrate the application of the general methods to the calculation of the equilibrium composition of particular systems.

The computation programs will be written for calculations at specified pressure. We do not present explicitly the relations for calculations at specified density. We have observed in a preceding section that the relations for the latter case are easily obtained from those for the former case in a formal way by simple and systematic substitutions that have been given explicitly.

The rapidity with which a particular computational program converges is largely determined by the abundance in the mixture of those constituents chosen as components relative to the abundance in the mixture of the remaining derived constituents. The equilibrium composition of carbon, hydrogen, oxygen, nitrogen systems varies greatly if considerable variation of the gross composition parameters and of the temperature and pressure are to be considered. Consequently, the program that is suitable for a given set of conditions of state and composition may converge very slowly or even diverge if applied to another region of different characteristics. For the efficient consideration of all possible gross compositions over considerable ranges of temperature and pressure a number of different programs, corresponding to different choices of the components, will be required. Each of these programs will be most appropriately employed for particular regions of the complete set of systems. It is unnecessary to specify closely the region of applicability of a particular program, since there is considerable overlap with the regions appropriate for alternative programs. It will be noted that the procedure for setting up a particular program is routine, once the constituents to be considered have been specified and a choice of components has been made.

It will generally be assumed that the equilibrium composition of the combustion products of fuel-oxidant systems, composed only of compounds of carbon, hydrogen, oxygen, and nitrogen, can be adequately represented by a consideration of the constituents: $C_{(solid)}$, CO, CO_2, H_2,

H_2O, N_2, O_2, O, OH, H, NO, N, NH_3, CH_4. Solid carbon will be assumed to be in the form of graphite. If the oxidant is air, argon will be introduced as an additional constituent. Argon will necessarily be chosen as an additional component, and, as it is inert, it does not affect in any important way the computational programs. We assume that the ideal gas law provides an adequate equation of state. In the previous section, the modifications necessary to take account of gas imperfections have been described.

The General Method for Lean Mixtures

Fuel-oxidant mixtures containing an excess of oxygen over the amount required for stoichiometric conversion of the carbon to carbon dioxide and the hydrogen to steam are called lean mixtures and are characterized by $C > 1/2$, where C is the composition parameter defined by equation (3.3). The predominant constituents of the combustion products satisfying the condition of independence required for their choice as components are

$$CO_2, H_2O, O_2, N_2,$$

except at very high temperatures. A more convenient set of components for mixtures at such temperatures (ca. 4000° K.) is described in a later section. If the oxidant is air, a fifth component, argon, must be considered.

The solution of equations (3.13) and (3.14) for this choice of components results in the equations

$$\begin{aligned}
q(CO_2) &= \frac{4\,(C/O)}{2 + (H/O) + 2\,(N/O) + 4\,(A/O)}, \\
q(H_2O) &= \frac{2\,(H/O)}{2 + (H/O) + 2\,(N/O) + 4\,(A/O)}, \\
q(O_2) &= \frac{2 - 4\,(C/O) - (H/O)}{2 + (H/O) + 2\,(N/O) + 4\,(A/O)}, \\
q(N_2) &= \frac{2\,(N/O)}{2 + (H/O) + 2\,(N/O) + 4\,(A/O)}, \\
q\,(A) &= \frac{4\,(A/O)}{2 + (H/O) + 2\,(N/O) + 4\,(A/O)},
\end{aligned} \tag{5.1}$$

relating the normalized stoichiometric constants to the atomic ratios. These relations can be employed together with equations (3.6) or (3.7) to evaluate the stoichiometric constants for assigned values of the parameters descriptive of the gross composition of the system. If the oxidant is not air, $(A/O) = 0$, $q\,(A) = 0$, and we obtain

$$\begin{aligned}
q(CO_2) &= \frac{(1-A)(1-B)(1-C)}{(1-C)(2A+B-AB)+C(1-A)},\\
q(H_2O) &= \frac{2B(1-A)(1-C)}{(1-C)(2A+B-AB)+C(1-A)},\\
q(O_2) &= \frac{(1-A)(2C-1)}{(1-C)(2A+B-AB)+C(1-A)},\\
q(N_2) &= \frac{2A(1-C)}{(1-C)(2A+B-AB)+C(1-A)},
\end{aligned} \tag{5.2}$$

by substitution of equations (3.5) into equations (5.1).

In lean mixtures, we assume that methane and ammonia are absent from the equilibrium mixture, an assumption that is confirmed by test calculations for the temperatures of interest in combustion research. The chemical reactions in the form of equations (3.11) for the formation of the dependent constituents from the components are

$$\begin{aligned}
&CO_2 - (1/2)O_2 = CO,\\
&H_2O - (1/2)O_2 = H_2,\\
&(1/2)O_2 = O,\\
&(1/2)H_2O + (1/4)O_2 = OH\\
&(1/2)H_2O - (1/4)O_2 = H,\\
&(1/2)N_2 + (1/2)O_2 = NO,\\
&(1/2)N_2 = N,
\end{aligned}$$

in which the symbols of all of the components are written on the left-hand side of the equations. The coefficients ν_{ij} of these equations can be summarized in matrix form,

$$(\nu_{ij}) = \begin{array}{c|ccccc}
 & CO_2 & H_2O & O_2 & N_2 & A \\
\hline
CO & 1 & 0 & -1/2 & 0 & 0 \\
H_2 & 0 & 1 & -1/2 & 0 & 0 \\
O & 0 & 0 & 1/2 & 0 & 0 \\
OH & 0 & 1/2 & 1/4 & 0 & 0 \\
H & 0 & 1/2 & -1/4 & 0 & 0 \\
NO & 0 & 0 & 0 & 1/2 & 0 \\
N & 0 & 0 & 0 & 1/2 & 0
\end{array} \tag{5.3}$$

The constants k_i of the mass action expressions, equations (4.9), are given for stated values of the temperature and pressure by

$$\begin{aligned} k(CO) &= p^{-1/2}K(CO), & k(H) &= p^{-3/4}K(H), \\ k(H_2) &= p^{-1/2}K(H_2), & k(NO) &= K(NO), \\ k(O) &= p^{-1/2}K(O), & k(N) &= p^{-1/2}K(N), \\ k(OH) &= p^{-1/4}K(OH), \end{aligned} \tag{5.4}$$

where the thermodynamic equilibrium constants can be calculated from the equilibrium constants of formation by means of the relations

$$\begin{aligned} K(CO) &= Kf(CO)/Kf(CO_2), & K(H) &= Kf(H)/[Kf(H_2O)]^{1/2}, \\ K(H_2) &= 1/Kf(H_2O), & K(NO) &= Kf(NO), \\ K(O) &= Kf(O), & K(N) &= Kf(N), \\ K(OH) &= Kf(OH)/[Kf(H_2O)]^{1/2}. \end{aligned} \tag{5.5}$$

In writing down equations (5.5), we have taken account of the fact that the equilibrium constant of formation of an element is unity.

The mole fractions of the dependent constituents are determined, for assumed values of the mole fractions of the components, by equations (4.9) in the form

$$\begin{aligned} x(CO) &= k(CO)x(CO_2)/[x(O_2)]^{1/2}, \\ x(H_2) &= k(H_2)x(H_2O)/[x(O_2)]^{1/2}, \\ x(O) &= k(O)[x(O_2)]^{1/2}, \\ x(OH) &= k(OH)[x(H_2O)]^{1/2}[x(O_2)]^{1/4}, \\ x(H) &= k(H)[x(H_2O)]^{1/2}/[x(O_2)]^{1/4}, \\ x(NO) &= k(NO)[x(O_2)]^{1/2}[x(N_2)]^{1/2}, \\ x(N) &= k(N)[x(N_2)]^{1/2}. \end{aligned} \tag{5.6}$$

The values of the mole fractions of the components leading to an exact calculation of the equilibrium composition satisfy the conditions

$$F(CO_2) = 0, \ F(H_2O) = 0, \ F(O_2) = 0, \ F(N_2) = 0,$$

where the functions, defined by equations (4.11), are given by

$$
\begin{aligned}
F(CO_2) &= Gq(CO_2) - x(CO_2) - x(CO), \\
F(H_2O) &= Gq(H_2O) - x(H_2O) - x(H_2) - x(OH)/2 - x(H)/2, \\
F(O_2) &= Gq(O_2) - x(O_2) + x(CO)/2 + x(H_2)/2 - x(O)/2 \\
&\qquad x(OH)/4 + x(H)/4 - x(NO)/2, \\
F(N_2) &= Gq(N_2) - x(N_2) - x(NO)/2 - x(N)/2,
\end{aligned}
\tag{5.7}
$$

and where

$$
G = 1 - x(CO)/2 - x(H_2)/2 - x(O)/2 - x(OH)/4 - 3x(H)/4 - x(N)/2. \tag{5.8}
$$

The application of the Newton-Raphson method to the improvement of an approximate set of values of the mole fractions of the components requires the solution of equations (4.12) in the form

$$
\begin{pmatrix}
A_{11} & A_{12} & A_{13} & A_{14} \\
A_{21} & A_{22} & A_{23} & A_{24} \\
A_{31} & A_{32} & A_{33} & A_{34} \\
A_{41} & A_{42} & A_{43} & A_{44}
\end{pmatrix}
\begin{pmatrix}
h(CO_2) \\ h(H_2O) \\ h(O_2) \\ h(N_2)
\end{pmatrix}
=
\begin{pmatrix}
F(CO_2) \\ F(H_2O) \\ F(O_2) \\ F(N_2)
\end{pmatrix}
\tag{5.9}
$$

where $h(CO_2)$, $h(H_2O)$, $h(O_2)$, and $h(N_2)$ are estimates of the fractional errors of a particular approximation to the mole fractions of the respective components, to be employed as indicated by equations (4.13) in obtaining the next approximation, and where the coefficients, defined by equations (4.14), are given by

$$
\begin{aligned}
A_{11} &= U_{11} - V_1q(CO_2), & A_{31} &= U_{13} - V_1q(O_2), \\
A_{12} &= U_{12} - V_2q(CO_2), & A_{32} &= U_{23} - V_2q(O_2), \\
A_{13} &= U_{13} - V_3q(CO_2), & A_{33} &= U_{33} - V_3q(O_2), \\
A_{14} &= U_{14} - V_4q(CO_2), & A_{34} &= U_{34} - V_4q(O_2), \\
A_{21} &= U_{12} - V_1q(H_2O), & A_{41} &= U_{14} - V_1q(N_2), \\
A_{22} &= U_{22} - V_2q(H_2O), & A_{42} &= U_{24} - V_2q(N_2), \\
A_{23} &= U_{23} - V_3q(H_2O), & A_{43} &= U_{34} - V_3q(N_2), \\
A_{24} &= U_{24} - V_4q(H_2O), & A_{44} &= U_{44} - V_4q(N_2),
\end{aligned}
$$

with

$$U_{11} = x(CO_2) + x(CO), \qquad U_{12} = 0, \qquad U_{13} = -x(CO)/2,$$
$$U_{14} = 0, \; U_{22} = x(H_2O) + x(H_2) + x(OH)/4 + x(H)/4,$$
$$U_{23} = x(H_2)/2 + x(OH)/8 - x(H)/8, \; 7 \; U_{24} = 0,$$
$$U_{33} = x(O_2) + x(CO)/4 + x(H_2)/4 + x(O)/4 + x(OH)/16 + x(H)/16 + x(NO)/4,$$
$$U_{34} = x(NO)/4, \; U_{44} = x(N_2) + x(NO)/4 + x(N)/4,$$

and

$$V_1 = -x(CO)/2, \; V_2 = -x(H_2)/2 - x(OH)/8 - 3x(H)/8,$$
$$V_3 = x(CO)/4 + x(H_2)/4 - x(O)/4 - x(OH)/16 + 3x(H)/16, \; V_4 = -x(N)/4.$$

If the oxidant is air, the value of the mole fraction of argon in the equilibrium mixture can be calculated from

$$x(A) = Gq(A). \tag{5.10}$$

The total number of moles n contained in M_o grams of mixture is equal to G^{-1}, where

$$M_o = 44.010\, q(CO_2) + 18.016\, q(H_2O) + 32.000\, q(O_2) + 28.016\, q(N_2) + 39.944\, q(A),$$

and where the quantity G is defined by equation (5.8).

A Special Method for Lean Mixtures

The special method of computation can profitably be employed in calculations for conditions such that the convergence of the general method is inconveniently slow. This will be the case for mixtures near the stoichiometric point $C = 1/2$ and for mixtures at temperatures such that dissociation of the components into atomic species is important. Although the special method converges more rapidly than the general method, each iteration of the special method involves a considerably longer and less systematic computational routine than is required by the general method.

We take the variable μ, defined by equation (4.17), to be

$$\mu = [n(O_2)]^{1/2} \tag{5.11}$$

and employ equation (5.11) to eliminate $n(O_2)$ from the set of equations describing the equilibrium conditions. The stoichiometric conditions, equations (4.1), on the components CO_2, H_2O, and N_2 are given by

$$n(CO_2) + n(CO) = q(CO_2),$$
$$n(H_2O) + n(H_2) + n(OH)/2 + n(H)/2 = q(H_2O), \qquad (5.12)$$
$$n(N_2) + n(NO)/2 + n(N)/2 = q(N_2).$$

The mass action expressions, equations (4.19), can be written explicitly

$$\begin{aligned} n(CO) &= k'(CO)x/\mu, & n(H) &= k'(H)y/\mu^{1/2}, \\ n(H_2) &= k'(H_2)y^2/\mu, & n(NO) &= k'(NO)z\mu, \\ n(O) &= k'(O)\mu, & n(N) &= k'(N)z, \\ n(OH) &= k'(OH)y\mu^{1/2}, \end{aligned} \qquad (5.13)$$

where

$$\begin{aligned} k'(CO) &= n^{1/2}k(CO), & k'(H) &= n^{3/4}k(H), \\ k'(H_2) &= n^{1/2}k(H_2), & k'(NO) &= k(NO), \\ k'(O) &= n^{1/2}k(O), & k'(N) &= n^{1/2}k(N), \\ k'(OH) &= n^{1/4}k(OH), \end{aligned} \qquad (5.14)$$

and where we have employed the abbreviations

$$x = n(CO_2), \quad y^2 = n(H_2O), \quad z^2 = n(H_2). \qquad (5.15)$$

Substituting equations (5.13) into equations (5.14), we obtain

$$x[1 + k'(CO)/\mu] - q(CO_2) = 0,$$
$$y^2[1 + k'(H_2)/\mu] + y[k'(OH)\mu^{1/2} + k'(H)/\mu^{1/2}]/2 - q(H_2O) = 0,$$
$$z^2 + z\,[k'(NO)\mu + k'(N)]/2 - q(N_2) = 0,$$

with the solutions,

$$x = \frac{q(CO_2)}{1 + k'(CO)/\mu} \qquad (5.16)$$

$$y = -\frac{k'(OH)\mu^{1/2} + k'(H)/\mu^{1/2}}{4 + 4k'(H_2)/\mu} + \sqrt{\left[\frac{K'(OH)\mu^{1/2} + k'(H)\mu^{1/2}}{4 + 4k'(H_2)/\mu}\right]^2 + \frac{q(H_2O)}{1 + k'(H_2)/\mu}},$$

$$z = -\frac{k'(NO)\mu + k'(N)}{4} + \sqrt{\left[\frac{k'(NO)\mu + k'(N)}{4}\right]^2 + q(N_2)}.$$

Equations (5.16), together with equations (5.11), (5.13), and (5.15), determine the equilibrium composition for assumed values of n and μ.

The values of n and μ leading to an exact calculation of the equilibrium composition satisfy the conditions,

$$F(\mu) = 0, \quad F(n) = 0,$$

where the functions are defined by equations (4.22) and have the explicit form

$$\begin{aligned} F(\mu) &= q(O_2) - n(O_2) + n(CO)/2 + n(H_2)/2 - n(O)/2 - n(OH)/4 + n(H)/4 - n(NO)/2, \\ F(n) &= n - 1 - n(CO)/2 - n(H_2)/2 - n(O)/2 - n(OH)/4 - 3n(H)/4 - n(N)/2. \end{aligned} \tag{5.17}$$

If F and G do not vanish, the application of the Newton-Raphson method to obtain an improved pair of values of n and μ requires the solution of equations (4.23),

$$\begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} \begin{pmatrix} h(u) \\ h(n) \end{pmatrix} = \begin{pmatrix} F(u) \\ F(n), \end{pmatrix} \tag{5.18}$$

where h(μ) and h(n) are estimates of the fractional error of the approximation to μ and n, respectively, to be employed as indicated by equations (4.24) in obtaining the next approximation, and where the coefficients, defined by equations (4.25), are given by

$$\begin{aligned} A_{11} = {} & 2n(O_2) + n(CO)/2 + n(H_2)/2 + n(O)/2 + n(OH)/8 + n(H)/8 + n(NO)/2 \\ & + U\,[-n(CO)/2] + V\,[-n(H_2) + n(OH)/4 - n(H)/4] + W\,[n(NO)/2] \\ A_{12} = {} & -n(CO)/4 - n(H_2)/4 + n(O)/4 + n(OH)/16 - 3n(H)/16 \\ & + X\,[-n(CO)/2] + Y\,[-n(H_2) + n(OH)/4 - n(H)/4] + Z\,[n(NO)/2] \\ A_{21} = {} & -n(CO)/2 - n(H_2)/2 + n(O)/2 + n(OH)/8 - 3n(H)/8 \\ & + U\,[n(CO)/2] + V\,[n(H_2) + n(OH)/4 + 3n(H)/4] + W\,[n(N)/2] \\ A_{22} = {} & -n + n(CO)/4 + n(H_2)/4 + n(O)/4 + n(OH)/16 + 9n(H)/16 + n(N)/4 \\ & + X\,[n(CO)/2] + Y\,[n(H_2) + n(OH)/4 + 3n(H)/4] + Z\,[n(N)/2] \end{aligned}$$

where

$$U = \frac{n(CO)}{q(CO_2)}, \qquad X = -\frac{n(CO)/2}{q(CO_2)},$$

$$V = \frac{n(H_2) - n(OH)/4 + n(H)/4}{q(H_2O) + n(H_2O) + n(H_2)}, \qquad Y = -\frac{n(H_2)/2 + n(OH)/8 + 3n(H)/8}{q(H_2O) + n(H_2O) + n(H_2)},$$

$$W = \frac{n(NO)/2}{q(N_2) + n(N_2)}, \qquad Z = -\frac{n(N)/4}{q(N_2) + n(N_2)}.$$

If the oxidant is air, the concentration of argon is given by

$$n(A) = q(A). \qquad (5.19)$$

The equilibrium composition is expressed in terms of mole fractions by dividing the number of moles of each constituent by the total number of moles n of the mixture. The mass of the mixture in grams containing a total number of gram moles n is M_o, where

$$M_o = 44.010\, q(CO_2) + 18.016\, q(H_2O) + 32.000\, q(O_2) + 28.016\, q(N_2) + 39.944\, q(A).$$

The General Method for Rich Mixtures Without Solid Carbon

Fuel-oxidant mixtures containing a deficit of oxygen compared to the amount required for stoichiometric conversion of the carbon to carbon dioxide and the hydrogen to steam are called rich mixtures and are characterized by $C < 1/2$, where C is the composition parameter defined by equation (3.2). If $C > C_1$, where C_1 is the critical value of C defining the solid carbon boundary surface, equation (3.31), the equilibrium mixture will consist of a gas phase only. The predominant constituents of the combustion products satisfying the conditions of independence required for their choice as components are

$$CO,\ H_2,\ H_2O,\ N_2,$$

except at very high temperatures. A more convenient set of components for mixtures at such temperatures (ca. 4000° K.) is described in a later section. If the oxidant is air, a fifth component, argon, must be considered.

The solution of equations (3.13) and (3.14) for this choice of components results in the equations

$$\begin{aligned}
q(CO) &= \frac{2(C/O)}{2(C/O) + (H/O) + (N/O) + 2(A/O)}, \\
q(H_2) &= \frac{(H/O) + 2(C/O) - 2}{2(C/O) + (H/O) + (N/O) + 2(A/O)}, \\
q(H_2O) &= \frac{2 - 2(C/O)}{2(C/O) + (H/O) + (N/O) + 2(A/O)}, \qquad (5.20) \\
q(N_2) &= \frac{(N/O)}{2(C/O) + (H/O) + (N/O) + 2(A/O)}, \\
q(A) &= \frac{2(A/O)}{2(C/O) + (H/O) + (N/O) + 2(A/O)},
\end{aligned}$$

relating the normalized stoichiometric constants to the atomic ratios. These relations can be employed, together with equations (3.6) or (3.7), to evaluate the stoichiometric constants for assigned values of the parameters descriptive of the gross composition of the system. If the oxidant is not air, (A/O) = 0, q(A) = 0, and we obtain

$$\begin{aligned} q(CO) &= \frac{(1-A)(1-B)}{1+A+B-AB}, \\ q(H_2) &= \frac{(1-A)\left[(1+B)(1-C)-2C\right]}{(1-C)\,(1+A+B-AB)}, \\ q(H_2O) &= \frac{(1-A)\left[2C-(1-B)(1-C)\right]}{(1-C)(1+A+B-AB)}, \\ q(N_2) &= \frac{2A}{1+A+B-AB} \end{aligned} \qquad (5.21)$$

by substitution of equations (3.5) into equations (5.20).

The chemical reactions in the form of equations (3.11) for the formation of the dependent constituents from the components are

$$\begin{aligned} &CO + H_2O - H_2 = CO_2, \\ &2H_2O - 2H_2 = O_2, \\ &H_2O - H_2 = O, \\ &H_2O - \frac{1}{2}H_2 = OH, \\ &\frac{1}{2}H_2 = H, \\ &H_2O + \frac{1}{2}N_2 - H_2 = NO, \\ &\frac{1}{2}N_2 = N, \\ &CO + 3H_2 - H_2O = CH_4, \\ &\frac{3}{2}H_2 + \frac{1}{2}N_2 = NH_3, \end{aligned}$$

in which the symbols of all of the components are written on the left-hand side of the equations. The coefficients ν_{ij} of these equations can be summarized in matrix form,

$$(\nu_{ij}) = \begin{array}{c|ccccc} & CO & H_2 & H_2O & N_2 & A \\ \hline CO_2 & 1 & -1 & 1 & 0 & 0 \\ O_2 & 0 & -2 & 2 & 0 & 0 \\ O & 0 & -1 & 1 & 0 & 0 \\ OH & 0 & -1/2 & 1 & 0 & 0 \\ H & 0 & 1/2 & 0 & 0 & 0 \\ NO & 0 & -1 & 1 & 1/2 & 0 \\ N & 0 & 0 & 0 & 1/2 & 0 \\ CH_4 & 1 & 3 & -1 & 0 & 0 \\ NH_3 & 0 & 3/2 & 0 & 1/2 & 0 \end{array} \tag{5.22}$$

The constants k_i of the mass action expressions, equations (4.9), are given for stated values of the temperature and pressure by

$$\begin{aligned} k(CO_2) &= K(CO_2),. & k(NO) &= p^{-1/2}K(NO), \\ k(O_2) &= p^{-1}K(O_2), & k(N) &= p^{-1/2}K(N), \\ k(O) &= p^{-1}K(O), & k(CH_4) &= p^{2}K(CH_4), \\ k(OH) &= p^{-1/2}K(OH), & k(NH_3) &= pK(NH_3), \\ k(H) &= p^{-1/2}K(H), \end{aligned} \tag{5.23}$$

where the thermodynamic equilibrium constants can be calculated from the equilibrium constants of formation by means of the relations,

$$\begin{aligned} K(CO_2) &= Kf(CO_2)/Kf(CO)Kf(H_2O), & K(NO) &= Kf(NO)/Kf(H_2O), \\ K(O_2) &= 1/[Kf(H_2O)]^2, & K(N) &= Kf(N), \\ K(O) &= Kf(O)/Kf(H_2O), & K(CH_4) &= Kf(CH_4)\,Kf(H_2O)/Kf(CO), \\ K(OH) &= Kf(OH)/Kf(H_2O), & K(NH_3) &= Kf(NH_3), \\ K(H) &= Kf(H). \end{aligned} \tag{5.24}$$

In writing down equations (5.25), we have taken account of the fact that the equilibrium constant of formation of an element is unity.

The mole fractions of the dependent constituents are determined, for assumed values of the mole fractions of the components, by equations (4.9) in the form

$$
\begin{aligned}
x(CO_2) &= k(CO_2)\, x(CO)x(H_2O)/x(H_2),\\
x(O_2) &= k(O_2)\,[x(H_2O)]^2/[x(H_2)]^2,\\
x(O) &= k(O)\, x(H_2O)/x(H_2),\\
x(OH) &= k(OH)x(H_2O)/[x(H_2)]^{1/2},\\
x(H) &= k(H)\,[x(H_2)]^{1/2},\\
x(NO) &= k(NO)x(H_2O)\,[x(N_2)]^{1/2}/x(H_2),\\
x(N) &= k(N)\,[x(N_2)]^{1/2},\\
x(CH_4) &= k(CH_4)x(CO)\,[x(H_2)]^3/x(H_2O),\\
x(NH_3) &= k(NH_3)\,[x(H_2)]^{3/2}[x(N_2)]^{1/2}.
\end{aligned}
\qquad (5.25)
$$

The values of the mole fractions of the components leading to an exact calculation of the equilibrium composition satisfy the conditions

$$F(CO) = 0,\ F(H_2) = 0,\ F(H_2O) = 0,\ F(N_2) = 0, \qquad (5.26)$$

where the functions, defined by equations (4.11), are given by

$$
\begin{aligned}
F(CO) &= Gq(CO) - x(CO) - x(CO_2) - x(CH_4),\\
F(H_2) &= Gq(H_2) - x(H_2) + x(CO_2) + 2x(O_2) + x(O) + x(OH)/2\\
&\quad -x(H)/2 + x(NO) - 3x(CH_4) - 3x(NH_3)/2,\\
F(H_2O) &= Gq(H_2O) - x(H_2O) - x(CO_2) - 2x(O_2) - x(O) - x(OH)\\
&\quad -x(NO) + x(CH_4),\\
F(N_2) &= Gq(N_2) - x(N_2) - x(NO)/2 - x(N)/2 - x(NH_3)/2,
\end{aligned}
\qquad (5.27)
$$

and where

$$
\begin{aligned}
G = 1 &- x(O_2) - x(O) - x(OH)/2 - x(H)/2 - x(NO)/2 - x(N)/2\\
&+ 2x(CH_4) + x(NH_3).
\end{aligned}
\qquad (5.28)
$$

The application of the Newton-Raphson method to the improvement of an approximate set of values of the mole fractions of the components requires the solution of equations (4.12) in the form

$$\begin{pmatrix} A_{11} & A_{12} & A_{13} & A_{14} \\ A_{21} & A_{22} & A_{23} & A_{24} \\ A_{31} & A_{32} & A_{33} & A_{34} \\ A_{41} & A_{42} & A_{43} & A_{44} \end{pmatrix} \begin{pmatrix} h(CO) \\ h(H_2) \\ h(H_2O) \\ h(N_2) \end{pmatrix} = \begin{pmatrix} F(CO) \\ F(H_2) \\ F(H_2O) \\ F(N_2) \end{pmatrix} \qquad (5.29)$$

where $h(CO)$, $h(H_2)$, $h(H_2O)$, and $h(N_2)$ are estimates of the fractional errors of a particular approximation to the mole fractions of the respective components, to be employed as indicated by equations (4.13) in obtaining the next approximation, and where the coefficients, defined by equations (4.14), are given by

$$A_{11} = U_{11} - V_1q(CO), \qquad A_{31} = U_{13} - V_1q(H_2O),$$
$$A_{12} = U_{12} - V_2q(CO), \qquad A_{32} = U_{23} - V_2q(H_2O),$$
$$A_{13} = U_{13} - V_3q(CO), \qquad A_{33} = U_{33} - V_3q(H_2O),$$
$$A_{14} = U_{14} - V_4q(CO), \qquad A_{34} = U_{34} - V_4q(H_2O),$$
$$A_{21} = U_{12} - V_1q(H_2), \qquad A_{41} = U_{14} - V_1q(N_2),$$
$$A_{22} = U_{22} - V_2q(H_2), \qquad A_{42} = U_{24} - V_2q(N_2),$$
$$A_{23} = U_{23} - V_3q(H_2), \qquad A_{43} = U_{34} - V_3q(N_2),$$
$$A_{24} = U_{24} - V_4q(H_2), \qquad A_{44} = U_{44} - V_4q(N_2),$$

with

$$U_{11} = x(CO) + x(CO_2) + x(CH_4), \quad U_{12} = -x(CO_2) + 3x(CH_4),$$
$$U_{13} = x(CO_2) - x(CH_4), \; U_{14} = 0,$$
$$U_{22} = x(H_2) + x(CO_2) + 4x(O_2) + x(O) + x(OH)/4 + x(H)/4 + x(NO) + 9x(CH_4) + 9x(NH_3)/4,$$
$$U_{23} = x(CO_2) - 4x(O_2) - x(O) - x(OH)/2 - x(NO) - 3x(CH_4),$$
$$U_{24} = -x(NO)/2 - 3x(NH_3)/4,$$
$$U_{33} = x(H_2O) + x(CO_2) + 4x(O_2) + x(O) + x(OH) + x(NO) + x(CH_4),$$
$$U_{34} = x(NO)/2, \; U_{44} = x(N_2) + x(NO)/4 + x(N)/4 + x(NH_3)/4,$$

and

$$
\begin{aligned}
V_1 &= 2x(CH_4),\\
V_2 &= 2x(O_2) + x(O) + x(OH)/4 + x(H)/4 + x(NO)/2 + 6x(CH_4) + 3x(NH_3)/2,\\
V_3 &= -2x(O_2) - x(O) - x(OH)/2 - x(NO)/2 - 2x(CH_4),\\
V_4 &= -x(NO)/4 - x(N)/4 + x(NH_3)/4.
\end{aligned}
$$

If the oxidant is air, so that $q(A) \neq 0$, the value of the mole fraction of argon in the equilibrium mixture, can be calculated from

$$x(A) = G\,q(A). \tag{5.30}$$

The total number of moles n contained in M_o grams of mixture is equal to G^{-1}, where

$$M_o = 28.010\ q(CO) + 2.016\ q(H_2) + 18.016\ q(H_2O) + 28.016\ q(N_2) + 39.944\ q(A),$$

and where the quantity G is defined by equation (5.28).

The rate of convergence of this method of computation can be increased substantially if the mole fractions of dependent constituents are calculated from an approximate set of values of the variables, y_1, y_2, y_3, and $x(N_2)$, where

$$
\begin{aligned}
y_1 &= x(CO) + x(CO_2),\\
y_2 &= x(H_2) - x(CO_2),\\
y_3 &= x(H_2O) + x(CO_2).
\end{aligned} \tag{5.31}
$$

We may determine a value of $x(CO_2)$, consistent with given values of y_1, y_2, and y_3 and with the first of equations (5.26), by means of

$$
\begin{aligned}
x(CO_2) &= -b + \sqrt{b^2 + c} \quad \text{for } k(CO_2) < 1,\\
x(CO_2) &= -b - \sqrt{b^2 + c} \quad \text{for } k(CO_2) > 1,
\end{aligned} \tag{5.32}
$$

where

$$b = \frac{y_2 + (y_1 + y_3)\,k(CO_2)}{2\cdot[1 - k(CO_2)]},$$

$$c = \frac{y_1 y_3 k(CO_2)}{1 - k(CO_2)}.$$

where $k(CO_2) = 1$, the solution is

$$x(CO_2) = \frac{y_1 y_3}{y_1 + y_2 + y_3}. \tag{5.33}$$

The values of $x(CO)$, $x(H_2)$, and $x(H_2O)$ can then be determined for given y_1, y_2, and y_3 by equations (5.31), and they may be employed with equations (5.26) to complete the determination of the equilibrium composition for assumed values of y_1, y_2, and y_3. If this determination does not satisfy the criteria for convergence, the next approximation can be obtained by means of

$$\begin{aligned} y'_1 &= y_1\,[1 + h(CO)] + x(CO_2)\,[-h(H_2) + h(H_2O)], \\ y'_2 &= y_2\,[1 + h(H_2)] + x(CO_2)\,[-h(CO) + 2h(H_2) - h(H_2O)], \\ y'_3 &= y_3\,[1 + h(H_2O)] + x(CO_2)\,[h(CO) - h(H_2)], \\ x'(N_2) &= x(N_2)\,[1 + h(N_2)], \end{aligned} \tag{5.34}$$

where $h(CO)$, $h(H_2)$, $h(H_2O)$, $h(N_2)$ are the solutions of equations (5.29) and where y'_1, y'_2, y'_3, $x'(N_2)$ are the new approximations to y_1, y_2, y_3, and $x(N_2)$, respectively.

A Special Method for Rich Mixtures without Solid Carbon

The special method of computation can profitably be employed in calculations for conditions such that the convergence of the general method is inconveniently slow. This will be the case for mixtures near the stoichiometric point $C = 1/2$ and for mixtures at temperatures such that dissociation of the components into atomic species is important. Although the special method converges more rapidly than the general method, each iteration of the special method involves a considerably longer and less systematic computational routine than is required by the general method.

At temperatures sufficiently high so that methane and ammonia can be assumed to be absent from the equilibrium mixture, we take the variable μ, defined by equation (4.17), to be

$$\mu = n(H_2O)/n(H_2), \tag{5.35}$$

and employ equation (5.35) to eliminate $n(H_2O)$ from the set of equations describing the equilibrium conditions. The stoichiometric conditions, equations (4.1), can be written in the form,

$$\begin{aligned} &n(CO) + n(CO_2) = q(CO), \\ &n(H_2)\,[1 + \mu] + n(OH)/2 + n(H)/2 = q'(H_2) = q(H_2) + q(H_2O), \\ &n(N_2) + n(NO)/2 + n(N)/2 = q(N_2), \end{aligned} \tag{5.36}$$

where the second equation is a linear combination of the stoichiometric conditions on the components H_2 and H_2O. The mass action expressions, equations (4.19), can be written explicitly

$$\begin{aligned} n(CO_2) &= k'(CO_2)\,x\,\mu, & n(O_2) &= k'(O_2)\,\mu^2, \\ n(OH) &= k'(OH)\,y\,\mu, & n(O) &= k'(O)\,\mu, \\ n(H) &= k'(H)\,y, & n(NO) &= k'(NO)\,z\,\mu, \\ & & n(N) &= k'(N)\,z, \end{aligned} \tag{5.37}$$

where

$$\begin{aligned} k'(CO_2) &= k(CO_2), & k'(O_2) &= nk(O_2), \\ k'(OH) &= n^{1/2}k(OH), & k'(O) &= nk(O), \\ k'(H) &= n^{1/2}k(H), & k'(NO) &= n^{1/2}k(NO), \\ & & k'(N) &= n^{1/2}k(N), \end{aligned} \tag{5.38}$$

and where we have employed the abbreviations

$$x = n(CO),\ y^2 = n(H_2),\ z^2 = n(N_2). \tag{5.39}$$

Substituting equations (5.37) into equations (5.36), we obtain

$$\begin{aligned} &x\ [1 + k'(CO_2)\mu]\ -q(CO) = 0, \\ &y^2(1+\mu) + y\ [k'(OH)\mu + k'(H)]/2 - q'(H_2) = 0, \\ &z^2 + z\ [k'(NO)\ \mu + k'(N)]/2 - q(N_2) = 0, \end{aligned}$$

with the solutions

$$\begin{aligned} x &= \frac{q(CO)}{1 + k'(CO_2)\mu}, \\ y &= \frac{k'(OH)\mu + k'(H)}{4(1+\mu)} + \sqrt{\left[\frac{k'(OH)\mu + k'(H)}{4(1+\mu)}\right]^2 + \frac{q'(H_2)}{1+\mu}}, \\ z &= -\frac{k'(NO)\mu + k'(N)}{4} + \sqrt{\left[\frac{k'(NO)\mu + k'(N)}{4}\right]^2 + q(N_2)}. \end{aligned} \tag{5.40}$$

Equations (5.40), together with equations (5.35), (5.37), and (5.39), determine the equilibrium composition for assumed values of n and μ.

The values of n and μ leading to an exact calculation of the equilibrium composition satisfy the conditions,

$$F(\mu) = 0, \quad F(n) = 0,$$

where the functions are defined by equations (4.22) and have the explicit form,

$$\begin{aligned} F(\mu) &= q(H_2O) - n(H_2O) - n(CO_2) - 2n(O_2) - n(O) - n(OH) - n(NO), \\ F(n) &= n - 1 - n(O_2) - n(O) - n(OH)/2 - n(H)/2 - n(NO)/2 - n(N)/2. \end{aligned} \tag{5.41}$$

If F and G do not vanish, the application of the Newton-Raphson method to obtain an improved pair of values of n and μ requires the solution of equations (4.23),

$$\begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} \begin{pmatrix} h(\mu) \\ h(n) \end{pmatrix} = \begin{pmatrix} F(\mu) \\ F(n) \end{pmatrix} , \tag{5.42}$$

where h(μ) and h(n) are estimates of the fractional error of the approximation to μ and n, respectively, to be employed as indicated by equations (4.24) in obtaining the next approximation, and where the coefficients, defined by equations (4.25), are given by

$$\begin{aligned}
A_{11} &= n(H_2O) + n(CO_2) + 4n(O_2) + n(O) + n(OH) + n(NO) \\
&\quad + U\,n(CO_2) + V\,[2n(H_2O) + n(OH)] + W\,n(NO), \\
A_{12} &= 2n\,(O_2) + n(O) + n(OH)/2 + n(NO)/2 \\
&\quad + X\,n(CO_2) + Y\,[2n(H_2O) + n(OH)] + Z\,n(NO), \\
A_{21} &= 2n(O_2) + n(O) + n(OH)/2 + n(NO)/2 \\
&\quad + V\,[n(OH)/2 + n(H)/2] + W\,[n(NO)/2 + n(N)/2], \\
A_{22} &= -n + n(O_2) + n(O) + n(OH)/4 + n(H) + n(NO)/4 + n(N)/4 \\
&\quad + Y\,[n(OH)/2 + n(H)/2] + W\,[n(NO)/2 + n(N)/2],
\end{aligned}$$

where

$$U = -\frac{n(CO_2)}{q(CO)}, \qquad X = O,$$

$$V = -\frac{n(H_2O) - n(OH)/2}{q'(H_2) + n(H_2) + n(H_2O)}, \qquad Y = -\frac{n(OH)/4 + n(H)/4}{q'(H_2) + n(H_2) + n(H_2O)},$$

$$W = -\frac{n(NO)/2}{q(N_2) \quad n(N_2)}, \qquad Z = -\frac{n(NO)/4 + n(H)/4}{q(N_2) + n(N_2)}.$$

If the oxidant is air, the concentration of argon is given by

$$n(A) = q(A). \tag{5.43}$$

The equilibrium composition is expressed in terms of mole fractions by dividing the number of moles of each constituent by the total number of moles n of the mixture. The mass of the mixture, in grams, containing a total number of gram moles n is M_o, where

$$M_o = 28.010\ q(CO) + 2.016\ q(H_2) + 18.016\ q(H_2O) + 28.016\ q(N_2) + 39.944\ q(A).$$

It should be noted that this computation program remains determinate for the case where the system contains no hydrogen ($B = O$), since μ remains finite as $n(H_2)$ and $n(H_2O)$ tend to zero.

A Special Method for Homogeneous Mixtures at High Temperatures

At high temperatures (ca. 4,000° K.), a considerable amount of dissociation results in the formation of atomic species at the expense of the substances employed as components for the previously described computational methods for both lean and rich mixtures. Under these circumstances, these methods are inconveniently slow in converging, and it is useful to employ a special computation program for these temperatures. The predominant constituents of the combustion products satisfying the conditions of independence required for their choice as components are

$$CO, \; H, \; O, \; N_2.$$

If the oxidant is air, a fifth component, argon, must be considered. At these temperatures, ammonia and methane need not be considered as possible constituents of the equilibrium mixture.

The solution of equations (3.13) and (3.14) for this choice of components results in the equations

$$\begin{aligned}
q(CO) &= \frac{2(C/O)}{2 + 2(H/O) + (N/O) + 2(A/O)}, \\
q(H) &= \frac{2(H/O)}{2 + 2(H/O) + (N/O) + 2(A/O)}, \\
q(O) &= \frac{2 - 2(C/O)}{2 + 2(H/O) + (N/O) + 2(A/O)}, \\
q(N_2) &= \frac{(N/O)}{2 + 2(H/O) + (N/O) + 2(A/O)}, \\
q(A) &= \frac{2(A/O)}{2 + 2(H/O) + (N/O) + 2(A/O)},
\end{aligned} \qquad (5.44)$$

relating the normalized stoichiometric constants to the atomic ratios. These relations can be employed, together with equations (3.6) or (3.7), to evaluate the stoichiometric constants for assigned values of the parameters descriptive of the gross composition of the system. If the oxidant is not air, $(A/O) = O$, $q(A) = O$, and we obtain by substitution of equations (3.5)

$$\begin{aligned}
q(CO) &= \frac{(1-A)(1-B)(1-C)}{2C(1-A) + 2(1-C)(A + 2B - 2AB)}, \\
q(H) &= \frac{2B(1-A(1-C)}{C(1-A) + (1-C)(A + 2B - 2AB)}, \\
q(O) &= \frac{(1-A)(B + 3C - BC - 1)}{2C(1-A) + 2(1-C)(A + 2B - 2AB)}, \\
q(N_2) &= \frac{A(1-C)}{C(1-A) + (1-C)(A + 2B - 2AB)}.
\end{aligned} \qquad (5.45)$$

The stoichiometric constants for this program can be computed from those for the program for rich mixtures without solid carbon at lower temperatures by means of the relations

$$
\begin{aligned}
q(CO) &= q(CO)^{(r)} / [q(CO)^{(r)} + 2q(H_2)^{(r)} + 3q(H_2O)^{(r)} + q(N_2)^{(r)}], \\
q(H) &= [2q(H_2)^{(r)} + 2q(H_2O)^{(r)}] / [q(CO)^{(r)} + 2q(H_2)^{(r)} + 3q(H_2O)^{(r)} + q(N_2)^{(r)}], \\
q(O) &= q(H_2O)^{(r)} / [q(CO)^{(r)} + 2q(H_2)^{(r)} + 3q(H_2O)^{(r)} + q(N_2)^{(r)}], \\
q(N_2) &= q(N_2)^{(r)} / [q(CO)^{(r)} + 2q(H_2)^{(r)} + 3q(H_2O)^{(r)} + q(N_2)^{(r)}],
\end{aligned}
\tag{5.46}
$$

where the superscript r is employed to designate the previously defined constants for homogeneous, rich mixtures at lower temperatures. Similarly, in terms of the constants for lean mixtures at lower temperatures,

$$
\begin{aligned}
q(CO) &= q(CO_2)^{(\ell)} / [2q(CO_2)^{(\ell)} + 3q(H_2O)^{(\ell)} + 2q(O_2)^{(\ell)} + q(N_2)^{(\ell)}], \\
q(H) &= 2q(H_2O)^{(\ell)} / [2q(CO_2)^{(\ell)} + 3q(H_2O)^{(\ell)} + 2q(O_2)^{(\ell)} + q(N_2)^{(\ell)}], \\
q(O) &= [q(CO_2)^{(\ell)} + q(H_2O)^{(\ell)} + 2q(O_2)^{(\ell)}] / [2q(CO_2)^{(\ell)} + 3q(H_2O)^{(\ell)} + 2q(O_2)^{(\ell)} \\
&\quad + q(N_2)^{(\ell)}], \\
q(N_2) &= q(N_2)^{(\ell)} / [2q(CO_2)^{(\ell)} + 3q(H_2O)^{(\ell)} + 2q(O_2)^{(\ell)} + q(N_2)^{(\ell)}],
\end{aligned}
\tag{5.47}
$$

where the superscript ℓ is employed to designate the previously defined constants for lean mixtures at lower temperatures.

$$
\begin{aligned}
&CO + O = CO_2, \\
&2H = H_2, \\
&2H + O = H_2O, \\
&2O = O_2, \\
&O + H = OH, \\
&(1/2)N_2 + O = NO, \\
&(1/2)N_2 = N.
\end{aligned}
$$

The coefficients ν_{ij} of these equations can be summarized in matrix form,

$$
(\nu_{ij}) = \begin{array}{c|ccccc}
 & CO & H & O & N_2 & A \\
\hline
CO_2 & 1 & 0 & 1 & 0 & 0 \\
H_2 & 0 & 2 & 0 & 0 & 0 \\
H_2O & 0 & 2 & 1 & 0 & 0 \\
O_2 & 0 & 0 & 2 & 0 & 0 \\
OH & 0 & 1 & 1 & 0 & 0 \\
NO & 0 & 0 & 1 & 1/2 & 0 \\
N & 0 & 0 & 0 & 1/2 & 0
\end{array}
\qquad (5.48)
$$

The constants k_i of the mass action expressions, equations (4.9), are given for stated values of the temperature and pressure by

$$
\begin{array}{ll}
k(CO_2) = pK(CO_2), & k(OH) = pK(OH), \\
k(H_2) = pK(H_2), & k(NO) = p^{1/2}K(NO), \\
k(H_2O) = p^2K(H_2O), & k(N) = p^{-1/2}K(N), \\
k(O_2) = pK(O_2), &
\end{array}
\qquad (5.49)
$$

where the thermodynamic equilibrium constants can be calculated from the equilibrium constants of formation by means of the relations

$$
\begin{array}{ll}
K(CO_2) = Kf(CO_2)/Kf(CO)Kf(O), & K(OH) = Kf(OH)/Kf(H)Kf(O), \\
K(H_2) = 1/[Kf(H)]^2, & K(NO) = Kf(NO)/Kf(O), \\
K(H_2O) = Kf(H_2O)/[Kf(H)]^2 Kf(O), & K(N) = Kf(N), \\
K(O_2) = 1/[Kf(O)]^2. &
\end{array}
\qquad (5.50)
$$

In writing equations (5.50) we have taken account of the fact that the equilibrium constant of formation of an element is unity.

The mass action expressions, equations (4.19) can be written in the form

$$
\begin{array}{ll}
n(CO_2) = k'(CO_2)\, x\mu, & n(OH) = k'(OH)\, y\mu, \\
n(H_2) = k'(H_2)\, y^2, & n(NO) = k'(NO)\, z\mu, \\
n(H_2O) = k'(H_2O)\, y^2\mu, & n(N) = k'(N)\, z, \\
n(O_2) = k'(O_2)\, \mu^2, &
\end{array}
\qquad (5.51)
$$

where we have introduced the variable

$$\mu = n(O), \qquad (5.52)$$

and the abbreviations

$$x = n(CO),\ y = n(H),\ z^2 = n(N_2), \qquad (5.53)$$

and where

$$
\begin{aligned}
k'(CO_2) &= n^{-1}k(CO_2), & k'(OH) &= n^{-1}k(OH),\\
k'(H_2) &= n^{-1}k(H_2), & k'(NO) &= n^{-1/2}k(NO),\\
k'(H_2O) &= n^{-2}k(H_2O), & k'(N) &= n^{-1/2}k(N),\\
k'(O_2) &= n^{-1}k(O_2). & &
\end{aligned}
\qquad (5.54)
$$

We employ the stoichiometric conditions in the form given by equations (4.1). The conditions on the components CO, H, and N_2 are

$$
\begin{aligned}
&n(CO) + n(CO_2) = q(CO),\\
&n(H) + 2n(H_2) + 2n(H_2O) + n(OH) = q(H),\\
&n(N_2) + n(NO)/2 + n(N)/2 = q(N_2).
\end{aligned}
\qquad (5.55)
$$

Substituting equations (5.57) and (5.53) into equations (5.55), there are obtained

$$
\begin{aligned}
&x\,[1 + k'(CO)\mu] - q(CO) = 0,\\
&2y^2\,[k'(H_2) + k'(H_2O)\mu] + y\,[1 + k'(OH)\mu] - q(H) = 0,\\
&z^2 + z\,[k'(NO)\mu + k'(N)]/2 - q(N_2) = 0,
\end{aligned}
$$

with the solutions

$$
\begin{aligned}
x &= \frac{q(CO)}{1 + k'(CO)\mu},\\
y &= -\frac{1 + k'(OH)\mu}{4k'(H_2) + 4k'(H_2O)\mu} + \sqrt{\left[\frac{1 + k'(OH)\mu}{4k'(H_2) + 4k'(H_2O)\mu}\right]^2 + \frac{q(H)}{2k'(H_2) + 2k'(H_2O)\mu}},\\
z &= \frac{k'(NO)\mu + k'(N)}{4} + \sqrt{\left[\frac{k'(NO)\mu + k'(N)}{4}\right]^2 + q(N_2)}.
\end{aligned}
\qquad (5.56)
$$

Equations (5.56), together with equations (5.51), (5.52), and (5.53), determine the equilibrium composition for assumed values of n and μ.

The values of n and μ leading to an exact calculation of the equilibrium composition satisfy the conditions

$$F(\mu) = 0, \quad F(n) = 0,$$

where the functions, defined by equations (4.22), are given by

$$
\begin{aligned}
F(\mu) &= q(O) - n(O) - n(CO_2) - n(H_2O) - 2n(O_2) - n(OH) - n(NO),\\
F(n) &= n - 1 + n(CO_2) + n(H_2) + 2n(H_2O) + n(O_2) + n(OH) + n(NO)/2 - n(N)/2.
\end{aligned}
\qquad (5.57)
$$

If F and G do not vanish, the application of the Newton-Raphson method to obtain an improved pair of values of n and μ requires the solution of equations (4.23),

$$\begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} \begin{pmatrix} h(u) \\ h(n) \end{pmatrix} = \begin{pmatrix} F(u) \\ F(n) \end{pmatrix}, \tag{5.58}$$

where $h(\mu)$ and $h(n)$ are estimates of the fractional error of the approximation to μ and n, respectively, to be employed as indicated by equations (4.24) in obtaining the next approximation, and where the coefficients, defined by equations (4.25), are given by

$$\begin{aligned} A_{11} &= n(O) + n(CO_2) + n(H_2O) + 4n(O_2) + n(OH) + n(NO) \\ &\quad + Un(CO_2) + V[2n(H_2O) + n(OH)] + Wn(NO), \\ A_{12} &= -n(CO_2) - 2n(H_2O) - 2n(O_2) - n(OH) - n(NO)/2 \\ &\quad + Xn(CO_2) + Y[2n(H_2O) + n(OH)] + Zn(NO), \\ A_{21} &= -n(CO_2) - 2n(H_2O) - 2n(O_2) - n(OH) - n(NO)/2 \\ &\quad + U[-n(CO_2)] + V[-2n(H_2) - 4n(H_2O) - n(OH)] + W[-n(NO)/2 + n(N)/2], \\ A_{22} &= -n + n(CO_2) + n(H_2) + 4n(H_2O) + n(O_2) + n(OH) + n(NO)/4 + n(N)/4 \\ &\quad + X[-n(CO_2)] + Y[-2n(H_2) - 4n(H_2O) - n(OH)] + Z[-n(NO)/2 + n(N)/2], \end{aligned}$$

where

$$U = -\frac{n(CO_2)}{q(CO)}, \qquad X = \frac{n(CO_2)}{q(CO)},$$

$$V = -\frac{2n(H_2O) + n(OH)}{q(H) + 2n(H_2) + 2n(H_2O)}, \qquad Y = \frac{n(H_2) + 2n(H_2O) + n(OH)}{q(H) + 2n(H_2) + 2n(H_2O)},$$

$$W = -\frac{n(NO)/2}{q(N_2) + n(N_2)}, \qquad Z = \frac{n(NO)/2 - n(N)/2}{q(N_2) + n(N_2)}.$$

If the oxidant is air, the concentration of argon is given by

$$n(A) = q(A). \tag{5.59}$$

The mass of the mixture containing a total of n moles is M_o, where

$$M_o = 28.010\, q(CO) + 1.008\, q(H) + 16.000\, q(O) + 28.016\, q(N_2) + 39.944\, q(A).$$

The General Method for Rich Mixtures with Solid Carbon

Rich fuel-oxidant mixtures that are characterized by $C<C_1$, where C is the composition parameter defined by equation (3.2) and C_1 is the critical value of C defining the solid carbon boundary surface, equation (3.31), consist of a gas phase in equilibrium with solid carbon. The predominant constituents of the combustion products satisfying the conditions of independence required for their choice as components are

$$C_{(s)},\ CO,\ H_2,\ N_2.$$

Because the system is heterogeneous, it possesses only two degrees of freedom for the specification of composition, and the computation program is based upon the gaseous components only. If the oxidant is air, a fifth component, argon, must be considered.

The solution of equations (3.13) and (3.14) for this choice of components results in the equations

$$\begin{aligned} q(CO) &= \frac{2}{2+(H/O)+(N/O)+2(A/O)}, \\ q(H_2) &= \frac{(H/O)}{2+(H/O)+(N/O)+2(A/O)}, \\ q(N_2) &= \frac{(N/O)}{2+(H/O)+(N/O)+2(A/O)}, \\ q(A) &= \frac{2(A/O)}{2+(H/O)+(N/O)+2(A/O)}, \end{aligned} \qquad (5.60)$$

relating the normalized stoichiometric constants to the atomic ratios. These relations are independent of the amount of carbon available, which is assumed to be in excess. They can be employed, together with equations (3.6) or (3.7) to evaluate the stoichiometric constants for assigned values of the parameters descriptive of the gross composition of the system. If the oxidant is not air, $(A/O) = 0$, $q(A) = 0$, and we obtain by substitution of equations (3.5) the relations

$$\begin{aligned} q(CO) &= E(1-D), \\ q(H_2) &= (1-D)(1-E), \\ q(N_2) &= D \end{aligned} \qquad (5.61)$$

for a system described by the parameters D and E.

We shall determine, in addition to the equilibrium composition of the gas phase, the location of the solid carbon boundary surface in the form $B_1 = B_1(D, E, p, T)$.

The chemical reactions in the form of equations (3.11) for the formation of the dependent constituents from the components are

$$2CO - C_{(s)} = CO_2,$$

$$CO + H_2 - C_{(s)} = H_2O,$$

$$2CO - 2C_{(s)} = O,$$

$$CO - C_{(s)} = O,$$

$$CO + \frac{1}{2} H_2 - C_{(s)} = OH,$$

$$\frac{1}{2} H_2 = H,$$

$$CO + \frac{1}{2} N_2 - C_{(s)} = NO,$$

$$\frac{1}{2} N_2 = N,$$

$$C_{(s)} + 2H_2 = CH_4,$$

$$\frac{3}{2} H_2 + \frac{1}{2} N_2 = NH_3,$$

in which the symbols of all of the components are written on the left-hand side of the equations. The coefficients ν_{ij} of these equations can be summarized in matrix form,

$$
(\nu_{ij}) = \begin{array}{l|ccccc}
 & C_{(s)} & CO & H_2 & N_2 & A \\
\hline
CO_2 & (-1) & 2 & 0 & 0 & 0 \\
H_2O & (-1) & 1 & 1 & 0 & 0 \\
O_2 & (-2) & 2 & 0 & 0 & 0 \\
O & (-1) & 1 & 0 & 0 & 0 \\
OH & (-1) & 1 & 1/2 & 0 & 0 \\
H & 0 & 0 & 1/2 & 0 & 0 \\
NO & (-1) & 1 & 0 & 1/2 & 0 \\
N & 0 & 0 & 0 & 1/2 & 0 \\
CH_4 & (1) & 0 & 2 & 0 & 0 \\
NH_3 & 0 & 0 & 3/2 & 1/2 & 0
\end{array}
\qquad (5.62)
$$

where the entries in the column for solid carbon are enclosed in parentheses to indicate that these elements are not to be taken into account in summations over the gaseous components. The constants k_i of the mass action expressions, equations (4.9), are given for stated values of the temperature and pressure by

$$
\begin{aligned}
k(CO_2) &= pK(CO_2), & k(H) &= p^{-1/2}K(H),\\
k(H_2O) &= pK(H_2O), & k(NO) &= p^{1/2}K(NO),\\
k(O_2) &= pK(O_2), & k(N) &= p^{-1/2}X(N),\\
k(O) &= K(O), & k(CH_4) &= pK(CH_4),\\
k(OH) &= p^{1/2}K(OH), & k(NH_3) &= pK(NH_3),
\end{aligned}
\tag{5.63}
$$

where the thermodynamic equilibrium constants can be calculated from the equilibrium constants of formation by means of the relations

$$
\begin{aligned}
K(CO_2) &= Kf(CO_2)Kf(C)/[Kf(CO)]^2, & K(H) &= Kf(H),\\
K(H_2O) &= Kf(H_2O)Kf(C)/Kf(CO), & K(NO) &= Kf(NO)Kf(C)/Kf(CO),\\
K(O_2) &= [Kf(C)]^2/[Kf(CO)]^2, & K(N) &= Kf(N),\\
K(O) &= Kf(O)Kf(C)/Kf(CO), & K(CH_4) &= Kf(CH_4)/Kf(C),\\
K(OH) &= Kf(OH)Kf(C)/Kf(CO), & K(NH_3) &= Kf(NH_3).
\end{aligned}
\tag{5.64}
$$

In writing equations (5.64), we have taken account of the fact that the equilibrium constant of formation of a gaseous element is unity. If solid carbon is assumed to be in the form of graphite, then $Kf(C) = 1$. However, if the solid carbon is assumed to exist in an activated form, the equilibrium constant of formation of the activated form can be used explicitly in equations (5.66).

The mole fractions of the dependent constituents are determined by equations (4.9) in the form

$$
\begin{aligned}
x(CO_2) &= k(CO)\,[x(CO)]^2,\\
x(H_2O) &= k(H_2O)\,x(CO)\,x(H_2),\\
x(O_2) &= k(O_2)\,[x(CO)]^2,\\
x(O) &= k(O)\,x(CO),\\
x(OH) &= k(OH)\,x(CO)\,[x(H_2)]^{1/2},\\
x(H) &= k(H)\,[x(H_2)]^{1/2},\\
x(NO) &= k(NO)\,x(CO)\,[x(N_2)]^{1/2},\\
x(N) &= k(N)\,[x(N_2)]^{1/2},\\
x(CH_4) &= k(CH_4)\,[x(H_2)]^2,\\
x(NH_3) &= k(NH_3)\,[x(H_2)]^{3/2}\,[x(N_2)]^{1/2}
\end{aligned}
\tag{5.65}
$$

for assumed values of the mole fractions of the components. The values of the mole fractions of the gaseous components leading to an exact calculation of the equilibrium composition of the gaseous phase satisfy the conditions

$$F(CO) = 0,\ F(H_2) = 0,\ F(N_2) = 0,$$

where the functions, defined by equations (4.11) are given by

$$\begin{aligned} F(CO) &= Gq(CO) - x(CO) - 2x(CO_2) - x(H_2O) - 2x(O_2) - x(O) - x(OH) - x(NO), \\ F(H_2) &= Gq(H_2) - x(H_2) - x(H_2O) - x(OH)/2 - x(H)/2 - 2x(CH_4) - 3x(NH_3)/2, \\ F(N_2) &= Gq(N_2) - x(N_2) - x(NO)/2 - x(N)/2 - x(NH_3)/2, \end{aligned} \tag{5.66}$$

and where

$$G = 1 + x(CO_2) + x(H_2O) + x(O_2) + x(OH)/2 - x(H)/2 + x(NO)/2 - x(N)/2 + x(CH_4) + x(NH_3). \tag{5.67}$$

The application of the Newton-Raphson method to the improvement of an approximate set of values of the mole fractions of the gaseous components requires the solution of equations (4.12) in the form

$$\begin{pmatrix} A_{11} & A_{12} & A_{13} \\ A_{21} & A_{22} & A_{23} \\ A_{31} & A_{32} & A_{33} \end{pmatrix} \begin{pmatrix} h(CO) \\ h(H_2) \\ h(N_2) \end{pmatrix} = \begin{pmatrix} F(CO) \\ F(H_2) \\ F(N_2) \end{pmatrix}, \tag{5.68}$$

where h(CO), $h(H_2)$, and $h(N_2)$ are estimates of the fractional errors of a particular approximation to the mole fractions of the respective gaseous components, to be employed as indicated by equations (4.13) in obtaining the next approximation, and where the coefficients, defined by equations (4.14), are given by

$$\begin{aligned} A_{11} &= U_{11} - V_1 q(CO), & A_{23} &= U_{23} - V_3 q(H_2), \\ A_{12} &= U_{12} - V_2 q(CO), & A_{31} &= U_{13} - V_1 q(N_2), \\ A_{13} &= U_{13} - V_3 q(CO), & A_{32} &= U_{23} - V_2 q(N_2), \\ A_{21} &= U_{21} - V_1 q(H_2), & A_{33} &= U_{33} - V_3 q(N_2), \\ A_{22} &= U_{22} - V_2 q(H_2), \end{aligned} \tag{5.69}$$

with

$$\begin{aligned} U_{11} &= x(CO) + 4x(CO_2) + x(H_2O) + 4x(O_2) + x(O) + x(OH) + x(NO), \\ U_{12} &= x(H_2O) + x(OH)/2, \qquad U_{13} = x(NO)/2, \\ U_{22} &= x(H_2) + x(H_2O) + x(OH)/4 + x(H)/4 + 4x(CH_4)/4 + 9x(NH_3)/4, \\ U_{23} &= 3x(NH_3)/4, \qquad U_{33} = x(N_2) + x(NO)/4 + x(N)/4 + x(NH_3)/4, \end{aligned} \tag{5.70}$$

and

$$\begin{aligned} V_1 &= 2x(CO_2) + x(H_2O) + 2x(O_2) + x(OH)/2 + x(NO)/2, \\ V_2 &= x(H_2O) + x(OH)/4 - x(H)/4 + 2x(CH_4) + 3x(NH_3)/2, \\ V_3 &= x(NO)/4 - x(N)/4 + x(NH_3)/2. \end{aligned} \tag{5.71}$$

If the oxidant is air, so that $q(A) = 0$, the value of the mole fraction of argon in the equilibrium mixture can be calculated from

$$x(A) = G\, q(A). \tag{5.72}$$

The total number of moles n contained in M_o grams of the gaseous mixture is G^{-1}, where

$$M_o = 28.010\, q(CO) + 2.016\, q(H_2) + 28.016\, q(N_2) + 39.944\, q(A)$$

and where the quantity G is defined by equation (5.67).

In order to determine the location of the solid carbon boundary surface, the number of gram atoms of carbon contained in M_o grams of gas phase in the form of compounds of carbon is calculated by

$$Q'_C = \frac{1}{G}\left[x(CO) + x(CO_2) + x(CH_4)\right]. \tag{5.73}$$

It is evident from equations (5.66) that the number of gram atoms of hydrogen in the same weight of gas phase is

$$Q_H = 2q(H_2). \tag{5.74}$$

If these relations are substituted into the definition of B given in equations (3.3), we obtain

$$B_1 = \frac{q(H_2)}{2Q'_C + q(H_2)}. \tag{5.75}$$

Now $q(H_2)$ is a function of D and E, given by equations (5.61), and Q'_C is a function of the equilibrium composition, and therefore an implicitly prescribed function of D, E, the temperature, and the pressure. It follows that equation (5.75) is a relation of the form

$$B_1 = B_1(D, E, p, T)$$

for the location of the solid carbon boundary surface.

If the amount of carbon available to the system is limited and specified by a value of the parameter $B < B_1$, the amount of solid carbon in the heterogeneous mixture at equilibrium is given by equation (3.29), which can be written in the form

$$n(C_{(s)}) = (1-D)(1-E)(B_1-B)/B_1B, \tag{5.76}$$

where $n(C_{(s)})$ is the number of gram atoms of solid carbon in equilibrium with M_o grams of gaseous mixture.

The foregoing computation method has been based essentially upon a specification of the amounts of hydrogen, oxygen, and nitrogen available to a system with an excess of carbon. This method affords the most convenient basis for treating systems that are known in advance to be heterogeneous. However, it is not convenient in determining the range of applicability of a computation method for rich homogeneous mixtures described by the parameters A, B, and C. For the latter purpose, a representation of the solid carbon boundary surface in the form

$$C_1 = C_1 (A, B, p, T)$$

is desired, requiring a computation method based upon a specification of the amounts of carbon, hydrogen, and nitrogen available to the system. Such a description of the composition is not the natural one to employ, and the computation program for this case can not be formulated by the routine application of the general principles. However, it is possible to devise a computation method for the heterogeneous mixture whose composition is described by specification of the parameters A and B, and this method is similar, except in detail, to the one that has been described.

An alternative solution of equations (3.13) and (3.14), appropriate to the present application, can be written in the form

$$\begin{aligned} q(CO) &= \frac{2(C/O)}{2(C/O) + (H/O) + (N/O) + 2(A/O)}, \\ q(H_2) &= \frac{(H/O)}{2(C/O) + (H/O) + (N/O) + 2(A/O)}, \\ q(N_2) &= \frac{(N/O)}{2(C/O) + (H/O) + (N/O) + 2(A/O)}, \\ q(A) &= \frac{2(A/O)}{2(C/O) + (H/O) + (N/O) + 2(A/O)}, \end{aligned} \qquad (5.77)$$

in which q(CO) is determined by the relative amount of carbon available instead of by the relative amount of oxygen available, as in equations (5.60). Equations (5.77) are independent of the relative amount of oxygen available to the system. They yield

$$\begin{aligned} q(CO) &= \frac{(1-A)(1-B)}{1 + A + B - AB}, \\ q(H_2) &= \frac{2B(1-A)}{1 + A + B - AB}, \\ q(N_2) &= \frac{W\,2A}{1 + A + B - AB}, \end{aligned} \qquad (5.78)$$

for a system described by the parameters A and B.

The mole fractions of the dependent constituents are determined by equations (5.65) for assumed values of the mole fractions of the components. The mass action constants appearing in these expressions are defined by equations (5.63) and (5.64).

The values of the mole fractions of the gaseous components leading to an exact calculation of the equilibrium composition of the gaseous phase satisfy the conditions

$$F(CO) = 0, \quad F(H_2) = 0, \quad F(N_2) = 0,$$

where the functions are given by

$$\begin{aligned} F(CO) &= Gq(CO) - x(CO) - x(CO_2) - x(CH_4), \\ F(H_2) &= Gq(H_2) - x(H_2) - x(H_2O) - x(OH)/2 - x(H)/2 - 2x(CH_4) - 3x(NH_3)/2, \\ F(N_2) &= Gq(N_2) - x(N_2) - x(NO)/2 - x(N)/2 - x(NH_3)/2, \end{aligned} \tag{5.79}$$

and where

$$G = 1 - x(OH)/2 - x(H)/2 - x(NO)/2 - x(N)/2 + 2x(CH_4) + x(NH_3). \tag{5.80}$$

The first member of equations (5.79) differs from the corresponding member of equations (5.66) because the value of $q(CO)$ is determined for the former case by the relative amount of carbon available to the gaseous phase and for the latter case by the relative amount of oxygen available to this phase. As a result, the definition of G given by equation (5.80) differs from that given by equation (5.67).

The application of the Newton-Raphson method to the improvement of an approximate set of values of the mole fractions of the components requires the solution of equations (5.68), the coefficients of which are given by equations (5.69). However, in the evaluation of equations (5.69), the definitions of the quantities $U_{jj'}$ and V_j, given for the former case by equations (5.70) and (5.71), respectively, must be replaced by the relations

$$\begin{aligned} U_{11} &= x(CO) + x(CO_2) + x(CH_4), \\ U_{12} &= 2x(CH_4), \quad U_{13} = 0, \\ U_{22} &= x(H_2) + x(H_2O) + x(OH)/4 + x(H)/4 + 4x(CH_4) + 9x(NH_3)/4, \\ U_{23} &= 3x(NH_3)/4, \quad U_{33} = x(N_2) + x(NO)/4 + x(N)/4 + x(NH_3)/4 \end{aligned} \tag{5.81}$$

and

$$\begin{aligned} V_1 &= 2x(CH_4), \\ V_2 &= -x(OH)/4 - x(H)/4 + 4x(CH_4) + 3x(NH_3)/2, \\ V_3 &= -x(NO)/4 - x(N)/4 + x(NH_3)/2. \end{aligned} \tag{5.82}$$

If the oxidant is air, the value of the mole fraction of argon is given by equation (5.72), with G defined by equation (5.80). The total number of moles n contained in M_0 grams of the gaseous mixture is G^{-1}, where M_0 is again given by

$$M_0 = 28.010\ q(CO) + 2.016\ q(H_2) + 28.016\ q(N_2) + 39.944\ q(A),$$

and where the quantity G is defined by equation (5.80).

The number of gram atoms of oxygen contained in M_o grams of gas phase is given by

$$Q_O' = \frac{1}{G} \left[x(CO) + 2x(CO_2) + x(H_2O) + 2x(O_2) + x(O) + x(OH) + x(NO)\right]. \qquad (5.83)$$

The number of gram atoms of carbon and hydrogen in the same weight of gas phase are

$$Q_C = q(CO), \quad Q_H = 2q(H_2). \qquad (5.84)$$

If these quantities are substituted into the definition of C given in equations (3.2), we obtain

$$C_1 = \frac{Q_O'}{2q(CO) + q(H_2) + Q_O'}. \qquad (5.85)$$

Now $q(CO)$ and $q(H_2)$ are functions of A and B, given by equations (5.78), and Q_O' is a function of the equilibrium composition, and therefore an implicitly prescribed function of A, B, the temperature, and the pressure. It follows that equation (5.85) is a relation of the form

$$C_1 = C_1(A, B, p, T)$$

for the location of the solid carbon boundary surface.

VI. THE THERMODYNAMIC PROPERTIES OF GAS MIXTURES

The thermodynamic properties of a gas mixture of known composition are easily determined by means of well-known relations. These relations are discussed in detail in standard treatises on thermodynamics.[17] In the present section, we list without derivation the relations that are conveniently employed in the evaluation of the thermodynamic properties of combustion gases. We include in general form the relations for taking into account the effect of gas imperfection on these calculations.

The State Variables

The gross composition of the system has been quantitatively described for the purpose of the calculation of the equilibrium composition by the parameters q_j, $j = 1, 2, \ldots c$, expressing the composition of the hypothetical mixture consisting of components only. The normalization of the q_j, expressed by equation (3.14), implies that q_j is the number of gram moles of the j-th component in the hypothetical mixture of components only whose gaseous phase is of weight M_o, where

$$M_o = \sum_j{}' q_j M_j \qquad (3.15)$$

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[17] See for example, MacDougall, F. H., Thermodynamics and Chemistry: John Wiley & Sons, Inc., New York, 3d ed., 1939.

See also Beattie, J. A., Work cited in footnote 13.

and where M_j is the molecular weight of the j-th component. Explicit expressions for M_o have been given for each of the particular computation programs. The total number of moles of gas contained in a gas phase of weight M_o has been shown to be

$$n = G^{-1}, \tag{6.1}$$

where the general definition of G is

$$G = 1 + \sum_{i=c+1}^{s} (\nu_i - 1)\, x_i. \tag{4.11}$$

Explicit expressions for G have been given for each of the particular computation programs. We have also shown that

$$n = 1 + \sum_{i=c+1}^{s} (1 - \nu_i)\, n_i \tag{4.16}$$

for a computation conducted in terms of the number of moles n_k instead of the mole fractions x_k of the constituents $k = 1, 2, \ldots s$. The mean molecular weight M of the gas phase is evidently given by

$$M = M_o/n. \tag{6.2}$$

We have assumed that the gas phase is described by a law in one or the other of the alternative forms

$$p/\rho = \frac{nRT}{M_o}\, \varphi(p,T), \tag{6.3}$$

$$p/\rho = \frac{nRT}{M_o}\, \psi(\varphi\, T). \tag{6.4}$$

For an ideal gas, $\varphi = 1$ and $\psi = 1$. The first expression determines the density as a function of pressure, temperature, and composition. The second expression determines the pressure as a function of density, temperature, and composition. The molar volume v and the density are related by

$$v = M/\rho = M_o/n\,\rho. \tag{6.5}$$

The Thermodynamic Properties of Ideal Gas Mixtures

The enthalpy and energy of a system are undefined to the extent of an arbitrary additive constant. This fact is of no consequence in practical applications, as one always wishes to know the difference of enthalpy (or energy) between two different states, and this difference is unambiguously defined. The enthalpy or energy of an equilibrium mixture of combustion gases must therefore be evaluated relative to some convenient state taken as standard. Evidently, in calculating the difference of enthalpy or energy between two states, the functions for each state must be evaluated relative to the same standard state.

As standard state for the equilibrium mixture of combustion gases, we shall usually employ the stoichiometrically equivalent mixture of elements, each element being in its customary standard state. The standard state of carbon is taken to be solid graphite at 0° K., and that for hydrogen, oxygen, or nitrogen to be hypothetical ideal gas at 0° K.

We define the relative molar enthalpy H of a gas mixture as the difference between the enthalpy of 1 mole of the mixture and the enthalpy of the stoichiometrically equivalent mixture of elements in their standard states. For an ideal gas mixture, we write

$$H^* (p,T) = \sum_{k=1}^{s} x_k (H^o - E_o^o)_k + \sum_{k=1}^{s} x_k (\Delta_f E_o^o)_k, \tag{6.6}$$

where the asterisk is employed to specify that the quantity is evaluated for an ideal gas mixture. In this expression, $(H^o - E_o^o)_k$ is the change in enthalpy when 1 mole of the k-th constituent is taken from its standard state to a state of temperature T and sufficiently low pressure such that the ideal gas law and the Gibbs-Dalton law are applicable, and $(\Delta_f E_o^o)_k$ is the change of energy (equal to the enthalpy at 0° K.) accompanying the formation of 1 mole of the k-th constituent in its standard state from the elements in their standard states. The quantity $(H^o - E_o^o)_k$ is a function of the temperature only that can be calculated by statistical methods from the spectroscopically observed energy levels of the k-th constituent. $(\Delta_f E_o^o)_k$ is a constant for given k that can be deduced from appropriate colorimetric experiments. The relative molar enthalpy H* of the gas mixture is a function of both temperature and pressure, as the mole fractions x_k are functions of both temperature and pressure.

For an ideal gas mixture, the relative molar energy E of the mixture is given by

$$E^* (p,T) = \sum_{k=1}^{s} x_k (E^o - E_o^o)_k + \sum_{k=1}^{s} x_k (\Delta_f E_o^o)_k, \tag{6.7}$$

where $(E^o - E_o^o)_k$ is the change in energy when 1 mole of the k-th constituent is taken from its standard state to a state of temperature T and sufficiently low pressure so that the ideal gas laws are applicable. For ideal gas mixtures, we also have the well-known relation

$$H^* = E^* + pv = E^* + RT, \tag{6.8}$$

where v is the molar volume and R is the gas constant.

The molar heat capacity at constant pressure Cp* and the molar heat capacity at constant volume Cv* can be computed by the relations

$$\begin{aligned} Cp^* &= \sum_{k=1}^{s} x_k \, Cp_k^o, \\ Cv^* &= \sum_{k=1}^{s} x_k \, Cv_k^o, \end{aligned} \tag{6.9}$$

where Cp_k^o and Cv_k^o are the heat capacities at constant pressure and at constant volume, respectively, of the k-th constituent at temperature T and pressure sufficiently low so that the ideal gas laws are applicable. For an ideal gas mixture, we also have the well-known relation

$$Cp^* = Cv^* + R. \tag{6.10}$$

The adiabatic exponent γ^* can be calculated from the relations

$$\gamma^* = \frac{Cp^*}{Cv^*} = 1 + \frac{R}{Cv^*} = \frac{Cp^*}{Cp^* - R}. \tag{6.11}$$

Cp_k^o and Cv_k^o are functions of temperature only that can be calculated by statistical methods from the spectroscopically observed energy levels of the k-th constituent.

The molar entropy of an ideal gas mixture is given by

$$S^* (p,T) = \sum_{k=1}^{s} x_k \, S_k^o - R \sum_{k=1}^{s} x_k \log x_k - R \log p, \tag{6.12}$$

where S_k^o is the entropy of the k-th constituent in the hypothetical ideal gas at unit pressure and temperature T and can be calculated by statistical methods from the spectroscopically determined energy levels of the k-th constituent.

In the consideration of combustion processes, it is frequently desirable to refer the extensive thermodynamic properties to a fixed weight of the system. The specific enthalpy h* is the enthalpy per unit weight and is given by

$$h^* (p,T) = \frac{1}{M} H^* (p,T) = \frac{n}{M_o} H^* (p,T), \tag{6.13}$$

the specific energy e* by

$$e^* (p,T) = \frac{1}{M} E^* (p,T) = \frac{n}{M_o} E^* (p,T), \tag{6.14}$$

and the specific entropy s* by

$$s^* (p,T) = \frac{1}{M} S^* (p,T) = \frac{n}{M_o} S^* (p,T). \tag{6.15}$$

The thermodynamic properties of the gas mixture, assumed to be ideal, may be considered to be functions of the temperature and density. The dependence of the properties considered on the pressure (or density) is explicit only in the case of the entropy. In the case of all of the other properties, the dependence on pressure (or density) is implicit, arising from the dependence of the equilibrium compositions on the pressure (or density). The relations given can be employed without modification for computation of the enthalpy, energy content, and heat capacities of the equilibrium mixture at specified density and temperature. The entropy is given by the relation

$$S^* (\rho,T) = \sum_{k=1}^{s} x_k \, S_k^o - R \sum_{k=1}^{s} x_k \log x_k - R \log \frac{RT\rho}{M} \tag{6.16}$$

Beattie[18] has comprehensively discussed the thermodynamics of imperfect gas mixtures that contains a systematic derivation of the general relations required to take account of the effect of gas imperfection on the calculation of the thermodynamic properties. In the present section we assemble those relations of interest in the consideration of combustion gases.

If the equation of state is of the form

$$pv = RT\,\varphi\,(p,T), \tag{6.17}$$

where $v = M/\rho$ is the molar volume, one obtains the following relations

$$\begin{aligned} H(p,T) &= H^*(p,T) - RT^2 \int_o^P \frac{\partial\varphi}{T}\,\frac{dp}{p}, \\ S(p,T) &= S^*(p,T) - R \int_o^P [\varphi - 1 + T\,\frac{\partial\varphi}{\partial T}\,]\,\frac{dp}{p}, \\ Cp(p,T) &= C_p^*(p,T) - RT \int_o^P [T\,\frac{\partial^2\varphi}{\partial T^2} + 2\,\frac{\partial\varphi}{\partial T}\,]\,\frac{dp}{p} \end{aligned} \tag{6.18}$$

for the relative molar enthalpy H, molar entropy S, and molar heat capacity C_p of the real gas mixture at temperature T and pressure p. The quantities designated by an asterisk are evaluated as described in the preceding section. The integrals can be evaluated explicitly for particular forms of the equation of state. The relative molar energy content is evaluated from the relation

$$E(p,T) = H(p,T) - RT\,\varphi, \tag{6.19}$$

and the heat capacity at constant volume, if required, may be evaluated with the aid of the well-known relation

$$C_p - C_v = T\left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_p . \tag{6.20}$$

If the equation of state is of the form

$$\frac{p}{\rho} = \frac{RT}{M}\,\psi\,(\rho,T), \tag{6.21}$$

one obtains the following relations,

$$\begin{aligned} E(\rho,T) &= E^*\,(\rho,T) - RT^2 \int_o^\rho \frac{\partial\psi}{\partial T}\,\frac{d\rho}{\rho}, \\ S(\rho,T) &= S^*\,(\rho,T) - R \int_o^\rho [\psi - 1 + T\frac{\partial\psi}{\partial T}\,]\,\frac{d\rho}{\rho}, \\ C_v\,(\rho,T) &= C_v^*\,(\rho,T) - RT \int_o^\rho [T\,\frac{\partial^2\psi}{\partial T^2} + 2\,\frac{\partial\psi}{\partial T}\,]\,\frac{d\rho}{\rho}, \end{aligned} \tag{6.22}$$

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[18] Beattie, J. A., Work cited in footnote 13.

for the relative molar energy content E, molar entropy S, and molar heat capacity C_V at temperature T and density ρ. The quantities designated by an asterisk are evaluated as described in the preceding section. The integrals can be evaluated explicitly for particular forms of the equation of state. The relative molar entropy can be evaluated from the relation

$$H(\rho,T) = E(\rho,T) + RT\psi, \tag{6.23}$$

and the heat capacity at constant pressure, if required, can be evaluated with the aid of equation (6.20).

VII. DESCRIPTION OF A GENERALIZED TABLE OF THE EQUILIBRIUM COMPOSITION AND THERMODYNAMIC PROPERTIES OF COMBUSTION GASES

The Explosives and Physical Sciences Division of the Bureau of Mines is calculating a massive table that will list the equilibrium composition and thermodynamic properties at equilibrium, over an extended range of temperature and pressure, of gas mixtures containing compounds of carbon, hydrogen, nitrogen, and oxygen. The methods of computation described in this report have been employed in the tabulation.[19]

The table includes all possible combinations of the four elements, the spacing of calculated points being small enough to permit accurate interpolation in the table. The temperature ranges from 1,000° to 5,000° K. and the pressure from 0.1 atmosphere to pressures great enough to include those of interior ballistics. The table is the result of nearly a million individual computations.

The results of the individual computations are recorded on punched cards. Because of the size of the project, publication in tabular form of the complete table is impractical. However, the file of punched cards constitutes a reference table with all of the computational results in easily accessible form. This reference table can readily be employed in the consideration of specific problems. The results of such applications will be published in a series of reports to be issued by this laboratory.

It is anticipated that the table will have a wide range of application to the special interests of many organizations. The cooperation of interested organizations is invited so that the greatest possible utilization of the table may be achieved. The Bureau will welcome suggestions for applying the table to specific problems.

The state is uniquely determined by specification of two state variables, for which purpose we select the temperature and pressure. In the table, the temperature takes on the values

$$T(^{\circ}K.) = 1{,}000\ (100)\ 1{,}600\ (200)\ 5{,}000,$$

where the interval spacing of the argument of a table is given in parentheses, and the lower and upper limits for which the interval applies are given to the left and right, respectively, of the

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[19] A preliminary announcement of this table appeared in Chem. Eng. News, vol. 27, Sept. 5, 1949, p. 2540-2541.

number in parentheses. This statement is to be read "The temperature, in degrees Kelvin, ranges from 1,000 to 1,600 with an interval of 100 and from 1,600 to 5,000 with an interval of 200."

A closer spacing is necessary at low than at high temperatures to permit accurate interpolation with respect to temperature in the table. It has been found by means of sample calculations that interpolation with respect to the pressure is facilitated by the use of a logarithmic scale. In the table, the pressure ranges from 0.1 to 100 atmospheres in the following way:

$$\log p = -1.0\ (0.2)\ 2.0.$$

It is intended subsequently to extend the portion of the table that is of interest in considering gun propellants to pressures high enough to permit its application to the calculations of interior ballistics. In this portion of the table the temperature and density will be taken as the independent state variables.

In selecting the table arguments that define the gross composition, we have employed, for the heterogeneous region containing solid carbon, the quantities D and E given by equations (3.3). In the table, these variables take on the values

$$D = 0\ (0.1)\ 0.9$$

$$E = 0\ (0.1)\ 1.0.$$

For the homogeneous part of the table we employ the parameters A, B, and C, defined by equations (3.2). In the table, the variables A, B, and C take on the following values:

$$A = 0\ (0.1)\ 0.9$$

$$B = 0\ (0.1)\ 0.5,\ 1.0$$

$$C = 0.1\ (0.05)\ 0.9 \text{ subject to } C \geqslant C_1.$$

For each composition defined as indicated and for each temperature and pressure, the composition at thermodynamic equilibrium is calculated by the numerical methods that have been described in this report. We have assumed that the mixture at equilibrium may contain the following gaseous constituents: CO, CO_2, H_2, H_2O, N_2, O_2, OH, NO, H, N, O, NH_3, CH_4. This selection neglects a number of additional possible constituents, and it was dictated by the storage capacity of the computer. However, it is believed that the constituents of major importance have been considered. In exceptional cases, where it is desired to consider the existence of additional constituents, the present work will provide the starting basis for a more detailed calculation, which should be very simple.

The mole fraction of each constituent of the gas at equilibrium is recorded in punched-card form. In addition, for the heterogeneous mixtures the punched cards record the value of the dependent gross composition parameter, which defines the location of the carbon boundary surface.

The results of the calculation of the equilibrium composition are employed in the usual manner to calculate the density, energy content, heat content (enthalpy), and entropy of the equilibrium mixture. The table of thermodynamic properties may be considered to be a Mollier chart, in punched-card form, for each of the different mixtures of the four elements considered.

In constructing the table we employed the values of the thermodynamic properties of the individual constituents recommended by the National Bureau of Standards.[20/] For pressures below 100 atmospheres we employed the ideal gas equation of state.

Only brief reference can be made here to some of the applications anticipated for the table. The flame temperatures of a variety of fuels burning under a wide range of conditions can readily be estimated.[21/] Hottel and Eberhardt[22/] have discussed the application of Mollier diagrams to performance studies of internal combustion engines, and Sucrow[23/] summarizes their application to performance studies of jet-propulsion and gas-turbine engines. The table will be useful in predicting the operating conditions for various gas-synthesis processes that will produce a product gas of desired characteristics.

[20/] Tables of Selected Values of Chemical Thermodynamic Properties: Issued at irregular intervals by the National Bureau of Standards, Washington, D. C.

[21/] Lewis, B., and von Elbe, G., Combustion, Flames, and Explosion in Gases: Cambridge University Press, Cambridge, 1938, Chap. XIX.

[22/] Hottel, H. C., and Eberhardt, J. E., Mollier Diagrams for the Internal-Combustion Engine: Chem. Rev., vol. 21, Dec. 1937, pp. 439-460.

[23/] Sucrow, M. J., Principles of Jet Propulsion and Gas Turbines: John Wiley & Sons, Inc., New York, 1947, Chap. III.

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