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TECHNICAL NOTE 2113

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

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GENERAL METHOD FOR COMPUTATION OF EQUILIBRIUM COMPOSITION
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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.)

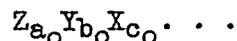
(b) A set of linear simultaneous correction equations are given that determine a new composition and a new temperature.

(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

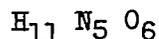
The substances entering a reaction process will be designated the reactants and can be represented by the equivalent formula



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 (NH_3) for fuel and 2 moles of nitric acid (HNO_3) for an oxidant are

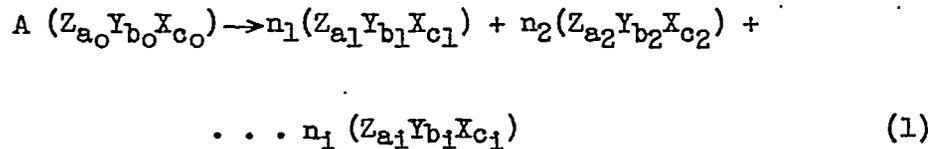


and the equivalent formula would be



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



where n_i is the number of moles of the i th 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 i th 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

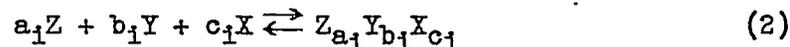
$$p_i = n_i$$

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



and the corresponding equation for the equilibrium constant K_1 of gaseous molecules is

$$K_1 = \frac{p_1}{p_Z^{a_1} p_Y^{b_1} p_X^{c_1}} \quad (3)$$

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

$$K_1 = \frac{1}{p_Z^{a_1} p_Y^{b_1} p_X^{c_1}} \quad (4)$$

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 $(\Delta F_T^0)_1$ across the dissociation reactions represented by equation (2) or

$$\log_e K_1 = \left(\frac{-\Delta F_T^0}{RT} \right)_1 \quad (5)$$

Because the assumed composition may not correspond to that at chemical equilibrium, variables k_1 are conveniently defined so that for gaseous molecules

$$\log_e k_1 = \log_e p_1 - a_1 \log_e p_Z - b_1 \log_e p_Y - c_1 \log_e p_X - \left(\frac{-\Delta F_T^0}{RT} \right)_1 \quad (6)$$

and for liquid or solid molecules

$$\log_e k_1 = -a_1 \log_e p_Z - b_1 \log_e p_Y - c_1 \log_e p_X - \left(\frac{-\Delta F_T^0}{RT} \right)_1 \quad (7)$$

The value of each k_1 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 , . . . 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 , and c approach the values of a_0 , b_0 , and 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 ρ is defined as

$$\rho = \frac{AM_T}{V} = \frac{AM_T}{RT} \quad (12)$$

where M_r is the molecular weight of the equivalent formula. For a reaction process with an assigned density, the value of ρ must approach the assigned value ρ_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 $Z_{a_0} Y_{b_0} X_{c_0}$ is denoted by h_0 and is given by the expression

$$h_0 = n_f (H_T^0)_f + n_g (H_T^0)_g \quad (13)$$

where n_f and n_g are the number of moles of fuel and oxidant, respectively, corresponding to the equivalent formula $Z_{a_0} Y_{b_0} X_{c_0}$ and $(H_T^0)_f$ and $(H_T^0)_g$ are the molar enthalpies of the fuel and the oxidant, respectively, at the initial conditions. The molar enthalpy H_T^0 is defined by the equation

$$H_T^0 = \int_0^T C_p^0 dT + H_0^0$$

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 0^0 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

$$h = \frac{1}{A} \sum_1 (H_{T1}^0) n_1 \quad (14)$$

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:

Type	Number of equations
Dissociative equilibrium	N_d
Conservation of mass	N_e
Constant pressure	1
Conservation of energy	1

These equations are to be solved simultaneously. Values for n_1 , A , and T can be estimated and the values of the parameters k_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_p+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 ΔQ_1 and ΔQ_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 $\log_e k_i$, a , b , c , . . . , h , and P can similarly be expanded in a Taylor's series; for example, equation (6) for $\log_e k_i$ for gases expanded in the logarithmic form would be

$$\Delta \log_e k_i = \Delta \log_e p_i - a_i \Delta \log_e p_Z - b_i \Delta \log_e p_Y - c_i \Delta \log_e p_X -$$

$$\left(\frac{\Delta H_T^0}{RT} \right)_i \Delta \log_e T \quad (15)$$

The term $\left(\frac{\Delta H_T^0}{RT} \right)_i$ appears because

$$\frac{\partial \left(\frac{-\Delta F_T^0}{RT} \right)_i}{\partial \log_e T} = \left(\frac{\Delta H_T^0}{RT} \right)_i$$

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

$$\Delta a = \frac{1}{A} \sum_i a_i \Delta n_i - \sum_i \frac{a_i n_i}{A^2} \Delta A \quad (16)$$

Some of these equations are expressed in terms of $\Delta \log_e p_i$ and Δp_i , whereas the others are expressed in terms of Δn_i . In order to convert to a common variable $\Delta \log_e n_i$, the following substitutions can be made:

For gases, $p_i = n_i$ therefore

$$\Delta \log_e p_i = \Delta \log_e n_i \quad (17)$$

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

$$\Delta q = q \Delta \log_e q \quad (18)$$

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,

$$\Delta \log n_i - a_i \Delta \log n_Z - b_i \Delta \log n_Y - c_i \Delta \log n_X -$$

$$\frac{(\Delta H_T^0)_i}{RT} \Delta \log T = - \log k_i \quad (19)$$

For liquid or solid products,

$$-a_i \Delta \log n_Z - b_i \Delta \log n_Y - c_i \Delta \log n_X - \frac{(\Delta H_T^0)_i}{RT} \Delta \log T = - \log k_i \quad (20)$$

For all products of reaction,

$$\sum_i a_i n_i \Delta \log n_i - Aa \Delta \log A = Aa \log \frac{a_0}{a} \quad (21a)$$

$$\sum_i b_i n_i \Delta \log n_i - Ab \Delta \log A = Ab \log \frac{b_0}{b} \quad (21b)$$

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$$\sum_i c_i n_i \Delta \log n_i - A c \Delta \log A = A c \log \frac{c_0}{c} \quad (21c)$$

$$\sum_i p_i \Delta \log n_i = P \log \frac{P_0}{P} \quad (22)$$

$$\begin{aligned} \sum_i (H_T^0)_i n_i \Delta \log n_i - A h \Delta \log A + T \sum_i (C_p^0)_i n_i \Delta \log T \\ = A h \log \frac{h_0}{h} \end{aligned} \quad (23)$$

where the desired values of the parameters ($\log_e k_i = 0, a = a_0, \dots$) are substituted in the form

$$\Delta \log_e k_i = - \log_e k_i \quad (24)$$

$$\Delta a = a \log_e \frac{a_0}{a} \quad (25)$$

.....

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)

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

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

$$\begin{aligned} \sum_i (E_T^0)_i n_i \Delta \log n_i - A e \Delta \log A + T \sum_i (C_V^0)_i n_i \Delta \log T \\ = A e \log \frac{e_0}{e} \end{aligned} \quad (27)$$

where e_0 is the assigned internal energy per equivalent formula at initial given conditions and C_V^0 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 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.

$$s_0 = \left\{ \frac{1}{A} \sum_i \left[n_i (S_T^0)_i - R p_i \log_e p_i \right] \right\} \quad (28)$$

combustion
conditions

where $(S_T^O)_i$ is the absolute entropy of the product i 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

$$s = \left\{ \frac{1}{A} \sum_i \left[n_i (S_T^O)_i - R p_i \log_e p_i \right] \right\}_{\text{exit conditions}} \quad (29)$$

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_i , 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):

$$\sum s_i' \Delta \log n_i - A s \Delta \log A + \sum_i (C_p^O)_i n_i \Delta \log T = A s \log \frac{s_0}{s} \quad (30)$$

where

$$s_i' = (S_T^O)_i n_i - R p_i (1 + \log_e p_i)$$

The values of $\Delta \log n_i$, $\Delta \log A$, 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

$$u^2 = \left(\frac{dP}{d\rho} \right)_s \quad (31)$$

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

$$dP = \sum_i dp_i \quad (32)$$

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

$$d\rho = \frac{M_r}{RT} dA - \frac{A}{RT^2} dT \quad (33)$$

Thus, equation (31) can be written

$$u^2 = \left(\frac{\sum_i dp_i}{\frac{M_r}{RT} dA - \frac{A}{RT^2} dT} \right)_s$$

and by dividing the numerator and the denominator by dT and changing to logarithmic variables

$$u^2 = \left[\frac{\sum_i p_i \frac{d \log_e p_i}{d \log_e T}}{\frac{AM_r}{RT} \left(\frac{d \log_e A}{d \log_e T} - 1 \right)} \right]_s \quad (34)$$

This expression will permit evaluation of u^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,

$$\frac{d \log p_1}{d \log T} - a_1 \frac{d \log p_Z}{d \log T} - b_1 \frac{d \log p_Y}{d \log T} - c_1 \frac{d \log p_X}{d \log T} - \frac{(\Delta H_T^0)_1}{RT} = \frac{d \log k_1}{d \log T} \quad (35)$$

For liquid and solid products,

$$-a_1 \frac{d \log p_Z}{d \log T} - b_1 \frac{d \log p_Y}{d \log T} - c_1 \frac{d \log p_X}{d \log T} - \frac{(\Delta H_T^0)_1}{RT} = \frac{d \log k_1}{d \log T} \quad (36)$$

For all products of reaction,

$$\sum_i a_i n_i \frac{d \log n_i}{d \log T} - Aa \frac{d \log A}{d \log T} = Aa \frac{d \log a}{d \log T} \quad (37a)$$

$$\sum_i b_i n_i \frac{d \log n_i}{d \log T} - Ab \frac{d \log A}{d \log T} = Ab \frac{d \log b}{d \log T} \quad (37b)$$

$$\sum_i c_i n_i \frac{d \log n_i}{d \log T} - Ac \frac{d \log A}{d \log T} = Ac \frac{d \log c}{d \log T} \quad (37c)$$

$$\sum_i s_i \frac{d \log n_i}{d \log T} - As \frac{d \log A}{d \log T} + \sum_i (C_p^0)_i n_i = As \frac{d \log s}{d \log T} \quad (38)$$

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

$\left(\frac{d \log n_1}{d \log T}\right)_S$ and $\left(\frac{d \log A}{d \log T}\right)_S$ 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:

$$C_p^o = \frac{A}{P} \left(\frac{dh}{dT}\right)_P = \frac{1}{PT} \left[\sum_1 (H_T^o)_1 n_1 \left(\frac{d \log n_1}{d \log T}\right)_P - Ah \left(\frac{d \log A}{d \log T}\right)_P + T \sum_1 n_1 (C_p^o)_1 \right] \quad (39)$$

Equation (32) can be written as

$$\sum_1 p_1 \frac{d \log n_1}{d \log T} = \frac{P d \log P}{d \log T} \quad (40)$$

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 $\left(\frac{d \log n_1}{d \log T}\right)_P$ 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_p^o .

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 energy to the point in question. From this relation, the velocity squared at any point z is

$$v^2 = 2 \left[\frac{h_0}{M_r} - \left(\frac{\sum_1 (H_T^0)_1 n_1}{AM_r} \right)_z \right] \quad (41)$$

where the subscript z indicates that the variables are evaluated at point z in the nozzle. The Mach number M is

$$M = \frac{v}{u} \quad (42)$$

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:

$$h^* = \frac{\sum_1 (H_T^0)_1 n_1}{A} + M^2 \left[\frac{RT \sum_1 p_1 \frac{d \log_e n_1}{d \log T}}{2A \left(\frac{d \log_e A}{d \log_e T} - 1 \right)} \right]_s \quad (43)$$

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

$$\sum_1 h_1' \Delta \log n_1 - Ah^* \Delta \log A + T \sum_1 (C_p^0)_1' \Delta \log T = Ah^* \log \frac{h_0}{h^*} \quad (44)$$

where

$$h_1' = n_1 (H_T^0)_1 + M^2 p_1 \left[\frac{RT \frac{d \log n_1}{d \log T}}{2 \left(\frac{d \log A}{d \log T} - 1 \right)} \right]$$

$$(C_p^0)_i' = n_i \left[(C_p^0)_i + \frac{M^2 R p_i \frac{d \log n_i}{d \log T}}{2 \left(\frac{d \log A}{d \log T} - 1 \right)} \right]$$

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 n_1 , A , and T are estimated for the assigned conditions; the

value 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

$$\frac{t}{m} = \frac{RT}{AM_T u} \quad (45)$$

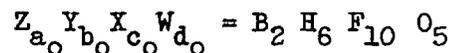
where m is the mass flow per second. This equation can be applied to mixtures of liquid or solid phases in equilibrium provided that the volume occupied by the liquid and the solid phases is negligible compared with that of the gas phase and that the particles of liquid and solid are in thermal and velocity 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 (B_2H_6) with 5 moles of fluorine oxide (F_2O) is illustrated in this example for processes of

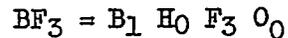
- (a) constant-pressure adiabatic combustion
- (b) isentropic expansion to 1 atmosphere
- (c) isentropic expansion to the local velocity of sound

An equivalent formula of these reactants is



and $a_0 = 2$, $b_0 = 6$, $c_0 = 10$, and $d_0 = 5$.

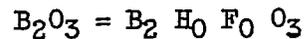
The following gaseous products will be considered as the products of reaction: boron trifluoride BF_3 , boron trioxide B_2O_3 , boron fluoride BF , boron hydride BH , boron oxide BO , diatomic boron B_2 , hydrogen H_2 , water vapor H_2O , hydroxyl radical OH , hydrogen fluoride HF , oxygen O_2 , fluorine F_2 , atomic hydrogen H , atomic boron B , atomic fluorine F , and atomic oxygen 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:



and therefore

$$a_1 = 1, b_1 = 0, c_1 = 3, \text{ and } d_1 = 0$$

Similarly,



and

$$a_2 = 2, b_2 = 0, c_2 = 0, \text{ and } d_2 = 3$$

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 B_2H_6 at $298.16^\circ K$ and of liquid F_2O at $128.3^\circ K$, 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 B_2H_6 (reference 6) and 5.5 kilocalories per mole for F_2O (reference 7). (Heat liberated is considered to be negative.) The enthalpy values using the base previously described are

$$(H^\circ_{298.16}) \text{ liquid } B_2H_6 = 570.149 \text{ kilocalories per mole}$$

$$(H^\circ_{128.3}) \text{ liquid } F_2O = 67.077 \text{ kilocalories per mole}$$

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

$$h_o = 570.149 + 5 (67.077) = 905.534 \frac{\text{kilocalories}}{\text{equivalent formula}} \quad (46)$$

The values of a_1 , b_1 , c_1 , d_1 , and h_o 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_1 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 $p_1 = n_1$, hence

$$P = \sum_1 p_1 = 16.000 \quad (47)$$

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

$$1.000 \Delta \log P_{\text{BF}_3} + 1.000 \Delta \log P_{\text{B}_2\text{O}_3} + 1.000 \Delta \log P_{\text{BF}} + \dots + \\ 1.000 \Delta \log p_0 = 16.000 \log \frac{20.400}{16.000} \quad (48)$$

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

$$Aa = \sum_1 a_1 n_1 = 1 n_{\text{BF}_3} + 2 n_{\text{B}_2\text{O}_3} + 1 n_{\text{BF}} + 1 n_{\text{BH}} + 1 n_{\text{BO}} + 2 n_{\text{B}_2} + \\ 1 n_{\text{B}} = 9.000 \quad (49)$$

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):

$$1.000 \Delta \log n_{\text{BF}_3} + 2.000 \Delta \log n_{\text{B}_2\text{O}_3} + 1.000 \Delta \log n_{\text{BF}} + \\ 1.000 \Delta \log n_{\text{BH}} + 1.000 \Delta \log n_{\text{BO}} + 2.000 \Delta \log n_{\text{B}_2} + \\ 1.000 \Delta \log n_{\text{B}} - 9.000 \Delta \log A = 9.000 \log \frac{2}{9.000} \quad (50)$$

Similarly, the correction equation based on the conservation of hydrogen atoms is

$$\begin{aligned}
 & 1.000 \Delta \log n_{\text{BH}} + 2.000 \Delta \log n_{\text{H}_2} + 2.000 \Delta \log n_{\text{H}_2\text{O}} + \\
 & 1.000 \Delta \log n_{\text{OH}} + 1.000 \Delta \log n_{\text{HF}} + 1.000 \Delta \log n_{\text{H}} - 8.000 \Delta \log A \\
 & = 8.000 \log \frac{6}{8.000} \quad (51)
 \end{aligned}$$

the conservation of fluorine atoms is

$$\begin{aligned}
 & 3.000 \Delta \log n_{\text{BF}_3} + 1.000 \Delta \log n_{\text{BF}} + 1.000 \Delta \log n_{\text{HF}} + \\
 & 2.000 \Delta \log n_{\text{F}_2} + 1.000 \Delta \log n_{\text{F}} - 8.000 \Delta \log A = 8.000 \log \frac{10}{8.000} \\
 & \quad (52)
 \end{aligned}$$

and the conservation of oxygen atoms is

$$\begin{aligned}
 & 3.000 \Delta \log n_{\text{B}_2\text{O}_3} + 1.000 \Delta \log n_{\text{BO}} + 1.000 \Delta \log n_{\text{H}_2\text{O}} + \\
 & 1.000 \Delta \log n_{\text{OH}} + 2.000 \Delta \log n_{\text{O}_2} + 1.000 \Delta \log n_{\text{O}} - 9.000 \Delta \log A \\
 & = 9.000 \Delta \log \frac{5}{9.000} \quad (53)
 \end{aligned}$$

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 $(-\Delta F_{\text{T}}^{\circ}/RT)_1 \log e = \log K_1$) 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

$$\Delta \log p_{\text{BF}_3} - \Delta \log p_{\text{B}} - 3 \Delta \log p_{\text{F}} - (-62.075) \Delta \log T = 5.695 \quad (54)$$

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

$$\begin{aligned} \Delta \log p_{\text{B}_2\text{O}_3} - 2\Delta \log p_{\text{B}} - 3\Delta \log p_{\text{O}} - (-80.593) \Delta \log T \\ = -\log k_{\text{B}_2\text{O}_3} = 5.109 \end{aligned}$$

For H_2O , equation (19) is

$$\begin{aligned} \Delta \log p_{\text{H}_2\text{O}} - 2\Delta \log p_{\text{H}} - \Delta \log p_{\text{O}} - (-29.209) \Delta \log T = -\log k_{\text{H}_2\text{O}} \\ = -0.347 \end{aligned}$$

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

$$\begin{aligned} (72.172) \Delta \log p_{\text{BF}_3} + (233.435) \Delta \log p_{\text{B}_2\text{O}_3} + \dots + \\ (79.493) \Delta \log p_{\text{O}} - (2734.615) \Delta \log A + (644.651) \Delta \log T \\ = (2734.615) \log \frac{905.534}{2734.615} \quad (55) \end{aligned}$$

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

$$\begin{array}{ll}
 \Delta \log n_{\text{BF}_3} = 0.708 & \Delta \log n_{\text{OH}} = 0.490 \\
 \Delta \log n_{\text{B}_2\text{O}_3} = -1.098 & \Delta \log n_{\text{HF}} = 1.378 \\
 \Delta \log n_{\text{BF}} = 1.116 & \Delta \log n_{\text{O}_2} = 0.172 \\
 \Delta \log n_{\text{BH}} = 1.664 & \Delta \log n_{\text{F}_2} = -2.038 \\
 \Delta \log n_{\text{BO}} = 0.613 & \Delta \log n_{\text{H}} = 1.299 \\
 \Delta \log n_{\text{B}_2} = -2.138 & \Delta \log n_{\text{B}} = 0.929 \\
 \Delta \log n_{\text{H}_2} = 0.014 & \Delta \log n_{\text{F}} = 1.221 \\
 \Delta \log n_{\text{H}_2\text{O}} = -0.799 & \Delta \log n_{\text{O}} = 1.457 \\
 \Delta \log A = 0.123 & \Delta \log T = 0.154
 \end{array}$$

These values are to be applied to the initial estimates for n_i , A, and T according to the equation

$$(\log n_i)_{\text{second estimate}} = (\log n_i)_{\text{first estimate}} + \Delta \log n_i \quad (56)$$

For example, the second estimate of n_{BF_3} would be

$$\begin{aligned}
 (\log n_{\text{BF}_3})_{\text{second estimate}} &= \log 1.000 + 0.708 \\
 (n_{\text{BF}_3})_{\text{second estimate}} &= 5.105
 \end{aligned}$$

Another set of correction equations based on the second estimates of n_i , 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_i , A , and T :

$$\begin{array}{ll}
 p_{\text{BF}_3} = 2.6593 & p_{\text{OH}} = 0.6785 \\
 p_{\text{B}_2\text{O}_3} = 0.1235 & p_{\text{HF}} = 7.1456 \\
 p_{\text{BF}} = 0.1936 & p_{\text{O}_2} = 0.9210 \\
 p_{\text{BH}} = 0.0001 & p_{\text{F}_2} = 0.0003 \\
 p_{\text{BO}} = 0.1669 & p_{\text{H}} = 1.7694 \\
 p_{\text{B}_2} = 0 & p_{\text{B}} = 0.0577 \\
 p_{\text{H}_2} = 0.1271 & p_{\text{F}} = 1.3043 \\
 p_{\text{H}_2\text{O}} = 0.0627 & p_{\text{O}} = 5.1903 \\
 A = 1.6622 & T = 4775.5^\circ \text{K}
 \end{array}$$

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 δ are shown in the following table where δ is defined as

$$\delta = \sum_i \left| \log k_i \right| + \left| \log \frac{a_0}{a} \right| + \left| \log \frac{b_0}{b} \right| + \left| \log \frac{c_0}{c} \right| + \left| \log \frac{d_0}{d} \right| + \left| \log \frac{P_0}{P} \right| + \left| \log \frac{h_0}{h} \right|$$

RESULTS OF APPROXIMATIONS								
Parameter	First estimate	Trial number						Desired value
		1	2	3	4	5	6	
a	8	36.840	7.005	6.286	6.079	6.002	6.000	6.000
b	9	23.346	11.605	2.653	2.325	2.008	2.000	2.000
c	8	51.540	24.082	13.104	10.541	10.016	10.000	10.000
d	9	29.641	11.954	33.660	5.240	5.022	5.000	5.000
P	16	125.485	38.000	52.434	21.416	20.436	20.400	20.400
h	2734.615	12055.015	2090.090	2909.950	965.968	912.368	905.594	905.534
δ	26.892	5.861	4.092	2.505	.537	.011	.002	0

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 $^{\circ}\text{K}$ 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.

$$P_{BF_3} = 0.1304$$

$$P_{HF} = 0.3503$$

$$P_H = 0.0867$$

$$P_O = 0.2544$$

$$A = 0.0815$$

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

$$0 = \log 0.3503 - \log 0.0867 - \log p_F - 1.8944$$

$$\log p_F = -0.45556 + 1.06198 - 1.8944$$

$$= -1.28798$$

$$p_F = 0.0515$$

Similarly, p_B can be estimated with the assumed values of P_{BF_3} and p_F

$$0 = \log 0.1304 - \log p_B - 3 \log 0.0515 - 5.6953$$

$$\log p_B = -0.88472 + 3.86394 - 5.6953$$

$$p_B = 0.0019$$

If this procedure is followed for all the remaining constituents, the following list of first estimates can be made:

$$\begin{array}{ll}
 p_{\text{BF}_3} = 0.1304 & p_{\text{OH}} = 0.0150 \\
 p_{\text{B}_2\text{O}_3} = 0.0078 & p_{\text{HF}} = 0.3503 \\
 p_{\text{BF}} = 0.0043 & p_{\text{O}_2} = 0.0269 \\
 p_{\text{BH}} = 0 & p_{\text{F}_2} = 0 \\
 p_{\text{BO}} = 0.0053 & p_{\text{H}} = 0.0867 \\
 p_{\text{B}_2} = 0 & p_{\text{B}} = 0.0019 \\
 p_{\text{H}_2} = 0.0029 & p_{\text{F}} = 0.0515 \\
 p_{\text{H}_2\text{O}} = 0.0009 & p_{\text{O}} = 0.2544 \\
 A = 0.0815 & T = 4000^\circ \text{K}
 \end{array}$$

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°K for n_1 , A , and T , respectively, were again made.

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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

$$\left(\frac{d \log n_1}{d \log T} \right)_S \text{ and } \left(\frac{d \log A}{d \log T} \right)_S, \text{ which are used in equation (44)}$$

(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, . . .	summation of each atomic type over products of reaction per equivalent formula; with subscript, number of atoms of each element within chemical formula
C_p^0	molar specific heat at constant pressure and standard conditions
$C_p^{0'}$	specific heat coefficient for matrix
C_v^0	molar specific heat at constant volume and standard conditions
E_T^0	molar internal energy at standard conditions
e	internal energy per equivalent formula
F_T^0	molar free energy at standard conditions
H_0^0	molar enthalpy at 0° K and standard conditions
H_T^0	molar enthalpy at standard conditions
h	enthalpy per equivalent formula
h'	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_T^0	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
α 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 $\left(-\frac{d \log n_i}{d \log T}\right)_s$ and $\left(-\frac{d \log A}{d \log T}\right)_s$ 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

$$\left[\begin{array}{ccc|c} U_m & & & \\ \alpha_1 & & & \\ \alpha_2 & & & \\ & & & \alpha_3 \\ & & & \end{array} \right] \quad (B1)$$

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

$$\left[\begin{array}{c|c} U_m & \alpha_1 \\ \hline \alpha_2 & \alpha_4 \end{array} \right] \quad (B2)$$

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

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

For computation, equation (B3) is written

$$[\alpha_5] = [\alpha_2 \mid \alpha_3] \begin{bmatrix} -\alpha_1 \\ -U_k \end{bmatrix} \quad (B4)$$

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 $x_{(m+1)}, \dots, x_{(N_p+2)}$ 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

$$\begin{bmatrix} x_1 \\ \cdot \\ \cdot \\ \cdot \\ x_m \end{bmatrix} = - [\alpha_1] \begin{bmatrix} x_{m+1} \\ \cdot \\ \cdot \\ x_{N_p+2} \\ -1 \end{bmatrix}$$

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For illustration, the submatrices $[\alpha_1]$, $[\alpha_2]$, and $[\alpha_3]$ were taken from figure 4 and used to construct figure 7. The last six rows of figure 4 correspond to the matrix $\begin{bmatrix} \alpha_2 & \alpha_3 \end{bmatrix}$ and are shown in figure 7(a). The matrix $\begin{bmatrix} -\alpha_1 \\ U_m \end{bmatrix}$ 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 $[\alpha_5]$ are indicated in figure 8(a) and the results for the example given in figure 7 are shown in figure 8(b). The operation $\sum (\textcircled{1} \textcircled{A})$ is illustrated in detail as follows:

$$\begin{aligned} &0 \times 0 + 0 \times 0 + 0 \times 0 + 1 \times 1.000 + 0 \times 0 + 0 \times 0 + 2 \times 2.000 + \\ &2 \times 2.000 + 1 \times 1.000 + 1 \times 1.000 + 0 \times 0 + 0 \times 0 + \\ &1 \times 1.000 + 0 \times 0 + 0 \times 0 + 0 \times 0 = 12.000 \end{aligned}$$

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_i are entered in row E.
2. Values of the elements of rows \textcircled{A} , \textcircled{B} , \textcircled{C} , and \textcircled{D} for columns 1 through N are obtained by multiplying the elements of row \textcircled{E} by the elements of row $\textcircled{1}$, $\textcircled{2}$, $\textcircled{3}$, and $\textcircled{4}$, respectively.
3. Values of the elements of row \textcircled{F} for columns 1 through N are obtained by multiplying the elements of row \textcircled{E} by the values of $(H_T^0)_i$ 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 (E) 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 (6) is obtained by entering the values of $(\Delta H_T^0)_1/RT$ 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.

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TABLE I - VALUES OF CONSTANTS FOR REACTION OF DIBORANE WITH FLUORINE OXIDE ($B_2H_6 + 5F_2O$)

Product	Fixed					Determined at estimated temperature of 4000° K				
	i	a _i	b _i	c _i	d _i	(H _T ^o) _i	(ΔH _T ^o /RT) _i	(S _T ^o) _i	(C _p ^o) _i	log K _i
Equivalent formula	0	2	6	10	5					
BF ₃	1	1	0	3	0	72.172	-62.0753	105.951	19.738	5.6953
B ₂ O ₃	2	2	0	0	3	233.435	-80.5932	116.760	25.660	5.1094
BF	3	1	0	1	0	262.961	-17.2884	73.904	8.905	1.6342
BH	4	1	1	0	0	356.994	-8.3004	61.412	8.826	-2.6110
BO	5	1	0	0	1	252.739	-18.1834	69.620	9.065	1.0327
B ₂	6	2	0	0	0	572.053	-7.9892	70.580	8.923	-2.7625
H ₂	7	0	2	0	0	99.593	-13.9385	51.054	9.151	-0.4061
H ₂ O	8	0	2	0	1	57.706	-29.2092	72.458	13.300	-0.3470
OH	9	0	1	0	1	76.560	-13.6031	63.989	9.165	-0.1668
HF	10	0	1	1	0	32.016	-19.6736	61.054	9.045	1.8944
O ₂	11	0	0	0	2	37.310	-15.3125	70.783	9.932	-0.3804
F ₂	12	0	0	2	0	96.012	-8.7047	70.813	9.451	-3.1373
H	13	0	1	0	0	105.192		40.306	4.968	
B	14	1	0	0	0	317.778		49.549	4.968	
F	15	0	0	1	0	82.601		51.230	4.974	
O	16	0	0	0	1	79.493		51.479	5.091	

Equation	Gaseous molecules					Atoms			Solid or liquid				
	$\Delta \log n_1$	$\Delta \log n_2$	$\Delta \log n_3$	$\Delta \log n_4$...	$\Delta \log n_Z$	$\Delta \log n_Y$	$\Delta \log n_X$...	$\Delta \log n_1$	$\Delta \log A$	$\Delta \log T$	
(19)	1					$-a_1$	$-b_1$	$-c_1$				$\left(-\frac{\Delta H_1^0}{RT}\right)_1$	$-\log k_1$
		1				$-a_2$	$-b_2$	$-c_2$				$\left(-\frac{\Delta H_2^0}{RT}\right)_2$	$-\log k_2$
			1			$-a_3$	$-b_3$	$-c_3$				$\left(-\frac{\Delta H_3^0}{RT}\right)_3$	$-\log k_3$
				1		$-a_4$	$-b_4$	$-c_4$				$\left(-\frac{\Delta H_4^0}{RT}\right)_4$	$-\log k_4$
				
(21)	$a_1 n_1$	$a_2 n_2$	$a_3 n_3$	$a_4 n_4$...	$a_Z n_Z$	$a_Y n_Y$	$a_X n_X$...	$a_1 n_1$	$-Aa$		$Aa \log \frac{a_0}{a}$
	$b_1 n_1$	$b_2 n_2$	$b_3 n_3$	$b_4 n_4$...	$b_Z n_Z$	$b_Y n_Y$	$b_X n_X$...	$b_1 n_1$	$-Ab$		$Ab \log \frac{b_0}{b}$
	$c_1 n_1$	$c_2 n_2$	$c_3 n_3$	$c_4 n_4$...	$c_Z n_Z$	$c_Y n_Y$	$c_X n_X$...	$c_1 n_1$	$-Ac$		$Ac \log \frac{c_0}{c}$
(20)									$\left(-\frac{\Delta H_T^0}{RT}\right)_1$	$-\log k_1$
(22)	P_1	P_2	P_3	P_4	...	P_Z	P_Y	P_X					$P \log \frac{P_0}{P}$
(23)	$(H_T^{0n})_1$	$(H_T^{0n})_2$	$(H_T^{0n})_3$	$(H_T^{0n})_4$...	$(H_T^{0n})_Z$	$(H_T^{0n})_Y$	$(H_T^{0n})_X$...	$(H_T^{0n})_1$	$-Ah$	$T \sum_1^i (C_P^{0n})_i$	$Ah \log \frac{h_0}{h}$

(a) Adiabatic combustion.

(30)	s_1'	s_2'	s_3'	s_4'	...	s_Z'	s_Y'	s_X'	...	s_1'	$-As$	$\sum_1^i (C_P^{0n})_i$	$As \log \frac{s_0}{s}$
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(b) Isentropic expansion to fixed pressure (substitute in place of heat-balance equation in Fig. 1(a)).

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.



Equation	Gaseous molecules					Atoms			Solid or liquid			
	$\left(\frac{d \log n_1}{d \log T}\right)_a$	$\left(\frac{d \log n_2}{d \log T}\right)_a$	$\left(\frac{d \log n_3}{d \log T}\right)_a$	$\left(\frac{d \log n_4}{d \log T}\right)_a$...	$\left(\frac{d \log n_2}{d \log T}\right)_a$	$\left(\frac{d \log n_Y}{d \log T}\right)_a$	$\left(\frac{d \log n_X}{d \log T}\right)_a$...	$\left(\frac{d \log n_1}{d \log T}\right)_b$		$\left(\frac{d \log A}{d \log T}\right)_b$
(35)	1					-a ₁	-b ₁	-c ₁				$\left(\frac{\Delta H_1^0}{RT}\right)_1$
		1				-a ₂	-b ₂	-c ₂				$\left(\frac{\Delta H_2^0}{RT}\right)_2$
			1			-a ₃	-b ₃	-c ₃				$\left(\frac{\Delta H_3^0}{RT}\right)_3$
				1		-a ₄	-b ₄	-c ₄				$\left(\frac{\Delta H_4^0}{RT}\right)_4$
				
(37)	a ₁ n ₁	a ₂ n ₂	a ₃ n ₃	a ₄ n ₄	...	a ₂ n ₂	a _Y n _Y	a _X n _X	...	a ₁ n ₁	-Aa	
	b ₁ n ₁	b ₂ n ₂	b ₃ n ₃	b ₄ n ₄	...	b ₂ n ₂	b _Y n _Y	b _X n _X	...	b ₁ n ₁	-Ab	
	c ₁ n ₁	c ₂ n ₂	c ₃ n ₃	c ₄ n ₄	...	c ₂ n ₂	c _Y n _Y	c _X n _X	...	c ₁ n ₁	-Ac	
(38)					
						-a ₁	-b ₁	-c ₁				$\left(\frac{\Delta H_1^0}{RT}\right)_1$
(38)	s ₁ '	s ₂ '	s ₃ '	s ₄ '	...	s ₂ '	s _Y '	s _X '	...	s ₁ '	-As	$\sum_1^2 (s_2 n_2)_1$

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; (38), entropy balance. All blank spaces denote zeros.



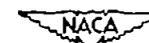
Equation	Gaseous molecules					Atoms			Solid or liquid		$\Delta \log T$		
	$\Delta \log n_1$	$\Delta \log n_2$	$\Delta \log n_3$	$\Delta \log n_4$...	$\Delta \log n_Z$	$\Delta \log n_Y$	$\Delta \log n_X$...	$\Delta \log n_1$			$\Delta \log A$
(19)	1					$-a_1$	$-b_1$	$-c_1$				$\left(\frac{\Delta H_T^0}{-RT}\right)_1$	$-\log k_1$
		1				$-a_2$	$-b_2$	$-c_2$				$\left(\frac{\Delta H_T^0}{-RT}\right)_2$	$-\log k_2$
			1			$-a_3$	$-b_3$	$-c_3$				$\left(\frac{\Delta H_T^0}{-RT}\right)_3$	$-\log k_3$
				1		$-a_4$	$-b_4$	$-c_4$				$\left(\frac{\Delta H_T^0}{-RT}\right)_4$	$-\log k_4$
				
(21)	$a_1 n_1$	$a_2 n_2$	$a_3 n_3$	$a_4 n_4$...	$a_Z n_Z$	$a_Y n_Y$	$a_X n_X$...	$a_1 n_1$	$-Aa$		$Aa \log \frac{a_0}{a}$
	$b_1 n_1$	$b_2 n_2$	$b_3 n_3$	$b_4 n_4$...	$b_Z n_Z$	$b_Y n_Y$	$b_X n_X$...	$b_1 n_1$	$-Ab$		$Ab \log \frac{b_0}{b}$
	$c_1 n_1$	$c_2 n_2$	$c_3 n_3$	$c_4 n_4$...	$c_Z n_Z$	$c_Y n_Y$	$c_X n_X$...	$c_1 n_1$	$-Ac$		$Ac \log \frac{c_0}{c}$
(20)					
						$-a_1$	$-b_1$	$-c_1$				$\left(\frac{\Delta H_T^0}{-RT}\right)_1$	$-\log k_1$
(30)	s_1'	s_2'	s_3'	s_4'	...	s_Z'	s_Y'	s_X'	...	s_1'	$-As$	$\sum_I (C_P^0)_I$	$As \log \frac{s_0}{s}$
(44)	h_1'	h_2'	h_3'	h_4'	...	h_Z'	h_Y'	h_X'	...	h_1'	$-Ah^*$	$T \sum_I (C_P^0)_I$	$Ah^* \log \frac{h_0}{h^*}$

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.



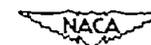
Equation	Gaseous molecules												Atoms						⑥	⑦
	$\Delta \log \frac{n_{B_2}}{n_{F_2}}$	$\Delta \log \frac{n_{B_2O_3}}{n_{F_2O_3}}$	$\Delta \log \frac{n_{BF_3}}{n_{BF_3}}$	$\Delta \log \frac{n_{BF_2}}{n_{BF_2}}$	$\Delta \log \frac{n_{B_2O}}{n_{B_2O}}$	$\Delta \log \frac{n_{B_2O_2}}{n_{B_2O_2}}$	$\Delta \log \frac{n_{B_2O_3}}{n_{B_2O_3}}$	$\Delta \log \frac{n_{H_2O}}{n_{H_2O}}$	$\Delta \log \frac{n_{OH}}{n_{OH}}$	$\Delta \log \frac{n_{HF}}{n_{HF}}$	$\Delta \log \frac{n_{OF_2}}{n_{OF_2}}$	$\Delta \log \frac{n_{BF_2}}{n_{BF_2}}$	$\Delta \log \frac{n_H}{n_H}$	$\Delta \log \frac{n_B}{n_B}$	$\Delta \log \frac{n_F}{n_F}$	$\Delta \log \frac{n_O}{n_O}$	$\Delta \log \frac{n_A}{n_A}$	$\Delta \log \frac{n_T}{n_T}$		
	①	②	③	④	⑤	⑥	⑦	⑧	⑨	⑩	⑪	⑫	⑬	⑭	⑮	⑯	⑰	⑱		
(19)	1														-1	-3		62.075	5.698	
		1													-2		-3	60.663	5.109	
			1												-1	-1		17.826	1.634	
				1											-1	-1		8.300	-2.611	
					1										-1		-1	18.183	1.033	
						1									-4			7.989	-2.765	
							1								-3			15.639	-0.406	
								1							-2		-1	29.809	-0.547	
									1						-1		-1	18.663	-0.167	
										1					-1	-1		19.674	1.594	
										1						-2	15.815	-0.380		
											1				-2		8.706	-2.157		
①				1.000			2.000	2.000	1.000	1.000			1.000				-8.000		-0.992	
②	1.000	2.000	1.000	1.000	1.000	2.000								1.000			-9.000		-2.879	
③	3.000		1.000						1.000		2.000				1.000		-8.000		0.775	
④		3.000			1.000			1.000	1.000		2.000					1.000	-9.000		-2.207	
⑤ (22)	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000			1.688	
⑥ (23)	78.173	235.435	262.961	558.394	252.736	572.063	99.566	57.708	76.660	32.016	27.510	96.012	105.193	317.778	82.801	79.463	-3734.618	644.650	-1512.532	

Figure 4. - Matrix for solution of correction equations for adiabatic combustion of diborane and fluorine oxide after first estimate of n_1 , A, and T. Equations: (19), dissociation of gaseous molecules; (21), mass balance; (22), pressure; (23) heat balance. All blank spaces denote zeros.



Equation	Gaseous molecules												Atoms				$\Delta \log A$	$\Delta \log F$	
	$\Delta \log B_{BF_3}$	$\Delta \log B_{B_2O_3}$	$\Delta \log B_{BF}$	$\Delta \log B_{BF_2}$	$\Delta \log B_{BO}$	$\Delta \log B_{B_2}$	$\Delta \log B_{BF_2}$	$\Delta \log B_{H_2O}$	$\Delta \log B_{OH}$	$\Delta \log B_{HF}$	$\Delta \log B_{O_2}$	$\Delta \log B_{F_2}$	$\Delta \log B_H$	$\Delta \log B_B$	$\Delta \log B_F$	$\Delta \log B_O$			
(19)	1													-1	-3			63.075	0
		1												-2		-3		80.693	0
			1											-1	-1			17.288	0
				1									-1	-1				8.500	0
					1									-1		-1		16.168	0
						1								-2				7.969	0
							1						-2					15.939	0
								1						-2			-1	29.209	0
									1					-1		-1		13.803	0
										1				-1		-1		19.874	0
											1					-2		15.313	0
											1				-2		8.765	0	
(21)							0.0058	0.0019	0.0150	0.5503			0.0867				-0.4598		0.01258
	0.1304	0.0156	0.0043		0.0058									0.0019			-0.1578		0.00235
	0.3913		0.0043						0.3505						0.0818		-0.7978		0.00760
		0.0234			0.0053			0.0009	0.0150		0.0588					0.2544	-0.5596		0.02206
(22)	0.1304	0.0078	0.0045		0.0053		0.0029	0.0009	0.0150	0.3503	0.0269		0.0867	0.0019	0.0515	0.2544		0.02695	
(30)	14.0648	0.9704	0.3569		0.4137		0.1751	0.0760	1.0568	21.4318	2.0458		3.7455	0.1140	2.8395	13.2827	-63.4405	8.464	0.09447

Figure 5. - Matrix for solution of correction equations for isentropic expansion to 1 atmosphere for the reaction of diborane with fluorine oxide. Equations: (19), dissociation of gaseous molecules; (21), mass balance; (22), pressure; (30), entropy balance. All blank spaces denote zeros.



Equation	Gaseous molecules												Atoms						
	$\Delta \log n_{BF_3}$	$\Delta \log n_{B_2O_3}$	$\Delta \log n_{BF}$	$\Delta \log n_{BH}$	$\Delta \log n_{BO}$	$\Delta \log n_{B_2}$	$\Delta \log n_{H_2}$	$\Delta \log n_{H_2O}$	$\Delta \log n_{OH}$	$\Delta \log n_{HF}$	$\Delta \log n_{O_2}$	$\Delta \log n_{F_2}$	$\Delta \log n_H$	$\Delta \log n_B$	$\Delta \log n_F$	$\Delta \log n_O$	$\Delta \log A$	$\Delta \log T$	
(19)	1													-1	-3			68.078	3.695
		1												-2		-5		60.593	8.109
			1											-1	-1			17.288	1.634
				1										-1	-1			8.800	-3.611
					1									-1		-1		18.188	1.033
						1								-2				7.989	-2.765
							1							-2				15.939	-0.406
								1						-2			-1	29.809	-0.347
									1					-1			-1	13.603	-0.167
										1				-1		-1		19.874	1.634
											1						-2	16.313	-0.560
											1				-2		8.705	-3.157	
(21)				1.000			2.000	2.000	1.000	1.000			1.000				-8.000		-0.999
	1.000	2.000	1.000	1.000	1.000	2.000								1.000			-9.000		-5.879
	5.000		1.000							1.000		2.000			1.000		-8.000		0.778
		3.000			1.000			1.000	1.000		2.000					1.000	-9.000		-2.297
(30)	103.964	114.775	71.917	69.425	67.633	68.593	49.067	70.471	68.002	59.067	66.798	66.222	38.519	47.568	49.243	49.492	-1080.944	161.162	-163.234
(44)	0.750	2.564	2.672	3.623	2.569	5.778	1.035	0.664	0.815	0.547	0.437	1.025	1.066	5.215	0.269	0.639	-88.035	-7.113	-13.760

Figure 6. - Matrix for solution of correction equations for isentropic expansion to local velocity of sound for reaction of diborane 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.



Equation	Gaseous molecules												Atoms							
	$\Delta \log_{P_{HF_6}}$	$\Delta \log_{P_{B_2O_6}}$	$\Delta \log_{P_{HF}}$	$\Delta \log_{P_{RH}}$	$\Delta \log_{P_{BO}}$	$\Delta \log_{P_{B_2}}$	$\Delta \log_{P_{H_2}}$	$\Delta \log_{P_{H_2O}}$	$\Delta \log_{P_{OH}}$	$\Delta \log_{P_{HF}}$	$\Delta \log_{P_{O_2}}$	$\Delta \log_{P_{F_2}}$	$\Delta \log_{P_H}$	$\Delta \log_{P_B}$	$\Delta \log_{P_F}$	$\Delta \log_{P_O}$	$\Delta \log_A$	$\Delta \log_T$		
Ⓐ				1.000			2.000	2.000	1.000	1.000			1.000				-8.000	-0.999		
Ⓑ	(21)	1.000	2.000	1.000	1.000	2.000								1.000			-8.000	-5.979		
Ⓒ		5.000		1.000						1.000		2.000			1.000		-8.000	0.776		
Ⓓ			5.000			1.000		1.000	1.000		2.000					1.000	-8.000	-2.297		
Ⓔ	(22)	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000		1.000		
Ⓕ	(23)	72.172	253.435	282.961	556.894	252.729	572.052	99.596	57.706	76.560	22.016	57.510	96.012	105.192	517.778	82.601	79.493	-2724.615	644.651	-1512.592

(a) Submatrix $[a_2|a_3]$ taken from lower portion of figure 4. Equations: (21), mass balance; (22), pressure; (23), heat balance.

Ⓐ	$\Delta \log_{P_H}$				1			2	2	1	1			1					
Ⓑ	$\Delta \log_{P_B}$	1	2	1	1	1	2							1					
Ⓒ	$\Delta \log_{P_F}$	3		1						1		2				1			
Ⓓ	$\Delta \log_{P_O}$		3			1			1	1		2					1		
Ⓔ	$\Delta \log_A$																1		
Ⓕ	$\Delta \log_T$	-82.076	-80.895	-17.288	-8.500	-18.165	-7.969	-13.959	-29.209	-15.605	-19.674	-15.515	-6.706					1	
Ⓖ		-5.698	-5.109	-1.624	2.611	-1.063	2.765	0.406	0.347	0.187	-1.694	0.580	5.157						1

(b) Submatrix $\begin{bmatrix} -a_1 \\ U_m \end{bmatrix}$ transposed ($-[a_1]$ taken from fig. 4).



Figure 7. - Breakdown of complete matrix of example to facilitate calculation. All blank spaces denote zeros.

$\Delta \log n_H$	$\Delta \log n_B$	$\Delta \log n_F$	$\Delta \log n_O$	$\Delta \log A$	$\Delta \log T$	
$\Sigma(1A)$	$\Sigma(2A)$	$\Sigma(3A)$	$\Sigma(4A)$	$\Sigma(5A)$	$\Sigma(6A)$	$\Sigma(7A)$
$\Sigma(1B)$	$\Sigma(2B)$	$\Sigma(3B)$	$\Sigma(4B)$	$\Sigma(5B)$	$\Sigma(6B)$	$\Sigma(7B)$
$\Sigma(1C)$	$\Sigma(2C)$	$\Sigma(3C)$	$\Sigma(4C)$	$\Sigma(5C)$	$\Sigma(6C)$	$\Sigma(7C)$
$\Sigma(1D)$	$\Sigma(2D)$	$\Sigma(3D)$	$\Sigma(4D)$	$\Sigma(5D)$	$\Sigma(6D)$	$\Sigma(7D)$
$\Sigma(1E)$	$\Sigma(2E)$	$\Sigma(3E)$	$\Sigma(4E)$	$\Sigma(5E)$	$\Sigma(6E)$	$\Sigma(7E)$
$\Sigma(1F)$	$\Sigma(2F)$	$\Sigma(3F)$	$\Sigma(4F)$	$\Sigma(5F)$	$\Sigma(6F)$	$\Sigma(7F)$
(a) Method of calculation of reduced matrix.						
12.000	1.000	1.000	3.000	-8.000	-127.873	1.391
1.000	13.000	4.000	7.000	-9.000	-283.010	-16.322
1.000	4.000	16.000	0	-8.000	-240.597	-13.564
3.000	7.000	0	17.000	-9.000	-333.400	-17.383
8.000	9.000	8.000	9.000	0	-294.871	-3.866
885.360	2873.620	786.118	1241.423	-2734.615	-45475.661	-766.321

(b) Numerical value of reduced matrix.



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