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CHEMICAL KINETICS AND ROCKET
NOZZLE DESIGN

F. J. Krieger

P-237

20 September 1951

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CHEMICAL KINETICS AND ROCKET
NOZZLE DESIGN

F. J. Krieger¹

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ABSTRACT

The effect of chemical kinetics on rocket nozzle design was investigated for the particular case of hydrogen gas flowing adiabatically through a typical rocket nozzle having a chamber-to-throat-area ratio of 2 to 1. For comparative purposes the following types of flow were considered: (a) constant composition (frozen equilibrium), (b) instantaneous chemical equilibrium (shifting equilibrium), and (c) kinetic chemical equilibrium. A stepwise iteration process was employed to perform the integration of the differential equation in case (c). In each case the gas entered the nozzle at a temperature of 3500°K and a pressure of 20 atm and was allowed to expand isentropically to an exhaust pressure of 1 atm. The results for a mass flow rate of 1000 gm sec^{-1} are presented in Figs. 2 through 6. The instantaneous equilibrium flow assumption not only gives a higher specific impulse, but also requires a larger nozzle than either the kinetic or the constant composition flow assumption. The kinetic equilibrium flow results are intermediate between those for instantaneous equilibrium flow and those for constant composition flow, the relative position depending on the magnitude of the reaction rate which governs the kinetic equilibrium.

INTRODUCTION

It has been standard practice in the field of rocketry to compute the specific impulse (i.e., the jet velocity divided by the acceleration of gravity) of a propellant system on the basis of either of two fundamental assumptions, namely, that the adiabatic flow of propellant gases from the combustion chamber through the nozzle is such that either (a) constant composition or (b) instantaneous chemical equilibrium is maintained. For an adiabatic process, assumption (a), which says that the inherent reaction rate is zero, gives a minimum value for the specific impulse, whereas assumption (b), which says that the inherent reaction rate is infinite, gives a maximum value for the specific impulse. The introduction of reaction rate equations into the computation of specific impulse so complicates the problem that heretofore investigators have, perforce, been generally satisfied with a knowledge of the limiting values obtained on the basis of the above assumptions.

Aside from the computational difficulties which it entails, the kinetic approach, because it requires close adherence to physical reality, tends not only to establish the true specific impulse for a propellant system, but also to give some insight into the design of the nozzle for that system. In general, specific impulse values computed under assumptions (a) and (b) are made without regard to nozzle configuration and with the added simplifying assumption that the chamber gases enter the nozzle with zero velocity. Since this latter assumption has no physical justification and is erroneous, it leads to spurious values . . .

specific impulse. In order to obviate this condition it is necessary at the outset to determine the chamber velocity at the entrance to the nozzle for the type of gas flow under consideration. This may be done only by consideration of nozzle configuration.

The nozzle generally accepted by rocket designers is the convergent-divergent de Laval type, which is formed from two intersecting right circular cones. The half angle of the convergent cone is usually 30° and that of the divergent cone, 15° . To prevent discontinuity of flow, the throat section is rounded off with a radius of curvature which is equal to the throat diameter $2r_t$. Such a nozzle was considered by Altman and Penner.^{(1),(2)} The nozzle considered in this study is shown in Fig. 1. It differs from the Altman and Penner nozzle in two respects. First, according to current design practice, the entrance area A_c is twice the throat area A_t . This restriction permits one to establish, among other things, the origin of a rectangular coordinate system at the entrance to the nozzle. Secondly, the convergent cone is replaced with a sphere of radius r_c . The sphere is tangent to the rounded throat section at a point where the slope makes an angle of $23^\circ 31'$ with the nozzle axis. The use of a spherical section instead of a convergent cone ensures continuity of flow from the combustion chamber into the nozzle entrance.

The propellant system in this study is pure hydrogen having a chamber temperature of 3500°K and a chamber pressure of 20 atm. Its history prior to its arrival at the entrance to the nozzle is irrelevant. From the basic nozzle design parameters and mass flow rate considerations, the following properties may be computed:

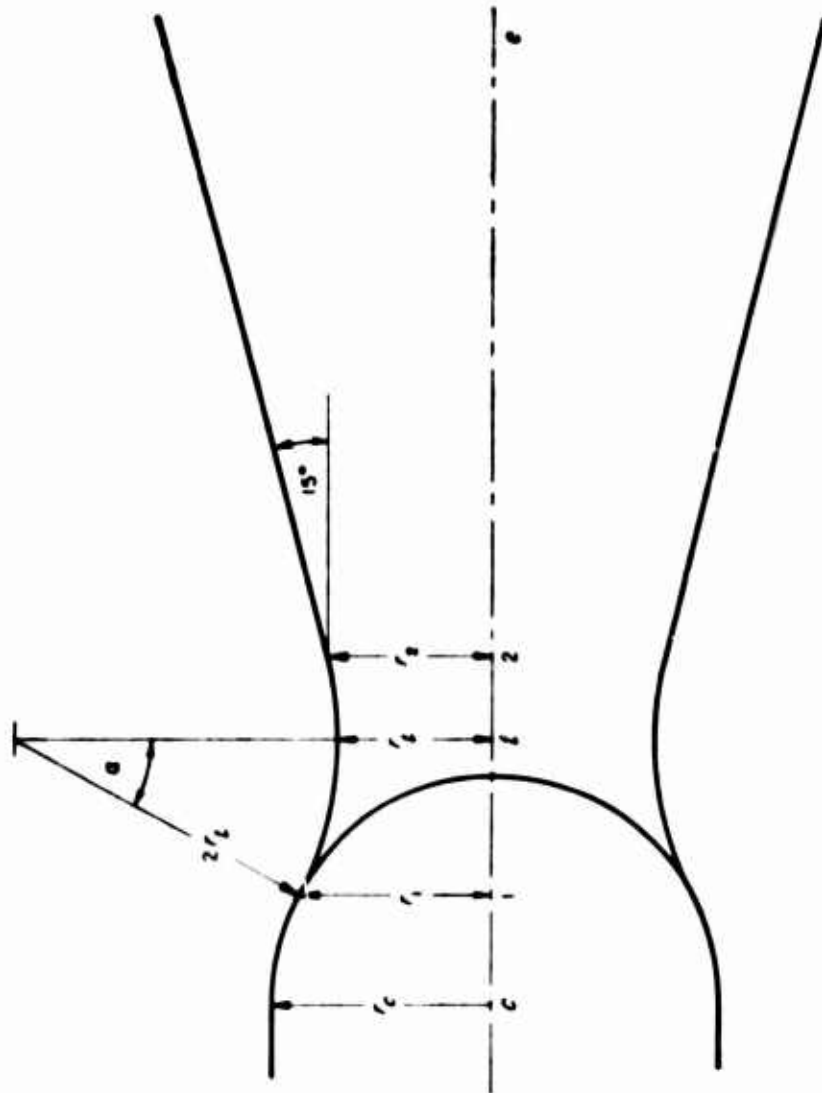


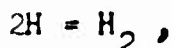
FIG. 1 CROSS SECTION THROUGH ROCKET NOZZLE

1. Chamber velocity v_c
2. Nozzle throat area A_t
3. Nozzle length L
4. Jet velocity v_e or equivalent specific impulse I

In this study, the above properties are determined not only for (a) constant composition flow and (b) instantaneous chemical equilibrium flow, but also for (c) kinetic chemical equilibrium flow. Case (c) makes use of the expression for the rate of recombination of hydrogen atoms during the adiabatic expansion process of the propellant gas as it flows through the nozzle.

GENERAL THERMODYNAMIC EQUATIONS

Several basic equations may be derived from a thermodynamic consideration of the propellant gas mixture. For the association reaction



the equilibrium constant K_p is given by the expression

$$K_p = N_{H_2} / N_H^2 P , \quad (1)$$

where N_{H_2} and N_H are the mole fractions of H_2 and H , respectively, and P is the total pressure in atmospheres. The mole fractions satisfy the obvious relation

$$N_{H_2} + N_H = 1 . \quad (2)$$

The molecular weight of the gas mixture is given by the relationship

$$M = \sum N_i M_i \quad (i = 1, 2) , \quad (3)$$

where N_i and M_i are the mole fraction and the molecular weight, respectively, of component i .

The expansion of the propellant gas is assumed to be isentropic. The specific entropy of the gas mixture is given by the expression

$$s = \frac{1}{M} (\sum N_i S_i^0 - R \sum N_i \ln N_i - R \ln P) , \quad (4)$$

where s is the entropy in calories per degree per gram, M is the molecular weight of the gas mixture, S_i^0 is the entropy per mole of component i at one atmosphere and at a given temperature, N_i is the mole fraction

of component i , R is the gas constant, and P is the given pressure in atmospheres.

The specific enthalpy of the gas mixture at any point in the expansion process is given by the expression

$$h = \frac{1}{M} \left[\sum N_i (\Delta H_{f_i} + \Delta H_{298.16, i}^T) \right] , \quad (5)$$

where h is the enthalpy in calories per gram, M is the molecular weight of the gas mixture, and N_i , ΔH_{f_i} , and $\Delta H_{298.16, i}^T$ are the mole fraction, the heat of formation, and the sensible heat content, respectively, of component i .

By equating the change in kinetic energy of the expanding gas to its change in enthalpy, the velocity at any point in the expansion is found to be

$$v = \left[v_c^2 + 2J(h_c - h) \right]^{1/2} , \quad (6)$$

where v is the velocity in centimeters per second, h is the specific enthalpy in calories per gram, J is the mechanical equivalent of heat, and the subscript c refers to the chamber conditions.

Specific impulse and velocity are related by means of the simple expression

$$I = v/g , \quad (7)$$

where I is the specific impulse in seconds, v is the velocity in centimeters per second, and g is the acceleration of gravity. This concept of specific impulse assumes complete or perfect expansion of the propellant gas.

MASS FLOW EQUATIONS

A fundamental relationship between nozzle configuration and propellant gas mass flow may be derived from the following considerations. The time rate of mass flow μ in grams per second may be defined by the expression

$$\mu = \rho A v, \quad (8)$$

where ρ is the density of the gas in grams per cubic centimeter, A is the cross-sectional area of the nozzle in square centimeters, and v is the velocity in centimeters per second. The ideal gas equation may be written in the form

$$P = \frac{\rho}{M} RT, \quad (9)$$

where P is the absolute pressure in atmospheres, ρ is the density of the gas in grams per cubic centimeter, M is the molecular weight of the gas, R is the gas constant, and T is the absolute temperature in degrees Kelvin. Equations (8) and (9) may be combined to give the expression

$$A = \frac{\mu RT}{P \mu v}, \quad (10)$$

for the area associated with a given mass flow rate at any point in the nozzle. The corresponding cross-sectional radius is given by the expression

$$r = \left[\frac{\mu RT}{2 P \mu v} \right]^{1/2} \quad (11)$$

From the equation

$$x^2 + y^2 = r_c^2, \quad (12)$$

which defines the spherical section of the nozzle depicted in Fig. 1, and the fact that $y = r$, the following expression is obtained for the distance downstream from the nozzle entrance through the spherical section

$$x = (r_c^2 - r^2)^{1/2}. \quad (13)$$

An expression for the distance downstream through the rounded throat section may be derived from the equation which defines the shape of the throat. In terms of an x, y coordinate system having its origin at the center of the nozzle entrance, the equation of such a defining circle is simply

$$(x - x_t)^2 + (y - y_t)^2 = 2r_c^2, \quad (14)$$

where x_t and y_t are the coordinates of the center of the circle whose radius is $2r_t$ or $2^{1/2}r_c$. Reference to Fig. 1 shows that

$$y_t = 3r_c/2^{1/2} \quad (15)$$

and that

$$x_t = x_1 + r_c/2^{1/2}, \quad (16)$$

where x_1 is the abscissa of the point at station 1 where the circles defined by Eqs. (12) and (14) are tangent. By combining Eqs. (14) and (15) and remembering that $y = r$, the following expression for the distance downstream through the throat section is obtained:

$$x = x_t \mp \left[2r_c^2 - (r - 3r_c/2^{1/2})^2 \right]^{1/2}. \quad (17)$$

In Eq. (17) the minus sign is valid in the convergent section of the nozzle and the positive sign in the divergent.

Inspection of Fig. 1 shows that the expression for the distance downstream from station 2 is given by the relation

$$x = (r - r_2) \cot \theta , \quad (18)$$

where r_2 is the radius of the throat at station 2 where the divergent cone of half angle θ is tangent to the circle which defines the shape of the throat.

Further inspection of Fig. 1 indicates the following particular relations. The angle α , associated with the point of tangency at station 1, is given by equation

$$\cos \alpha = \frac{3(2^{1/2})}{2(1 + 2^{1/2})} = 0.87868 , \quad (19)$$

so that $\alpha = 23.516^\circ$.

Thus at station 1

$$r_1 = r_c \cos \alpha = 0.87868 r_c \quad (20)$$

and

$$x_1 = r_c \sin \alpha = 0.47741 r_c . \quad (21)$$

At the throat

$$r_t = r_c / 2^{1/2} = 0.70711 r_c \quad (22)$$

and

$$x_t = x_1 + 2^{1/2} r_c \sin \alpha = 1.1526 r_c . \quad (23)$$

At station 2

$$r_2 = (3 - 2 \cos 15^\circ) r_t = 0.75529 r_c \quad (24)$$

and

$$x_2 = x_t + 2^{1/2} \sin 15^\circ r_c = 1.5136 r_c . \quad (25)$$

KINETIC EQUATIONS

The recombination of hydrogen atoms to form hydrogen molecules may be represented by the triple-body collision reaction equation



where k_f and k_b are the forward and backward reaction rate constants, respectively, and Z is any third body*. If $[H]$ denotes the concentration of H in moles per cubic centimeter, then the time rate of change of $[H]$ for a process in which the volume V is changing is given by the expression

$$-\frac{1}{2} \frac{d[H]}{dt} = k_f [H]^2 [Z] - k_b [H_2] [Z] + \frac{1}{2} \frac{[H]}{V} \frac{dV}{dt}. \quad (27)$$

The validity of the third term on the right-hand side of Eq. (27) may be easily verified by a consideration of the identity $[H] = n_H/V$, where n_H is the number of moles of H in the volume V of expanding gas.

In this study it is more convenient to deal with the concept of mole fraction N_H than with that of molar concentration $[H]$. By making use of the identities

$$[H] = N_H P/RT \quad (28)$$

and

$$[Z] = P/RT, \quad (29)$$

Eq. (27) may be written in the form

$$\begin{aligned} -\frac{dN_H}{dt} &= P \left[k_f N_H^2 (P/RT)^2 - k_b N_{H_2} (P/RT) \right] \\ &+ N_H \frac{d}{dt} \ln (PV/RT). \end{aligned} \quad (30)$$

*Compare this treatment with that of Penner³.

For a mass of m grams of gas the ideal gas law may be written in the form

$$PV = mRT/M, \quad (31)$$

so that

$$\frac{d}{dt} \ln (PV/T) = \frac{d}{dt} \ln (mR/M) = - \frac{1}{M} \frac{dM}{dt}. \quad (32)$$

Hence, Eq. (30) becomes

$$- \frac{dN_H}{dt} = 2 \left[k_f N_H^2 (P/RT)^2 - k_b N_{H_2} (P/RT) \right] - \frac{N_H}{M} \frac{dM}{dt}. \quad (33)$$

By using Eqs. (2) and (3) and the value 1.008 for the atomic weight of hydrogen, the expression for the molecular weight of the gas mixture becomes

$$M = 1.008 (2 - N_H). \quad (34)$$

Equation (33) thus reduces to the following:

$$- \frac{dN_H}{dt} = (2 - N_H) \left[k_f N_H^2 (P/RT)^2 - k_b N_{H_2} (P/RT) \right]. \quad (35)$$

Since the equilibrium constant K_p defined by Eq. (1) and the rate constants in Eq. (26) are related by the expression

$$K_p RT = k_f/k_b, \quad (36)$$

Eq. (35) may be written in the form

$$- \frac{dN_H}{dt} = \frac{k_f (2 - N_H)}{(RT)^2} (N_H^2 P^2 - N_{H_2} P/K_p). \quad (37)$$

Finally, since the velocity v at any distance x downstream is given by the relation

$$v = dx/dt, \quad (38)$$

the rate of change of N_H with distance is given by the expression

$$- \frac{dN_H}{dx} = \frac{k_f (2 - N_H)}{v(RT)^2} (N_H^2 P^2 - N_{H_2} P/K_p). \quad (39)$$

BASIC DATA

The pertinent thermodynamic data used in this study were taken from the National Bureau of Standards⁽⁴⁾. They include the total enthalpy above the reference temperature 298.16°K and the absolute entropy for the chemical species H and H₂ and the logarithms of the equilibrium constants for the reaction 2H = H₂ at temperatures from 1600°K to 3500°K. The heats of formation for H and H₂ at 298.16°K are 52,089 and 0 cal mol⁻¹, respectively.

The pertinent physical constants have the following values: the acceleration of gravity $g = 980.665 \text{ cm sec}^{-2}$; the gas constant $R = 82.0567 \text{ cm}^3 \text{ atm deg}^{-1} \text{ mol}^{-1}$; the mechanical equivalent of heat $J = 4.1840 \text{ abs joules cal}^{-1}$.

The forward reaction rate constant k_f in Eq. (26) is assumed to have the value $10^{16} \text{ cm}^6 \text{ mol}^{-2} \text{ sec}^{-1}$ over the entire range of temperatures and pressures covered by this investigation. This assumption is made (a) because the chemical literature is singularly lacking in kinetic data for the hydrogen recombination reaction* and (b) because the primary purpose of this study is to show how a rate equation may be dealt with in a propellant gas expansion problem.

* In this connection, see Refs. 5 and 6.

COMPUTATIONAL PROCEDURE

In general, the composition of the expanding gas may be determined at any temperature and pressure by the simultaneous solution of Eqs. (1) and (2). The entropy of the system, the expansion of which is assumed to be isentropic, may be determined from the initial chamber conditions by means of Eq. (4). Once the value of the entropy has been established, Eq. (4) may be used to determine the pressure at any temperature and composition. The velocity of the expanding gas at any point may be computed by means of Eq. (6). The chamber velocity may be determined from the following considerations.

If, for a given mass flow rate μ , a plot of area A versus temperature T is made for various temperatures between T_c and T_e , a smooth curve having a well-defined minimum is obtained. This point of minimum area corresponds to the throat of the nozzle. The chamber velocity may, therefore, be computed from Eq. (10) when the design condition

$$A_c = 2 A_t \quad (40)$$

is satisfied.

Since A_t cannot be computed explicitly, a tentative value for A_c must be assumed on the basis of some nonzero chamber velocity. Then values of A may be computed for various values of T . From a plot of these data a throat area corresponding to the assumed chamber area may be determined. If this process is repeated for several values of A_c and if a plot of A_c/A_t versus A_c is made, then, by interpolation, values of A_c and A_t may be obtained which satisfy Eq. (40). This procedure for determining A_c , A_t , and v_c is perfectly general and is independent of the type of

flow considered.

The length of the nozzle may be computed from a knowledge of end conditions only by means of Eqs. (13), (17), and (18) for constant composition flow and for instantaneous chemical equilibrium flow. The kinetic case, however, requires a stepwise procedure which involves the integration of Eq. (39) as well as the use of Eqs. (13), (17), and (18). For this purpose it is convenient to use temperature as a parameter and to perform the integration over temperature intervals which are small enough to ensure a degree of accuracy consistent with the data used. The two regions where particular care must be exercised are (a) at the very entrance to the nozzle, where the temperature gradient is a maximum, and (b) at the throat, where the parameters must be determined precisely in order to satisfy the design conditions.

The integration of Eq. (39) may be accomplished by writing it in the form

$$dN_H/dT = \frac{dN_H/dL}{dL/dT} , \quad (41)$$

where L denotes the length of the nozzle, and by subjecting it to an iterative process which makes use of the methods and equations of the numerical calculus for equal intervals of the argument T. A list of such equations is given by Milne⁽⁷⁾. For the present the following four-point integration formula is satisfactory:

$$N_3 = N_0 + (h/8)(N'_0 + 3N'_1 + 3N'_2 + N'_3) . \quad (42)$$

In this equation h is the temperature interval and the primed quantities are the first derivatives with respect to temperature of the function N at four consecutive temperatures.

In order to carry out the integration process effectively, it is expedient to construct tables of dN_H/dL and L values for a judicious spread of N_H values at the various temperatures considered. Starting values of N_H may be obtained by reference to those calculated for the instantaneous equilibrium case.

Once a set of values of N_H is obtained for the temperature range from T_c to some arbitrary T_c , corresponding values of dN_H/dL and of L may be obtained from the previously constructed tables by interpolation. Values of dL/dT may be derived from a plot of L versus T or by means of an appropriate differentiation formula as given in Ref. 7. Equation (42) may then be used to correct the original rough values of N_H as often as necessary to achieve convergence.

RESULTS AND DISCUSSION

The mole fraction composition of the gas entering the nozzle at a temperature of 3500°K and a pressure of 20 atm is 0.1235 H and 0.8765 H_2 , and its specific entropy is $22.918 \text{ cal deg}^{-1} \text{ gm}^{-1}$. With these data as initial conditions, a mass flow rate of 1000 gm sec^{-1} , the nozzle configuration of Fig. 1, and a 2-to-1 chamber-to-throat-area ratio, the adiabatic flow of hydrogen to an exhaust pressure of 1 atm was studied, assuming first, constant composition flow, then instantaneous chemical equilibrium flow, and finally, kinetic chemical equilibrium flow. The results are presented graphically in Figs. 2 through 6.

Inspection shows that the shape of the kinetic flow nozzle is identical with that of the instantaneous flow nozzle. This is due to the fact that, since the magnitude (10^{16}) of the forward rate constant k_f is for all practical purposes infinite, the chamber parameters are numerically equal (as far as significant figures are concerned) for the kinetic and the instantaneous equilibrium flow cases. Since the chamber parameters determine the geometry of the nozzle, it follows that the shape of the nozzles must be identical.

As was to be expected the kinetic results are for the most part intermediate between the constant composition and the instantaneous equilibrium flow results. This fact was invaluable in estimating starting values for the iteration process used to integrate Eq. (39). A temperature interval of 50°K was employed throughout the integration process. A smaller interval might have given smoother results, but the increased

labor would have been greater than the accuracy of either the initial data or the final results would warrant.

Figure 6 depicts the nozzle configuration for the three types of flow investigated. It is interesting to note (a) that instantaneous equilibrium flow requires a longer (and larger) nozzle than does constant composition flow and (b) that for kinetic equilibrium flow the nozzle is slightly shorter than for instantaneous equilibrium flow.

It may also be noted that nozzle design affects specific impulse in the following manner. The specification of a 2-to-1 chamber-to-throat-area ratio results in a chamber specific impulse of 141.4 sec for the constant composition flow nozzle and 136.0 sec for both the instantaneous and the kinetic equilibrium flow nozzles. It is obvious from Eq. (10) that a zero chamber velocity would require an infinite chamber area, a factor which is not feasible in practice. Furthermore, a zero chamber velocity would yield, at an exhaust pressure of 1 atm, a specific impulse of 823.2 sec instead of 835.1 for constant composition flow and 873.8 sec instead of 884.3 for instantaneous equilibrium flow. It is thus evident that nozzle configuration, specifically chamber-to-throat-area ratio, has a definite effect on the magnitude of specific impulse or jet velocity.

In the present example the effect of chemical kinetics, i.e., the rate of recombination of hydrogen atoms, on specific impulse is not very pronounced, as the figures 884.3 and 879.6 at an exhaust pressure of 1 atm for instantaneous and kinetic equilibrium flow, respectively, indicate. This is due, of course, to the magnitude of the forward reaction rate constant k_f and to the nature of the chemical species. In other

expanding propellant gases in which the rate constants associated with the pertinent chemical reactions are numerically smaller than the hydrogen rate constant and the chemical species themselves are less active than hydrogen, the general effect would be to displace the kinetic results toward the constant composition flow values. In such cases, even if several differential equations similar to eq. (39) are involved, the method of integration indicated in this paper would be valid, but the computation would best be performed on automatic equipment.

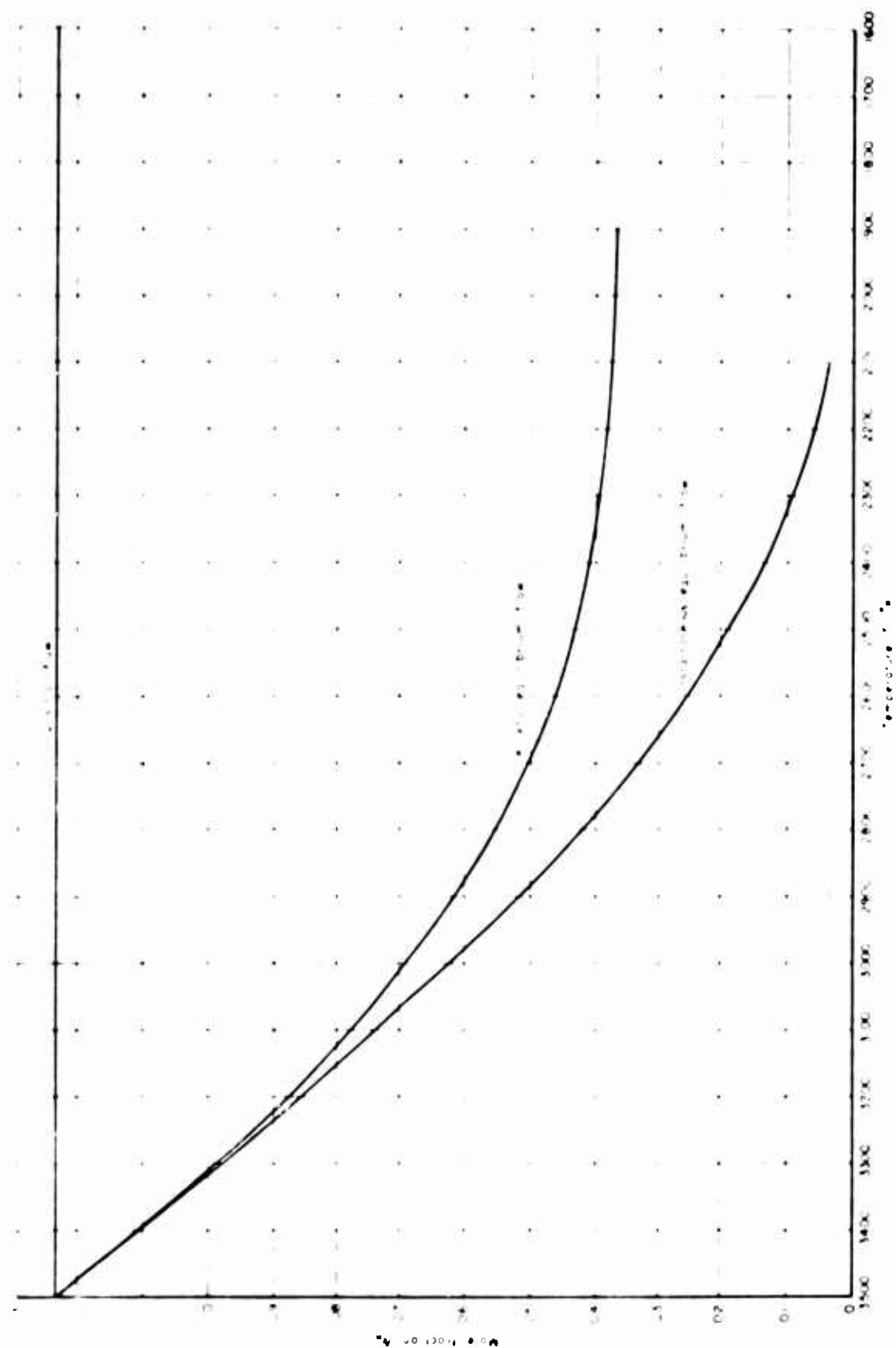


FIG. 2 COMPOSITION VERSUS TEMPERATURE FOR THE ADIABATIC EXPANSION OF HYDROGEN THROUGH A ROCKET NOZZLE

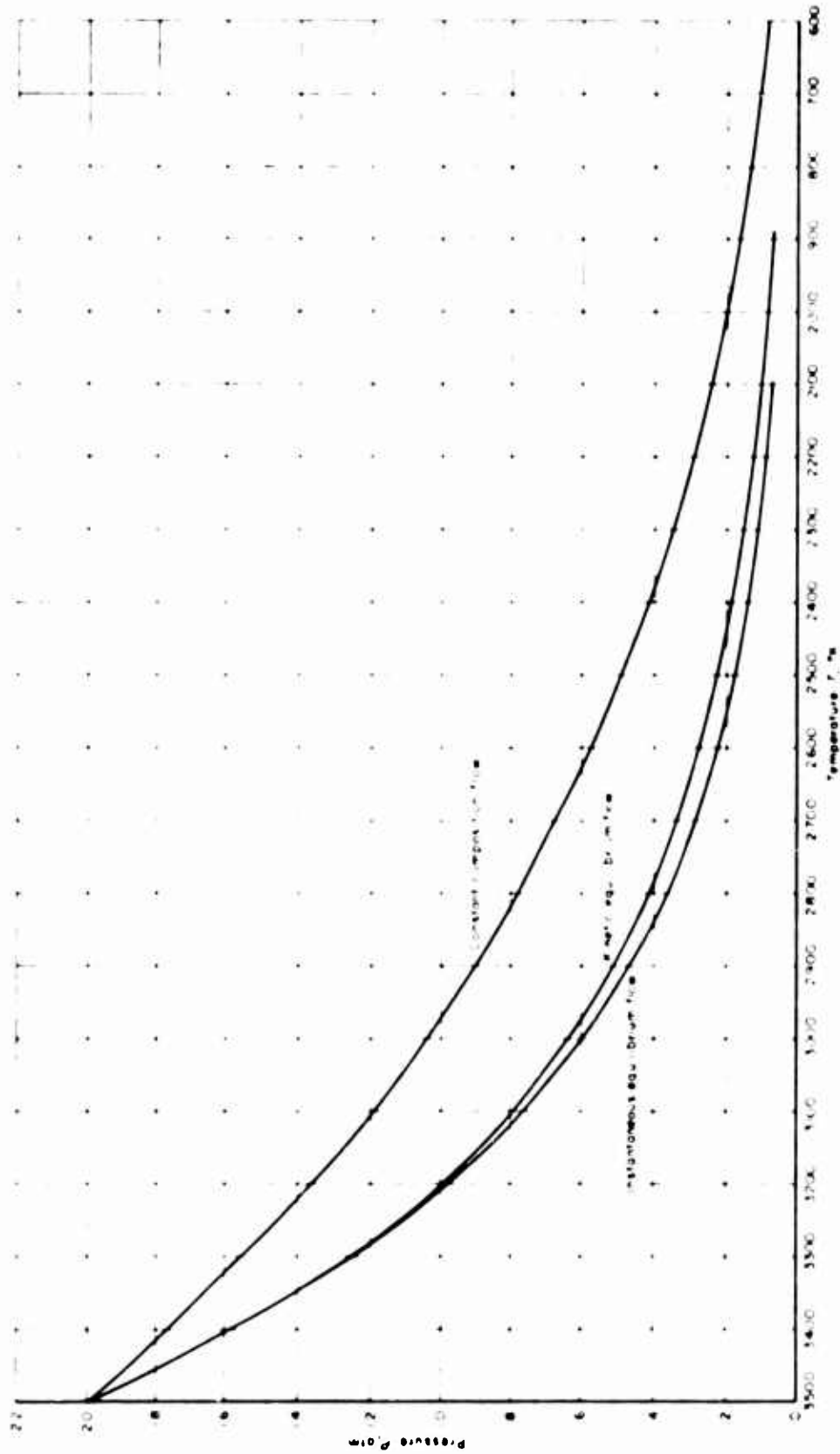


FIG. 3 PRESSURE VERSUS TEMPERATURE FOR THE ADIABATIC EXPANSION OF HYDROGEN THROUGH A ROCKET NOZZLE

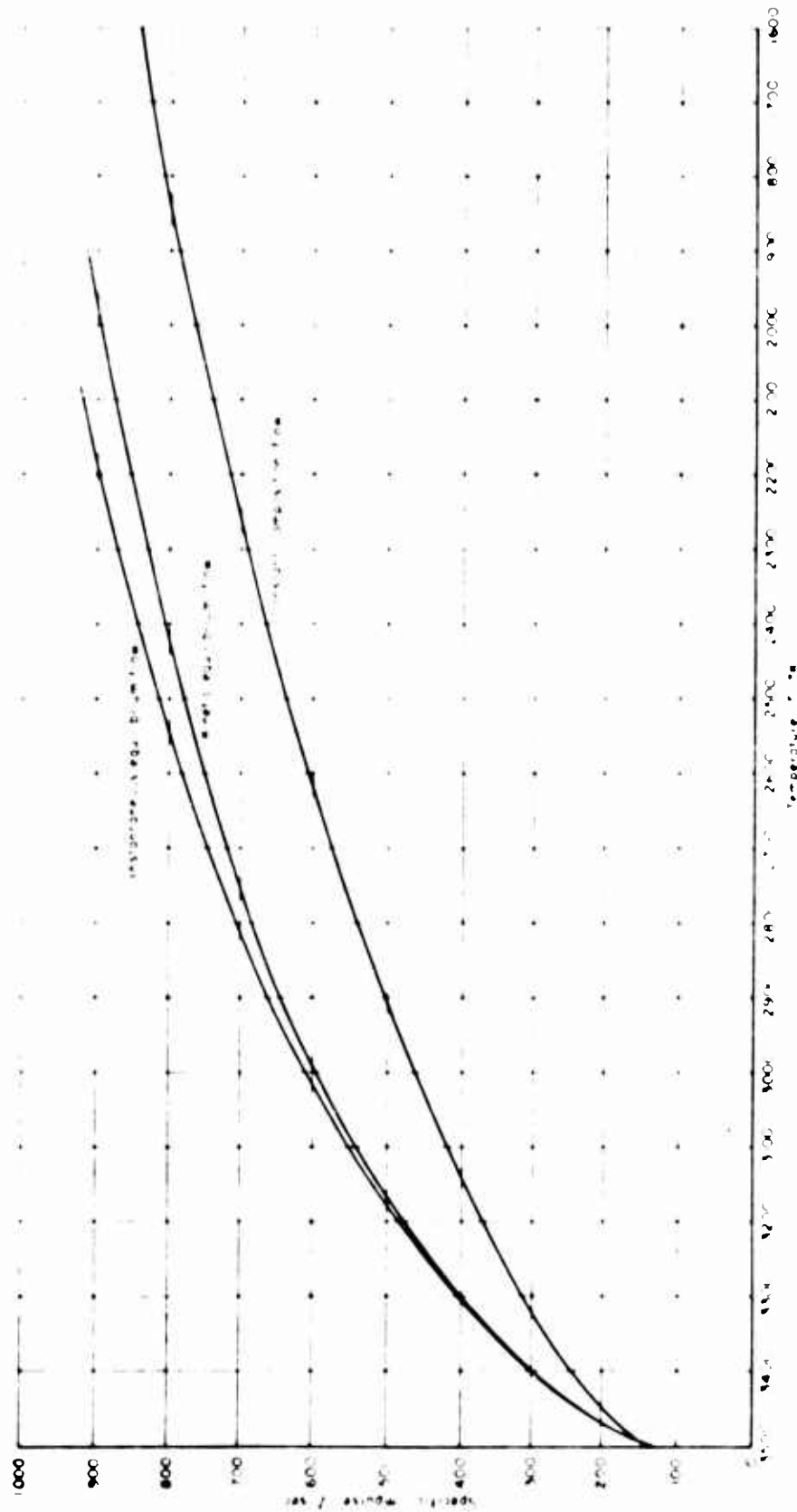


FIG. 4 SPECIFIC IMPULSE VERSUS TEMPERATURE FOR THE ADIABATIC EXPANSION OF HYDROGEN THROUGH A ROCKET NOZZLE

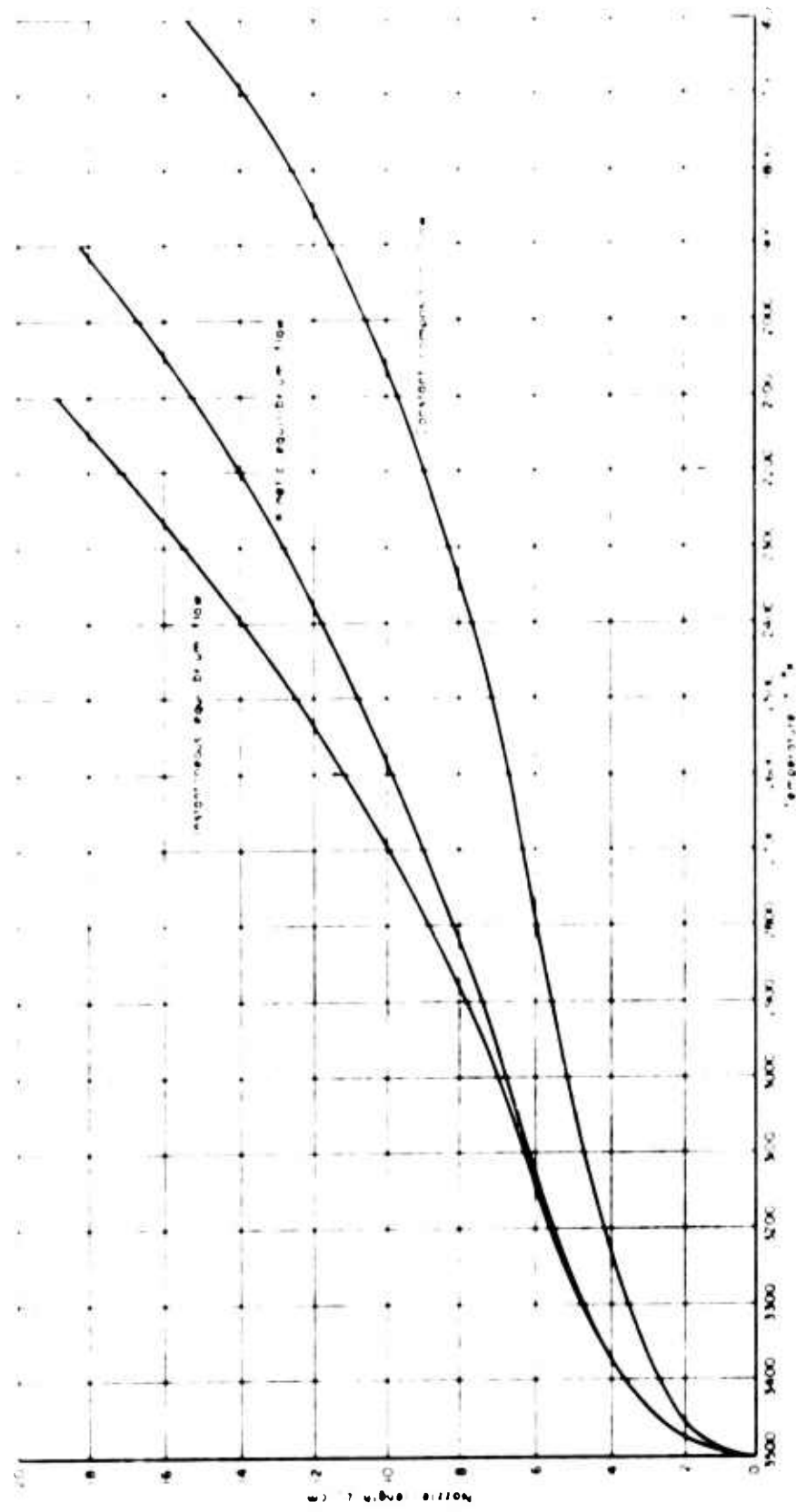


FIG. 5 NOZZLE LENGTH VERSUS TEMPERATURE FOR THE ADIABATIC EXPANSION OF HYDROGEN THROUGH A ROCKET NOZZLE

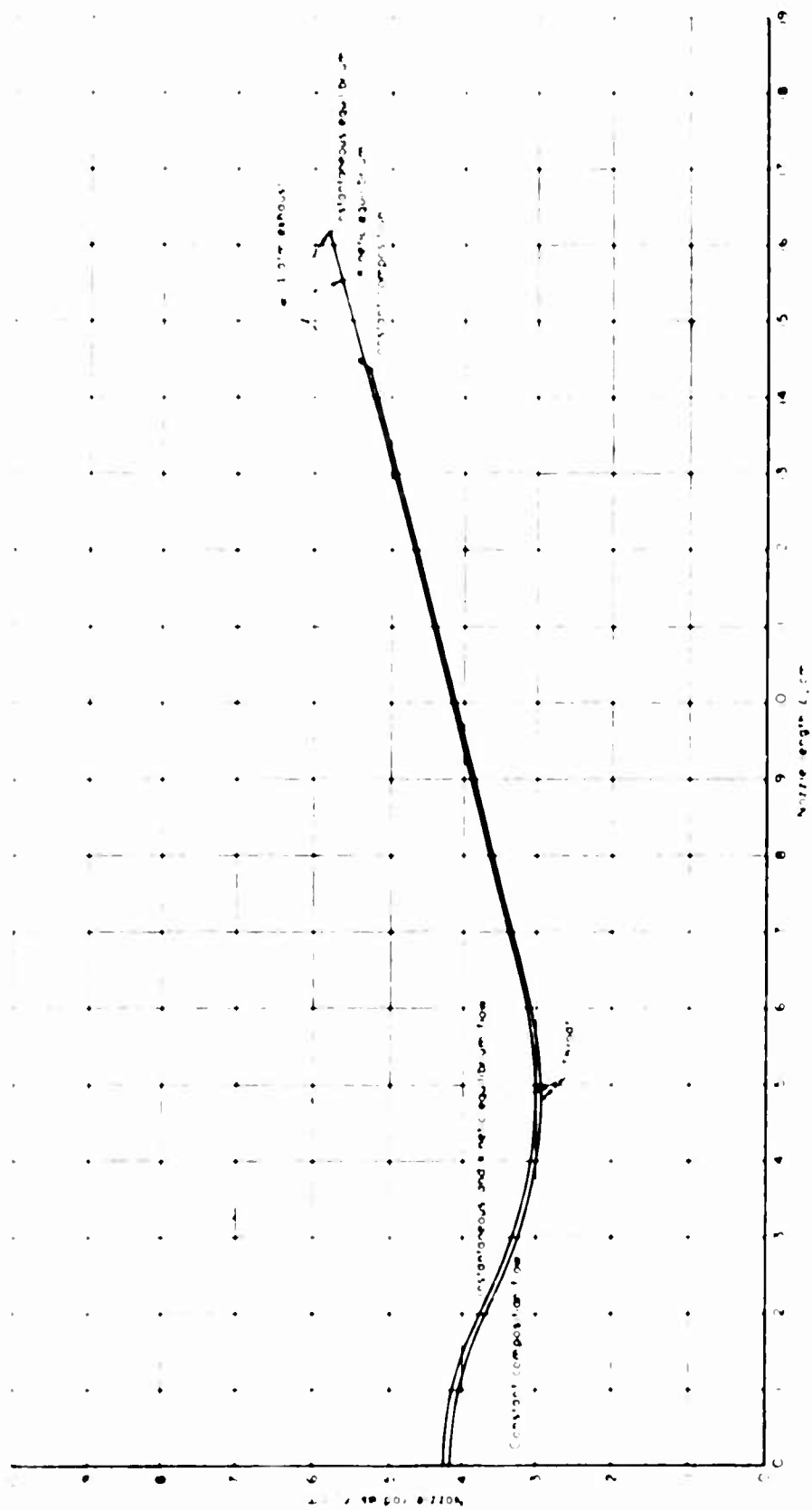


FIG. 6 NOZZLE RADIUS VERSUS NOZZLE LENGTH FOR THE ADIABATIC EXPANSION OF HYDROGEN THROUGH A ROCKET NOZZLE.

CONCLUSIONS

The following conclusions may be drawn from the foregoing study.

1. The effect of chemical kinetics on rocket propellant gases expanding through a nozzle has been determined by the simultaneous solution of three sets of equations based on thermodynamic, nozzle configuration, and chemical reaction rate considerations.
2. The fundamental design calculational requirement, aside from the mass flow rate, is the specification of a finite chamber-to-throat-area ratio.
3. Nozzles designed on the basis of chemical kinetics for perfect expansion are somewhat smaller than instantaneous equilibrium flow nozzles but are larger than constant composition flow nozzles, the difference depending on the magnitude of the reaction rates involved.
4. The method of stepwise integration described may be applied to propellant systems which involve several differential equations with, of course, a corresponding increase in computational labor.

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