GENERAL METHOD FOR COMPUTATION OF EQUILIBRIUM COMPOSITION

AND TEMPERATURE OF CHEMICAL REACTIONS

By Vearl N. Huff and Virginia E. Morrell

Lewis Flight Propulsion Laboratory
Cleveland, Ohio

Washington
June 1950
TECHNICAL NOTE 2113

GENERAL METHOD FOR COMPUTATION OF EQUILIBRIUM COMPOSITION
AND TEMPERATURE OF CHEMICAL REACTIONS

By Vearl N. Huff and Virginia E. Morrell

SUMMARY

A rapidly convergent successive approximation process is described that simultaneously determines both composition and temperature resulting from a chemical reaction. This method is suitable for use with any set of reactants over the complete range of mixture ratios as long as the products of reaction are ideal gases. An approximate treatment of limited amounts of liquids and solids is also included. This method is particularly suited to problems having a large number of products of reaction and to problems that require determination of such properties as specific heat or velocity of sound of a dissociating mixture.

The method presented is applicable to a wide variety of problems that include (1) combustion at constant pressure or volume; and (2) isentropic expansion to an assigned pressure, temperature; or Mach number.

INTRODUCTION

The theoretical performance of propulsion systems having high combustion temperatures can be calculated on the assumption that chemical equilibrium exists among the products of reaction. The equilibrium composition and the temperature for a system of \( N_p \) products of reaction are determined by the simultaneous solution of at least \( N_p+1 \) equations involving dissociation, mass balance, and energy or entropy balance. This calculation becomes increasingly difficult as \( N_p \) increases.

The usual method for solving these equations provides a successive approximation or trial-and-error process for determining the composition at an assumed temperature and pressure. Examples of these methods are found in references 1 to 4. When it is desired to find the temperature of a system in equilibrium, with a parameter
such as entropy or enthalpy assigned, the composition is usually computed at a sequence of temperatures that either converge to the correct temperature or are spaced to permit interpolation to obtain the correct temperature.

A rapidly convergent successive approximation process that determines composition at an assigned temperature or that simultaneously determines both composition and temperature for assigned values of another parameter, such as enthalpy or entropy, was developed at the NACA Lewis laboratory during 1948 and is presented herein. This process also permits computation of the partial derivatives required to compute such thermodynamic properties as specific heat and velocity of sound corresponding to chemical equilibrium. The equations are derived that are required for solution of the following cases: (1) combustion at constant pressure or volume; and (2) isentropic expansion to an assigned pressure, temperature, or Mach number. Examples are given for (1) constant-pressure adiabatic combustion; (2) isentropic expansion to an assigned pressure; and (3) isentropic expansion to an assigned Mach number.

This method is particularly suitable for problems having a large number of products of reaction and for problems that require determination of partial derivatives. Although it is possible, at least in special cases, to devise a procedure that involves less numerical computation, the method presented is applicable in a wide variety of cases and its numerical application to a given process is always simple and essentially the same for all reactions.

GENERAL METHOD

The thermodynamic state following a specific process, such as combustion at constant pressure, can be determined from an appropriate combination of the following equations: (a) dissociative equilibrium; (b) conservation of mass; (c) conservation of energy; (d) pressure; and (e) entropy. Equations (a) and (b) are used to specify chemical equilibrium and, when used with any two of the remaining equations, define a process.

The successive approximation procedure presented herein for finding the simultaneous solution of a specific combination of the aforementioned equations consists of the following steps:

(a) Estimates of composition and temperature are made and used in simple equations to compute the values of error parameters, which indicate inconsistency among the estimates of composition and
temperature. (These estimates need not be based on previous experience but for rapid convergence it is desirable that they be close to the final values.)

(b) A set of linear simultaneous correction equations are given that determine a new composition and a new temperature.

(c) The new composition is used to compute new values of the error parameters and step (b) is repeated until the desired accuracy is obtained.

In order to aid in computation, general instructions are given that permit construction of the correction equations in matrix form. The numerical values of the error parameters are obtained directly from the elements of the matrix of coefficients of the unknowns and the solution of the matrix equation provides the correction factors necessary for determination of the new composition and temperature.

Equations for Dissociation, Mass, Pressure, and Volume

The substances entering a reaction process will be designated the reactants and can be represented by the equivalent formula

\[ Z_{a_0} Y_{b_0} X_{c_0} \]

where the subscripts \( a_0, b_0, \) and \( c_0 \) are proportional to the total number of atoms of the elements \( Z, Y, \) and \( X, \) respectively, contained in a quantity of the entering substance at the initial conditions. (A complete list of symbols is included in appendix A.) For example, the reactants for a rocket combustion process using 3 moles of ammonia \((\text{NH}_3)\) for fuel and 2 moles of nitric acid \((\text{HNO}_3)\) for an oxidant are

\[ 3\text{NH}_3 + 2\text{HNO}_3 \]

and the equivalent formula would be

\[ 11 \text{H} 14 \text{N} 16 \text{O}_6 \]

where \( Z, \) \( Y, \) and \( X \) are the atoms hydrogen, nitrogen, and oxygen, respectively, and \( a_0, b_0, \) and \( c_0 \) are 11, 5, and 6, respectively.
The reaction under consideration can be written

\[ A (Z_{a_0}Y_{b_0}X_{c_0}) \rightarrow n_1(Z_{a_1}Y_{b_1}X_{c_1}) + n_2(Z_{a_2}Y_{b_2}X_{c_2}) + \cdots + n_i(Z_{a_i}Y_{b_i}X_{c_i}) \]

where \( n_i \) is the number of moles of the ith molecule or atom. The subscripts \( a_i, b_i, \) and \( c_i \), which can take on only integral values or zero, denote the number of \( Z, Y, \) and \( X \) atoms in the ith molecule. For example, if \( Z, Y, \) and \( X \) again represent hydrogen, nitrogen, and oxygen, respectively, the values of \( a_i, b_i, \) and \( c_i \) for a water molecule \( H_2O \) would be 2, 0, and 1, respectively.

Assumptions are made that the products of reaction are contained by a volume \( V \) numerically equal to the gas constant \( R \) times the absolute temperature \( T \) so that for ideal gases

\[ p_i = n_i \]

During the solution of the problem, determination of the number of formula weights of the reactants \( A \) that are required to balance the reaction given by equation (1) is necessary. Products of reaction in the gas phase are assumed to be ideal gases that form ideal mixtures and each condensed phase is assumed to have a partial pressure of zero, even when finely divided and suspended in the gas. For solids and liquids therefore

\[ p_i = 0 \]

As an approximation, the following assumptions are also made: Each condensed product is insoluble in all others, the fugacity of each condensed phase is equal to 1; the total volume occupied by the liquids and solids is negligible with respect to the volume occupied by the gases; and the liquid and solid particles have the same temperature and flow velocity as the gases.

Dissociation equations. - The equation for the dissociative equilibrium among gaseous atoms and molecules can be written as

\[ a_1Z + b_1Y + c_1X \rightleftharpoons Z_{a_1}Y_{b_1}X_{c_1} \]
and the corresponding equation for the equilibrium constant $K_i$ of gaseous molecules is

$$K_i = \frac{P_1}{P_Z \cdot P_Y \cdot P_X}$$

(3)

For liquid or solid molecules, assuming the fugacity of each condensed phase is equal to 1,

$$K_i = \frac{1}{P_Z \cdot P_Y \cdot P_X}$$

(4)

where $P_Z$, $P_Y$, and $P_X$ are the partial pressures of the $Z$, $Y$, and $X$ atoms in equation (1), respectively. The equilibrium constants can also be expressed in terms of the free-energy changes ($\Delta F^o_T$) across the dissociation reactions represented by equation (2) or

$$\log_{e} K_i = \left(\frac{-\Delta F^o_T}{RT}\right)_i$$

(5)

Because the assumed composition may not correspond to that at chemical equilibrium, variables $K_i$ are conveniently defined so that for gaseous molecules

$$\log_{e} K_i = \log_{e} P_1 - a_1 \log_{e} P_Z - b_1 \log_{e} P_Y - c_1 \log_{e} P_X - \left(\frac{-\Delta F^o_T}{RT}\right)_i$$

(6)

and for liquid or solid molecules

$$\log_{e} K_i = -a_1 \log_{e} P_Z - b_1 \log_{e} P_Y - c_1 \log_{e} P_X - \left(\frac{-\Delta F^o_T}{RT}\right)_i$$

(7)

The value of each $K_i$ must approach 1 as the solution to the problem is found. Applying equation (6) or (7) to each molecule results in $N_d$ equations, where $N_d$ denotes the number of different types of molecule considered.

For simplicity of nomenclature and presentation, the equations for dissociation are expressed in terms of the atomic gas, which
leads to a simple computational procedure when the atomic gases of most elements are present in significant quantities. If the atomic gas of an element is not to be considered as one of the products of reaction, however, a molecule containing the element may be substituted in equation (2) in place of the atomic gas. For example, carbon monoxide can be used in place of carbon gas and would then be treated as an atom.

**Mass-balance equations.** - A mass-balance equation stating the conservation of atomic type can be written for each chemical element present. Because a composition is initially assumed, it is convenient to define parameters \( a, b, c, \ldots \) as representing the summation over the products of reaction of each atomic type per equivalent formula.

\[
a = \frac{1}{A} \sum_{i} a_{i} n_{i} \quad (8)
\]

\[
b = \frac{1}{A} \sum_{i} b_{i} n_{i} \quad (9)
\]

\[
c = \frac{1}{A} \sum_{i} c_{i} n_{i} \quad (10)
\]

As the solution to the problem is found by successive adjustments of the initial assumptions, the values of \( a, b, c \) approach the values of \( a_{0}, b_{0}, c_{0} \), respectively. The mass-balance equations result in \( N_{e} \) equations, where \( N_{e} \) denotes the number of chemical elements.

**Total-pressure equation.** - The total pressure \( P \) is the sum of the partial pressures

\[
P = \sum_{i} P_{i} \quad (11)
\]

For a process with an assigned pressure, the value of \( P \) must approach the assigned value \( P_{0} \) as the solution of the problem is found.

**Constant volume.** - For processes that occur at constant volume, the density of the mixture is constant. The density \( \rho \) is defined as

\[
\rho = \frac{AM_{p}}{V} = \frac{AM_{p}}{RT} \quad (12)
\]
where $M_T$ is the molecular weight of the equivalent formula. For a reaction process with an assigned density, the value of $\rho$ must approach the assigned value $\rho_0$ as the solution of the problem is found.

**Combustion at Constant Pressure**

For given initial conditions, the temperature and the composition following a combustion process are to be found. When chemical energy is included in the enthalpy of each substance, the enthalpy of the products of reaction following an adiabatic combustion must be equal to the enthalpy of the reactants at the initial conditions. An arbitrary base may be adopted for assigning absolute values to the enthalpy of various substances because only differences are measurable. One such base (reference 4) assigned a chemical energy of zero to the oxidized form of the elements at 100° F. For calculations with the elements boron, hydrogen, fluorine, oxygen, nitrogen, and carbon, assigning a chemical energy of zero to water, oxygen, hydrogen fluoride, boron trifluoride, nitrogen, and carbon dioxide at the absolute temperature of 0° K was found to be more convenient. By using this base, the chemical energies of all other molecular types entering a combustion process containing these elements are positive, thus avoiding a possible source of difficulty that might occur in the recommended method of adjustment when a logarithm of a negative number (or zero) might be required.

**Enthalpy of fuel and oxidant.** - The enthalpy at initial conditions of the amount of fuel and oxidant corresponding to the equivalent formula $Z_{ao}Y_{bo}X_{co}$ is denoted by $h_0$ and is given by the expression

$$h_0 = n_f (H^0_T)_f + n_g (H^0_T)_g$$

(13)

where $n_f$ and $n_g$ are the number of moles of fuel and oxidant, respectively, corresponding to the equivalent formula $Z_{ao}Y_{bo}X_{co}$ and $(H^0_T)_f$ and $(H^0_T)_g$ are the molar enthalpies of the fuel and the oxidant, respectively, at the initial conditions. The molar enthalpy $H^0_T$ is defined by the equation

$$H^0_T = \int_0^T C_p \, dT + H^0_0$$
where $C_p^0$ is the molar specific heat at constant pressure, and $H_0^0$ is the chemical energy of the substance at an absolute temperature of $0^\circ$ K.

**Enthalpy of products of reaction.** - The enthalpy of the products of reaction per equivalent formula can be conveniently represented by a variable $h$ that is given by the equation

$$h = \frac{1}{A} \sum_1^A (H_T^0)_{i.n.}$$

(14)

as long as the kinetic energy is negligible. When enthalpy is assigned, the value of $h$ approaches $h_0$ as the solution of the problem is found by successive adjustments of the estimated quantities. If heat were lost, the value of $h_0$ would be accordingly reduced.

**Equations for constant-pressure combustion.** - The equations defining the constant-pressure combustion are:

<table>
<thead>
<tr>
<th>Type</th>
<th>Number of equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissociative equilibrium</td>
<td>$N_d$</td>
</tr>
<tr>
<td>Conservation of mass</td>
<td>$N_e$</td>
</tr>
<tr>
<td>Constant pressure</td>
<td>1</td>
</tr>
<tr>
<td>Conservation of energy</td>
<td>1</td>
</tr>
</tbody>
</table>

These equations are to be solved simultaneously. Values for $n_1$, $A$, and $T$ can be estimated and the values of the parameters $x_1$, $a$, $b$, $c$, ..., $P$, and $h$ can be computed from equations (6) to (11) and (14). Corrections are then required for $n_1$, $A$, and $T$.

**Correction equations.** - The adjustments to $n_1$, $A$, and $T$ are made by means of a set of $N_f + 2$ correction equations derived from equations (6) to (11) and (14) that adjust the estimates by the Newton-Raphson method for solving simultaneous equations (reference 5). This method can be illustrated by a simple example. If $Q_1$ and $Q_2$ are functions of $q$ and $r$,

$$Q_1 = f_1(q,r)$$

$$Q_2 = f_2(q,r)$$
By taking estimated values, for example $q_0$ and $r_0$, each function may be expanded in a Taylor's series about the point $(q_0, r_0)$ and when derivatives of higher order than the first are neglected

$$\Delta Q_1 = \frac{\partial Q_1}{\partial q} \Delta q + \frac{\partial Q_1}{\partial r} \Delta r$$

$$\Delta Q_2 = \frac{\partial Q_2}{\partial q} \Delta q + \frac{\partial Q_2}{\partial r} \Delta r$$

The desired changes $\Delta Q_1$ and $\Delta Q_2$ can be computed and if the partial derivatives can be numerically evaluated, solving for the approximate changes in $q$ and $r$ to effect simultaneously the desired changes in both $Q_1$ and $Q_2$ is comparatively simple because the equations are linear.

The equations for $\log_e k_1$, $a$, $b$, $c$, $\ldots$, $h$, and $P$ can similarly be expanded in a Taylor's series; for example, equation (6) for $\log_e k_1$ for gases expanded in the logarithmic form would be

$$\Delta \log_e k_1 = \Delta \log_e p_1 - a_1 \Delta \log_e p_2 - b_1 \Delta \log_e p_y - c_1 \Delta \log_e p_x - \frac{\left( \frac{\Delta H^0_T}{RT} \right)_1}{\frac{\partial}{\partial \log_e T}} \Delta \log_e T$$

(15)

The term $\left( \frac{\Delta H^0_T}{RT} \right)_1$ appears because

$$\frac{\partial}{\partial \log_e T} \left( \frac{\Delta H^0_T}{RT} \right)_1 = \left( \frac{\Delta H^0_T}{RT} \right)_1$$

where $\left( \frac{\Delta H^0_T}{RT} \right)_1$ is determined across the dissociation-reaction equation (2). Expanding equation (8) gives

$$\Delta a = \frac{1}{A} \sum a_i \Delta n_i - \sum \frac{a_i n_i}{A^2} \Delta A$$

(16)
Some of these equations are expressed in terms of $\Delta \log e p_1$ and $\Delta p_1$, whereas the others are expressed in terms of $\Delta n_1$. In order to convert to a common variable $\Delta \log e n_1$, the following substitutions can be made:

For gases, $p_1 = n_1$ therefore

$$\Delta \log e p_1 = \Delta \log e n_1 \quad \text{(17)}$$

A Taylor's expansion of the logarithm of a variable $\log e q$, by dropping terms of higher order than the first, yields

$$\Delta q = q \Delta \log e q \quad \text{(18)}$$

The expansion of equations (6) to (11) and (14) can be written in logarithmic variables with the aid of equations (17) and (18), as follows:

For gaseous products,

$$\Lambda \log n_1 - a_1 \Lambda \log n_2 - b_1 \Lambda \log n_Y - c_1 \Lambda \log n_X = \frac{(\Delta E^o_T)}{RT} \Delta \log T = - \log k_1 \quad \text{(19)}$$

For liquid or solid products,

$$-a_1 \Lambda \log n_2 - b_1 \Lambda \log n_Y - c_1 \Lambda \log n_X = \frac{(\Delta E^o_T)}{RT} \Lambda \log T = - \log k_1 \quad \text{(20)}$$

For all products of reaction,

$$\sum a_i n_i \Lambda \log n_i - Aa \Lambda \log A = Aa \log \frac{a_0}{a} \quad \text{(21a)}$$

$$\sum b_i n_i \Lambda \log n_i - Ab \Lambda \log A = Ab \log \frac{b_0}{b} \quad \text{(21b)}$$
\[ \sum_{i} c_{i} n_{i} \Delta \log n_{i} - Ac \Delta \log A = A \log \frac{\bar{\theta}}{\epsilon} \]  \hspace{1cm} (21c) \\
\[ \sum_{i} p_{i} \Delta \log n_{i} = P \log \frac{\bar{p}}{p} \]  \hspace{1cm} (22) \\
\[ \sum_{i} (c_{i}^{0} n_{i}) \Delta \log n_{i} + Ah \Delta \log A + T \sum_{i} (c_{i}^{0} n_{i}) \Delta \log T \]
\[ = Ah \log \frac{\bar{\theta}}{\bar{h}} \]  \hspace{1cm} (23)

where the desired values of the parameters \((\log_{e} k_{i} = \epsilon, a = a_{0}, \ldots)\) are substituted in the form

\[ \Delta \log_{e} k_{i} = - \log_{e} k_{i} \]  \hspace{1cm} (24) \\
\[ \Delta a = a \log_{e} \frac{a_{0}}{a} \]  \hspace{1cm} (25)

and logarithms to the base 10 are used for convenience.

**Matrix.** - The values of \(\Delta \log n_{i}, \Delta \log A,\) and \(\Delta \log T\) are then computed by means of the matrix shown in figure 1(a). These corrections are applied to the initial set of estimates of \(n_{i}, A,\) and \(T\) and the process is repeated until all the given conditions are simultaneously satisfied. This matrix, however, merely provides a convenient scheme for solving the simultaneous equations but any of the well-known methods for solving simultaneous equations may be used.

In order to permit rapid solution of the matrix, using the arrangement of rows and columns described in appendix B is desirable. With this arrangement, a single step reduces the order of the matrix by the number of gaseous molecular types.

**Combustion at Constant Volume**

The procedure given for finding the composition and the temperature of a combustion process at constant pressure can be applied to combustion at constant volume with the following changes:
(a) The correction equation for pressure is replaced by a correction equation for density obtained from equation (12)

$$\Delta \log A - \Delta \log T = \log \frac{\rho_0}{\rho}$$  \hspace{1cm} (26)

(b) The correction equation for conservation of energy must be written in terms of internal energy $E^0_T$ and thus becomes

$$\sum_i (E^0_T)_i n_i \Delta \log n_i - Ae \Delta \log A + T \sum_i (C^0_V)_i n_i \Delta \log T$$

$$= Ae \log \frac{e_0}{e}$$  \hspace{1cm} (27)

where $e_0$ is the assigned internal energy per equivalent formula at initial given conditions and $C^0_V$ is the molar specific heat at constant volume. Substitution of these two equations in the matrix of figure 1(a) will permit the composition and the temperature to be found for assigned values of density and internal energy. This application of constant-volume combustion, which, for example, is involved in reciprocating engines and pulse-jet engines, has not been made at the Lewis laboratory.

Isentropic Expansion to Assigned Pressure or Temperature

Assigned pressure. - The calculation of temperature and equilibrium composition of the products of reaction following isentropic expansion to a fixed pressure involves the simultaneous solution of dissociation, conservation of mass, pressure, and entropy-balance equations.

For the reaction of equation (1), the dissociation, conservation of mass, and pressure equations ((6) to (11)) can again be applied. For the conditions following an isentropic expansion, the entropy $s_0$ of the products of combustion per equivalent formula after expansion must be equal to the entropy $s_0$ of the products of combustion per equivalent formula before expansion.

$$s_0 = \left\{ \frac{1}{A} \sum_i \left[ n_i (E^0_T)_i - R p_i \log e_i \right] \right\}$$  \hspace{1cm} (28)
where \((S^0_T)_1\) is the absolute entropy of the product \(1\) at standard conditions. This formula is applicable for ideal solids and liquids, assuming \(p_i = 0\), as long as their volume is negligible. After the expansion takes place, the entropy per equivalent formula is given by the expression

\[
s = \left\{ \frac{1}{A} \sum_{i=1}^{n_i} (S^0_T)_1 - R_p \log p_i \right\} \text{exit conditions}
\]  

(29)

Whereas equation (28) is, of course, evaluated at combustion-chamber temperature and pressure, equation (29) is evaluated for exit temperature and pressure. As the solution of the problem is found by successive adjustment of estimated quantities, the value of \(s\) approaches \(s_0\).

In the adjustment of the values of \(n_1, A,\) and \(T\), the correction equations (19) to (22), which have been derived from equations (6) to (11), can be applied. In addition, the following correction equation for entropy can be written from equation (29):

\[
\sum s_i' \Delta \log n_1 = A \Delta \log A + \sum (c^0_p)_i n_i \Delta \log T = A \Delta \log \frac{s_0}{s} \]  

(30)

where

\[
s_i' = (S^0_T)_1 n_i - R_p (1 + \log p_i)
\]

The values of \(\Delta \log n_1, \Delta \log A,\) and \(\Delta \log T\) are then computed by means of the matrix of figure 1(b), which is identical to figure 1(a) except that equation (30) is substituted in the last row in place of equation (23).

Assigned temperature. - For the computation of data for enthalpy-entropy diagrams and for other practical computations, it is often necessary to find the exit pressure and composition as a function of exit temperature. The procedure required is the same as that described for isentropic expansion to an assigned pressure except that the pressure equation and the temperature column are dropped from the matrix of figure 1(b).
Isentropic Expansion to Local Velocity of Sound

The theoretical velocity of sound that includes the effect of dissociation can be computed at any point in a nozzle with a modification of the matrix previously derived to obtain the correction quantities.

**Velocity of sound.** - The velocity of sound \( u \) can be defined as

\[
u^2 = \left( \frac{dp}{d\rho} \right)_s\]  

(31)

where the subscript \( s \) denotes the condition of constant entropy. The total differential of pressure \( dp \) can be found from equation (11)

\[
dp = \sum \frac{dp_i}{i}
\]

(32)

and the total differential of density \( dp \) can be found from equation (12).

\[
d\rho = \frac{M_{T}}{RT} dA - \frac{A}{RT^2} dT
\]

(33)

Thus, equation (31) can be written

\[
u^2 = \left( \frac{\sum \frac{dp_i}{i}}{\frac{M_{T}}{RT} dA - \frac{A}{RT^2} dT} \right)_s
\]

and by dividing the numerator and the denominator by \( d\rho \) and changing to logarithmic variables

\[
u^2 = \left[ \frac{\sum p_i}{\frac{M_{T}}{RT} dA - \frac{A}{RT^2} dT} \right]_{\log} \left[ \frac{d \log_e p_i}{d \log_e T} \right]_s
\]

(34)

This expression will permit evaluation of \( \nu^2 \), provided the values of the derivatives \( \left( \frac{d \log_e p_i}{d \log_e T} \right)_s \) and \( \left( \frac{d \log_e A}{d \log_e T} \right)_s \) are found for...
conditions of chemical equilibrium and for an isentropic process. The conditions of chemical equilibrium and constant entropy are introduced by writing the total differentials of equations (6) to (10) and (29). The total differential of these equations expressed in logarithmic variables and divided by $d \log_e T$ can be written for gaseous products,

$$\frac{d \log p_1}{d \log T} - a_1 \frac{d \log p_2}{d \log T} - b_1 \frac{d \log p_Y}{d \log T} - c_1 \frac{d \log p_X}{d \log T} = \frac{(\Delta H^o)_1}{RT}$$

For liquid and solid products,

$$-a_i \frac{d \log p_z}{d \log T} - b_i \frac{d \log p_Y}{d \log T} - c_i \frac{d \log p_X}{d \log T} = \frac{(\Delta H^o)_1}{RT} = \frac{d \log k_1}{d \log T}$$

For all products of reaction,

$$\sum a_i n_i \frac{d \log n_i}{d \log T} = A_a \frac{d \log A}{d \log T} = A_a \frac{d \log a}{d \log T}$$

$$\sum b_i n_i \frac{d \log n_i}{d \log T} = A_b \frac{d \log A}{d \log T} = A_b \frac{d \log b}{d \log T}$$

$$\sum c_i n_i \frac{d \log n_i}{d \log T} = A_c \frac{d \log A}{d \log T} = A_c \frac{d \log c}{d \log T}$$

$$\sum s_i \frac{d \log n_i}{d \log T} = A_s \frac{d \log A}{d \log T} + \sum (C^o_P)_{i=1} n_i = A_s \frac{d \log s}{d \log T}$$

If $d \log s$ is taken as 0, $s$ is a constant; if $d \log a$, $d \log b$, $d \log c$, and $d \log k_1$ are taken as 0, mass is constant, atomic types are conserved, and rate of change in composition.
corresponds to constant values of \( \log k_1 \). With these assumptions, equations (35) to (38) constitute a set of simultaneous equations for partial derivatives. The augmented matrix formed from these equations is shown in figure 2 with the sign reversed. The matrix is identical to a portion of the matrix of figure 1(b). When

\[
\left( \frac{d \log n_i}{d \log T} \right) \quad \text{and} \quad \left( \frac{d \log A}{d \log T} \right)
\]

are determined by means of the matrix shown in figure 2, the velocity of sound can be calculated from equation (34). This equation can be applied to mixtures of liquid and solid products in equilibrium as long as their volume is negligible compared with the volume of the gas mixture and provided the liquid and solid particles move in velocity and temperature equilibrium with the gas.

**Specific heat.** - The specific heat at constant pressure of a mixture in equilibrium may be found from equation (14) as follows:

\[
C^o_p = \frac{A}{\sum_i n_i c_i^o} = \frac{1}{PT} \left[ \sum_i (E^o_i) n_i \left( \frac{d \log n_i}{d \log T} \right)_p - A_h \left( \frac{d \log A}{d \log T} \right)_p + \right]
\]

Equation (32) can be written as

\[
\sum_i p_i \frac{d \log n_i}{d \log T} = P \frac{d \log P}{d \log T}
\]

If \( d \log P \) is taken as 0, the pressure is constant; therefore, when equation (40) is substituted in the matrix of figure 2 in place of equation (38), the values of \( \left( \frac{d \log n_i}{d \log T} \right)_p \) and \( \left( \frac{d \log A}{d \log T} \right)_p \) can be found. These values can then be substituted in equation (39) to evaluate \( C^o_p \).

**Isentropic expansion to assigned Mach number.** - The kinetic energy of the gas at any point, by assuming no heat transfer, is
equal to the enthalpy change from the point of negligible kinetic
ergy to the point in question. From this relation, the velocity
squared at any point \( l \) is

\[
v^2 = 2 \left[ \frac{h_0}{M^2} - \frac{\left( \sum \left( E_T^0 \right) \right)}{AM_T^2} \right]
\]

(41)

where the subscript \( l \) indicates that the variables are evaluated
at point \( l \) in the nozzle. The Mach number \( M \) is

\[
M = \frac{v}{u}
\]

(42)

For convenience, a parameter \( h^* \) is defined as representing the sum
of heat energy plus kinetic energy of the products of reaction per
equivalent formula:

\[
h^* = \frac{\sum (E_T^0) n_1}{A} + M^2 \left[ \frac{RT \sum p_1 \frac{d \log n_1}{d \log T}}{2A \left( \frac{d \log A}{d \log T} - 1 \right)} \right]
\]

(43)

As the solution of the problem is found by successive adjustments
of the estimated quantities, \( h^* \) approaches \( h_0 \).

If equation (43) can be expanded in a manner similar to that
used to obtain equation (23) and if the differentials of derivatives
are assumed to be negligible, the correction equation is

\[
\sum h_1' \Delta \log n_1 = Ah^* \Delta \log A + T \sum (C_p^0)_{1'} \Delta \log T = Ah^* \Delta \log \frac{h_0}{h^*}
\]

(44)

where

\[
h_1' = n_1 \left( \frac{E_T^0}{p_1} \right) + M^2 p_1 \left[ \frac{\frac{d \log n_1}{d \log T}}{RT \frac{d \log A}{d \log T}} - 1 \right]
\]
Equation (44), together with equations (19) to (21) and (30), constitute the correction equations for the isentropic expansion to an assigned Mach number. The coefficients of these equations form the matrix shown in figure 3.

In order to carry out the numerical computations, values of \( \eta_1, A, \) and \( T \) are estimated for the assigned conditions; the values of \( \left( \frac{d \log n_1}{d \log T} \right)_s \) and \( \left( \frac{d \log A}{d \log T} \right)_s \) are obtained from the matrix of figure 2. The numerical values of the elements of the last column and bottom row of the matrix of figure 3 are then computed and by using the auxiliary matrix already completed for figure 2, the matrix of figure 3 may be reduced and the value of the corrections to \( n_1, A, \) and \( T \) found. This process can be repeated until the assigned conditions are satisfied.

Throat area of supersonic nozzle. - The process of isentropic expansion to a local Mach number of 1 is particularly interesting in the determination of the throat area of a nozzle having greater than critical pressure ratio. By assuming that the flow is isentropic and that chemical equilibrium is maintained throughout the expansion process, the flow velocity \( v \) at the throat must be equal to the velocity of sound \( u \) at the throat. The values \( n_1, A, T, \) and \( u \) can be found for a Mach number of 1 by use of the procedure given.

The throat area \( t \) can be calculated from the equation

\[
\frac{t}{m} = \frac{RT}{AM_T u}
\]

where \( m \) is the mass flow per second. This equation can be applied to mixtures of liquid or solid phases in equilibrium provided that the volume occupied by the liquid and the solid phases is negligible compared with that of the gas phase and that the particles of liquid and solid are in thermal and velocity equilibrium with the gas phase.
EXAMPLE OF COMBUSTION OF DIBORANE WITH FLUORINE OXIDE

The calculation of equilibrium temperature and composition of the reaction of 1 mole of diborane \((\text{B}_2\text{H}_6)\) with 5 moles of fluorine oxide \((\text{F}_2\text{O})\) is illustrated in this example for processes of

(a) constant-pressure adiabatic combustion

(b) isentropic expansion to 1 atmosphere

(c) isentropic expansion to the local velocity of sound

An equivalent formula of these reactants is

\[
Z_{a_0}X_{b_0}Y_{c_0}Z_{d_0} = \text{B}_2\text{H}_6\text{F}_{10}\text{O}_5
\]

and \(a_0 = 2, b_0 = 6, c_0 = 10, \) and \(d_0 = 5.\)

The following gaseous products will be considered as the products of reaction: boron trifluoride \(\text{BF}_3\), boron trioxide \(\text{B}_2\text{O}_3\), boron fluoride \(\text{BF}\), boron hydride \(\text{BH}\), boron oxide \(\text{B}_2\text{O}\), diatomic boron \(\text{B}_2\), hydrogen \(\text{H}_2\), water vapor \(\text{H}_2\text{O}\), hydroxyl radical \(\text{OH}\), hydrogen fluoride \(\text{HF}\), oxygen \(\text{O}_2\), fluorine \(\text{F}_2\), atomic hydrogen \(\text{H}\), atomic boron \(\text{B}\), atomic fluorine \(\text{F}\), and atomic oxygen \(\text{O}\). No liquids or solids are included. If the products are numbered in the order given, they can be identified in the terminology of equation (1) as follows:

\[
\text{BF}_3 = \text{B}_1\text{H}_0\text{F}_3\text{O}_0
\]

and therefore

\(a_1 = 1, b_1 = 0, c_1 = 3, \) and \(d_1 = 0.\)

Similarly,

\[
\text{B}_2\text{O}_3 = \text{B}_2\text{H}_0\text{F}_0\text{O}_3
\]

and

\(a_2 = 2, b_2 = 0, c_2 = 0, \) and \(d_2 = 3.\)
All values of $a_1$, $b_1$, $c_1$, and $d_1$ for this problem, together with the thermodynamic properties used, are listed in table I. Although these thermodynamic values have since been revised, they are adequate for the purpose of this example.

The enthalpies of liquid $\text{B}_2\text{H}_6$ at 298.16° K and of liquid $\text{F}_2\text{O}$ at 128.3° K, the assumed initial conditions, were computed from the heats of formation, the heats of vaporization, and the heat changes due to temperature changes together with the arbitrary chemical energy assigned to the elements. The value of the heats of formation were taken as -44 kilocalories per mole for $\text{B}_2\text{H}_6$ (reference 6) and 5.5 kilocalories per mole for $\text{F}_2\text{O}$ (reference 7). (Heat liberated is considered to be negative.) The enthalpy values using the base previously described are

\[
(H^0_{298.16}) \text{ liquid } \text{B}_2\text{H}_6 = 570.149 \text{ kilocalories per mole}
\]

\[
(H^0_{128.3}) \text{ liquid } \text{F}_2\text{O} = 67.077 \text{ kilocalories per mole}
\]

The enthalpy of the amount of fuel and oxidant at initial conditions corresponding to the equivalent formula is, from equation (13),

\[
h_0 = 570.149 + 5(67.077) = 905.534 \frac{\text{kilocalories}}{\text{equivalent formula}}
\]

(46)

The values of $a_1$, $b_1$, $c_1$, $d_1$, and $h_0$ are constant for all parts of this example.

Combustion Process

The adiabatic combustion process was assumed to occur at a constant pressure of 20.4 atmospheres.

First estimate. - From previous computations or from simple calculations using equilibrium constants, estimating reasonable values for the composition and the temperature is usually possible. This procedure is recommended inasmuch as close estimates reduce the number of trials that must be made. In order to show that an arbitrary composition that is not based on probable final values of
the composition can be used, however, the first estimates for this example for \( n_i \) and \( A \) have been taken equal to 1 mole and a temperature of 4000° K. The possibility of divergence is discussed in a later section. All estimated quantities will be used with three decimal places to distinguish them from numbers that are always integers.

**Correction equations.** - The total pressure from equation (11) can be computed because \( p_i = n_i \), hence

\[
P = \sum p_i = 16.000
given \quad (47)
\]

The correction equation for pressure (equation (22)) becomes

\[
1.000 \Delta \log p_{BF_3} + 1.000 \Delta \log p_{B_2O_5} + 1.000 \Delta \log p_{BF} + \ldots + 1.000 \Delta \log p_0 = 16.000 \log \frac{20.400}{16.000} \quad (48)
\]

The total amount of boron in the products of reaction can be determined from equation (8)

\[
Aa = \sum a_i n_i = 1 n_{BF_3} + 2 n_{B_2O_5} + 1 n_{BF} + 1 n_{BH} + 1 n_{BO} + 2 n_{B_2} + 1 n_B = 9.000
\]

and therefore the number of estimated boron atoms per equivalent formula is

\[
a = \frac{9.000}{1.000} = 9.000
\]

because \( A \) has been assumed to be 1.000 for the first estimate. The coefficient of each term in equation (8) is equal to the number of boron atoms in the molecule; the terms that do not contain boron atoms are 0. Each term of equation (49) then becomes the coefficient for its respective correction term in equation (21a):

\[
1.000 \Delta \log n_{BF_3} + 2.000 \Delta \log n_{B_2O_5} + 1.000 \Delta \log n_{BF} + \\
1.000 \Delta \log n_{BH} + 1.000 \Delta \log n_{BO} + 2.000 \Delta \log n_{B_2} + \\
1.000 \Delta \log n_B - 9.000 \Delta \log A = 9.000 \log \frac{2}{9.000} \quad (50)
\]
Similarly, the correction equation based on the conservation of hydrogen atoms is
\[1.000 \Delta \log n_{\text{BH}} + 2.000 \Delta \log n_{\text{H}_2} + 2.000 \Delta \log n_{\text{H}_2\text{O}} + 1.000 \Delta \log n_{\text{OH}} + 1.000 \Delta \log n_{\text{HF}} + 1.000 \Delta \log n_{\text{H}} - 8.000 \Delta \log \Lambda = 8.000 \log \frac{6}{8.000}\] (51)

the conservation of fluorine atoms is
\[3.000 \Delta \log n_{\text{BF}_3} + 1.000 \Delta \log n_{\text{BF}} + 1.000 \Delta \log n_{\text{HF}} + 2.000 \Delta \log n_{\text{F}_2} + 1.000 \Delta \log n_{\text{F}} - 8.000 \Delta \log \Lambda = 8.000 \log \frac{10}{8.000}\] (52)

and the conservation of oxygen atoms is
\[3.000 \Delta \log n_{\text{B}_2\text{O}_3} + 1.000 \Delta \log n_{\text{BO}} + 1.000 \Delta \log n_{\text{H}_2\text{O}} + 1.000 \Delta \log n_{\text{OH}} + 2.000 \Delta \log n_{\text{O}_2} + 1.000 \Delta \log n_{\text{O}} - 9.000 \Delta \log \Lambda = 9.000 \Delta \log \frac{5}{9.000}\] (53)

For dissociation, the numerical value of \(\log k_{\text{BF}_3}\) can be computed directly from equation (6) with the data of table I and (by using logarithms to the base 10 for convenience and by remembering that \((-\Delta F^o/RT)_1 \log e = \log K_1\)) is
\[\log k_{\text{BF}_3} = \log p_{\text{BF}_3} - \log p_{\text{B}} - 3 \log p_{\text{F}} = 5.695\]

As the partial pressures of all the constituents have been estimated to be 1.000 atmosphere,
\[\log k_{\text{BF}_3} = -5.695\]
The corresponding correction equation from equation (19) is

\[ \Delta \log p_{BF_3} - \Delta \log p_B - 3 \Delta \log p_F - (-62.075) \Delta \log T = 5.695 \]  

(54)

In a similar manner, equation (19) for \( B_2O_3 \) is

\[ \Delta \log p_{B_2O_3} - 2\Delta \log p_B - 3\Delta \log p_O - (-80.593) \Delta \log T \]

\[ = - \log k_{B_2O_3} = 5.109 \]

For \( H_2O \), equation (19) is

\[ \Delta \log p_{H_2O} - 2\Delta \log p_H - \Delta \log p_O - (-29.209) \Delta \log T = - \log k_{H_2O} \]

\[ = -0.347 \]

Correction equations for dissociation similar to those given for \( BF_3 \), \( B_2O_3 \), and \( H_2O \) molecules can be written for each molecular constituent considered in the reaction (a total of 12 in this example). The sum of the enthalpies of the products of reaction, as given in Table I and determined by equation (14), is 2734.615 because \( n_1 = 1.000 \). The heat-balance equation, as given by equation (23), is

\[ (72.172) \Delta \log p_{BF_3} + (233.435) \Delta \log p_{B_2O_3} + \ldots + \]

\[ (79.493) \Delta \log p_O - (2734.615) \Delta \log A + (644.651) \Delta \log T \]

\[ = (2734.615) \log \frac{905.534}{2734.615} \]  

(55)
A matrix (fig. 4) can now be constructed with the 12 equations similar to equation (54) and with equations (48), (50) to (53), and (55). The recommended arrangement and reduction of the matrix are given in appendix B. The solution to the correction equations is found to be

\[
\begin{align*}
\Delta \log n_{BF_3} &= 0.708 & \Delta \log n_{OH} &= 0.490 \\
\Delta \log n_{BF_2O_3} &= -1.098 & \Delta \log n_{HF} &= 1.378 \\
\Delta \log n_{BF} &= 1.116 & \Delta \log n_{O_2} &= 0.172 \\
\Delta \log n_{BH} &= 1.664 & \Delta \log n_{F_2} &= -2.038 \\
\Delta \log n_{BO} &= 0.613 & \Delta \log n_{H} &= 1.299 \\
\Delta \log n_{B_2} &= -2.138 & \Delta \log n_{B} &= 0.929 \\
\Delta \log n_{H_2} &= 0.014 & \Delta \log n_{F} &= 1.221 \\
\Delta \log n_{H_2O} &= -0.799 & \Delta \log n_{O} &= 1.457 \\
\Delta \log A &= 0.123 & \Delta \log T &= 0.154
\end{align*}
\]

These values are to be applied to the initial estimates for \( n_1 \), \( A \), and \( T \) according to the equation

\[
(log n_1)_{\text{second estimate}} = (log n_1)_{\text{first estimate}} + \Delta \log n_1
\]  

(56)

For example, the second estimate of \( \log n_{BF_3} \) would be

\[
\left( log n_{BF_3} \right)_{\text{second estimate}} = \log 1.000 + 0.708
\]

\[
\left( n_{BF_3} \right)_{\text{second estimate}} = 5.105
\]
Another set of correction equations based on the second estimates of $n_1$, $A$, and $T$ are set up and solved by means of a second matrix. The process is repeated until the values of equations (48) and (50) to (55) approach 0. For this example, six approximations were required to give the following final values of $n_1$, $A$, and $T$:

\[
\begin{align*}
P_{\text{BF}_3} &= 2.6593 & P_{\text{OH}} &= 0.6785 \\
P_{\text{B}_2\text{O}_3} &= 0.1235 & P_{\text{HF}} &= 7.1456 \\
P_{\text{BF}} &= 0.1936 & P_{\text{O}_2} &= 0.9210 \\
P_{\text{FH}} &= 0.0001 & P_{\text{F}_2} &= 0.0003 \\
P_{\text{BO}} &= 0.1669 & P_{\text{H}} &= 1.7694 \\
P_{\text{B}_2} &= 0 & P_{\text{B}} &= 0.0577 \\
P_{\text{H}_2} &= 0.1271 & P_{\text{F}} &= 1.3043 \\
P_{\text{H}_2\text{O}} &= 0.0627 & P_{\text{O}} &= 5.1903 \\
A &= 1.6622 & T &= 4775.5^\circ \text{K}
\end{align*}
\]

Discussion of Convergence. - In order to demonstrate the convergence of the process with large errors in the first estimate, the example of the combustion of diborane and fluorine oxide was solved by using 1 mole of each product, a value of 1 for $A$, and a temperature of 4000° K for the first estimate. Because these first estimates were made without regard for the probable final values, large errors were present in the second approximation and six approximations were required to eliminate the error. These values of parameters $a$, $b$, $c$, $d$, $p$, $h$, and $\delta$ are shown in the following table where $\delta$ is defined as

\[
\delta = \sum_{i=1}^{n} \left( \log k_i + \log a_i^{c_i} + \log b_i^{d_i} + \log c_i^{e_i} + \log d_i^{f_i} + \log e_i^{g_i} + \log f_i^{h_i} \right)
\]
This method has been used in routine computation for a year without encountering a divergent case in a practical problem. At least for special cases when temperature is assigned, the process will converge for all values of the first estimates. Divergence is known to occur for certain cases where temperature is used as a variable when the first estimate of temperature and composition is sufficiently in error. Although no mathematical analysis has been made to determine the theoretical limits of convergence, the process appears to be satisfactory for practical computation.

Special treatment would be required if divergence is encountered. Obtaining convergence should be possible by a sufficiently close new estimate of composition and temperature. This procedure is recommended when it is feasible but other procedures are possible, depending on the individual case.

Isentropic Expansion to Fixed Pressure

The temperature and the composition of the products of reaction following an isentropic-expansion ratio of 20.4 at chemical equilibrium were also computed for the products of reaction of this example. The value of \( S_0 \) is found from equation (28) by using the final values of each constituent of the adiabatic combustion and the absolute entropy values corresponding to the final combustion temperature. The calculated value of \( S_0 \) was 763.476 calories per \(^\circ\)K per mole.
First estimates. - The number of approximations necessary for a complete calculation can be considerably reduced if the initial estimate is based on previous experience. The final values of $n_1$ and $A$ determined for the combustion process of this example can therefore be the basis for this first estimate.

Because the expansion ratio is 20.4, the four largest constituents can be estimated to be $1/20.4$ of their combustion value.

\[
\begin{align*}
PB_F &= 0.1304 \\
PH_F &= 0.3503 \\
P_H &= 0.0867 \\
P_0 &= 0.2544 \\
A &= 0.0815
\end{align*}
\]

For convenience of presentation, the temperature was estimated to be $4000^\circ K$ so that the values of table I could be used again. The remaining constituents can be estimated from the dissociation equations by setting $\log k_1 = 0$. For example, $P_F$ would be determined with the assumed values of $P_{HF}$ and $P_H$ from equation (6) and table I

\[
0 = \log 0.3503 - \log 0.0867 - \log P_F - 1.8944
\]

\[
\begin{align*}
\log P_F &= -0.45556 + 1.06198 - 1.8944 \\
&= -1.28798 \\
P_F &= 0.0515
\end{align*}
\]

Similarly, $P_B$ can be estimated with the assumed values of $P_{BF_3}$ and $P_F$

\[
0 = \log 0.1304 - \log P_B - 3 \log 0.0515 - 5.6953
\]

\[
\begin{align*}
\log P_B &= -0.88472 + 3.86394 - 5.6953 \\
P_B &= 0.0019
\end{align*}
\]
If this procedure is followed for all the remaining constituents, the following list of first estimates can be made:

\[
\begin{align*}
P_{BF_3} &= 0.1304 & P_{OH} &= 0.0150 \\
B_{B_2O_3} &= 0.0078 & P_{HF} &= 0.3503 \\
P_{BF} &= 0.0043 & P_{O_2} &= 0.0269 \\
P_{BH} &= 0 & P_{F_2} &= 0 \\
P_{BO} &= 0.0053 & P_{H} &= 0.0867 \\
P_{B_2} &= 0 & P_{B} &= 0.0019 \\
P_{H_2} &= 0.0029 & P_{F} &= 0.0515 \\
P_{H_2O} &= 0.0009 & P_{O} &= 0.2544 \\
A &= 0.0815 & T &= 4000^\circ K
\end{align*}
\]

Correction equations. - When these estimates are substituted in equations (8) to (11) and (29), the parameters \(a, b, c, d, P,\) and \(s\) are calculated to be 1.9325, 5.6393, 9.7828, 4.3288, 0.9383, and 766.297, respectively. The correction equations (given in matrix form in fig. 5) are then determined when these estimates and parameters are used in equations (19), (21), and (30). The remainder of this problem is continued in the same manner as the combustion calculation. The final solution is obtained in three trials.

Isentropic Expansion to Mach Number of 1

The temperature and the composition of the products of reaction following an isentropic expansion to the local velocity of sound by assuming chemical equilibrium was computed for the products of reaction considered in this example. The value of \(s_0\) is the same as that found for the isentropic expansion to 1 atmosphere.

First estimate. - For simplicity, the same first estimates of 1 mole, \(1,\) and \(4000^\circ K\) for \(n_1, A,\) and \(T,\) respectively, were again made.
Correction equations. - The matrix shown in figure 6 was constructed from the application of the data of table I to equations (19), (21), (30), and (44). The first sixteen rows are identical to the corresponding rows of figure 4 because the same equations are used; the next row is obtained from equation (30). These seventeen equations are then solved to determine the values of

\[
\left( \frac{d \log n_1}{d \log T} \right)_S \quad \text{and} \quad \left( \frac{d \log A}{d \log T} \right)_S
\]

(last row of fig. 6). As in the previous calculations, the resulting corrections are then applied to the first estimates of \( n_1 \), \( A \), and \( T \) by using equation (56) and the process is repeated until the assigned conditions are satisfied.

Lewis Flight Propulsion Laboratory,
National Advisory Committee for Aeronautics,
Cleveland, Ohio, September 7, 1949.
APPENDIX A

SYMBOLS

A
number of equivalent formulas

a, b, c, \ldots
summation of each atomic type over products of reaction per equivalent formula; with subscript, number of atoms of each element within chemical formula

C\text{P}^0
molar specific heat at constant pressure and standard conditions

C\text{P}^0\prime
specific heat coefficient for matrix

C\text{V}^0
molar specific heat at constant volume and standard conditions

E\text{P}^0_T
molar internal energy at standard conditions

e
internal energy per equivalent formula

E\text{P}^0_T
molar free energy at standard conditions

E^0\text{O}_T
molar enthalpy at 0^\circ \text{K} and standard conditions

E^0_T
molar enthalpy at standard conditions

h
enthalpy per equivalent formula

h\prime
enthalpy coefficient for matrix

h^*
sum of heat and kinetic energies per equivalent formula

K
equilibrium constant

k
ratio of equilibrium constant based on partial pressures to equilibrium constant based on free-energy change
M  Mach number

M_r  molecular weight of equivalent formula

m  mass flow per second

N_d  number of dissociation equations

N_e  number of chemical elements involved in reaction

N_p  number of products of reaction

n  number of moles

P  total pressure

p  partial pressure

Q  any function

q,r  any variables

R  gas constant

S^o_T  molar entropy at standard conditions

s  entropy per equivalent formula

s'  entropy coefficient for matrix

T  temperature

t  throat area

U  unit matrix

u  velocity of sound

V  volume

v  velocity of flow
... , X, Y, Z  elements within representative chemical formula
x  matrix variable
a  submatrix
δ  total-error parameter
ρ  density

Subscripts:
a, b, c, ...  number of atoms within chemical formula
f  fuel
g  oxidant
l  any point in nozzle
m  number of types of gaseous molecule
o  initial given condition
P  constant pressure
s  constant entropy
T  temperature, °K
... , X, Y, Z  product index numbers (i) that designate atomic gases
1, 2, 3, ... , i  product index number
APPENDIX B

MATRIX CONSTRUCTION AND REDUCTION

A coefficient matrix is a scheme of detached coefficients of a set of linear equations that are to be solved simultaneously. An augmented matrix is identical to a coefficient matrix except that the constants are included. Equations (19) to (23) constitute such a set of equations for the simultaneous determination of the variables \( \Delta \log n_1, \Delta \log A, \) and \( \Delta \log T. \)

Construction. - Because of the large number of zeros occurring in the matrix, a considerable saving in effort can be made by proper arrangement of the order of the rows and the columns. The following arrangement provides a partly symmetrical matrix that has been found to be among the easiest to evaluate as long as the products of reaction are principally gaseous and the dissociation constants are expressed in terms of the atomic species:

1. The order of the columns should be
   (a) \( \Delta \log n_1 \) of gaseous molecules
   (b) \( \Delta \log n_1 \) of atoms
   (c) \( \Delta \log n_1 \) of liquid and solid products
   (d) \( \Delta \log A \)
   (e) \( \Delta \log T \)
   (f) Constant terms of equations

2. The order of the rows is
   (a) Dissociation equations in same order as gaseous molecules in columns
   (b) Mass-balance equations in order of atoms in columns
(c) Dissociation equations for solid and liquid products in same order as solid and liquid in columns

(d) Total-pressure equation

(e) Heat-balance equation in combustion calculation; entropy-balance equation in calculation of isentropic expansion to fixed pressure.

In the calculation of isentropic expansion to an assigned Mach number, the order of the columns is not changed but the rows are modified as follows: (1) The entropy-balance equation is substituted for the total-pressure equation; and (2) the heat-balance equation is changed to include the kinetic energy in accordance with equation (44).

The values of \(- \frac{d \log n_1}{d \log T_s}\) and \(- \frac{d \log A}{d \log T_s}\) are first computed by means of the \(N_p+1\) order matrix and are then substituted in equations (45) and (46) to yield the \((N_p+2)\)nd row of the complete matrix.

Solution. - One of the best methods of solving simultaneous linear equations is given by Crout (reference 8). With this method, an auxiliary matrix is constructed from an original augmented matrix by a simple routine. This auxiliary matrix is of the order equal to the original matrix. The solution for the set of equations can be obtained by a process of back substitution in the auxiliary matrix.

For convenience, the order of the matrix is reduced before the Crout method is applied. A matrix arranged as recommended can be partitioned so that a unit matrix \([U_m]\) of the order \((m,m)\) appears in the upper left corner, where \(m\) is equal to the number of types of gaseous molecule. The original augmented matrix can then be written

\[
\begin{bmatrix}
U_m & a_2 \\
0 & a_3 \\
\end{bmatrix}
\]

(B1)
When the Crout method is applied to the original augmented matrix, the Crout auxiliary matrix can be expressed as

\[
\begin{bmatrix}
U_m & \alpha_1 \\
& U_{m+1} \\
& \alpha_2 \\
& \alpha_3 \\
& \alpha_4 \\
\end{bmatrix}
\] (B2)

where \([U_m]\), \([\alpha_1]\), and \([\alpha_2]\) are identical to the corresponding submatrices of the original matrix. By observing the operations involved in the construction of the Crout auxiliary matrix, \([\alpha_4]\) is shown to be identical to the auxiliary matrix of the augmented matrix \([\alpha_5]\) defined by

\[
[\alpha_5] = [\alpha_3] - [\alpha_2] [\alpha_1]
\] (B3)

For computation, equation (B3) is written

\[
[\alpha_5] = [\alpha_2 | \alpha_3] [-\alpha_1 | -U_k]
\] (B4)

where \(U_k\) is a unit matrix of order equal to the number of columns of \([\alpha_3]\). The numerical solution is then obtained by carrying out the matrix multiplication indicated in equation (B4) to find \([\alpha_5]\). The Crout auxiliary matrix \([\alpha_4]\) is constructed from \([\alpha_5]\). The values of the variable \(x(m+1), \ldots, x(N_p+2)\) are found from \([\alpha_4]\) by the process of back substitution given by Crout. The values of the remaining variables are found by the matrix equation

\[
[x_1] \\
\vdots \\
[x_m] \\
[x_{m+1}] \\
\vdots \\
[x_{N_p+2}]
\] = - \([\alpha_1]\) \begin{bmatrix}
-1 \\
\vdots \\
-1
\end{bmatrix}
For illustration, the submatrices \([a_1], [a_2],\) and \([a_3]\)
were taken from figure 4 and used to construct figure 7. The last six rows of figure 4 correspond to the matrix \([a_2, a_3]\) and are shown in figure 7(a). The matrix \([\frac{-a_1}{M_m}]\) is shown in figure 7(b) where, for convenience of computation, the columns have been tabulated as rows with the first row at the top. The operations required by equation (B4) to evaluate \([a_5]\) are indicated in figure 8(a) and the results for the example given in figure 7 are shown in figure 8(b). The operation \(\sum (1 A)\) is illustrated in detail as follows:

\[
0 \times 0 + 0 \times 0 + 0 \times 0 + 1 \times 1,000 + 0 \times 0 + 0 \times 0 + 2 \times 2,000 + 2 \times 2,000 + 1 \times 1,000 + 1 \times 1,000 + 0 \times 0 + 0 \times 0 + 1 \times 1,000 + 0 \times 0 + 0 \times 0 + 0 \times 0 + 0 = 12,000
\]

Practical computation. - In practical computations, writing the complete original matrix, as shown in figure 4, is unnecessary; instead, the matrices shown in figure 7(a) and 7(b) are written out so that figure 8(b) may be obtained. Except for the last two rows, figure 7(b) is always the same for a given group of chemical elements.

The process of obtaining figure 7 is as follows:

1. Values of \(n_1\) are entered in row E.

2. Values of the elements of rows \(A, E, O,\) and \(D\) for columns 1 through \(N\) are obtained by multiplying the elements of row \(E\) by the elements of row \(1, 2, 3,\) and \(4,\) respectively.

3. Values of the elements of row \(F\) for columns 1 through \(N\) are obtained by multiplying the elements of row \(E\) by the values of \((E^0)_{1}\) found from a table of the thermodynamic properties for the substances.
4. Column $\Delta \log A$ is found by summing the elements in each row and writing the negative of the total in column $\Delta \log A$ except for row 8 where the value is 0.

5. The elements of the $\Delta \log T$ and constant columns are evaluated by means of the expressions shown in figure 1.

6. Row 8 is obtained by entering the values of $(\Delta H^0_T)_{1}/RT$ from a table of thermodynamic properties.

7. Elements of row 7 are obtained from the equations defining $\log k_1$, by taking $\log k_1$ from a table of thermodynamic properties.

REFERENCES


<table>
<thead>
<tr>
<th>Product</th>
<th>Fixed Equivalent formula</th>
<th>Determined at estimated temperature of 4000° K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>i</td>
<td>a₁</td>
</tr>
<tr>
<td>BF₃</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>B₂O₃</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>BF</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>BH</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>BO</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>B₂</td>
<td>6</td>
<td>2</td>
</tr>
<tr>
<td>H₂</td>
<td>7</td>
<td>0</td>
</tr>
<tr>
<td>H₂O</td>
<td>8</td>
<td>0</td>
</tr>
<tr>
<td>OH</td>
<td>9</td>
<td>0</td>
</tr>
<tr>
<td>HF</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>O₂</td>
<td>11</td>
<td>0</td>
</tr>
<tr>
<td>F₂</td>
<td>12</td>
<td>0</td>
</tr>
<tr>
<td>H</td>
<td>13</td>
<td>0</td>
</tr>
<tr>
<td>B</td>
<td>14</td>
<td>1</td>
</tr>
<tr>
<td>F</td>
<td>15</td>
<td>0</td>
</tr>
<tr>
<td>O</td>
<td>16</td>
<td>0</td>
</tr>
</tbody>
</table>
Figure 1. General matrix for solution of correction equations for adiabatic combustion and isentropic expansion to assigned pressure. Equations: (19), dissociation of gaseous molecules; (21), mass balance; (20), dissociation of solids or liquids; (22), pressure; (23), heat balance; (30), entropy balance. All blank spaces denote zeros.
Figure 2. - General matrix for determination of derivatives used for calculating the local velocity of sound. Equations: (35), dissociation of gaseous molecules; (37), mass balance; (36), dissociation of solid or liquid molecules; (39), entropy balance. All blank spaces denote zero.
<table>
<thead>
<tr>
<th>Equation</th>
<th>Gaseous molecules</th>
<th>Atoms</th>
<th>Solid or liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta \log n_1$</td>
<td>$\Delta \log n_2$</td>
<td>$\Delta \log n_3$</td>
</tr>
<tr>
<td>(19)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(21)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_{1n_1}$</td>
<td>$a_{2n_2}$</td>
<td>$a_{3n_3}$</td>
<td>$a_{4n_4}$</td>
</tr>
<tr>
<td>$b_{1n_1}$</td>
<td>$b_{2n_2}$</td>
<td>$b_{3n_3}$</td>
<td>$b_{4n_4}$</td>
</tr>
<tr>
<td>$c_{1n_1}$</td>
<td>$c_{2n_2}$</td>
<td>$c_{3n_3}$</td>
<td>$c_{4n_4}$</td>
</tr>
<tr>
<td>(20)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(30)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$s_1$</td>
<td>$s_2$</td>
<td>$s_3$</td>
<td>$s_4$</td>
</tr>
<tr>
<td>(44)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$h_1$</td>
<td>$h_2$</td>
<td>$h_3$</td>
<td>$h_4$</td>
</tr>
</tbody>
</table>

Figure 3. - General matrix for solution of correction equations for the process of isentropic expansion to assigned Mach number. Equations: (19), dissociation of gaseous molecules; (21), mass balance; (20), dissociation of solid or liquid molecules; (30), entropy balance; (44), energy balance. All blank spaces denote zeros.
Figure 4. Matrix for solution of correction equations for adiabatic combustion of diborane and fluorine oxide after first estimate of n₁, A, and T. Equations: (19), dissociation of gaseous molecules; (21), mass balance; (22), pressure; (23) heat balance. All blank spaces denote zero.
### Table: Data for Reaction of Diborane with Fluorine

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Eqn. 1</th>
<th>Eqn. 2</th>
<th>Eqn. 3</th>
<th>Eqn. 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction</td>
<td>0.0014</td>
<td>0.0005</td>
<td>0.0006</td>
<td>0.0007</td>
</tr>
<tr>
<td>Product 1</td>
<td>0.0014</td>
<td>0.0005</td>
<td>0.0006</td>
<td>0.0007</td>
</tr>
<tr>
<td>Product 2</td>
<td>0.0014</td>
<td>0.0005</td>
<td>0.0006</td>
<td>0.0007</td>
</tr>
<tr>
<td>Product 3</td>
<td>0.0014</td>
<td>0.0005</td>
<td>0.0006</td>
<td>0.0007</td>
</tr>
<tr>
<td>Product 4</td>
<td>0.0014</td>
<td>0.0005</td>
<td>0.0006</td>
<td>0.0007</td>
</tr>
</tbody>
</table>

**Figure 1:** Matrix for solution of correlation equations for isotope expansion to 1 atmosphere for the reaction of diborane with fluorine. Equations: (1) = dissociation of diborane molecules; (2) = reaction of diborane with fluorine; (3) = dissociation of diborane molecules; (4) = reaction of diborane with fluorine.
### Figure 6 - Matrix for solution of correction equations for isentropic expansion to local velocity of sound for reaction of dibromine and fluorine oxide after first estimate of \( n_1 \), \( A \), and \( T \): Equations: (19), dissociation of gaseous molecules; (21), mass balance; (30), entropy balance; (44), energy balance. All blank spaces denote zeros.
Figure 7. - Breakdown of complete matrix of example to facilitate calculation. All blank spaces denote zeros.
### Table: Method of calculation of reduced matrix.

<table>
<thead>
<tr>
<th>Σ(1A)</th>
<th>Σ(2A)</th>
<th>Σ(3A)</th>
<th>Σ(4A)</th>
<th>Σ(5A)</th>
<th>Σ(6A)</th>
<th>Σ(7A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Σ(1B)</td>
<td>Σ(2B)</td>
<td>Σ(3B)</td>
<td>Σ(4B)</td>
<td>Σ(5B)</td>
<td>Σ(6B)</td>
<td>Σ(7B)</td>
</tr>
<tr>
<td>Σ(1C)</td>
<td>Σ(2C)</td>
<td>Σ(3C)</td>
<td>Σ(4C)</td>
<td>Σ(5C)</td>
<td>Σ(6C)</td>
<td>Σ(7C)</td>
</tr>
<tr>
<td>Σ(1D)</td>
<td>Σ(2D)</td>
<td>Σ(3D)</td>
<td>Σ(4D)</td>
<td>Σ(5D)</td>
<td>Σ(6D)</td>
<td>Σ(7D)</td>
</tr>
<tr>
<td>Σ(1E)</td>
<td>Σ(2E)</td>
<td>Σ(3E)</td>
<td>Σ(4E)</td>
<td>Σ(5E)</td>
<td>Σ(6E)</td>
<td>Σ(7E)</td>
</tr>
<tr>
<td>Σ(1F)</td>
<td>Σ(2F)</td>
<td>Σ(3F)</td>
<td>Σ(4F)</td>
<td>Σ(5F)</td>
<td>Σ(6F)</td>
<td>Σ(7F)</td>
</tr>
</tbody>
</table>

(a) Method of calculation of reduced matrix.

<table>
<thead>
<tr>
<th>Δ log n_H</th>
<th>Δ log n_B</th>
<th>Δ log n_F</th>
<th>Δ log n_0</th>
<th>Δ log A</th>
<th>Δ log T</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.000</td>
<td>1.000</td>
<td>1.000</td>
<td>3.000</td>
<td>-8.000</td>
<td>-127.873</td>
</tr>
<tr>
<td>1.000</td>
<td>13.000</td>
<td>4.000</td>
<td>7.000</td>
<td>-9.000</td>
<td>-283.010</td>
</tr>
<tr>
<td>1.000</td>
<td>4.000</td>
<td>16.000</td>
<td>0</td>
<td>-8.000</td>
<td>-240.597</td>
</tr>
<tr>
<td>3.000</td>
<td>7.000</td>
<td>0</td>
<td>17.000</td>
<td>-9.000</td>
<td>-333.400</td>
</tr>
<tr>
<td>8.000</td>
<td>9.000</td>
<td>8.000</td>
<td>9.000</td>
<td>0</td>
<td>-294.871</td>
</tr>
<tr>
<td>885.360</td>
<td>2873.620</td>
<td>786.118</td>
<td>1241.423</td>
<td>-2734.615</td>
<td>-45475.661</td>
</tr>
</tbody>
</table>

(b) Numerical value of reduced matrix.

Figure 8. - Method of reduction of order of example matrix.