CORRELATIONS FOR DETERMINING THERMODYNAMIC PROPERTIES OF HYDROGEN-HELIUM GAS MIXTURES AT TEMPERATURES FROM 7000 TO 35 000 K

Ernest V. Zoby, Peter A. Gnoffo, and Randolph A. Graves, Jr.

Langley Research Center
Hampton, Va. 23665

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • AUGUST 1976
Simple relations for determining the enthalpy and temperature of hydrogen-helium gas mixtures have been developed for hydrogen volumetric compositions from 1.0 to 0.7. These relations are expressed as a function of pressure and density and are valid for a range of temperatures from 7000 to 35,000 K and pressures from 0.10 to 3.14 MPa. The proportionality constant and exponents in the correlation equations were determined for each gas composition by applying a linear least-squares curve fit to a large number of thermodynamic calculations obtained from a detailed computer code. Although these simple relations yielded thermodynamic properties suitable for many engineering applications, their accuracy was improved significantly by evaluating the proportionality constants at postshock conditions and correlating these values as a function of the gas composition and the product of freestream velocity and shock angle. The resulting equations for the proportionality constants in terms of velocity and gas composition and the corresponding simple relations for enthalpy and temperature were incorporated into a flow-field computational scheme. Comparison was good between the thermodynamic properties determined from these relations and those obtained by using a detailed computer code to determine the properties. Thus, an appreciable savings in computer time was realized with no significant loss in accuracy.
CORRELATIONS FOR DETERMINING THERMODYNAMIC PROPERTIES
OF HYDROGEN-HELIUM GAS MIXTURES AT TEMPERATURES
FROM 7000 TO 35 000 K

Ernest V. Zoby, Peter A. Gnoffo, and Randolph A. Graves, Jr.
Langley Research Center

SUMMARY

Simple relations for determining the enthalpy and temperature of hydrogen-helium gas mixtures have been developed for hydrogen volumetric composition from 1.0 to 0.7. These relations are expressed as a function of pressure and density and are valid for a range of temperatures from 7000 to 35 000 K and pressures from 0.10 to 3.14 MPa. The proportionality constant and exponents in the correlation equations were determined for each gas composition by applying a linear least-squares curve fit to a large number of thermodynamic calculations obtained from a detailed computer code. Although these simple relations yielded thermodynamic properties suitable for many engineering applications, their accuracy was improved significantly by evaluating the proportionality constants at postshock conditions and correlating these values as a function of the gas composition and the product of free-stream velocity and shock angle. The resulting equations for the proportionality constants in terms of velocity and gas composition and the corresponding simple relations for enthalpy and temperature were incorporated into a flow-field computational scheme. Comparison was good between the thermodynamic properties determined from these relations and those obtained by using a detailed computer code to determine the properties. Thus, an appreciable savings in computer time was realized with no significant loss in accuracy.

INTRODUCTION

Scientific exploration of the outer planets (Jupiter, Saturn, and Uranus) is planned for the 1979-1984 time period. The instrumented probes used for these missions will experience a severe aerothermal environment during entry into the planetary atmospheres which consist primarily of hydrogen and helium. For successful missions, it is extremely important to define the environment. Since the contribution that present experimental facilities can make is not adequate at the conditions expected during entry into the outer
planetary atmospheres, most of the required information must be obtained from computational analyses. In general, the first step towards obtaining flow-field information about proposed entry configurations is to utilize the most complete and detailed codes possible. These codes (e.g., refs. 1 and 2) require excessively long run times; consequently, such programs are expensive to run and usually serve as "benchmark" solutions. One aspect of the benchmark programs which consumes an appreciable amount of computer storage and computational time is the complex equilibrium chemistry code for the calculation of thermodynamic properties. For parametric studies, engineering methods incorporating a simplified equation of state are required for computing the thermal environment about entry aeroshells. The engineering methods, such as presented in references 3 and 4 for Earth and Venusian entry, respectively, are verified by comparison with benchmark solutions.

Although the atmospheres of the outer planets are known to consist primarily of hydrogen and helium (refs. 5, 6, and 7), their precise elemental compositions are not presently known. For this reason and due to the need for a rapid method of determining thermodynamic properties to incorporate in flow-field codes, a simple and versatile means of determining the properties for arbitrary hydrogen-helium mixtures has been developed and is presented herein. Correlation equations have been developed for the enthalpy and temperature as functions of pressure and density that are applicable to a range of hydrogen-helium mixtures consisting of hydrogen volumetric compositions from 1.0 to 0.7 over a wide range of temperatures from 7000 to 35 000 K and pressures from 0.10 to 3.14 MPa. This range of temperature and pressure was chosen to encompass the values expected within the shock layer of a Jovian entry aeroshell.

A method used to develop the correlation equations and a procedure that improves the accuracy of the correlations for shock flow-field applications are discussed. Comparisons of these correlations with "exact" equilibrium thermodynamic and shock calculations are presented. For a proposed Jovian atmosphere model and body shape, the correlations are incorporated in a flow-field analysis and the results are compared with those obtained by using an exact chemistry code in the same flow-field procedure.

**SYMBOLS**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>matrix (see appendix)</td>
</tr>
<tr>
<td>C</td>
<td>unknown column vector (see appendix)</td>
</tr>
<tr>
<td>$C_h$</td>
<td>enthalpy coefficient (see eq. (1))</td>
</tr>
<tr>
<td>$C_T$</td>
<td>temperature coefficient (see eq. (2))</td>
</tr>
</tbody>
</table>
h  enthalpy
\( \hat{h} \)  nondimensional enthalpy, \( hM_o/RT_o \)
\( \lambda, k \)  temperature exponents in equation (2)
\( M_o \)  cold state molecular weight of hydrogen-helium mixture at \( T_o \)
m, n  enthalpy exponents in equation (1)
p  pressure
\( \tilde{p} \)  nondimensional pressure, \( p/p_o \)
p_o  reference pressure, 0.101325 MPa
R  universal gas constant
r  residual (see appendix)
\( r_n \)  body nose radius
s  distance along body surface
T  temperature
\( T_o \)  reference temperature, 273.15 K
U  velocity
\( U_t \)  transformed free-stream velocity (see eq. (15))
u  tangential velocity component behind oblique shock
v  normal velocity component behind oblique shock
X  mole fraction
y  column vector (see appendix)
\( \delta \)  
shock-layer detachment distance normal to body

\( \theta_s \)  
shock angle

\( \rho \)  
density

\( \bar{\rho} \)  
nondimensional density, \( \rho / \rho_0 \)

\( \rho_0 \)  
density of air at \( T_0 \) and \( p_0 \), 1.292 \( \text{kg/m}^3 \)

Subscripts:

\( b \)  
body

\( s \)  
shock

\( \infty \)  
free stream

**PROCEDURE AND DISCUSSION**

This section discusses the approach used to obtain the correlation equations for determining equilibrium enthalpy and temperature as a function of pressure and density over a range of temperatures, pressures, and real hydrogen-helium gas mixtures. Comparisons of the approximate and "exact" results are also given.

**Correlation Equations**

For the enthalpy, an equation of the form

\[
\bar{h} = C_h \frac{\bar{\rho}^m}{\bar{\rho}^n} \tag{1}
\]

is assumed. Equation (1) is similar to the enthalpy correlation used in reference 4 for a \( \text{CO}_2 - \text{N}_2 \) mixture. The temperature was correlated in reference 4 by a polynomial expression. In reference 8 the same correlation form presented in equation (1) was used to predict the temperature for air. This form was selected rather than the polynomial fit of reference 4 since the power law appeared to provide a better correlation form for variable gas mixtures. Hence, the relation for temperature as a function of pressure and density is given by

\[
T = C_T \frac{\bar{p}^l}{\bar{\rho}^k} \tag{2}
\]
Discussed first is a method using a linear least-squares curve fit applied to a large number of exact thermodynamic calculations for evaluating the proportionality constants and exponents in equations (1) and (2). This first method is referred to as method I, and it provides a technique for rapidly estimating the enthalpy and temperature over a range of pressure, temperature, and gas composition. It should be noted that the analysis of reference 4 used a technique different from that of method I to evaluate the proportionality constant $C_h$. In reference 4, the constant was correlated from normal-shock calculations as a function of the free-stream velocity and normal-shock density ratio. Even though the technique of reference 4 utilized a shock flow-field application to determine $C_h$, the technique requires easily obtainable parameters for the correlation. Based on the investigation of reference 4, correlations of the $C_h$ and $C_T$ proportionality constants in equations (1) and (2) referenced to a shock-crossing procedure are also presented. This second method involving a shock crossing is referred to as method II.

Sources of Thermodynamic Data

Before the procedures of method I and method II are discussed in detail, several computer codes for generating thermochemical equilibrium properties of arbitrary gases are discussed and the enthalpies for pure hydrogen calculated from these codes are compared. The purpose of this comparison is to illustrate why the particular code used in computing the exact properties was chosen and to illustrate differences between several computer codes.

The codes used for comparison were selected from references 9 to 11. The codes of references 9 and 10 employed the species $H_2$, $H$, $H_2^+$, $H^+$, $H^-$, and $e^-$ and essentially the same heats of formation and spectroscopic input data. Both codes are similar in that free energies for the individual species are calculated and a minimization procedure is used to determine the equilibrium composition. The method of reference 11 is less rigorous in that curve fits to data for the various species are used in obtaining the thermodynamic properties. These curve fits are applicable to temperatures of only 6000 K; five species ($H_2$, $H$, $H^+$, $H^-$, and $e^-$) were used in the method. Although less rigorous than the other two procedures (refs. 9 and 10), the method of reference 11 is widely used in flow-field computations because of two factors: First, its greater simplicity; second, comparisons with other gas mixtures such as air and CO₂ have demonstrated that the method yields thermodynamic properties in relatively good agreement with more rigorous computational schemes.

Since the proposed atmospheric models in references 5 to 7 generally indicate a predominance of hydrogen, the three selected codes were used to generate equilibrium properties for pure hydrogen at a pressure of 0.101325 MPa and temperatures from 7000 to 35 000 K. As discussed subsequently, the temperature range is representative of temperatures expected within the shock layer for outer planetary entry.
For comparison, the enthalpy generated by the three codes from references 9, 10, and 11 is shown in figure 1 as a function of temperature for a pressure of \( p/p_0 = 1 \). The values of enthalpy predicted by the codes of references 9 and 10 are observed to be in excellent agreement over the temperature range. The values of enthalpy calculated by the method of reference 11 are observed to be in very good agreement (within 2 percent) with the values calculated by the other two methods. It is believed that the more detailed computer codes of references 9 and 10 should be utilized to generate the exact thermodynamic properties in the present study. The method of reference 9 was selected since a shock-crossing procedure is included in the computer code of this reference, but not in reference 10. The importance of the fact that values of enthalpy predicted from the methods of references 9 and 11 were in good agreement will become apparent in a subsequent discussion.

Method I

From the results of references 5 to 7, three hydrogen-helium gas compositions which encompass the proposed compositions of the outer planets were selected for the present study. These selected compositions, given by percent volume, are \(1.00\text{H}_2-0\text{He}, 0.85\text{H}_2-0.15\text{He}, \) and \(0.70\text{H}_2-0.30\text{He} \). Normal-shock calculations for these gas compositions and for the free-stream conditions given in reference 5 indicate that for Jovian entry velocities the temperature and pressure, within the shock layer of an entry probe, range from approximately 7000 to 35 000 K and 0.101325 to 3.141018 MPa, respectively. Over this range of conditions, the exact thermodynamic equilibrium calculations were obtained by using the computer program discussed in reference 9. For each gas composition, 240 pressure-temperature combinations were selected.

A least-squares curve-fit routine was used to evaluate the proportionality constants and exponents appearing in equations (1) and (2) (i.e., \( C_h, m, n, C_T, l, \) and \( k \)) from the resulting matrix of 240 points. This least-squares routine is discussed in the appendix. The results of the curve fit for determining the proportionality constants and exponents are presented in table I and in figures 2 and 3 as a function of the initial volumetric composition of hydrogen. For application to other hydrogen-helium gas compositions contained within the range of the present compositions, the following formulas, obtained by a linear least-squares fit to the data in table I, may be written for enthalpy as

\[
C_h = 0.51455 + 0.27237 \ln X_{\text{H}_2} \tag{3}
\]

\[
m = 0.95252 - 0.1447 \ln X_{\text{H}_2} \tag{4}
\]

\[
n = 0.97556 - 0.16149 \ln X_{\text{H}_2} \tag{5}
\]
and for temperature as

\[ C_T = 97.48934 + 59.7632 (1 - X_{H_2}) \]  \hspace{1cm} (6)

\[ I = 0.67389 - 0.04637 \ln X_{H_2} \]  \hspace{1cm} (7)

\[ k = 0.65206 - 0.04407 \ln X_{H_2} \]  \hspace{1cm} (8)

Note that equations (3) to (8) are functions of the initial volumetric composition of hydrogen.

For the three hydrogen-helium gas mixtures considered, sample results obtained with method I are presented in table II along with the exact results obtained with the code of reference 9. The results of table II present comparisons for temperatures of 7000, 17 000, and 27 000 K with the pressure varying roughly from 0.1 to 2.1 MPa for a given temperature. These typical results were presented since it was not feasible to present comparisons for the enthalpy and temperature over the whole range of temperatures, pressures, and gas compositions considered. Over the complete range, the values of temperature predicted by equation (2) and about 85 percent of the values of enthalpy predicted by equation (1) were within 10 percent of the corresponding exact values. In some cases, comparisons of enthalpy revealed errors as large as 18 percent. The largest errors were concentrated mainly in the range from 11 000 to 21 000 K. For certain engineering applications, the uncertainties associated with method I for predicting enthalpy and temperature would be acceptable. However, since radiative heat transfer is proportional to the temperature to the fourth power, the relatively larger uncertainties associated with predicting temperatures, especially at temperatures 15 000 K or greater, could produce erroneous results for radiative flow-field calculations. In order to improve the accuracy of the predictions of method I, especially for application to radiative flow fields, a second method for determining the proportionality constants \( C_h \) and \( C_T \) was undertaken. This method involves a shock-crossing procedure similar to that utilized in reference 4 and is discussed in the next section.

Method II

The analysis of reference 4 implied that an improved correlation between approximate and exact properties for a CO\(_2\)-N\(_2\) mixture was obtained when the enthalpy coefficient (i.e., the proportionality constant of eq. (1)) was determined precisely for a condition characteristic of and close to the conditions of interest rather than determined as a least-squares fit over an extended range of conditions. For high Mach number flow-field calculations, such a condition is that behind a normal or oblique shock wave for the given
free-stream velocity and density. In reference 4, consequently, the enthalpy coefficient was correlated in terms of free-stream velocity and density. Somewhat similar correlations for the enthalpy and temperature coefficients were undertaken in the present study. Over the range of temperatures, pressures, and gas compositions noted for method I, normal-shock solutions were calculated by using a modified version of the code of reference 9. For each shock solution, the values of \( C_h \) and \( C_T \) that satisfied equations (1) and (2), respectively, were calculated. (The exponents of pressure and density employed for method I, which are presented in table I, were used.) These values of \( C_h \) and \( C_T \) are plotted in figure 4 as a function of the product of free-stream velocity and \( \sin \theta_s \). For a normal-shock calculation, the quantity \( \sin \theta_s \) is equal to 1, but incorporating this quantity into the correlation scheme will permit oblique-shock calculations.

If the value of \( C_h \) is correlated for the present range of gas compositions, the resulting correlations in conjunction with the oblique-shock relations

\[
\rho_\infty U_\infty \sin \theta_s = \rho_s v_s \quad (9)
\]
\[
U_\infty \cos \theta_s = u_s \quad (10)
\]
\[
p_\infty + \rho_\infty U_\infty^2 \sin^2 \theta_s = p_s + \rho_s v_s^2 \quad (11)
\]
\[
h_\infty + \frac{1}{2} U_\infty^2 = h_s + \frac{1}{2}(u_s^2 + v_s^2) \quad (12)
\]

and the equation of state (eq. (1))

\[
h = h(p,\rho)
\]

provide a simple technique for rapidly computing the postshock properties over a wide range of conditions.

It was noted that the trends of the three curves for \( C_h \) presented in figure 4(a) were similar, as were the trends of the three curves for \( C_T \) presented in figure 4(b). A shift of these curves was performed whereby the curves for \( X_{H_2} = 0.85 \) and \( X_{H_2} = 0.7 \) were essentially collapsed onto the curve for \( X_{H_2} = 1 \), thus yielding approximately a single curve. In figures 5 and 6, the terms \( C_{h,U_t} \) and \( C_{T,U_t} \) represent the values of \( C_h \) and \( C_T \) after undergoing this transformation into a single curve. These values of \( C_{h,U_t} \) and \( C_{T,U_t} \) are plotted as a function of \( U_t \), which represents the normal component of the free-stream velocity after a translation of the curves in the axial direction. A fifth-degree polynomial was then applied to these data; the resulting curve fits are also shown in figures 5 and 6. The corresponding expressions for \( C_{h,U_t} \) and \( C_{T,U_t} \) are given by the following relations:
\[ C_{h,U_t} = 5.6611 - 0.52661U_t + 0.020376U_t^2 - 0.00037861U_t^3 \\
+ 0.000034265U_t^4 - 0.00000012206U_t^5 \]  
(13)

and

\[ C_{T,U_t} = -545.37 + 61.608U_t - 2.2459U_t^2 + 0.039922U_t^3 \\
- 0.00035148U_t^4 + 0.0000012361U_t^5 \]  
(14)

The value of \( U_t \) in equations (13) and (14) is given by the relation

\[ U_t = U_\infty \sin \theta_S \left[ 1 + 0.7467 \left( 1 - X_{H_2} \right) \right] \]  
(15)

where \( U_t \) is in km/sec. The values of \( C_h \) and \( C_T \) can now be simply computed for a specified free-stream velocity, shock angle, and gas composition by using equations (13), (14), and (15) in conjunction with the relations

\[ C_h = C_{h,U_t} - 0.3167 \left( 1 - X_{H_2} \right) \]  
(16)

and

\[ C_T = C_{T,U_t} + 61.2 \left( 1 - X_{H_2} \right) \]  
(17)

For convenience a brief outline for the application of method II is given as follows:

1. Given free-stream thermodynamic properties, \( U_\infty, \sin \theta_S, \) and \( X_{H_2} \), compute \( U_t \) and \( C_{h,U_t} \) from equations (15) and (13), respectively.

2. Compute \( C_h \) by equation (16).

3. Select exponents \( m \) and \( n \) from table I or determine exponents from equations (4) and (5) for use in equation (1). At this point, an equation of state in the form

\[ h = h(p, \rho) \]

has been obtained.

4. Use the values from the first three steps with equation (1) and equations (9) to (12) to cross the shock. Once the shock solution is performed so that the postshock pressure and density are known, the corresponding temperature may be computed from equation (2), where the exponents \( l \) and \( k \) are obtained from table I or computed from equations (7) and (8) and where \( C_T \) is computed from equation (17).
Typical results of method II are compared in table III with the results of exact normal-shock calculations of reference 9 for the three hydrogen-helium compositions and temperatures from 7000 to 31000 K. In general, the approximate values of enthalpy and pressure from method II agree with the exact values within 1 percent. The comparisons between the approximate values and the exact values of temperature and density showed agreement within about 3 percent except at the lower temperature of 7000 and 9000 K where discrepancies as high as 7 to 9 percent were observed. The improved accuracy in results between method II, in the range 11000 to 21000 K, and method I (table II) is quite significant.

The correlation equations of method II were also incorporated in a one-strip integral flow-field computer code developed by Peter A. Gnoffo of the Langley Research Center. A calculation was performed with this program for a 60° half-angle spherically blunted cone at free-stream conditions, in a 0.89H₂-0.11He mixture, which correspond to peak heating conditions for a Jovian entry. The present program was exercised for the same conditions, but with the chemistry code of reference 11 replacing the correlation equation of method II as the means for determining the equilibrium properties of the hydrogen-helium gas mixture. As discussed previously, the method of reference 11 yields values of enthalpy which are in good agreement with the values calculated by the method of reference 9, referred to herein as exact. For identification purposes, the method of reference 11 is referred to as "more detailed." It is of interest to note that the computational time for the approximate case using method II was five times faster than for the case using the method of reference 11.

Initially in the comparison of flow-field parameters, results computed with method II were obtained by computing the values \( C_h \) and \( C_T \) at conditions behind the normal shock and by holding these values constant throughout the shock layer. The thermodynamic properties behind the normal shock and the corresponding body streamline results were in excellent agreement with the more detailed calculations. However, for calculations immediately behind the more oblique portions of the bow shock, the deviation between the more detailed results and the approximate results increased to approximately 10 percent. This problem was the primary reason for the inclusion of the \( \sin \theta_S \) term in equation (15). Consequently, the values of \( C_h \) and \( C_T \) were computed at each shock location as a function of the normal component of the free-stream velocity. The comparison of the approximate shock and body streamline values with the more detailed values is shown in table IV. The comparisons are very good, and it is recommended that the proportionality constants be evaluated at each shock location. The percent deviation in the body streamline values of enthalpy and temperature between the approximate and more detailed method is shown in figure 7. The comparisons are seen to be very good and consequently justify the use of method II in approximate flow-field analysis.
CONCLUDING REMARKS

Simple relations for determining the enthalpy and temperature of equilibrium hydrogen-helium gas mixtures have been developed for hydrogen volumetric compositions from 1.0 to 0.7. These relations are expressed as a function of pressure and density and are valid for a range of temperatures from 7000 to 35 000 K and pressures from 0.10 to 3.14 MPa. The proportionality constant and exponents in the correlation equations were determined for each gas composition by applying a linear least-squares routine to a large number of thermodynamic calculations obtained from a detailed computer code. While these simple expressions generally yield results in reasonably good agreement (within 10 percent) with the detailed results over the range of hydrogen-helium conditions examined, errors as large as approximately 18 percent were observed for enthalpy in the range 11 000 to 21 000 K. By evaluating the proportionality constants at conditions close to the conditions of interest, the accuracy of the correlation equations was significantly improved. For use in the flow-field programs, these proportionality constants were correlated as a function of free-stream velocity, shock angle, and gas composition. The simple relation for enthalpy, coupled with the shock equations, provides very good agreement with thermodynamic properties computed by a detailed normal-shock procedure over the range of temperature and pressure previously noted. Since these correlations are applicable to shock flow-field problems, they were incorporated in a flow-field analysis and the resulting thermodynamic properties were compared with those obtained using a more detailed chemistry code in the same flow-field procedure. The results from these two procedures are in excellent agreement and demonstrate that the local shock angle should be included in the correlation equations.

Langley Research Center
National Aeronautics and Space Administration
Hampton, Va. 23665
June 25, 1976
APPENDIX

LEAST-SQUARES FIT TO THERMODYNAMIC DATA

Taking the logarithm of equation (1) results in a linear equation of the form

\[ \ln h = \ln C_h + m \ln \tilde{p} - n \ln \tilde{\rho} \]  

(1)

Since a large number (240) of data points will be fitted by using equation (A1), there are \( j \) equations but only three unknowns \( (C_h, m, \text{ and } n) \). Equation (A1) can be written as

\[ \ln \tilde{h}_1 = \ln C_h + m \ln \tilde{p}_1 - n \ln \tilde{\rho}_1 \]

\[ \ln \tilde{h}_2 = \ln C_h + m \ln \tilde{p}_2 - n \ln \tilde{\rho}_2 \]

\[ \ln \tilde{h}_j = \ln C_h + m \ln \tilde{p}_j - n \ln \tilde{\rho}_j \]

or in matrix notation

\[ AC = Y \]

where

\[ y_i = \ln \tilde{h}_i \]
\[ c_1 = \ln C_h \]
\[ a_{1,1} = 1 \]
\[ c_2 = m \]
\[ a_{1,2} = \ln \tilde{p}_1 \]
\[ c_3 = n \]
\[ a_{1,3} = \ln \tilde{\rho}_1 \]

The ith residual is

\[ r_i = a_{i,1}c_1 + a_{i,2}c_2 + a_{i,3}c_3 - y_i \]

The least-squares solution to this problem is the point \( C \) which minimizes

\[ \frac{1}{2} \| r \| \]

or

\[ \frac{1}{2}(r_1^2 + r_2^2 + \ldots + r_j^2) \rightarrow \text{ Minimum} \]
Let
\[ f(c) = \frac{1}{2} \| r \| = \frac{1}{2} \langle r, r \rangle \]
where
\[ r = AC - Y \]
Thus
\[ f(c) = \frac{1}{2} \langle AC - Y, AC - Y \rangle = \frac{1}{2} \langle C, A^T AC \rangle - \langle A^T Y, C \rangle + \frac{1}{2} \langle Y, Y \rangle \]
The minimum point occurs when \( \nabla f(c) = 0 \). The solution is
\[ A^T AC = A^T Y \quad \text{(A2)} \]
The solution of equation (A2) yields a least-squares fit for \( C_h, m, \) and \( n \). Even though there are \( j \) points, \( A^T A \) is only a \( 3 \times 3 \) matrix and \( A^T Y \) is of length 3. Thus, there are relatively few matrix operations to be performed.
REFERENCES


TABLE I.- CORRELATION RESULTS

(a) Enthalpy, $\tilde{h} = C_h \frac{\tilde{p}^m}{\tilde{p}^n}$

<table>
<thead>
<tr>
<th>Hydrogen-helium volumetric composition</th>
<th>$C_h$</th>
<th>$m$</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00H$_2$-0He</td>
<td>0.51224</td>
<td>0.95270</td>
<td>0.97582</td>
</tr>
<tr>
<td>0.85H$_2$-0.15He</td>
<td>0.47453</td>
<td>0.97572</td>
<td>1.00134</td>
</tr>
<tr>
<td>0.70H$_2$-0.30He</td>
<td>0.41547</td>
<td>1.00428</td>
<td>1.03337</td>
</tr>
</tbody>
</table>

(b) Temperature, $T = C_T \frac{\tilde{p}^l}{\tilde{p}^k}$

<table>
<thead>
<tr>
<th>Hydrogen-helium volumetric composition</th>
<th>$C_T$</th>
<th>$l$</th>
<th>$k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00H$_2$-0He</td>
<td>97.4174</td>
<td>0.67390</td>
<td>0.65200</td>
</tr>
<tr>
<td>0.85H$_2$-0.15He</td>
<td>106.5977</td>
<td>0.68141</td>
<td>0.65933</td>
</tr>
<tr>
<td>0.70H$_2$-0.30He</td>
<td>115.3464</td>
<td>0.69044</td>
<td>0.66773</td>
</tr>
</tbody>
</table>
TABLE II.- COMPARISON OF EXACT VALUES AND VALUES APPROXIMATED
BY METHOD I FOR TEMPERATURE AND ENTHALPY

<table>
<thead>
<tr>
<th>Pressure, p, MPa</th>
<th>Temperature, T, K</th>
<th>Enthalpy, ( \tilde{h} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Exact</td>
<td>Approximate</td>
</tr>
<tr>
<td></td>
<td>Exact</td>
<td>Approximate</td>
</tr>
<tr>
<td>1.00H₂-0He</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0999</td>
<td>7 000</td>
<td>7 209</td>
</tr>
<tr>
<td>.9811</td>
<td>7 000</td>
<td>7 357</td>
</tr>
<tr>
<td>2.1181</td>
<td>7 000</td>
<td>7 614</td>
</tr>
<tr>
<td>.1102</td>
<td>17 000</td>
<td>18 307</td>
</tr>
<tr>
<td>1.0334</td>
<td>17 000</td>
<td>16 183</td>
</tr>
<tr>
<td>2.0828</td>
<td>17 000</td>
<td>15 711</td>
</tr>
<tr>
<td>.1019</td>
<td>27 000</td>
<td>27 280</td>
</tr>
<tr>
<td>.9854</td>
<td>27 000</td>
<td>28 214</td>
</tr>
<tr>
<td>2.0920</td>
<td>27 000</td>
<td>28 182</td>
</tr>
<tr>
<td>0.85H₂-0.15He</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0999</td>
<td>7 000</td>
<td>7 182</td>
</tr>
<tr>
<td>.9745</td>
<td>7 000</td>
<td>7 516</td>
</tr>
<tr>
<td>2.1007</td>
<td>7 000</td>
<td>7 602</td>
</tr>
<tr>
<td>.1088</td>
<td>17 000</td>
<td>18 086</td>
</tr>
<tr>
<td>1.0258</td>
<td>17 000</td>
<td>16 132</td>
</tr>
<tr>
<td>2.0683</td>
<td>17 000</td>
<td>15 691</td>
</tr>
<tr>
<td>.1038</td>
<td>27 000</td>
<td>27 515</td>
</tr>
<tr>
<td>.9787</td>
<td>27 000</td>
<td>28 162</td>
</tr>
<tr>
<td>2.0625</td>
<td>27 000</td>
<td>28 045</td>
</tr>
<tr>
<td>0.70H₂-0.30He</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0965</td>
<td>7 000</td>
<td>7 142</td>
</tr>
<tr>
<td>.9542</td>
<td>7 000</td>
<td>7 495</td>
</tr>
<tr>
<td>2.0694</td>
<td>7 000</td>
<td>7 593</td>
</tr>
<tr>
<td>.1039</td>
<td>17 000</td>
<td>17 806</td>
</tr>
<tr>
<td>1.0113</td>
<td>17 000</td>
<td>16 069</td>
</tr>
<tr>
<td>2.0557</td>
<td>17 000</td>
<td>15 670</td>
</tr>
<tr>
<td>.1031</td>
<td>27 000</td>
<td>27 756</td>
</tr>
<tr>
<td>.9669</td>
<td>27 000</td>
<td>28 099</td>
</tr>
<tr>
<td>2.0349</td>
<td>27 000</td>
<td>27 882</td>
</tr>
</tbody>
</table>
### Table III: Comparison of Exact Values and Values Approximated by Method II for Normal-Shock Properties

<table>
<thead>
<tr>
<th>h (Exact)</th>
<th>h (Approximate)</th>
<th>T, K</th>
<th>p (Exact)</th>
<th>p (Approximate)</th>
<th>(\rho) (Exact)</th>
<th>(\rho) (Approximate)</th>
<th>(U_\infty, \text{km/sec})</th>
</tr>
</thead>
<tbody>
<tr>
<td>359.64</td>
<td>358.54</td>
<td>9000</td>
<td>9120</td>
<td>4.367</td>
<td>4.374</td>
<td>4.598</td>
<td>4.658</td>
</tr>
<tr>
<td>421.55</td>
<td>422.14</td>
<td>11000</td>
<td>10884</td>
<td>5.088</td>
<td>5.109</td>
<td>4.303</td>
<td>4.445</td>
</tr>
<tr>
<td>530.57</td>
<td>528.94</td>
<td>13000</td>
<td>13047</td>
<td>6.422</td>
<td>6.431</td>
<td>4.378</td>
<td>4.432</td>
</tr>
<tr>
<td>707.01</td>
<td>704.63</td>
<td>15000</td>
<td>15045</td>
<td>8.615</td>
<td>8.623</td>
<td>4.682</td>
<td>4.719</td>
</tr>
<tr>
<td>950.80</td>
<td>947.72</td>
<td>17000</td>
<td>16816</td>
<td>11.660</td>
<td>11.681</td>
<td>5.023</td>
<td>5.086</td>
</tr>
<tr>
<td>1530.40</td>
<td>1524.82</td>
<td>21000</td>
<td>21199</td>
<td>18.887</td>
<td>18.845</td>
<td>5.343</td>
<td>5.220</td>
</tr>
<tr>
<td>2394.90</td>
<td>2387.15</td>
<td>31000</td>
<td>30719</td>
<td>29.200</td>
<td>29.236</td>
<td>4.633</td>
<td>4.678</td>
</tr>
</tbody>
</table>

#### 1.00H₂-0He

<table>
<thead>
<tr>
<th>h (Exact)</th>
<th>h (Approximate)</th>
<th>T, K</th>
<th>p (Exact)</th>
<th>p (Approximate)</th>
<th>(\rho) (Exact)</th>
<th>(\rho) (Approximate)</th>
<th>(U_\infty, \text{km/sec})</th>
</tr>
</thead>
<tbody>
<tr>
<td>279.43</td>
<td>279.26</td>
<td>7000</td>
<td>7384</td>
<td>3.417</td>
<td>3.398</td>
<td>5.772 \times 10^{-3}</td>
<td>5.462 \times 10^{-3}</td>
</tr>
<tr>
<td>318.54</td>
<td>318.57</td>
<td>9000</td>
<td>8960</td>
<td>3.848</td>
<td>3.850</td>
<td>5.026</td>
<td>5.043</td>
</tr>
<tr>
<td>376.11</td>
<td>376.29</td>
<td>11000</td>
<td>10898</td>
<td>4.523</td>
<td>4.524</td>
<td>4.745</td>
<td>4.749</td>
</tr>
<tr>
<td>472.26</td>
<td>476.89</td>
<td>13000</td>
<td>13243</td>
<td>5.756</td>
<td>5.733</td>
<td>4.866</td>
<td>4.712</td>
</tr>
<tr>
<td>639.40</td>
<td>638.82</td>
<td>15000</td>
<td>15338</td>
<td>7.772</td>
<td>7.744</td>
<td>5.241</td>
<td>5.073</td>
</tr>
<tr>
<td>860.40</td>
<td>859.92</td>
<td>17000</td>
<td>17098</td>
<td>10.534</td>
<td>10.520</td>
<td>5.641</td>
<td>5.561</td>
</tr>
<tr>
<td>1371.60</td>
<td>1370.58</td>
<td>21000</td>
<td>21310</td>
<td>16.894</td>
<td>16.852</td>
<td>5.999</td>
<td>5.849</td>
</tr>
<tr>
<td>2211.60</td>
<td>2211.42</td>
<td>31000</td>
<td>31272</td>
<td>27.012</td>
<td>26.958</td>
<td>5.376</td>
<td>5.277</td>
</tr>
</tbody>
</table>

#### 0.85H₂-0.15He

<table>
<thead>
<tr>
<th>h (Exact)</th>
<th>h (Approximate)</th>
<th>T, K</th>
<th>p (Exact)</th>
<th>p (Approximate)</th>
<th>(\rho) (Exact)</th>
<th>(\rho) (Approximate)</th>
<th>(U_\infty, \text{km/sec})</th>
</tr>
</thead>
<tbody>
<tr>
<td>241.65</td>
<td>241.89</td>
<td>7000</td>
<td>6754</td>
<td>2.936</td>
<td>2.947</td>
<td>6.087 \times 10^{-3}</td>
<td>6.298 \times 10^{-3}</td>
</tr>
<tr>
<td>277.44</td>
<td>277.85</td>
<td>9000</td>
<td>8425</td>
<td>3.330</td>
<td>3.357</td>
<td>5.342</td>
<td>5.692</td>
</tr>
<tr>
<td>330.50</td>
<td>330.72</td>
<td>11000</td>
<td>10544</td>
<td>3.950</td>
<td>3.966</td>
<td>5.088</td>
<td>5.239</td>
</tr>
<tr>
<td>423.25</td>
<td>422.82</td>
<td>13000</td>
<td>13135</td>
<td>5.083</td>
<td>5.064</td>
<td>5.277</td>
<td>5.122</td>
</tr>
<tr>
<td>570.10</td>
<td>569.51</td>
<td>15000</td>
<td>15341</td>
<td>6.908</td>
<td>6.883</td>
<td>5.728</td>
<td>5.554</td>
</tr>
<tr>
<td>2034.50</td>
<td>2034.64</td>
<td>31000</td>
<td>31085</td>
<td>24.872</td>
<td>24.890</td>
<td>6.154</td>
<td>6.189</td>
</tr>
</tbody>
</table>
TABLE IV.- COMPARISON OF FLOW-FIELD PARAMETERS FOR MORE DETAILED AND APPROXIMATE (METHOD II) CHEMISTRY CODES

\[ U_\infty = 39.09 \text{ km/sec; } \rho_\infty = 0.000465 \text{ kg/m}^3; \ T_\infty = 140 \text{ K; gas mixture, } 0.80 \text{H}_2-0.11 \text{He}; \text{ body, } 60^\circ \text{ half-angle spherically blunted cone} \]

<table>
<thead>
<tr>
<th>( s/\tau_n )</th>
<th>( \delta/\tau_n )</th>
<th>( T_s, K )</th>
<th>( T_i, K )</th>
<th>( p_s/p_\infty U_\infty^2 )</th>
<th>( p_i/p_\infty U_\infty^2 )</th>
<th>( \rho_s/\rho_\infty )</th>
<th>( \rho_i/\rho_\infty )</th>
</tr>
</thead>
<tbody>
<tr>
<td>More detailed</td>
<td>Approximate</td>
<td>More detailed</td>
<td>Approximate</td>
<td>More detailed</td>
<td>Approximate</td>
<td>More detailed</td>
<td>Approximate</td>
</tr>
<tr>
<td>0</td>
<td>0.0780</td>
<td>0.0794</td>
<td>15 514</td>
<td>15 690</td>
<td>15 619</td>
<td>15 809</td>
<td>0.9033</td>
</tr>
<tr>
<td>0.050</td>
<td>0.0784</td>
<td>0.0798</td>
<td>15 506</td>
<td>15 670</td>
<td>15 609</td>
<td>15 797</td>
<td>0.9023</td>
</tr>
<tr>
<td>0.100</td>
<td>0.0793</td>
<td>0.0808</td>
<td>15 477</td>
<td>15 632</td>
<td>15 584</td>
<td>15 766</td>
<td>0.8981</td>
</tr>
<tr>
<td>0.150</td>
<td>0.0807</td>
<td>0.0823</td>
<td>15 423</td>
<td>15 569</td>
<td>15 549</td>
<td>15 725</td>
<td>0.8904</td>
</tr>
<tr>
<td>0.200</td>
<td>0.0826</td>
<td>0.0842</td>
<td>15 346</td>
<td>15 477</td>
<td>15 510</td>
<td>15 677</td>
<td>0.8794</td>
</tr>
<tr>
<td>0.263</td>
<td>0.0856</td>
<td>0.0874</td>
<td>15 224</td>
<td>15 335</td>
<td>15 453</td>
<td>15 608</td>
<td>0.8624</td>
</tr>
<tr>
<td>0.341</td>
<td>0.0910</td>
<td>0.0930</td>
<td>15 056</td>
<td>15 140</td>
<td>15 376</td>
<td>15 515</td>
<td>0.8393</td>
</tr>
<tr>
<td>0.438</td>
<td>0.1020</td>
<td>0.1044</td>
<td>14 871</td>
<td>14 928</td>
<td>15 301</td>
<td>15 425</td>
<td>0.8146</td>
</tr>
<tr>
<td>0.520</td>
<td>0.1129</td>
<td>0.1155</td>
<td>14 800</td>
<td>14 848</td>
<td>15 284</td>
<td>15 403</td>
<td>0.8053</td>
</tr>
<tr>
<td>0.524</td>
<td>0.1172</td>
<td>0.1200</td>
<td>14 791</td>
<td>14 837</td>
<td>15 282</td>
<td>15 400</td>
<td>0.8042</td>
</tr>
<tr>
<td>0.550</td>
<td>0.1222</td>
<td>0.1251</td>
<td>14 772</td>
<td>14 841</td>
<td>15 295</td>
<td>15 416</td>
<td>0.8016</td>
</tr>
<tr>
<td>0.584</td>
<td>0.1284</td>
<td>0.1314</td>
<td>14 757</td>
<td>14 796</td>
<td>15 301</td>
<td>15 423</td>
<td>0.7997</td>
</tr>
<tr>
<td>0.625</td>
<td>0.1361</td>
<td>0.1392</td>
<td>14 745</td>
<td>14 782</td>
<td>15 300</td>
<td>15 422</td>
<td>0.7961</td>
</tr>
<tr>
<td>0.677</td>
<td>0.1454</td>
<td>0.1487</td>
<td>14 732</td>
<td>14 766</td>
<td>15 295</td>
<td>15 416</td>
<td>0.7965</td>
</tr>
<tr>
<td>0.742</td>
<td>0.1570</td>
<td>0.1604</td>
<td>14 716</td>
<td>14 747</td>
<td>15 289</td>
<td>15 408</td>
<td>0.7945</td>
</tr>
<tr>
<td>0.824</td>
<td>0.1710</td>
<td>0.1747</td>
<td>14 695</td>
<td>14 722</td>
<td>15 282</td>
<td>15 399</td>
<td>0.7918</td>
</tr>
<tr>
<td>0.926</td>
<td>0.1881</td>
<td>0.1920</td>
<td>14 690</td>
<td>14 688</td>
<td>15 272</td>
<td>15 386</td>
<td>0.7861</td>
</tr>
<tr>
<td>1.053</td>
<td>0.2084</td>
<td>0.2127</td>
<td>14 628</td>
<td>14 644</td>
<td>15 256</td>
<td>15 358</td>
<td>0.7833</td>
</tr>
<tr>
<td>1.212</td>
<td>0.2324</td>
<td>0.2369</td>
<td>14 574</td>
<td>14 580</td>
<td>15 238</td>
<td>15 343</td>
<td>0.7765</td>
</tr>
<tr>
<td>1.410</td>
<td>0.2596</td>
<td>0.2644</td>
<td>14 494</td>
<td>14 486</td>
<td>15 206</td>
<td>15 302</td>
<td>0.7664</td>
</tr>
<tr>
<td>1.610</td>
<td>0.2834</td>
<td>0.2886</td>
<td>14 392</td>
<td>14 367</td>
<td>15 163</td>
<td>15 248</td>
<td>0.7539</td>
</tr>
<tr>
<td>1.810</td>
<td>0.3030</td>
<td>0.3082</td>
<td>14 257</td>
<td>14 209</td>
<td>15 100</td>
<td>15 167</td>
<td>0.7377</td>
</tr>
<tr>
<td>2.010</td>
<td>0.3169</td>
<td>0.3220</td>
<td>14 061</td>
<td>13 983</td>
<td>14 994</td>
<td>15 032</td>
<td>0.7150</td>
</tr>
<tr>
<td>2.160</td>
<td>0.3224</td>
<td>0.3274</td>
<td>13 835</td>
<td>13 724</td>
<td>14 837</td>
<td>14 832</td>
<td>0.6897</td>
</tr>
<tr>
<td>2.232</td>
<td>0.3231</td>
<td>0.3280</td>
<td>13 678</td>
<td>13 547</td>
<td>14 673</td>
<td>14 629</td>
<td>0.6729</td>
</tr>
</tbody>
</table>

\( \delta/\tau_n \) is the normalized time for the flow to pass through the angle \( \delta \).
Figure 1. - Enthalpy as a function of temperature for hydrogen at pressure $p/p_0 = 1$. 
Figure 2.- Correlation factors for enthalpy as function of initial volumetric composition of hydrogen.
Figure 3.- Correlation factors for temperature as function of initial volumetric composition of hydrogen.
Hydrogen-helium volumetric composition

- 1.00H₂-0He
- 0.85H₂-0.15He
- 0.70H₂-0.30He

(a) Proportionality constant for enthalpy correlation.

Figure 4.- Correlation coefficients for enthalpy and temperature for shock solutions as function of normal free-stream velocity component.
Hydrogen-helium volumetric composition

- \( 1.00 \text{H}_2 - 0.00 \text{He} \)
- \( 0.85 \text{H}_2 - 0.15 \text{He} \)
- \( 0.70 \text{H}_2 - 0.30 \text{He} \)

(b) Proportionality constant for temperature correlation.

Figure 4.- Concluded.
Figure 5. - Transformed coefficients of enthalpy for shock solutions as function of transformed velocity.
Figure 6.- Transformed coefficients of temperature for shock solutions as function of transformed velocity.
(a) Temperature.

(b) Enthalpy.

Figure 7.- Percent differences of thermodynamic variables around body.

\[ U_\infty = 39.09 \text{ km/sec}; \quad \rho_\infty = 0.000465 \text{ kg/m}^3; \quad T_\infty = 140 \text{ K}; \quad \text{gas mixture,} \]

0.89H\textsubscript{2} - 0.11He; body, 60° half-angle spherically blunted cone.
"The aeronautical and space activities of the United States shall be conducted so as to contribute ... to the expansion of human knowledge of phenomena in the atmosphere and space. The Administration shall provide for the widest practicable and appropriate dissemination of information concerning its activities and the results thereof."

— National Aeronautics and Space Act of 1958

NASA SCIENTIFIC AND TECHNICAL PUBLICATIONS

TECHNICAL REPORTS: Scientific and technical information considered important, complete, and a lasting contribution to existing knowledge.

TECHNICAL NOTES: Information less broad in scope but nevertheless of importance as a contribution to existing knowledge.

TECHNICAL MEMORANDUMS: Information receiving limited distribution because of preliminary data, security classification, or other reasons. Also includes conference proceedings with either limited or unlimited distribution.

CONTRACTOR REPORTS: Scientific and technical information generated under a NASA contract or grant and considered an important contribution to existing knowledge.

TECHNICAL TRANSLATIONS: Information published in a foreign language considered to merit NASA distribution in English.

SPECIAL PUBLICATIONS: Information derived from or of value to NASA activities. Publications include final reports of major projects, monographs, data compilations, handbooks, sourcebooks, and special bibliographies.

TECHNOLOGY UTILIZATION PUBLICATIONS: Information on technology used by NASA that may be of particular interest in commercial and other non-aerospace applications. Publications include Tech Briefs, Technology Utilization Reports and Technology Surveys.

Details on the availability of these publications may be obtained from:

SCIENTIFIC AND TECHNICAL INFORMATION OFFICE

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Washington, D.C. 20546