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APPROXIMATE METHOD FOR THE CALCULATION OF FLOWS WITH RELAXATION†

R. PRUD'HOMME

Office National d'Études et de Recherches Aéronautiques
Chatillon-sous-Bagneux, Seine, France
Translated by James L. Lauer, Sun Oil Company,
Marcus Hook, Pennsylvania 19061

Abstract—A method is given for calculating the relaxed flow of gaseous mixtures consisting of a diatomic molecule together with atoms generated by its dissociation. Following this, the principal formulas are given for use in applying the method to a mixture consisting of a given number of chemical species and reactions. Computational results are provided for hydrogen, showing the tendency toward relaxed flow of the principal parameters and functions involved in the suggested method.

INTRODUCTION

THE calculation of the performance of a rocket motor can be made in different ways, depending on the hypotheses accepted *a priori*. Very simple methods have already been applied: thus, for example, when the temperature, pressure, and composition of the gaseous mixture in the combustion chamber are known, specific impulses and characteristic velocities have been calculated for a given nozzle by considering the flow isentropic, the chemical composition remaining invariable. This flow, called "frozen," is very easy to analyze. Similarly, flows have been determined by assuming that the different species composing the gaseous mixture react among themselves, the composition at any point being that of chemical equilibrium, the entropy remaining always constant. This kind of flow is called flow with equilibrium composition, or just equilibrium flow. The determination of the conditions at the nozzle throat, where the flow velocity is supposed to be equal to that of sound, is the only calculation which is a little difficult.

However, the performances thus obtained are either too pessimistic for frozen flow or optimistic for equilibrium flow in the majority of cases, the reality lying between the two. This is due to the many

† Translated from *Entropie*, No. 5, 21-34 (1965) with the kind permission of O.N.E.R.A.

phenomena which are ignored when one or the other of the two preceding hypotheses is made. Thus the flow is considered unidimensional, and the effects of a boundary layer, of heat transfer, of chemical reaction rates, and of vibrational relaxation of the molecules are neglected. In particular, in the temperature ranges considered, the phenomena of chemical relaxation assume importance. We will restrict ourselves here to their study.

In effect, relaxation phenomena are not important throughout the entire length of the nozzle.¹ We distinguish between three zones of flow: First of all, in the combustion chamber and in a large part of the convergent portion of the nozzle, the flow is practically equilibrium flow, then a zone of chemical relaxation appears, which is more or less extended and which may include the throat, and finally, the flow becomes frozen in the divergent part of the nozzle and remains that way to the outlet.

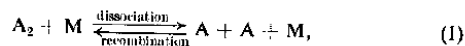
Bray² looks on the relaxation zone as being extremely narrow, the progression toward equilibrium being suddenly frozen, and the location of freezing being determined by a criterion related to the rates of dissociation and recombination. The real flow can thus be replaced by a succession of two flows, one at equilibrium and the other one frozen. Because of this view, Bray's method ignores any variation of entropy due to chemical reaction.

We, on the other hand, propose to calculate the flow as exactly as possible by supposing that relaxation phenomena play a more or less important role throughout the nozzle. In a problem of this type, we are going to encounter certain difficulties, in particular, if for frozen flow and for equilibrium flow the equations were ordinary because no differential equation came into play; on the other hand, in the case of flow with relaxation, we are meeting with a system of differential equations which is rather difficult to resolve by numerical integration, primarily in the first zone where the flow is close to equilibrium. Moreover, the curves of solution of the system contain a singular point somewhere in the divergent portion of the nozzle, which cannot be exactly determined. Thus we are forced to employ restrictive hypotheses and to utilize an approximate method of calculation.

Our aim is thus to find an approximate method of calculation which takes maximum account of chemical relaxation phenomena and gives better results for the evaluation of the performance of rocket motors than the limits of frozen and equilibrium flow.

METHOD OF CALCULATION OF FLOWS WITH
CHEMICAL RELAXATION

Our work refers to gaseous flow in a nozzle of axial symmetry. The gaseous mixture considered is composed of diatomic molecules A_2 and of atoms A obtained by dissociation of the molecules A_2 , the dissociation and recombination reactions being of the type:



Species M could be a molecule A_2 or an atom A or even a neutral species not participating in the reaction.

The gas mixture is supposed to obey the law of mixtures of perfect gases; it is proceeding from a combustion chamber where the gases are supposed to be at rest and the flow which follows is effected without heat exchange with the outside medium. Finally, the phenomenon shall be unidimensional, *i.e.*, all the thermodynamic variables as well as the composition of the gas mixture will be considered the same at any point of a cross-section at right angles to the axis of the nozzle, which has abscissa x and area $\Sigma_{(x)}$.

Kinetic Study of the Chemical Phenomena

In this section the origin of the chemical relaxation, *i.e.*, of the rates of reaction, is to be taken up. Classical chemical kinetics³ shows us that, at constant volume, the net rate of appearance of species A from the two reactions of Equation (1) is the following:

$$\frac{d\rho n_A}{dt} = 2[k_D \rho n_{A_2} - k_R (\rho n_A)^2] \rho n, \quad (2)$$

where it is assumed that the specific reaction rates of recombination, k_R , and thus also the specific rates of dissociation, k_D , are the same in the presence of species A_2 as of species A .

This equality, which brings into play the mass per unit volume, ρ , the concentrations in terms of number of moles per unit mass, n_A and n_{A_2} , the total number of moles per unit mass, n , and the time, t , can be replaced by the following one for the case of a dynamic flow at constant mass rate such as we are considering:

$$v \frac{dn_A}{dx} = 2(k_D n_{A_2} - k_R \rho n_A^2) \rho n, \quad (3)$$

where the time does not enter explicitly, but where the abscissa, x , and the speed of flow, V , appear. It should be observed that although the form of Equation (3) is well defined, this is not the case for the temperature-dependent functions, k_R and k_D ; here is the first problem posed by the study of relaxed flows. Several theories provide a way of determining the specific rates, k_R and k_D . Thus the collision theory^{4,5} or that of the activated complex⁶ result in expressions of the form

$$k = a \exp [-E/(RT)], \quad (4)$$

for k_R and k_D ; in this expression, E is the energy of activation of the

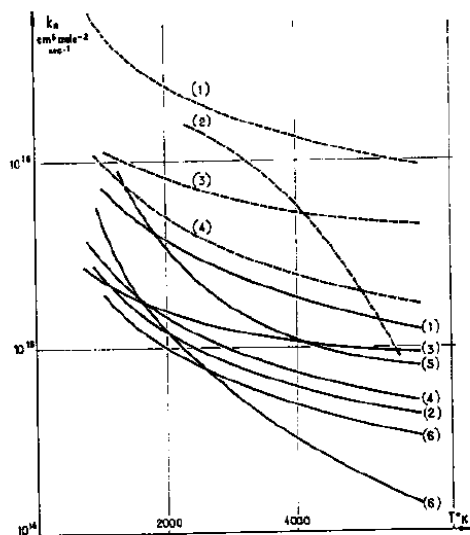
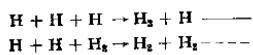


Figure 1.—Specific Reaction Rates as Functions of Temperature for:



According to the Formulas Given by Different Authors. (1) Patch, (2) Sutton, (3) Eschenroeder, (4) Rink, (5) Gardiner, (6) Westenberg.

reaction, R the universal gas constant, T the absolute temperature, and a the Arrhenius factor, which is a function of the temperature and whose expression is generally assumed to be of the form

$$a = \bar{A}T^{-\bar{s}}, \quad (5)$$

where the constants \bar{A} and \bar{s} differ according to the authors.

We will not discuss these diverse theories in detail, but will simply note that specific reaction rates differing by a factor of 100 are not uncommon. By way of example, Figure 1 shows the temperature-dependence of the specific recombination rate of hydrogen according to different authors. In our calculation, average values will be used, but the true influence of the errors in k_R and k_D upon the relaxed flow remains unknown.

General Equations

1. Equations of chemical concentration

The following relations are obvious. They bring together the concentrations and the atomic mass, W_A , of the element A:

$$n = n_A + n_{A_2} \quad (\text{conservation of species}); \quad (6)$$

$$1/W_A = n_A + 2n_{A_2} \quad (\text{conservation of mass}). \quad (7)$$

A third relation connects the concentrations, the temperature T and the pressure p , in the case of chemical equilibrium: It is the law of mass action, which introduces the equilibrium constant in terms of the pressures K_{A_2} :

$$\frac{n \cdot n_{A_2}}{n_A^2} = pK_{A_2}; \quad (8)$$

in the case of relaxed flows we write analogously:

$$\frac{n \cdot n_{A_2}}{n_A^2} = pK_{A_2} (1 - B). \quad (9)$$

This relation introduces the non-dimensional parameter B , which we will express, in what follows, as a function of the reaction velocity.

2. Equation given by the chemical kinetics

By taking into account the equilibrium relation

$$\frac{k_B}{k_D RT} = K_{A_2},$$

and putting

$$\Lambda = -\frac{V}{2\rho^2 k_B n \cdot n_{A_2}^2}, \quad (10)$$

the speed of appearance of species A can finally be written as

$$\frac{dn_A}{dx} = \frac{B}{\Lambda}. \quad (11)$$

3. Conservation of mass flow rate

The mass flow rate is conserved, whence:

$$\rho V = \frac{\dot{m}}{\sum_{(x)}}, \quad (12)$$

4. Conservation of energy

For adiabatic flow the conservation of energy can be expressed by a relation between the enthalpy per unit mass h at a point of flow, the velocity V , and the enthalpy per unit mass in the combustion chamber; thus

$$h_0 = h + \frac{1}{2}V^2, \quad (13)$$

where the expression for the enthalpy per unit mass h is the following:

$$h = n_A(H_T^\circ)_A + n_{A_2}(H_T^\circ)_{A_2}, \quad (14)$$

$(H_T^\circ)_A$ and $(H_T^\circ)_{A_2}$ being the standard molar enthalpies of species A and A_2 , respectively.

5. *Adiabaticity*

The nozzle plays the role of an adiabatic wall: during constant flow, the conservation of the quantity of heat Q can be expressed by

$$\frac{dQ}{dx} = 0. \quad (15)$$

Under these conditions, Gibbs' formula⁷ giving the elementary variation of the entropy per unit mass takes the following form:

$$\frac{ds}{dx} = -R \left(M_A \frac{dn_A}{dx} + M_{A_2} \frac{dn_{A_2}}{dx} \right). \quad (16)$$

The free enthalpies M_A and M_{A_2} can be expressed in terms of the standard free enthalpies by means of the following equations:

$$\begin{aligned} M_A &= (M_T^\circ)_A - \ln \frac{n_A}{n} p, \\ M_{A_2} &= (M_T^\circ)_{A_2} - \ln \frac{n_{A_2}}{n} p. \end{aligned} \quad (17)$$

Taking into account Equations (7) and (9) as well as the relation

$$\ln K_{A_2} = 2(M_T^\circ)_A - (M_T^\circ)_{A_2}, \quad (18)$$

we obtain at last:

$$\frac{ds}{dx} = \frac{R}{2} \ln(1-B) \frac{dn_A}{dx}. \quad (19)$$

To complete Equation (19), we now give the expression for the entropy per unit mass of the mixture:

$$\begin{aligned} s &= n_A (S_T^\circ)_A + n_{A_2} (S_T^\circ)_{A_2} \\ &\quad - R \left(n_A \ln \frac{n_A}{n} + n_{A_2} \ln \frac{n_{A_2}}{n} + n \ln p \right), \end{aligned} \quad (19')$$

$(S_T^\circ)_A$ and $(S_T^\circ)_{A_2}$ being the standard molar entropies of A and A_2 .

Study of the System Defining Relaxed Flow

The set of the following independent equations summarizes the preceding results and defines relaxed flow completely:

$$\begin{aligned}
 \text{(a)} \quad n &= n_A + n_{A_2}, \\
 \text{(b)} \quad \frac{1}{W_A} &= n_A + 2n_{A_2}, \\
 \text{(c)} \quad \frac{nn_{A_2}}{n_A^2} &= pK_{A_2}(1 - B), \\
 \text{(d)} \quad B &= \Lambda \frac{dn_A}{dx}, \\
 \text{(e)} \quad \Lambda &= -\frac{V}{2\rho^2 k_{11} n n_A^2}, \\
 \text{(f)} \quad \rho V &= \frac{\dot{m}}{\Sigma_{(x)}}, \quad (20) \\
 \text{(g)} \quad h &= n_A(H_T^\circ)_A + n_{A_2}(H_T^\circ)_{A_2}, \\
 \text{(h)} \quad h_0 &= h + \frac{1}{2}V^2, \\
 \text{(i)} \quad \frac{p}{\rho} &= nRT, \\
 \text{(j)} \quad s &= n_A(S_T^\circ)_A + n_{A_2}(S_T^\circ)_{A_2} \\
 &\quad - R \left(n_A \ln \frac{n_A}{n} + n_{A_2} \ln \frac{n_{A_2}}{n} + n \ln p \right), \\
 \text{(k)} \quad \frac{ds}{dx} &= \frac{R}{2} \ln(1 - B) \frac{dn_A}{dx}.
 \end{aligned}$$

1. *Elimination of the variables ρ and V*

Equations (g) and (h) give the following expression for velocity:

$$V = \sqrt{2(h_0 - (H_T^\circ)_A n_A - (H_T^\circ)_{A_2} n_{A_2})}; \quad (21)$$

V in the following equations is assumed defined by Equation (21)

where V is expressed as a function of the temperature T and of the concentrations.

Under these conditions, the set of Equations (20) can be reduced to the following three equations after elimination of p and V :

$$C_{pt} \frac{d \ln T}{dx} - Rn \frac{d \ln p}{dx} + \frac{H}{T} \frac{dn_A}{dx} = 0, \quad (22)$$

$$\left(1 + \frac{TC_{pt}}{V_2}\right) \frac{d \ln T}{dx} - \frac{d \ln p}{dx} + \left(\frac{1}{2n} + \frac{H}{V_2}\right) \frac{dn_A}{dx} = \frac{d \ln \Sigma}{dx}, \quad (23)$$

$$\frac{B}{A} = \frac{dn_A}{dx}, \quad (24)$$

to which Equations (20c) and (20e) must be added as well as the following definitions:

$$H = (H_T^0)_A - \frac{1}{2}(H_T^0)_{A_2}, \quad (25)$$

and

$$C_{pt} = n_A C_{pA} + n_{A_2} C_{pA_2}, \quad (26)$$

where C_{pA} and C_{pA_2} represent the specific heats of A and A_2 at constant pressure. C_{pt} will be called the specific heat at constant concentrations and pressure or, more simply, the frozen specific heat.

From Equations (22), (23), and (24) the following equations and sets of equations can be deduced; note that matrix ω^* is the following:

$$\omega^* = \begin{bmatrix} C_{pt} & -Rn \\ 1 + \frac{TC_{pt}}{V^2} & -1 \end{bmatrix}; \quad (27)$$

$$\left\{ \begin{array}{l} \left[\frac{d \ln T}{dx} \right] \\ \left[\frac{d \ln p}{dx} \right] \\ \frac{dn_A}{dx} = \frac{B}{A} \end{array} \right. = \left[\begin{array}{l} -\frac{H}{T} \frac{dn_A}{dx} \\ -\left(\frac{1}{2n} + \frac{H}{V^2}\right) \frac{dn_A}{dx} + \frac{d \ln \Sigma}{dx} \end{array} \right] \quad (28)$$

is a set of the differential equations

$$\left\{ \begin{array}{l} \omega^* \begin{bmatrix} d \ln T \\ d \ln p \end{bmatrix} = \begin{bmatrix} -\frac{H}{T} dn_A \\ -\left(\frac{1}{2n} + \frac{H}{V^2}\right) dn_A + d \ln \Sigma \end{bmatrix} \\ dn_A = \frac{B}{\Lambda} dx. \end{array} \right. \quad (29)$$

The corresponding difference equations are

$$\left\{ \begin{array}{l} \omega^* \begin{bmatrix} \Delta \ln T \\ \Delta \ln p \end{bmatrix} = \begin{bmatrix} -\frac{H}{T} \Delta n_A \\ -\left(\frac{1}{2n} + \frac{H}{V^2}\right) \Delta n_A + \Delta \ln \Sigma \end{bmatrix} \\ \Delta n_A = \frac{B}{\Lambda} \cdot \Delta x, \end{array} \right. \quad (30)$$

We will utilize (in an approximate method of calculation) this set of equations, connecting to the nearest second order the variations $\Delta \ln T$, $\Delta \ln p$, Δn_A , and Δx .

2. General remarks

With the help of Equations (f) and (i), the pressure p can be expressed as a function of the temperature T , of the abscissa x , and of the concentrations, so that B/Λ can be considered a function of these variables:

$$\frac{B}{\Lambda} = -\frac{2\rho^2 k_R n n_A^2}{V} \left[1 - \frac{n n_{A_2}}{p K_{A_2} n_A^2} \right], \quad (31)$$

and, after elimination of dp/dx , the set of Equations (28) can be written:

$$\left\{ \begin{array}{l} \det (\omega_{(n_A, T)}) \frac{d \ln T}{dx} \\ \quad = Rn \frac{d \ln \Sigma}{dx} - \left[\frac{H}{T} \left(\frac{nRT}{V^2} - 1 \right) + \frac{R}{2} \right] \left(\frac{B}{\Lambda} \right)_{(n_A, T, x)}, \\ \frac{dn_A}{dx} = \left(\frac{B}{\Lambda} \right)_{(n_A, T, x)}. \end{array} \right. \quad (32)$$

When the quantity $\det(\omega^*)$ is not zero, this system satisfies the Lipschitz⁸ conditions and therefore has a single solution $(T(x), n_A(x))$ provided two initial conditions, e.g., $T_0 = T(x_0)$ and $n_{A_0} = n_A(x_0)$, are fixed.

The calculations prove that there is a point in the nozzle which we will call F, where the determinant $\det(\omega^*)$ vanishes; this generally implies that dT/dx is infinite. Point F is located downstream of the geometric throat.

If we take it for granted that the real steady flow does not contain any point where the temperature gradient is zero or infinite, we must require the following conditions to be simultaneously satisfied at point F:

$$\begin{cases} \det(\omega^*) = 0 \\ Rn \frac{d \ln \Sigma}{dx} - \left[\frac{H}{T} \left(\frac{nRT}{V^2} - 1 \right) + \frac{R}{2} \frac{B}{A} \right] = 0. \end{cases} \quad (33)$$

These conditions can be interpreted in various ways. Thus Westenberg⁹ considers the rate \dot{m} as an *a priori* unknown, since the proper value of the rate satisfying conditions, Equations (33), can be determined by approximation. In the following we will assume that the rate \dot{m} has been chosen *a priori* and is close to the real rate, and we will see how it is possible to solve the problem in the case where the flow is close to equilibrium flow in the convergent portion of the nozzle.

3. Stability of the linearized system

Although the methods of linearization are subject to question in the totally general case, a study of the stability of the linearized system leads to conclusions well verified by calculation.

Let us therefore assume as known a relaxed flow and let us induce the following differences at a point of abscissa x_1 :

$$\begin{aligned} \bar{T}_1 &= \ln T_1' - \ln T_1 \\ \bar{p}_1 &= \ln p_1' - \ln p_1 \\ \bar{n}_{A_1} &= n_{A_1}' - n_{A_1}. \end{aligned} \quad (34)$$

We want to follow the variations of the differences \bar{T} , \bar{p} , and \bar{n}_A which differentiate the perturbed system of temperature T' , pressure p' , and concentration n_A' from the given relaxed flow of temperature T , pressure p , and concentration n_A . Let us designate the difference

$x - x_1$ by \bar{x} . Then we will be able to reach conclusions concerning the stability of the linearized system.

The linearized system, Equations (28), can be written:

$$\begin{aligned} \frac{C_{pt} dT}{d\bar{x}} - Rn \frac{d\bar{p}}{d\bar{x}} + \frac{H}{T} \frac{d\bar{n}_A}{d\bar{x}} &= 0, \\ \left(1 + \frac{TC_{pt}}{V^2}\right) \frac{dT}{d\bar{x}} - \frac{d\bar{p}}{d\bar{x}} + \left(\frac{1}{2n} + \frac{H}{V^2}\right) \frac{d\bar{n}_A}{d\bar{x}} &= 0, \\ \Lambda \frac{pK_{A_2} n_{A_2}^2}{nn_{A_2}} \frac{d\bar{n}_A}{d\bar{x}} + \frac{2H}{RT} T - \bar{p} - \frac{1}{2\pi} n_A &= 0, \end{aligned} \quad (35)$$

π being equal to $n_A^2 n_{A_2} n_{A_2}$.

From the definitions of the following matrices

$$\begin{aligned} \bar{X}^* &= \begin{bmatrix} T \\ \bar{p} \\ \bar{n}_A \end{bmatrix}, \\ A^* &= \begin{bmatrix} C_{pt} & -Rn & \frac{H}{T} \\ 1 + \frac{TC_{pt}}{V^2} & -1 & \frac{1}{2n} + \frac{H}{V^2} \\ 0 & 0 & \Lambda \frac{pK_{A_2}^2 n_{A_2}}{nn_{A_2}} \end{bmatrix}, \\ C^* &= \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ \frac{2H}{RT} & -1 & -\frac{1}{2\pi} \end{bmatrix}, \end{aligned} \quad (36)$$

we obtain the following matrix equation with constant coefficients:

$$A^* \frac{d\bar{X}^*}{d\bar{x}} + C^* \bar{X}^* = 0. \quad (37)$$

This differential equation has the following general solution:

$$\bar{X}^* = a_1 X_1^* + a_2 X_2^* + a_3 X_3^* e^{-\lambda \bar{x}}, \quad (38)$$

where the constant coefficients a_1 , a_2 , and a_3 are determined by the initial difference.

X_1^* and X_2^* are column matrices associated with two independent fixed vectors perpendicular to the vector of components,

$$\frac{2H}{RT}, -1, -\frac{1}{2\pi};$$

X_3^* is the column matrix,

$$X_3^* = \begin{bmatrix} Y \\ Z \\ 1 \end{bmatrix}, \text{ where the quantities } Y \text{ and } Z \text{ are defined by the equations:}$$

$$Y = -\frac{\frac{H}{T}\left(\frac{nRT}{V^2} - 1\right) + \frac{R}{2}}{\det(\omega^*)}, \quad Z = \frac{\frac{H}{T} - \frac{C_{pf}}{2n}}{\det(\omega^*)}. \quad (39)$$

λ is the only non-zero eigenvalue of the characteristic equation associated with Equation (37); it is expressed by

$$\lambda = \frac{1}{2\pi\Lambda} \frac{nn_{A2}}{pK_{A2}n_A^2} \frac{\det(\Omega^*)}{\det(\omega^*)}, \quad (40)$$

where Ω^* is the following matrix:

$$\Omega^* = \begin{bmatrix} C_{pf} & -\frac{2\pi H}{T} & -\frac{2\pi H}{T} - nR \\ -\frac{2H}{RT} & -1 & 0 \\ 1 + \frac{TC_{pf}}{V^2} & -\pi\left(\frac{1}{n} + \frac{2H}{V^2}\right) & -1 - \pi\left(\frac{1}{n} + \frac{2H}{V^2}\right) \end{bmatrix} \quad (41)$$

whose precise significance we will see further down. Calculations made for hydrogen show that $\det(\Omega^*)$ vanishes at a point E located up-stream of the geometric throat. It is negative upstream of E and positive downstream of E. λ is thus negative between points E and F and positive

elsewhere. When λ is negative, the system is unstable; when λ is positive, the following situations can arise:

(1) a_1 and a_2 are not both zero; then when \bar{x} becomes infinite, the difference X^* tends toward $a_1 X_1^* + a_2 X_2^*$, a non-zero column matrix. The new flow does not rejoin the initial flow but becomes stabilized along a new progression.

(2) $a_1 = a_2 = 0$. When \bar{x} becomes infinite, all differences tend toward zero; stability is obtained. Stability of the linear oscillator associated with the equations of relaxed flow thus occurs when λ is positive and when the initial differences are proportional respectively to Y for T_1 , to Z for β_1 , and to unity for n_A .

This last conclusion is important to the method we are about to explain, for the differences satisfying the preceding proportionality relations are precisely those applying to the possible first-order errors which our calculation procedure might introduce.

Thus we see that a brief study of the stability of the linearized system can also provide interesting information on the real system.

Method of Corrections

The particular form of the matrix equation of Equations (28) allows us to consider a family of progressions along the nozzle. In effect, we can look on the collection of progressions as satisfying the matrix equation of Equations (28), with the second equation:

$$\frac{dn_A}{dx} = \frac{B}{\Lambda}$$

replaced by a relation of the type:

$$f(i) \left(T, p, n_A, \frac{d \ln T}{dx}, \frac{d \ln p}{dx}, \frac{dn_A}{dx}, x \right) = 0, \quad (42)$$

index i designating the progression considered.

The relaxed flow forms a part of the family of progressions (i), where the function $f(i)$ has a particular form f_{rel} ; Equation (42) becomes:

$$f_{rel} = \frac{nn_{A_2}}{pK_{A_2}n_A^2} - 1 + \Lambda \frac{dn_A}{dx} = 0. \quad (43)$$

Thus a progression (i) will be characterized by the following two equations:

$$\omega^* \begin{bmatrix} \frac{d \ln T_{(i)}}{dx} \\ \frac{d \ln p_{(i)}}{dx} \end{bmatrix} = \begin{bmatrix} -\frac{H}{T} \frac{dn_{A(i)}}{dx} \\ -\left(\frac{1}{2n} + \frac{H}{V^2}\right) \frac{dn_{A(i)}}{dx} + \frac{d \ln \Sigma}{dx} \end{bmatrix}, \quad (44)$$

$$f_1\left(T, p, n_A, \frac{d \ln T}{dx}, \frac{d \ln p}{dx}, \frac{dn_A}{dx}, x\right) = 0, \quad (45)$$

and we will further assume that it satisfies Equations (20), except, in general, Equations (c), (d), (e), and (k) which are peculiar to relaxed flow.

Progression (i) will be utilized in the calculation of the relaxed flow between abscissas x_1 and $x_1 + \Delta x$.

Therefore, at abscissa x_1 , the temperature, pressure, and concentrations are assumed equal for the two flows; however, the derivatives are different and a first-order calculation of the variations $\Delta \ln T$, $\Delta \ln p$, and Δn_A will give different values of T , p , and n_A at the abscissa $x_1 + \Delta x$.

Putting

$$\begin{aligned} (\Delta \ln T)_{(i)}^{\text{rel.}} &= (\Delta \ln T)_{\text{rel.}} - (\Delta \ln T)_{(i)}, \\ (\Delta \ln p)_{(i)}^{\text{rel.}} &= (\Delta \ln p)_{\text{rel.}} - (\Delta \ln p)_{(i)}, \\ (\Delta n_A)_{(i)}^{\text{rel.}} &= (\Delta n_A)_{\text{rel.}} - (\Delta n_A)_{(i)}, \end{aligned} \quad (46)$$

the values of $x_1 + \Delta x$ will be the following, approximately to the second order:

$$\begin{aligned} T_{\text{rel.}}(x_1 + \Delta x) &= T_{(i)}(x_1 + \Delta x) + T_{\text{rel.}}(x_1)(\Delta \ln T)_{(i)}^{\text{rel.}}, \\ p_{\text{rel.}}(x_1 + \Delta x) &= p_{(i)}(x_1 + \Delta x) + p_{\text{rel.}}(x_1)(\Delta \ln p)_{(i)}^{\text{rel.}}, \\ n_{A\text{rel.}}(x_1 + \Delta x) &= n_{A(i)}(x_1 + \Delta x) + (\Delta n_A)_{(i)}^{\text{rel.}}. \end{aligned} \quad (47)$$

In the following the first members of Equations (46) will be called corrections. The corrections thus verify the following matrix equality approximately to the second order:

$$\omega^* \begin{bmatrix} (\Delta \ln T)_{(i)}^{\text{rel.}} \\ (\Delta \ln p)_{(i)}^{\text{rel.}} \end{bmatrix} = \begin{bmatrix} -\frac{H}{T} (\Delta n_A)_{(i)}^{\text{rel.}} \\ -\left(\frac{1}{2n} + \frac{H}{V^2}\right) (\Delta n_A)_{(i)}^{\text{rel.}} \end{bmatrix} \quad (48)$$

Thus we see that if we know how to calculate progression (*i*), we will have an approximation of the relaxed flow by utilizing Equations (47) and (48).

The present problem is to determine progression (*i*), which should be the one most acceptable for our calculations.

In the following paragraphs we will study two progressions which we will call "pseudo-equilibrium" and "pseudo-frozen," respectively. The quantities pertaining to these progressions will be provided with indices (*e'*) and (*f*), respectively.

The advantage of these two progressions lies in the circumstance that their associated systems of differential equations have integrals which make their calculation just as easy as the calculations of equilibrium and frozen flow.

On the other hand, they are defined in large portions of the nozzle and are very close to relaxed flow. As they do not present instability problems, we can regard them as a stable basis for relaxed flow.

1. Pseudo-equilibrium

We will call pseudo-equilibrium a progression (*e'*) whose associated function $f_{(e')}$ is the following:

$$f_{(e')} = \frac{nn_{\Delta_2}}{pK_{\Delta_2}n_{\Delta}^2} - 1 + B_{e'} = 0, \quad (49)$$

where $B_{e'}$ is a numerical constant with values between 0 and 1. Such a progression has the following first integrals:

$$s' = n_{\Delta}(S_{T^{\circ}})_{\Delta} + n_{\Delta_2}(S_{T^{\circ}})_{\Delta_2} - R \left(n_{\Delta} \ln \frac{n_{\Delta}}{n} + n_{\Delta_2} \ln \frac{n_{\Delta_2}}{n} + n \ln p(1 - B_{e'}) \right), \quad (50)$$

$$\dot{m} = \frac{pV}{nRT} \cdot \Sigma(x), \quad (51)$$

$$B_{e'} = 1 - \frac{nn_{\Delta_2}}{pK_{\Delta_2}n_{\Delta}^2}, \quad (52)$$

where s' , \dot{m} , and $B_{e'}$ are constants.

All the thermodynamic functions can be calculated from Equations (50) and (52) by means of the temperature T only.

In particular, it is possible to determine the maximum impulse $(\rho V)_e$; we note that this maximum is reached when

$$\det(\Omega^*) = 0.$$

We observe that point E, which was defined in the study of the stability, is such that, in it, $(\rho V)_e$ is a maximum and we will call it for this reason the *throat of pseudo-equilibrium*.

On the other hand, we note that the pseudo-equilibrium becomes a progression in a state of equilibrium and of entropy s' , when $B_e = 0$ in Equations (50), (51), and (52); with this equilibrium in the nozzle, the flow rate \dot{m} will be defined by the sound velocity in the geometric throat. The situation will be analogous for pseudo-equilibrium in the nozzle. But, in the following, our preoccupation with this question will be unnecessary, as the flow rate chosen will be that of relaxed flow and we will not need to consider pseudo-equilibrium for the entire nozzle but rather a sequence of pseudo-equilibria in intervals of small length Δx .

We are now in the position to list expressions for the corrections satisfying the matrix Equation (48). By putting $B_e = B_{(x_1)}$, the following values are obtained:

$$\begin{aligned} (\Delta \ln T)_e^{rel} &= Y \left[\left(\frac{B}{\Lambda} \right)_{(x_1)} - \left(\frac{dn_A}{dx} \right)_{e'(x_1)} \right] \Delta x, \\ (\Delta \ln p)_e^{rel} &= Z \left[\left(\frac{B}{\Lambda} \right)_{(x_1)} - \left(\frac{dn_A}{dx} \right)_{e'(x_1)} \right] \Delta x, \\ (\Delta n_A)_e^{rel} &= \left[\left(\frac{B}{\Lambda} \right)_{(x_1)} - \left(\frac{dn_A}{dx} \right)_{e'(x_1)} \right] \Delta x, \end{aligned} \quad (53)$$

where Y and Z are defined by Equations (39).

Equations (47) finally give the values of T, p , and n_A at the abscissa $x_1 + \Delta x$.

In fact the calculation of the pseudo-equilibrium is easier when the temperature rather than the abscissa is fixed so that $T_e(x_1 + \Delta x)$ is given instead of $x_1 + \Delta x$; and we will write:

$$T_e(x_1 + \Delta x) = T(x_1) - \Delta T. \quad (54)$$

This remark does not alter our method at all.

Finally Equations (53) show that, because of Equation (38), an error in the value of

$$\left[\left(\frac{B}{\Lambda} \right)_{(x_1)} - \left(\frac{dn_A}{dx} \right)_{e(x_1)} \right] \Delta x$$

is of little importance because the relaxed flow is stable with respect to such differences.

2. Practical utilization of the method of corrections with pseudo-equilibrium.

Two problems become evident:

(1) When the mass flow rate \dot{m} and the initial conditions are fixed, the progression obtained will not, in general, correspond to a real flow.

(2) To apply the method of corrections, the real conditions at at least one point of abscissa x must be known.

These two problems require us to make restrictive hypotheses which will limit the range of applicability of our method.

a. First hypothesis.

We assume that between the combustion chamber and the geometric throat of the nozzle the real flow is close to the equilibrium flow. This means that Equation (43) should be satisfied to the second order by the equilibrium values; *i.e.*, we must have

$$\left(\frac{nn_{A_2}}{pK_{A_2}n_{A_1}} \right)_e - 1 + \Lambda_e \left(\frac{dn_A}{dx} \right)_e = 0, \quad (55)$$

or because of Equation (8):

$$\Lambda_e \left(\frac{dn_A}{dx} \right)_e \simeq 0. \quad (56)$$

Now only has it become possible to assume that equilibrium flow constitutes a good approximation of relaxed flow. To specify Equation (56), we note that the following inequality:

$$\Lambda_e \left(\frac{dn_A}{dx} \right)_e < \varepsilon, \quad (57)$$

must be verified in the convergent part of the nozzle. Here ε is a positive number given in advance and always much less than one.

As

$$\Lambda_e \left(\frac{dn_A}{dx} \right)_e$$

is an increasing function of the abscissa x , it will suffice that the inequality, Equation (57), be verified in the throat.

Under these conditions we will assume that the value m_e of the mass flow rate of the equilibrium flow appropriate to the given nozzle can be chosen to take the place of the mass flow rate \dot{m} . This first restrictive hypothesis is satisfied when the temperature T in the convergent portion of the nozzle is sufficiently elevated for chemical equilibrium to be practically realized there.

It should be observed that the first term of the inequality, Equation (57), is analogous to that employed in Bray's criterion². However, when the inequality is realized with ε close to one and at times even equal to 2, Bray assumes that chemical equilibrium occurs and that the flow becomes frozen when

$$\Lambda_e \left(\frac{dn_A}{dx} \right)_e$$

becomes greater than a chosen value of ε .

Our procedure thus differs significantly from the one proposed by Bray.

b. Second Hypothesis.

To resolve the second problem, the actual conditions at the nozzle entrance must be known.

But only the conditions in the combustion chamber are given, where thermodynamic equilibrium is assumed to hold vigorously at zero velocity. To express our second hypothesis, we fall back on the basic equations of relaxed flow. Obviously the following matrix equation can be deduced from Equations (30):

$$\Omega^* \begin{bmatrix} \Delta \ln T \\ \Delta \ln [K_{A_2}(1 - B)] \\ \Delta \ln p \end{bmatrix} = \begin{bmatrix} 0 \\ \frac{\Delta B}{1 - B} \\ \Delta \ln \Sigma \end{bmatrix}, \quad (58)$$

where Ω^* is the matrix defined by Equation (41).

In the case of pseudo-equilibrium we find an equation of the same form:

$$\Omega^* \begin{bmatrix} (\Delta \ln T)_{e'} \\ (\Delta \ln [K_{A_2}(1 - B_{e'})]_{e'}) \\ (\Delta \ln p)_{e'} \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ \Delta \ln \Sigma \end{bmatrix}. \quad (59)$$

By subtraction of Equation (58) from Equation (59) member by member, the following equation is deduced on the assumption that at the point of abscissa x_1 considered the quantities are chosen as in the treatment of pseudo-equilibrium.

$$\Omega^* \begin{bmatrix} (\Delta \ln T)_{e'}^{rel.} \\ (\Delta \ln [K_{A_2}(1 - B)]_{e'}^{rel.}) \\ (\Delta \ln p)_{e'}^{rel.} \end{bmatrix} = \begin{bmatrix} 0 \\ \frac{\Delta B}{1 - B} \\ 0 \end{bmatrix}. \quad (60)$$

The correction of temperature and pressure can be calculated from Equation (60) by means of the variation of the parameter B and independently of the abscissa x .

Finally, the following expressions are obtained for the corrections:

$$\begin{aligned} (\Delta \ln T)_{e'}^{rel.} &= -2\pi \frac{\det(\omega^*)}{\det(\Omega^*)} Y \frac{\Delta B}{1 - B}, \\ (\Delta \ln p)_{e'}^{rel.} &= -2\pi \frac{\det(\omega^*)}{\det(\Omega^*)} Z \frac{\Delta B}{1 - B}, \\ (\Delta n_{A_2})_{e'}^{rel.} &= -2\pi \frac{\det(\omega^*)}{\det(\Omega^*)} \frac{\Delta B}{1 - B}. \end{aligned} \quad (61)$$

Our second hypothesis consists of the assumption that, between the combustion chamber and a point of abscissa x_1 near the entrance of the nozzle, the values of B are equal to those of the product

$$\Lambda_e \left(\frac{dn_A}{dx} \right)_e.$$

Starting with the combustion chamber where the velocity is zero, we finally obtain the following set of equalities where the values in the

combustion chamber are designated by the index (0):

$$\frac{\Delta B}{1 - B} = \Lambda_{e(x_1)} \left(\frac{dn_A}{dx} \right)_{e(x_1)}, \quad (62)$$

$$\begin{cases} T(x_1) = T_{e(x_1)} + T_0 \left(\frac{-2\pi \frac{H}{T}}{C_{p_f} + \frac{4\pi H^2}{RT^2}} \right) \Lambda_{e(x_1)} \left(\frac{dn_A}{dx} \right)_{e(x_1)} \\ p(x_1) = p_{e(x_1)}, \\ n_{A(x_1)} = n_{Ae(x_1)} + \left(\frac{2\pi \frac{H}{T}}{C_{p_f} + \frac{4\pi H^2}{RT^2}} \right) \Lambda_{e(x_1)} \left(\frac{dn_A}{dx} \right)_{e(x_1)}. \end{cases} \quad (63)$$

Beginning with a point of abscissa x_1 , we are thus in a position to apply the method of corrections step by step. The scheme of calculation carried out between points of abscissas x_n and x_{n+1} is outlined below.

Values known for X_n : all the thermodynamic parameters and their first derivatives with respect to x , all the concentrations and their first derivatives:

1. Determination of the pseudo-equilibrium by calculation of B_e and s'
2. Calculation of $p_{e'(x_{n+1})}$ and $(n_A)_{e'(x_{n+1})}$ such that

$$T_{e'(x_{n+1})} = T_{(x_n)} - \Delta T$$

with the help of Equations (50) and (52).

3. Calculation of $\Sigma(x_{n+1})$ with the help of Equation (51), then calculation of x_{n+1} .

4. Calculation of the corrections with the help of Equations (53).

5. Calculation of $T(x_{n+1})$, $p(x_{n+1})$, $n_A(x_{n+1})$ with the help of Equations (47) and determination of $B(x_{n+1})$ by means of Equation (c) of Equations (20).

We note that our method cannot be applied between points E and F and that in the vicinity of these points the corrections are so lacking in precision that its application there is not advised either. This restriction, by the way, is true for all approximate methods.

Therefore, we will choose two points E' and F' of abscissas $x_{E'} < x_E$ and $x_{F'} > x_F$, respectively, and assume that the values of $x_{E'}$ are deduced from those obtained for x_E by a pseudo-equilibrium calculation without correction. Points E' and F' will be chosen very close to the geometric throat, and their choice will be determined by the signs of the quantities $\det(\omega^*)$ and $\det(\Omega^*)$, respectively.

The values found for F' are false, but as the zone E'F' is very small, the values of T , p , and n_A vary little and, furthermore, the errors committed satisfy the stability conditions of the linearized system.

3. Pseudo-frozen

We will call "pseudo-frozen" a progression satisfying Equation (44) and the following:

$$f_r\left(T, p, n_A, \frac{d \ln T}{dx}, \frac{d \ln p}{dx}, \frac{dn_A}{dx}, x\right) = \left(\frac{dn_A}{dx}\right)_r = 0. \quad (64)$$

We will assume that progression (f') also satisfies the other conditions defining a progression (i). The system of equations associated with this progression possesses the following three first integrals:

$$s^r = n_A(S_T^{\circ})_A + n_A(S_T^{\circ})_{A_1} - Rn \ln p, \quad (65)$$

where s^r is a constant

$$\dot{m} = \frac{pV}{nRT} \Sigma(x), \quad (66)$$

$$\text{constant} = n_A. \quad (67)$$

As in the case of pseudo-equilibrium, Equations (65) and (67) allow the determination of all the thermodynamic parameters independently of the abscissa x and as a function only of the temperature T .

Furthermore, we observe that the quantity $(\rho V)_r$ is a maximum when the following equality is realized at point F, which, therefore, is called the throat of pseudo-frozen flow:

$$\det(\omega^*) = C_{pl} \left(\frac{nRT}{V^2} - 1 \right) + Rn = 0. \quad (68)$$

The corrections obtained by utilizing pseudo-frozen flow are the following:

$$\begin{aligned}(\Delta \ln T)_i^{\text{rel}} &= Y \left(\frac{B}{\Lambda} \right)_{(x_i)} \Delta x, \\(\Delta \ln p)_i^{\text{rel}} &= Z \left(\frac{B}{\Lambda} \right)_{(x_i)} \Delta x, \\(\Delta n_A)_i^{\text{rel}} &= \left(\frac{B}{\Lambda} \right)_{(x_i)} \Delta x.\end{aligned}\quad (69)$$

Possible errors in the values of

$$\left(\frac{B}{\Lambda} \right)_{(x_i)} \Delta x$$

will not be disturbing, for they satisfy the stability conditions. The calculation itself is performed in the same manner as in the case of the pseudo-equilibrium.

In general, the values of B/Λ decrease rather rapidly in proportion to the advance into the divergent part of the nozzle, and it will be interesting to use the method of corrections starting with a certain abscissa for which we will have

$$\left| \frac{B}{\Lambda} \right| < \left| \frac{B}{\Lambda} - \left(\frac{dn_A}{dx} \right)_e \right|. \quad (70)$$

(See figure 2.)

Furthermore, pseudo-frozen flow with correction will advantageously replace relaxed flow for large abscissas where B is close to unity.

Utilization of pseudo-frozen flow from the point E' of the preceding paragraph gives for F' results rather different from those obtained by the assumption of pseudo-equilibrium, but the values begin to coincide again after a certain abscissa, as calculations made for hydrogen have shown. This result is very encouraging, and can be considered as confirmation of the stability of relaxed flow.

4. Real flow

On account of our hypotheses and the results obtained in the case of hydrogen, it appears likely that the flow found by the method of pseudo-equilibrium with corrections is close to relaxed flow.

However, the region of the geometric throat, *i.e.*, the region of the nozzle contained between points E' and F', remains indeterminate. We have employed a pseudo-equilibrium to determine the conditions at F' from a knowledge of those existing at E', but the fact nevertheless remains that we know nothing about the flow between these two points. In fact, there is no reason why the pseudo-equilibrium employed should

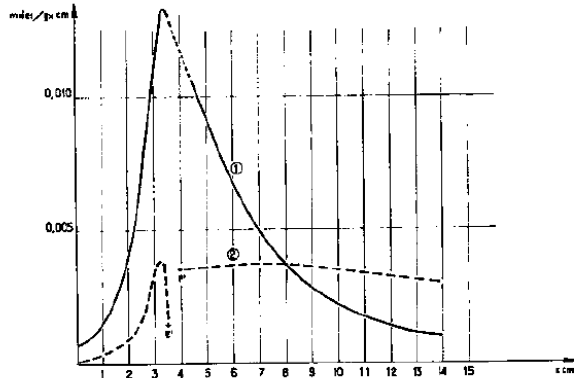


Figure 2.—① Trace of $\left| \frac{B}{A} \right|$ along the Nozzle, ② Trace of $\left| \frac{B}{A} - \left(\frac{dR^H}{dx} \right)_{e'} \right|$ in the Case of Hydrogen at $T^0 = 4000^\circ\text{K}$ and $p = 10$ atm.

be adapted to the nozzle considered, for the maximum of the quantity $(\rho V)_{e'}$ is probably not equal to \dot{m}/Σ_c , the ratio of the rate of mass flow to the area of the cross-section of the nozzle at the geometric throat C.

If we assume that between E' and F' pseudo-equilibrium is a good approximation of relaxation, the shape of the nozzle between these two points and, in particular, the radius of the throat's cross-section must be modified in such a way as to adapt the pseudo-equilibrium to the new nozzle thus obtained.

To find the area of the perpendicular cross-section $\Sigma_{(a)}$, the point where $(\rho V)_{e'}$ is a maximum must be found, *i.e.*, the point where $\det(\Omega^*)_{e'}$ is zero. This calculation is analogous to that employed for determining the values of the thermodynamic parameters at the throat in the case of equilibrium flow.

Thus it does not matter which profile, tangent to the old profile at the points of abscissas x_E and x_F , and satisfying the preceding condition, will be suitable. Point F will be determined by writing that $\det(\Omega^*)_E$ vanishes there and that the simultaneous conditions of Equations (33) are verified there with $B = B_E$, since both for equilibrium and for pseudo-equilibrium there is no indeterminacy at the frozen throat.

By replacing the relaxed flow by a pseudo-equilibrium between E' and F' , we therefore have eliminated the problem posed by the frozen throat; thus another condition shows up:

$$\begin{cases} \det(\Omega^*)_{E'} = 0, \\ \frac{d \ln \Sigma}{dx} = 0. \end{cases} \quad (71)$$

Finally, we must assume that the radius of curvature of the nozzle profile be continuous at E' and at F' .

RESULTS OBTAINED IN THE CASE OF A FLOW OF HYDROGEN

Figure 3 shows the profile of the nozzle considered. The reactions taking place are of the type of Equation (1), element A being the atom of hydrogen; the specific recombination rate is that used by Westenberg:⁹

$$k_R = 2 \times 10^{18} T^{-1} \text{ cm}^6 \text{ mole}^{-2} \text{ sec}^{-1}. \quad (72)$$

The case where the temperature in the combustion chamber is about 4000 °K and the pressure about 10 atm was studied in more detail. This case satisfies the hypothesis of Equation (55) well with $\varepsilon = 0.3$; increments of temperature $\Delta T = 5$ °K were chosen. The results obtained were plotted in Figures 4, 5, 6, 7, 8, and 9. These results have allowed us to make the following observations: First of all, when the abscissa x_1 at the start of the calculations is rather small, the subsequent flow is very close to equilibrium flow, and the values obtained are found to oscillate in a significant manner up to a certain abscissa and then to become stabilized. This result appears to be disconcerting at first, but we have found that the representative curves obtained by the use of different starting points converge to a unique curve.

The choice of the characteristic temperature steps (initially $\Delta T = 5$ °K was chosen, then $\Delta T = 100$ °K) has little influence on the flow in the convergent portion, and when we employed steps of

$\Delta T = 5^\circ\text{K}$. again in the divergent portion, the flow was found to be identical with the preceding one.

Thus the determination of the thermodynamic parameters in the convergent portion is rather rapidly made without need for the employment of very small steps. On the other hand, we are forced to use

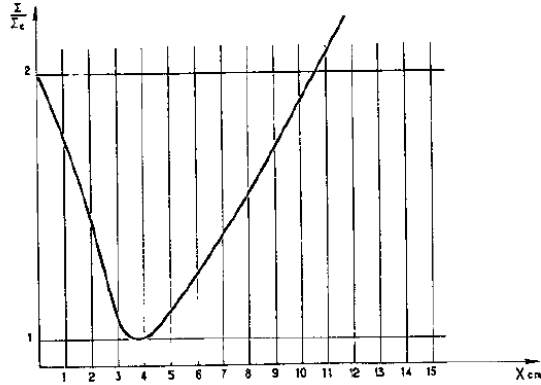


Figure 3.—Plot of the Cross-sectional Area Ratio as a Function of the Abscissa for the Nozzle Whose Parametric Equations are the Following, for the Abscissa and the Radius of the Cross-section, respectively:

$$x = \frac{2.125t - 0.03t^2 + 0.0012889t^3}{1 + 0.0012889t^3}$$

$$r = 70.71067812 + \frac{0.26794916t^3 - 27.00004119t^2 - 65113583000}{t^3 + 931.3691427}$$

rather small steps in the divergent portion, for the corrections become important and the precision of the results will depend on the step size.

In the region downstream of the divergent portion the parameter B tends to unity asymptotically; there is thus rapid "freezing" and our development can be replaced to advantage by a pseudo-frozen flow, *e.g.*, from $B = 0.99$ on.

We also made calculations for cases that do not satisfy the hypothesis of Equations (55). Thus, by maintaining a combustion chamber temperature of 4000°K , but taking pressures of 1 atm or 0.1 atm, the flow obtained is not likely to correspond to a real flow and, in particular,

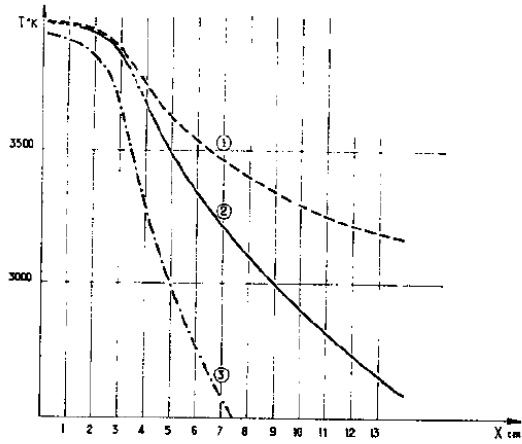


Figure 4.—Temperature Profile of Hydrogen Expansion with $T^0 = 4000^\circ\text{K}$ and $p^0 = 10$ atm. ① Equilibrium, ② Relaxed, ③ Frozen from the Combustion Chamber.

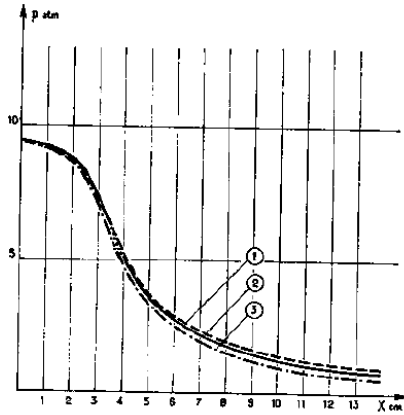


Figure 5.—Pressure Profile of Hydrogen Expansion with $T^0 = 4000^\circ\text{K}$ and $p^0 = 10$ atm. ① Equilibrium, ② Relaxed, ③ Frozen.

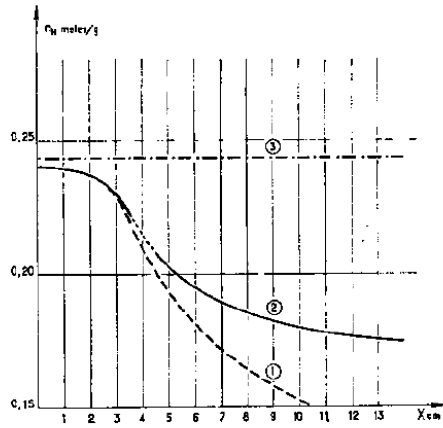


Figure 6.—Profile of Atomic Hydrogen Concentration in Hydrogen Expansion with $T^{\circ} = 4000^{\circ}\text{K}$ and $p^{\circ} = 10$ atm. ① Equilibrium, ② Relaxed, ③ Frozen.

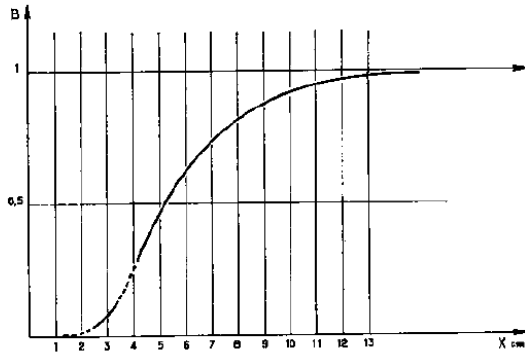


Figure 7.—Change of the Parameter B in Relaxed Flow of Hydrogen Expansion with $T^{\circ} = 4000^{\circ}\text{K}$ and $p^{\circ} = 1$ atm.

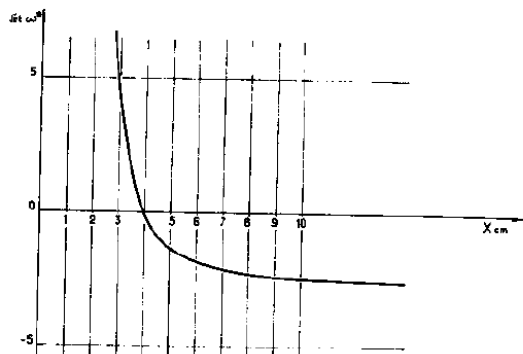


Figure 8.—Change of $\det(\omega^*)$ in Relaxed Flow of Hydrogen Expansion with $T^\circ = 4000^\circ\text{K}$ and $p^\circ = 10$ atm.

the flow rate \dot{m} chosen is surely false; but the criteria of stability have been found to be well verified.

However, in the present state of our method's development, it seems that we should limit ourselves to the cases for which the restrictive hypotheses for pseudo-equilibrium are verified.

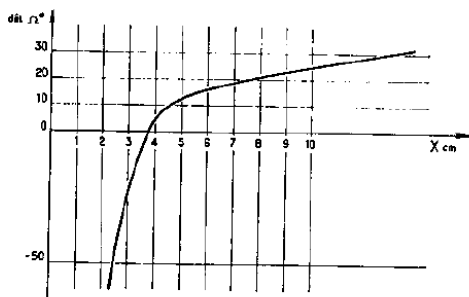


Figure 9.—Change of $\det(\Omega^*)$ in Relaxed Flow of Hydrogen Expansion with $T^\circ = 4000^\circ\text{K}$ and $p^\circ = 10$ atm.

Figure 10 shows the modification of the nozzle profile in the region of the throat, as indicated in the discussion of real flow.

Figure 2 shows that, from an abscissa of $x = 8$ cm on, we should use the method of corrections for "pseudo-frozen" flow, as the corrections for this case are less.

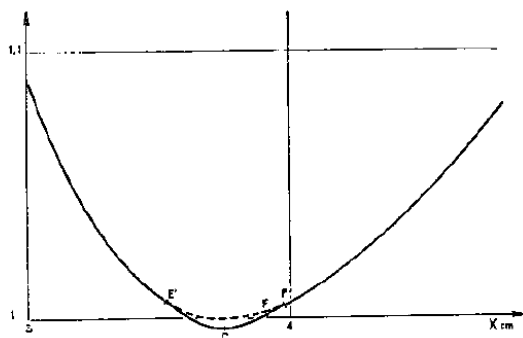


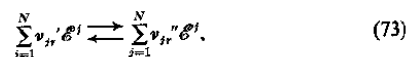
Figure 10.—Modification of the Throat Between Points E' and F'.

EXTENSION OF THE METHOD OF CORRECTIONS TO SEVERAL REACTIONS

When the gaseous mixture includes N chemical species formed from L elements so that K reactions are possible, our method can be generalized very well. This is due to the linear character of the equations.

The detail of the theory will be the subject of a later publication. Nevertheless, the principal equations obtained are given here.

The r th equation between the species \mathcal{E}^j can be written:



where v_{jr}' and v_{jr}'' are the stoichiometric coefficients with respect to the species \mathcal{E}^j in the two terms of the reaction.

It is always possible to choose L independent chemical species, *i.e.*, none of them can be obtained by a reaction among the other $L - 1$.

Let n_j be the number of moles of species \mathcal{E}^j per gram of mixture and

let us designate by α^* the column matrix of the other species numbered $L+1$ to N .

$$\alpha^* = \begin{bmatrix} n_{L+1} \\ \vdots \\ n_N \end{bmatrix}. \quad (74)$$

The L independent species are thus determined as a function of α^* by the following equation:

$$\begin{bmatrix} n_1 \\ \vdots \\ n_L \end{bmatrix} = (D^*)^{-1} \left\{ \begin{bmatrix} n_1^0 \\ \vdots \\ n_L^0 \end{bmatrix} - E^* \alpha^* \right\} \quad (75)$$

The quantities n_i^0 represent the number of gram atoms of element A^i contained in a gram of mixture.

The matrices D^* and E^* are the following (the α_i stand for the number of atoms of element A^i contained in the formula weight of species \mathcal{S}^j):

$$D^* = \begin{bmatrix} \alpha_{11} & \cdots & \alpha_{1L} \\ \vdots & & \vdots \\ \alpha_{L1} & \cdots & \alpha_{LL} \end{bmatrix}; \quad (76)$$

matrix D^* has an inverse,

$$E^* = \begin{bmatrix} \alpha_{1,L+1} & \cdots & \alpha_{1N} \\ \vdots & & \vdots \\ \alpha_{L,L+1} & \cdots & \alpha_{LN} \end{bmatrix}. \quad (77)$$

Furthermore, by defining matrix H^* as the following

$$H^* = \begin{bmatrix} (H_T^0)_{L+1} \\ \vdots \\ (H_T^0)_N \end{bmatrix} - (E^*)^t [(D^*)^{-1}]^t \begin{bmatrix} (H_T^0)_1 \\ \vdots \\ (H_T^0)_L \end{bmatrix}, \quad (78)$$

an equality of differential forms is obtained which is fully comparable to the matrix equality of Equations (29) obtained for molecule A_2 :

$$\omega^* \begin{bmatrix} d \ln T \\ d \ln p \end{bmatrix} = \begin{bmatrix} -\frac{(H^*)'}{T} d\alpha^* \\ -\frac{1}{n} dn - \frac{(H^*)'}{T^2} d\alpha^* + d \ln \Sigma \end{bmatrix}. \quad (79)$$

The relaxed flow is thus perfectly defined when we add the following equations to Equation (79):

$$B^* = -(G^*)' \left\{ \begin{bmatrix} M_{L+1} \\ \vdots \\ M_N \end{bmatrix} - (E^*)' [(D^*)^{-1}]' \begin{bmatrix} M_1 \\ \vdots \\ M_L \end{bmatrix} \right\}, \quad (80)$$

$$\frac{d\alpha^*}{dx} = \psi^*(B^*), \quad (81)$$

B^* is a column matrix of $N - L$ rows corresponding to $N - L$ reactions numbered from 1 to $N - 1$, e.g., whose matrix of the stoichiometric coefficients G^* has an inverse and is the following:

$$G^* = \begin{bmatrix} (v'_{L+1,1} - v'_{L+1,L}) & \cdots & (v'_{L+1,N-L} - v'_{L+1,N-L}) \\ \vdots & & \\ (v'_{N1} - v'_{N1}) & \cdots & (v'_{N,N-L} - v'_{N,N-L}) \end{bmatrix}. \quad (82)$$

The terms M_j of Equation (80) are numerically close to the free enthalpies of species \mathcal{E}^j divided by the product RT .

The vectorial function ψ^* depends on the specific rates of the reactions, the thermodynamic functions, and the concentrations.

Just as in the case of the diatomic molecule A_2 , we can bring together a family (i) of progressions which satisfy Equations (79) and $N - L$ supplementary equations of type:

$$f_{(i)} \left(T, p, \alpha^*, \frac{d \ln T}{dx}, \frac{d \ln p}{dx}, \frac{d\alpha^*}{dx}, x \right) = 0. \quad (83)$$

Two arbitrary progressions of family (i) have been chosen:

(1) the pseudo-equilibrium defined by Equation (79) and the matrix equation:

$$B_{e^*} + (G^*)' \left\{ \begin{bmatrix} M_{L+1} \\ \vdots \\ M_N \end{bmatrix} - (E^*)' (D^*)^{-1}' \begin{bmatrix} M_1 \\ \vdots \\ M_L \end{bmatrix} \right\} = \begin{bmatrix} O \\ \vdots \\ O \end{bmatrix}, \quad (84)$$

where B_{e^*} is a constant column matrix;

(2) the pseudo-frozen flow for which there are $N - L$ equations summarized by the matrix equation:

$$\frac{d\alpha^*}{dx} = \begin{bmatrix} O \\ \vdots \\ O \end{bmatrix}. \quad (85)$$

The throat of the pseudo-equilibrium case satisfies the equation:

$$\begin{vmatrix} C_{pt} & -R\eta & \frac{(H^*)^t}{T} - R(U^*)^t \\ 1 + \frac{TC_{pt}}{\nu^2} & -1 & \frac{(H^*)^t}{\nu^2} \\ \frac{H^*}{RT} & -U^* & -\Gamma^* \end{vmatrix} = 0, \quad (86)$$

with the following definitions:

$$U^* = \begin{bmatrix} 1 \\ \vdots \\ 1 \end{bmatrix} - (E^*)' (D^*)^{-1}' \begin{bmatrix} 1 \\ \vdots \\ 1 \end{bmatrix}, \quad (87)$$

$$\Gamma^* = \begin{bmatrix} n_{L+1}^{-1} & \cdots & 0 \\ \vdots & & \vdots \\ 0 & \cdots & n_N^{-1} \end{bmatrix} + (E^*)' [(D^*)^{-1}]' \begin{bmatrix} n_1^{-1} & \cdots & 0 \\ \vdots & & \vdots \\ 0 & \cdots & n_L^{-1} \end{bmatrix} (D^*)^{-1} E^* \quad (88)$$

The throat of the pseudo-frozen flow satisfies the equation:

$$\det(\omega^*) = 0.$$

Thus it is obvious that relaxed flow can be determined by means of restrictive hypotheses, starting with calculations of pseudo-equilibria, which are not more complicated than calculations of equilibrium and corrections.

Finally we want to give the relations which connect the corrections:

$$\omega^* \begin{bmatrix} (\Delta \ln T)_e^{\text{rel.}} \\ (\Delta \ln p)_e^{\text{rel.}} \end{bmatrix} = \begin{bmatrix} -\frac{(H^*)_t}{T} (\Delta \alpha^*)_e^{\text{rel.}} \\ -\frac{1}{n} (\Delta n)_e^{\text{rel.}} - \frac{(H^*)_t}{V^2} (\Delta \alpha^*)_e^{\text{rel.}} \end{bmatrix}$$

The pseudo-frozen state could be employed equally well.

CONCLUSION

First results of the calculations indicate that the proposed method of corrections leads to an approximate determination of relaxed flows. In the case of hydrogen flow, the calculation has been performed by means of an IBM 610. The calculation of one point by the method of corrections on the basis of pseudo-equilibrium takes about twenty minutes, while on the basis of a pseudo-frozen state it takes only ten minutes. The method of corrections employs calculational programs of the performances with equilibrium flow and frozen flow of the kind such that the calculation time could be considerably reduced with a more powerful machine. However, we believe that we have reached our goal, which was the approximate determination of the performance of a rocket on the basis of relaxed flow; in fact, the proposed method leads to calculation of the specific impulse and, especially, of the characteristic velocity.

We think we will be able eventually to determine the errors caused by our first-order approximation, as well as to learn the influence of the values of the specific reaction rate k_R on the relaxed flow. This will be the subject of later calculations. Finally, the calculations of relaxed flows in the case of several species will be the subject of a later publication.

NOMENCLATURE

A, A_2, M	Species present
$\Sigma_{(x)}$	A cross-sectional area normal to the axis of the nozzle
B	Non-dimensional parameter equal to $1 - \frac{nn_{A_2}}{pK_{A_2}n_{A_2}^2}$
B_0	Numerical constant
C_{pA}, C_{pA_2}	Molar specific heat at constant pressure of species A and A_2 , respectively
C_{pt}	Specific heat per unit mass of the mixture at constant pressure and concentrations
$f(i)$	Function characterizing a progression (i)
h	Enthalpy per unit mass
H_T°	Standard molar enthalpy
k_D, k_R	Specific reaction rates of dissociation and recombination, respectively
K_{A_2}	Equilibrium constant in terms of partial pressures
M_A, M_{A_2}	Free enthalpies of species A and A_2 , respectively
M_T°	Standard molar free enthalpy
n_A, n_{A_2}	Number of moles of species A and A_2 , respectively, contained in a unit mass of mixture
n	Total number of moles per unit mass of mixture
\dot{m}	Rate of mass flow
p	Static pressure
Q	Quantity of heat
R	Perfect gas constant
S_T°	Standard molar entropy
s	Entropy per unit mass of mixture
T	Absolute static temperature
t	Time
V	Velocity of flow
W_A	Atomic mass of A
x	Abscissa of a cross-section normal to the axis of the nozzle
ρ	Mass per unit volume of the mixture
*	Exponent indicating a matrix
ln	Natural logarithm
det	Determinant of a square matrix
t	Exponent indicating the transpose of a matrix
-1	Exponent indicating the inverse of a matrix or of an operator

- (i) Index signifying a progression of family (*i*)
- e' Index referring to a pseudo-equilibrium
- f' Index referring to a pseudo-frozen state
- e Index referring to equilibrium flow

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