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EMPIRICAL EQUATIONS FOR THE THERMODYNAMIC PROPERTIES OF AIR AND NITROGEN TO 15,000 °K

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ARNOLD ENGINEERING DEVELOPMENT CENTER

AIR FORCE SYSTEMS COMMAND

UNITED STATES AIR FORCE

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FOREWORD

The authors gratefully acknowledge the assistance of Mr. C. H. Link, Scientific Computing Services, Office of the Director of Engineering, in developing the empirical surface fit procedure used in this work.

ABSTRACT

Empirical equations are obtained for equilibrium dissociating and ionizing air and nitrogen for temperatures up to 15,000°K and in the entropy range $1.42 \leq \log (S/R) \leq 2.06$. The corresponding density range is approximately 10^{-6} to 10^{2} amagats. The density $\rho(p, S)$, enthalpy $H(p, S)$, compressibility factor $Z(p, S)$, and speed of sound $a(p, S)$ are presented in equation form and as an IBM Fortran subroutine program. The errors in each empirical surface are indicated.

PUBLICATION REVIEW

This report has been reviewed and publication is approved.

Darreld K Calkins

Darreld K. Calkins
Major, USAF
AF Representative, VKF
DCS/Test

Jean A. Jack

Jean A. Jack
Colonel, USAF
DCS/Test

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NOMENCLATURE

a	Speed of sound, ft/sec
C_p	Specific heat at constant pressure, ft^2/sec^2-°K
C_v	Specific heat at constant volume, ft^2/sec^2-°K
H	Enthalpy, ft^2/sec^2
k	Parameter in empirical equations
p	Pressure, atm
R	Gas constant, ft^2/sec^2-°K
S	Entropy, ft^2/sec^2-°K
T	Temperature, °K
x	Log p
x_o	Parameter in empirical equations
y	Log (S/R)
Z	Compressibility factor
γ	Ratio of specific heats, C_p/C_v
γ_E	Isentropic exponent, $(\partial \log p/\partial \log \rho)_S$
ρ	Mass density in amagats where one amagat is the density of the perfect gas at one atmosphere pressure and 273.15°K

SUBSCRIPTS

a	Reference condition at one atmosphere pressure and 273.15°K
S	At constant entropy

All logarithms are to the base 10

REFERENCE QUANTITIES

T_a = 273.15°K

p_a = 14.696 psia = 2116.224 lb_f/ft^2

	Air	Nitrogen
ρ_a, lb_f-sec^2/ft^4	2.507542×10^{-3}	2.423609×10^{-3}
R, ft^2/sec^2-°K	3089.67	3196.67
γ_a	1.4	1.4
a_a, ft/sec	1086.98	1105.64

1.0 INTRODUCTION

In making numerical calculations with high-speed digital computers where gas properties are needed at high temperature, the need for accurate and quickly obtainable data is obvious. The data usually exist in tabular form which may provide the necessary accuracy but does not facilitate fast operation especially where large quantities of data are needed.

A method of empirically fitting thermodynamic properties of air at high temperature was devised by Grabau (Ref. 1). The method assumes a family of curves, e.g., straight lines which are joined by transition functions which are asymptotic at both ends. If an inflection point occurs at x_0, then the form is

$$y = f_1(x) + \frac{f_2(x) - f_1(x)}{1 + \exp[k(x - x_0)]}$$

where $f_1(x)$ and $f_2(x)$ represent the equations of the two limiting curves (see Fig. 1a), and k is a parameter which depends on the rate at which the curve moves from $f_1(x)$ to $f_2(x)$. If no inflection point occurs in the transition, the form is then

$$y = f_1(x) + \frac{f_2(x) - f_1(x)}{1 - \exp[k(x - x_0)]}$$

where x_0 is now the intersection of $f_1(x)$ and $f_2(x)$ (see Fig. 1b).

After determining the parameters x_0 and k for each curve in the family, the parameters are then fitted as functions of the second independent variable. The interested reader can find more detail in Ref. 1. The method which is largely done by hand gives good accuracy, but it requires considerable effort.

Recently a machine program was developed by the Scientific Computing Services, Office of the Director of Engineering, Arnold Engineering Development Center (AEDC), Air Force Systems Command (AFSC), which permits accurate fitting of data almost entirely by machine. In this method as applied to the present investigation, all the data were plotted in the form $w = w(x, y)$. The resulting surface was examined for changes in curvature, and those regions where the curvature appeared to be slowly changing were considered as sub-regions of the entire domain. These sub-regions were fitted independently in the form $w = w(x, y)$. The resulting surfaces were connected by the Grabau-type transitions to form the entire surface.

Manuscript received June 1963.

2.0 THERMODYNAMIC SURFACES

2.1 AIR

The data of Hilsenrath, Klein, and Woolley (Ref. 2) for equilibrium dissociating and ionizing air neglecting intermolecular force effects were interpolated at constant $\log S$, and the results were plotted as $H(p, S)$, $\rho(p, S)$, and $Z(p, S)$. The surfaces were then fitted as described, and the results are shown plotted in Figs. 2-4. The symbols denote the errors in the surface fit when compared with the interpolated data. Similar comparisons were made with the original data of Ref. 2, and the errors caused by the interpolation at constant S were completely negligible in comparison with the errors in the surface fit.

The data of Landis and Nilson (Ref. 3) for the speed of sound in air based on the properties given in Ref. 2 were also fit, and the results are shown in Fig. 5. The results of the interpolation at constant S were used to compute the isentropic exponent $\gamma_E = (\partial \log p/\partial \log \rho)_S$, and then the speed of sound $a = (\gamma_E ZRT)^{1/2}$ was computed and compared with Landis and Nilson (Ref. 3). The results agreed within five significant figures.

The data of Humphrey and Neel (Ref. 4) below 1500°K were interpolated at constant S neglecting the intermolecular force effects in the data, and the results were fitted as those above 1500°K except for the speed of sound. The speed of sound was computed from the data of Ref. 4 as described above and fitted in the form $a/a_a = f\left[(T/T_a)^{1/2}\right]$.

The results for the air surface fit are given in Appendix I in terms of equations and an IBM Fortran subroutine listing. A Fortran source deck can be obtained from the authors.

2.2 NITROGEN

The data of Hilsenrath (Ref. 5) for equilibrium dissociating and ionizing nitrogen neglecting intermolecular force effects between 2000 and 15,000°K were interpolated at constant $\log S$ and $H(p, S)$, $\rho(p, S)$, and $Z(p, S)$ were fitted as were the air data. Hilsenrath gave $\gamma = C_p/C_v$ which, as seen from the air data of Landis and Nilson, is not equal to γ_E at high temperature; hence, γ_E and a were computed for nitrogen, and a surface fit was obtained. The nitrogen surface fit results are shown in Figs. 6-9.

Below 2000°K the data of Hilsenrath et al. (Ref. 6) were used. The two sources introduced a discontinuity in the thermodynamic surfaces at 2000°K. The data were faired in the vicinity of 2000°K with favor given to those data above that temperature.

The results of the nitrogen surface fit are given in Appendix II as equations and an IBM Fortran subroutine listing. A Fortran source deck can be obtained from the authors.

3.0 CONCLUDING REMARKS

The equilibrium dissociating and ionizing thermodynamic properties of air and nitrogen neglecting intermolecular force effects have been fitted to sufficient accuracy for most engineering purposes. An example of the maximum errors in the surface fits is given in the following table where the ranges were $-1 \leq \log p \leq 1$ and $2000 \leq T \leq 15{,}000$°K :

PERCENT ERROR

	ρ	H/R	Z	T	a
Air	2.42	1.96	0.75	2.24	2.78*
Nitrogen †	4.74	3.62	0.86	5.09	1.88

The results of the speed of sound surface fit can be used to compute the isentropic exponent γ_E, and the resulting error will be about twice that in the speed of sound (i. e., on the order of 4 percent). This also may be sufficiently accurate for many engineering calculations.

REFERENCES

1. Grabau, M. "A Method of Forming Continuous Empirical Equations for the Thermodynamic Properties of Air from Ambient Temperatures to 15,000°K, with Applications." AEDC-TN-59-102, August 1959.

*Maximum error for $T \geq 2200$°K was less than 2 percent.

†Maximum errors for $T \leq 12{,}000$°K were 2.49 percent for ρ and 2.42 percent in T.

2. Hilsenrath, J., Klein, M., and Woolley, H. W. "Tables of Thermodynamic Properties of Air Including Dissociation and Ionization from 1500°K to 15,000°K." AEDC-TR-59-20, December 1959.

3. Landis, F. and Nilson, E. N. "Thermodynamic Properties of Ionized and Dissociated Air from 1500°K to 15,000°K." Pratt and Whitney Aircraft Report No. 1921, January 1961.

4. Humphrey, R. L. and Neel, C. A. "Tables of Thermodynamic Properties of Air from 90 to 1500°K." AEDC-TN-61-103, August 1961.

5. National Bureau of Standards. Private communication from J. Hilsenrath, May 1959.

6. Hilsenrath, J., et al. "Tables of Thermal Properties of Gases." National Bureau of Standards Circular 564, November 1955.

APPENDIX I

Thermodynamic Properties of Air from 90° to 15,000°K

1. The compressibility factor $Z = f(x, y)$ where $x = \log p$ and $y = \log(S/R)$, let A denote surface above 1500°K and B denote surface below 1500°K.

$$Z_A = 1 + (Z_2 - 1)\,TZ_{12} + (Z_3 - Z_2)\,TZ_{23} + (Z_4 - Z_3)\,TZ_{34} + (4 - Z_4)\,TZ_{45}$$

where

$$Z_i = a_o + a_1x + a_2y + a_3x^2 + a_4xy + a_5y^2 + a_6x^3 + a_7x^2y + a_8xy^2 + a_9y^3$$

$$x = \log p \text{ and } y = \log(S/R)$$

$$TZ_{ij} = 1/\left\{1 + \exp[k(x - xZ_{ij})]\right\}, \quad k = -10$$

$$xZ_{ij} = a_o + a_1y$$

$$Z_B = 1 + (Z_A - 1)\,T_{BA}$$

$$T_{BA} = 1/\left\{1 + \exp[k(x - x_{BA})]\right\}, \quad k = -10$$

$$x_{BA} = a_o + a_1y + a_2y^2$$

2. The enthalpy $\log(H/R) = f(x, y)$

where $x = \log p$ and $y = \log(S/R)$

$$\log(H/R) = \log(H/R)_B + [\log(H/R)_A - \log(H/R)_B]\,T_{BA}$$

where

$$\log(H/R)_B = H_B$$

and

$$H_i = a_o + a_1x + a_2y + a_3x^2 + a_4xy + a_5y^2 + a_6x^3 + a_7x^2y + a_8xy^2 + a_9y^3$$

For

i) $y \leq 1.6$, $\log (H/R)_A = H_1$

ii) $1.6 < y \leq 1.76$,

$$\log (H/R)_A = H_2$$

where $H_2 = H_{21} + (H_{22} - H_{21})\, T H_{12}$

$$TH_{12} = 1/\left\{1 + \exp\left[k(x - xH_{12})\right]\right\}, \quad k = -10$$

$$xH_{12} = a_0 + a_1 y + a_2 y^2$$

iii) $1.76 < y \leq 1.92$, $\log (H/R)_A = H_3$

iv) $1.92 < y$, $\log (H/R)_A = H_4$

3. The density $\log \rho = f(x, y)$ where $x = \log p$ and $y = \log (S/R)$.

$$\log \rho = \log \rho_B + [\log \rho_A - \log \rho_B]\, T_{BA}$$

where $\log \rho_B = R_B$

and

$$\log \rho_A = R_1 + (R_2 - R_1)\, TR_{12} + (R_3 - R_2)\, TR_{23} + (R_4 - R_3)\, TR_{34} + (R_5 - R_4)\, TR_{45}$$

$$TR_{ij} = 1/\left\{1 + \exp\left[k(x - xR_{ij})\right]\right\}, \quad k = -10$$

$$xR_{ij} = a_0 + a_1 y + a_2 y^2 + a_3 y^3$$

4. The speed of sound $a/a_a = f(x, y)$ where $x = \log p$ and $y = \log (S/R)$.

i) For $2100 \leq T \leq 14{,}600°K$

$$a/a_a = F_1 + (F_2 - F_1)\, TR_1 + (F_3 - F_2)\, TR_2 + (F_4 - F_3)\, TR_3$$

where

$$TR_1 = 1/\left\{1 + \exp\left[k(x - x_1)\right]\right\}, \quad k = -10$$

$$x_1 = a_0 + a_1 y + a_2 y^2 + a_3 y^3$$

$$TR_2 = 1/\left\{1 + \exp\left[k(x - x_2)\right]\right\}, \quad k = -10$$

$$x_2 = a_0 + a_1 y + a_2 y^2 + a_3 y^3$$

$$TR_3 = 1/\left\{1 + \exp\left[k(x - x_3)\right]\right\}, \quad k = -10$$

$$x_3 = a_0 + a_1 y + a_2 y^2 + a_3 y^3$$

$$F_1 = a_0 + a_1 x + a_2 y + a_3 x^2 + a_4 xy + a_5 y^2 + a_6 x^3 + a_7 x^2 y + a_8 xy^2 + a_9 y^3$$

$$F_2 = F_{21} + (F_{22} - F_{21})\, TR_{21}$$

$$TR_{21} = 1/\left\{1 + \exp\left[k(x - x_{21})\right]\right\}, \quad k = -10$$

$$x_{21} = a_0 + a_1 y + a_2 y^2 + a_3 y^3$$

$$F_{21} = a_0 + a_1 x + a_2 y + a_3 x^2 + a_4 xy + a_5 y^2 + a_6 x^3 + a_7 x^2 y + a_8 xy^2 + a_9 y^3$$

$$F_{22} = a_0 + a_1 x + a_2 y + a_3 x^2 + a_4 xy + a_5 y^2$$

$$F_3 = a_0 + a_1 x + a_2 y + a_3 x^2 + a_4 xy + a_5 y^2 + a_6 x^3 + a_7 x^2 y + a_8 xy^2 + a_9 y^3$$

$$F_4 = a_0 + a_1 x + a_2 y + a_3 x^2 + a_4 xy + a_5 y^2$$

ii) For $T < 2100°K$

$$a/a_a = F_5 = a_0 + a_1 (T/T_a)^{1/2} + a_2 (T/T_a)$$

TABLE 1

The Coefficients in the Air Surface Fits

	a_o	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8	a_9
Z_2	519.80374	-23.753514	-983.90729	0.37296957	30.084379	620.04168	-0.0021648826	-0.23710079	-9.496903	-129.78921
Z_3	366.40674	-15.517444	-647.42436	0.18701758	18.040383	379.59834	-0.00087958438	-0.10580129	-5.1888254	- 73.504269
Z_4	516.07331	-16.59277	-808.49823	0.071256235	16.526813	418.45341	0.00094183347	-0.019727817	-3.9948906	- 71.038921
H_1	12.693869	5.3975312	- 48.729217	-0.14961521	-5.8788774	48.19278	0.00090144132	0.091151473	1.6282829	- 13.065267
H_{21}	-84.008522	2.5761318	107.06198	-0.014352904	-1.5313194	-32.316439				
H_{22}	-156.37194	6.6959228	269.93097	-0.097179965	-7.5379714	-152.13866	0.00057029937	0.058364795	2.1592755	28.940926
H_3	-35.160671	0.5366924	56.99585	-0.022661358	-0.48470305	-27.641087	0.00058568839	0.016299962	0.14073606	4.712261
H_4	-114.94796	4.004583	180.08427	-0.041327787	-4.0366535	-90.76006	0.00040320694	0.024360248	1.0462299	15.467804
R_1	15.951867	- 0.00228295	-15.994242	0.0065187267	0.53079685	3.175974				
R_2	1541.1666	-63.03935	-2993.1662	0.935437	84.30375	1938.7061	-0.004746016	-0.6128404	-27.422666	-419.0881
R_3	427.4745	-18.126622	-765.47626	0.29343169	22.926877	456.717	-0.0017033404	-0.18068309	- 6.9143617	- 91.131851
R_4	206.23144	- 8.2270278	-329.5465	0.1324191	9.8884165	175.03931	-0.0010178454	-0.07654371	- 2.6920144	- 31.237834
R_5	-399.52358	12.899477	411.64144	-0.097694919	-6.2204477	-106.6733				
H_B	28.160664	- 2.2339873	- 59.053694	0.054973544	3.7183257	40.986503	-0.0004292698	-0.040726332	- 1.3704505	- 8.253645
R_B	- 79.282533	6.3537078	179.22721	-0.12607098	-8.4013122	-129.95269	0.0010037437	0.094185511	3.1256966	30.203862
X_1	635.054	-1220.46	803.882	-180.845						
X_2	373.702	- 663.358	408.854	- 86.8056						
X_3	1703.78	-2602.97	1337.93	-231.422						
X_{21}	1043.37	-1820.34	1076.36	-215.445						
F_{21}	-1814.5117	86.096078	3315.6099	-1.7593034	-107.2534	-2023.201	0.016287679	1.1398134	33.659607	413.41945
F_{22}	2651.2944	-81.405596	-3099.0064	0.69752668	48.062596	907.70889				
F_1	-4409.6241	196.82259	8746.4634	-3.1650299	-262.32947	-5786.449	0.020004186	2.1429825	87.589029	1227.6718
F_3	-3217.8037	195.34964	5348.2143	-4.6268475	-221.12705	-2970.8649	0.044614358	2.7079177	63.042803	553.12007
F_4	16976.939	-476.10242	-17445.315	3.6534057	246.41125	4486.3118				
F_5	-0.0753808	1.12644	-0.0552696							
XZ_{12}	62.91	- 41.5								
XZ_{23}	72.945	- 45.75								
XZ_{34}	65.75	- 37.5								
XZ_{45}	62.92	- 32.0								
XH_{12}	-61.2053	114.103	-47.5532							
XR_{12}	-16.5527	57.45	-30.8036							
XR_{23}	499.544	-938.91	609.028	-135.995						
XR_{34}	360.507	-634.538	389.174	- 82.4653						
XR_{45}	489.628	-458.5	106.25							
X_{BA}	-39.1442	83.0558	-38.2842							

```
      SUBROUTINE WRKHAT (I,PLOG,SRLOG,ZHRT,AOAO)
C     AIR
C     I=1 , Z IS RETURNED
C     I=2 , LOG(H/R) IS RETURNED
C     I=3 , LOG(RHO/RHOA) IS RETURNED
C     I=4 , T AND A/AO ARE RETURNED
C     PLOG= LOG(P/PA)
C     SRLOG=LOG(S/R)
C     ZHRT= Z,LOG(H/R),LOG(RHO/RHOA), OR T CORRESPONDING TO THE
C    1 SELECTION OF I
C     R=3089.66
      X15=-39.1442+83.0558*SRLOG-38.2842*SRLOG*SRLOG
      X151=-10.*(PLOG-X15)
      IF (X151-40.)306,305,305
  305 T15=0.0
      GO TO 309
  306 IF (X151+40.)307,308,308
  307 T15=1.0
      GO TO 309
  308 T15=1./(1.+EXP F(X151))
  309 A=PLOG*PLOG
```

```
      B=SRLOG*SRLOG
      C=A*PLOG
      D=B*SRLOG
      GO TO (303,304,310,303),I
C     Z=F(LOGP,LOG(S/R))
  303 XZ12=62.91-41.5*SRLOG
      XZ23=72.945-45.75*SRLOG
      XZ34=65.75-37.5*SRLOG
      XZ45=62.92-32.0*SRLOG
      XZ121=-10.*(PLOG-XZ12)
      XZ231=-10.*(PLOG-XZ23)
      XZ341=-10.*(PLOG-XZ34)
      XZ451=-10.*(PLOG-XZ45)
      ZCAL2=519.80374-23.753514*PLOG-983.90729*SRLOG+.37296957*A
     1 +30.084379*PLOG*SRLOG+620.04168*B-.0021648826*C-.23710079*A*SRLOG
     2 -9.496903*PLOG*B-129.78921*D
      ZCAL3=366.40674-15.517444*PLOG-647.42436*SRLOG+.18701758*A
     1 +18.040383*PLOG*SRLOG+379.59834*B-.00087958438*C-.10580129*A*SRLOG
     2 -5.1888254*PLOG*B-73.504269*D
      ZCAL4=516.07331-16.59277*PLOG-808.49823*SRLOG+.071256235*A
     1 +16.526813*PLOG*SRLOG+418.45341*B+.00094183347*C-.019727817*A*
```

```
     2 SRLOG-3.9948906*PLOG*B-71.038921*D
       IF(XZ121-40.) 7,10,10
    7  IF(XZ121+40.) 8, 9, 9
    8  TZ12=1.
       GO TO 11
    9  TZ12=1./(1.+EXP F(XZ121))
       GO TO 11
   10  TZ12=0.0
   11  IF(XZ231-40.)12,15,15
   12  IF (XZ231+40.)13,14,14
   13  TZ23=1.
       GO TO 16
   14  TZ23=1./(1.+EXP F(XZ231))
       GO TO 16
   15  TZ23=0.0
   16   IF(XZ341-40.)17,20,20
   17  IF(XZ341+40.)18,19,19
   18  TZ34=1.
       GO TO 21
   19  TZ34=1./(1.+EXP F(XZ341))
       GO TO 21
```

```
20    TZ34=0.0
21    IF(XZ451-40.)22,25,25
22    IF(XZ451+40.)23,24,24
23    TZ45=1.
      GO TO 26
24    TZ45=1./(1.+EXP F(XZ451))
      GO TO 26
25    TZ45=0.0
26    ZCAL=1.0+ (ZCAL2-1.)*TZ12+(ZCAL3-ZCAL2)*TZ23+(ZCAL4-ZCAL3)*TZ34
     1 +(4.0-ZCAL4)*TZ45
      ZCAL=1.+(ZCAL-1.)*T15
      ZHRT=ZCAL
      GO TO (600,600,600,310),I
C     LOG(H/R)=F(LOGP,LOG(S/R))
304   IF (SRLOG-1.6)27,27,28
27    HRCAL=12.693869+5.3975312*PLOG-48.729217*SRLOG-.14961521*A
     1 -5.8788774*PLOG*SRLOG+48.19278*B+.00090144132*C+.091151473*A*SRLOG
     2 +1.6282829*PLOG*B-13.065267*D
      GO TO 33
28    IF (SRLOG-1.76)29,29,30
29    HR22 =-156.37194+6.6959228*PLOG+269.93097*SRLOG-.097179965*A
```

```
     1 -7.5379714*PLOG*SRLOG-152.13866*B+.00057029937*C+.058364795*A*
     2 SRLOG+2.1592755*PLOG*B+28.940926*D
       HR21=-84.008522+2.5761318*PLOG+107.06198*SRLOG-.014352904*A
     1 -1.5313194*PLOG*SRLOG-32.316439*B
       XH=-61.2053+114.103*SRLOG-47.5532*B
       XH1=-10.*(PLOG-XH)
       IF (XH1-40.)291,294,294
 291   IF (XH1+40.)292,293,293
 292   TH=1.
       GO TO 295
 293   TH=1./(1.+EXP F(XH1))
       GO TO 295
 294   TH=0.0
 295   HRCAL= HR21+  (HR22-HR21)*TH
       GO TO 33
  30   IF (SRLOG-1.92)31,31,32
  31   HRCAL=-35.160671+.5366924*PLOG+56.99585*SRLOG-.022661358*A
     1 -.48470305*SRLOG*PLOG-27.641087*B+.00058568839*C+.016299962*A*
     2 SRLOG+.14073606*B*PLOG+4.712261*D
       GO TO 33
  32   HRCAL=-114.94796+4.004583*PLOG+180.08427*SRLOG-.041327787*A
```

```
     1 -4.0366535*PLOG*SRLOG-90.76006*B+.00040320694*C+.024360248*A*SRLOG
     2 +1.0462299*PLOG*B+15.467804*D
   33  HR15=28.160664-2.2339873*PLOG-59.053694*SRLOG+.054973544*A
     1 +3.7183257*PLOG*SRLOG+40.986503*B-.0004292698*C-.040726332*A*SRLOG
     2 -1.3704505*PLOG*B-8.253645*D
       HRCAL=HR15+ (HRCAL-HR15)*T15
       ZHRT=HRCAL
       GO TO 600
C      LOG(RHO/RHOA)=F(LOGP,LOG(S/R))
  310  XR12=-16.5527+57.45*SRLOG-30.8036*B
       XR23=499.544-938.91*SRLOG+609.028*B-135.995*D
       XR34=360.507-634.538*SRLOG+389.174*B-82.4653*D
       XR45=489.628-458.5*SRLOG+106.25*B
       XR121=-10.*(PLOG-XR12)
       XR231=-10.*(PLOG-XR23)
       XR341=-10.*(PLOG-XR34)
       XR451=-10.*(PLOG-XR45)
       IF (XR121-40.)34,37,37
   34  IF (XR121+40.)35,36,36
   35  TR12=1.0
       GO TO 38
```

```
36    TR12=1./(1.+EXP F(XR121))
      GO TO 38
37    TR12=0.0
38    IF (XR231-40.)39,42,42
39    IF (XR231+40.)40,41,41
40    TR23=1.0
      GO TO 43
41    TR23=1./(1.+EXP F(XR231))
      GO TO 43
42    TR23=0.0
43    IF (XR341-40.)44,47,47
44    IF (XR341+40.)45,46,46
45    TR34=1.
      GO TO 48
46    TR34=1./(1.+EXP F(XR341))
      GO TO 48
47    TR34=0.0
48    IF (XR451-40.)49,52,52
49    IF (XR451+40.)50,51,51
50    TR45=1.0
      GO TO 53
```

```
51    TR45=1./(1.+EXP F(XR451))
      GO TO 53
52    TR45=0.0
53    RHCL1=15.951867-.00228295*PLOG-15.994242*SRLOG+.0065187267*A
     1 +.53079685*PLOG*SRLOG+3.175974*B
      RHCL2=1541.1666-63.93035*PLOG-2993.1662*SRLOG+.935437*A
     1 +84.30375*SRLOG*PLOG+1938.7061*B-.004746016*C-.6128404*A*SRLOG
     2 -27.422666*B*PLOG-419.0881*D
      RHCL3=427.4745-18.126622*PLOG-765.47626*SRLOG+.29343169*A
     1 +22.926877*PLOG*SRLOG+456.717*B-.0017033404*C-.18068309*A*SRLOG
     2 -6.9143617*B*PLOG-91.131851*D
      RHCL4=206.23144-8.2270278*PLOG-329.5465*SRLOG+.1324191*A
     1 +9.8884165*PLOG*SRLOG+175.03931*B-.0010178454*C-.07654371*A*SRLOG
     2 -2.6920144*B*PLOG-31.237834*D
      RHCL5=-399.52358+12.899477*PLOG+411.64144*SRLOG-.097694919*A
     1 -6.2204477*PLOG*SRLOG-106.6733*B
      RHCAL=RHCL1+  (RHCL2-RHCL1)*TR12+(RHCL3-RHCL2)*TR23+(RHCL4-RHCL3)*
     1 TR34+(RHCL5-RHCL4)*TR45
      RH15=-79.282533+6.3537078*PLOG+179.22721*SRLOG-.12607098*A
     1 -8.4013122*PLOG*SRLOG-129.95269*B+.0010037437*C+.094185511*A*SRLOG
     2 +3.1256966*PLOG*B+30.203862*D
```

```
      RHCAL=RH15+(RHCAL-RH15)*T15
      ZHRT=RHCAL
      GO TO (600,600,600,500),I
  500 T=(EXPXF(PLOG)*273.15)/(ZCAL*EXPXF(RHCAL))
      ZHRT=T
      IF (T-2100.)501,501,400
  501 IF (T-1500.)503,503,502
  502 IF (PLOG+1.)400,400,503
  503 CON1=SQRTF(T/273.15)
      A0A0=-.0753808+CON1*(1.12644-.0552696*CON1)
      GO TO 600
C     A/A0=F(LOG(P),LOG(S/R)) T IN DEG. K 2100-14600
  400 XA12=635.054-1220.46*SRLOG+803.882*B-180.845*D
      XA23=373.702-663.358*SRLOG+408.854*B-86.8056*D
      XA34=1703.78-2602.97*SRLOG+1337.93*B-231.422*D
      XA22=1043.37-1820.34*SRLOG+1076.36*B-215.445*D
      XA121=-10.*(PLOG-XA12)
      XA231=-10.*(PLOG-XA23)
      XA341=-10.*(PLOG-XA34)
      XA221=-10.*(PLOG-XA22)
      A1=-4409.6241+196.82259*PLOG+8746.4634*SRLOG-3.1650299*A
```

```
     1 -262.32947*PLOG*SRLOG-5786.449*B+.020004186*C+2.1429825*A*SRLOG
     2 +87.589029*PLOG*B+1277.6718*D
       A21= -1814.5117+86.096078*PLOG+3315.6099*SRLOG-1.7593034*A
     1 -107.2534*PLOG*SRLOG-2023.201*B+.016287679*C+1.1398134*A*SRLOG
     2 +33.659607*PLOG*B+413.41945*D
       A22=2651.2944-81.405596*PLOG-3099.0064*SRLOG+.69752668*A
     1 +48.062596*PLOG*SRLOG+907.70889*B
       IF (XA221-40.)402,401,401
401    TA22=0.0
       GO TO 405
402    IF (XA221+40.)403,403,404
403    TA22=1.0
       GO TO 405
404    TA22=1./(1.+EXPF(XA221))
405    A2= A21+(A22-A21)*TA22
       A3=-3217.8037+195.34964*PLOG+5348.2143*SRLOG-4.6268475*A
     1 -221.12705*PLOG*SRLOG-2970.8649*B+.044614358*C +2.7079177*A*SRLOG
     2 +63.042803*PLOG*B+553.12007*D
       A4=16976.939-476.10242*PLOG-17445.315*SRLOG+3.6534057*A
     1 +246.41125*PLOG*SRLOG+4486.3118*B
       IF (XA121-40.)407,406,406
```

```
406   TA12=0.0
      GO TO 410
407   IF (XA121+40.)408,408,409
408   TA12=1.0
      GO TO 410
409   TA12=1./(1.+EXPF(XA121))
410   IF (XA231-40.)412,411,411
411   TA23=0.0
      GO TO 415
412   IF (XA231+40.)413,413,414
413   TA23=1.0
      GO TO 415
414   TA23=1./(1.+EXPF(XA231))
415   IF (XA341-40.)417,416,416
416   TA34=0.0
      GO TO 420
417   IF (XA341+40.)418,418,419
418   TA34=1.0
      GO TO 420
419   TA34=1./(1.+EXPF(XA341))
420   AOAO=A1+(A2-A1)*TA12+(A3-A2)*TA23+(A4-A3)*TA34
600   RETURN
      END
```

APPENDIX II

Thermodynamic Properties of Nitrogen from 400 to 15,000°K

1. The compressibility factor $Z = f(x, y)$ where $x = \log p$ and $y = \log (S/R)$

$$Z = 1 + (Z_2 - 1)\,TZ_{12} + (Z_3 - Z_2)\,TZ_{23}$$

where

$$Z_i = a_0 + a_1 x + a_2 y + a_3 x^2 + a_4 xy + a_5 y^2 + a_6 x^3 + a_7 x^2 y + a_8 xy^2 + a_9 y^3$$

$$TZ_{ij} = 1/\left\{1 + \exp\left[k\,(x - xZ_{ij})\right]\right\}, \quad k = -30$$

$$xZ_{ij} = a_0 + a_1 y + a_2 y^2$$

2. The enthalpy $\log (H/R) = f(x, y)$ where $x = \log p$ and $y = \log (S/R)$

For

i) $y \leq 1.67$, $\log (H/R) = H_1$

ii) $y > 1.67$, $\log (H/R) = H_2$

where

$$H_i = a_0 + a_1 x + a_2 y + a_3 x^2 + a_4 xy + a_5 y^2 + a_6 x^3 + a_7 x^2 y + a_8 xy^2 + a_9 y^3 + a_{10} x^4 + a_{11} x^3 y + a_{12} x^2 y^2 + a_{13} xy^3 + a_{14} y^4$$

3. The density $\log \rho = f(x, y)$ where $x = \log p$ and $y = \log (S/R)$

$$\log \rho = R_3 + (R_2 - R_3)\,TR_{23} + (R_1 - R_2)\,TR_{12}$$

where

$$R_i = \frac{a_0 + a_1 x + a_2 y + a_3 x^2 + a_4 xy + a_5 y^2 + a_6 x^3 + a_7 x^2 y + a_8 xy^2 + a_9 y^3}{1 + b_1 x + b_2 y}$$

$$TR_{ij} = 1/\left\{1 + \exp\left[k\,(x - xR_{ij})\right]\right\}, \quad k = -30$$

$$xR_{ij} = a_0 + a_1 y + a_2 y^2$$

4. The speed of sound $a/a_a = f(x, y)$ where $x = \log p$ and $y = \log (S/R)$

i) For $2000 \leq T \leq 15{,}000°K$

$$a/a_a = F_1 + (F_2 - F_1)\,TR_1 + (F_3 - F_2)\,TR_2 + (F_4 - F_3)\,TR_3$$

where

$$TR_1 = 1/\left\{1 + \exp\left[k(x - x_1)\right]\right\}, \quad k = -10$$

$$x_1 = a_o + a_1 y + a_2 y^2$$

$$TR_2 = 1/\left\{1 + \exp\left[k(x - x_2)\right]\right\}, \quad k = -10$$

$$x_2 = a_o + a_1 y + a_2 y^2 + a_3 y^3$$

$$TR_3 = 1/\left\{1 + \exp\left[k(x - x_1)\right]\right\}, \quad k = -10$$

$$x_1 = a_o + a_1 y + a_2 y^2 + a_3 y^3$$

$$F_1 = a_o + a_1 x + a_2 y + a_3 x^2 + a_4 xy + a_5 y^2$$

$$F_2 = a_o + a_1 x + a_2 y + a_3 x^2 + a_4 xy + a_5 y^2 + a_6 x^3 + a_7 x^2 y + a_8 xy^2 + a_9 y^3$$

$$F_3 = a_o + a_1 x + a_2 y + a_3 x^2 + a_4 xy + a_5 y^2 + a_6 x^3 + a_7 x^2 y + a_8 xy^2 + a_9 y^3$$

$$F_4 = a_o + a_1 x + a_2 y + a_3 x^2 + a_4 xy + a_5 y^2$$

ii) For $T < 2000°K$

$$a/a_a = F_5 = a_o\,(T)^{1/2} + a_1 - \frac{a_2\left[(T)^{1/2} - (a_3 + a_4 y)\right]}{1 - \exp\left\{a_5\left[(T)^{1/2} - (a_3 + a_4 y)\right]\right\}}$$

TABLE 2

The Coefficients in the Nitrogen Surface Fits

	a_o	a_1	a_2	a_3	a_4	a_5	a_6	a_7
Z_2	220.49467	- 7.107162	-392.70071	0.056027391	8.157166	231.27257	-0.00020321316	-0.028109498
Z_3	522.48867	- 18.092783	-822.20488	0.042489392	18.065191	427.59538	0.0015140981	-0.001219524
H_1	489.55741	- 55.049214	-1216.5424	1.5942474	108.02105	1117.1136	-0.017158685	-2.095931
H_2	-521.74875	41.654096	1179.5552	-0.99243287	-70.12461	-995.19092	0.0064153564	1.1103749
R_1	32.641296	-0.38756741	-52.217392	-0.0075626552	0.90033723	27.205865	0.00015729175	-0.0051697773
R_2	1880.1145	-122.3931	-4430.137	3.209142	219.61577	3908.248	-0.036075276	-3.8264955
R_3	2.872289	-1.6432766	7.368364	0.091353715	2.7334952	-10.340992	-0.0007031218	-0.056173475

	a_8	a_9	a_{10}	a_{11}	a_{12}	a_{13}	a_{14}
Z_2	-2.2827033	- 44.684431					
Z_3	-4.3819551	- 72.976708					
H_1	-69.772324	-446.31509	0.000081375758	0.011380104	0.6840628	14.889246	65.601564
H_2	39.413318	374.20789	0.0000149833	-0.0033178953	-0.30857129	- 7.3757847	-52.774942
R_1	- 0.34481455	- 4.6250012					
R_2	-130.12534	-1530.282	0.00018329152	0.021413897	1.1360325	25.639507	224.23844
R_3	-0.74623782	2.4727295					

	b_1	b_2
R_1	-0.020398785	-0.50736384
R_2		
R_3		

	a_o	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8	a_9
X_1	- 90.3953	153.064	-61.657							
X_2	318.959	-562.976	346.466	-73.7847						
X_3	1391.18	-2145.3	1111.12	-193.399						
F_1	154.02215	-4.9427938	-226.16395	0.06434176	3.8196588	83.667474				
F_2	-1160.0377	56.321429	2166.1955	-1.2476059	-72.070582	-1351.0662	0.012951044	0.83628876	23.292021	282.61871
F_3	-1334.5733	82.105159	2227.5893	-1.9854366	-95.040801	-1247.3112	0.020908233	1.2247047	27.960659	235.86875
F_4	5392.7139	-155.01043	-5636.037	1.1554369	82.033548	1476.3358				
F_5	0.0566	0.0748	0.0338	254.2	-125.0	- 1.62				
XZ_{12}	-27.07215	+73.841795	-36.953212							
XZ_{23}	+29.380383	-2.0308333	-8.5416666							
XR_{12}	+219.6	-122.5								
XR_{23}	-23.2167	+79.1667	-41.6667							

```
      SUBROUTINE WRKHAT (I,PLOG,SRLOG,ZHRT,AOAO)
C     NITROGEN
C     I=1 , Z IS RETURNED
C     I=2 , LOG(H/R) IS RETURNED
C     I=3 , LOG(RHO/RHOA) IS RETURNED
C     I=4 , T AND A/AO ARE RETURNED
C     PLOG = LOG(P/PA)
C     SRLOG= LOG(S/R)
C     ZHRT = Z,LOG(H/R),LOG(RHO/RHOA),OR  T CORRESPONDING TO THE
C    1 SELECTION OF I
C     R=3196.66
      A=PLOG**2
      B=SRLOG**2
      C=PLOG*A
      D=SRLOG*B
      GO TO (1,181,211,  1),I
C     Z=F(LOG(P),LOG(S/R))
    1 XZ12=-27.07215+73.841795*SRLOG-36.953212*B
      XZ23=29.380383-2.0308333*SRLOG-8.5416666*(SRLOG**2)
      XZ121=-30.*(PLOG-XZ12)
      XZ231=-30.*(PLOG-XZ23)
```

```
      ZCAL2=220.49467-7.107162*PLOG-392.70071*SRLOG+.056027391*( PLOG**2
     1 )+8.157166*PLOG*SRLOG+231.27257*(SRLOG**2)-.00020321316*(PLOG**3)
     2 -.028109498*SRLOG*(PLOG**2)-2.2827033*PLOG*(SRLOG**2)-44.684431*
     3 (SRLOG**3)
      ZCAL3=522.48867-18.092783*PLOG-822.20488*SRLOG+.042489392*A
     1 +18.065191*PLOG*SRLOG+427.59538*B+.0015140981*C-.001219524*A*SRLOG
     2 -4.3819551*PLOG*B-72.976708*D
      IF (XZ121-40.)13,14,14
 13   IF (XZ121+40.)131,132,132
131   TZ12=1.
      GO TO 15
132   TZ12=1./(1.+EXP F(XZ121))
      GO TO 15
 14   TZ12=0.0
 15   IF (XZ231-40.)16,17,17
 16   IF (XZ231+40.)161,162,162
161   TZ23=1.
      GO TO 18
162   TZ23=1./(1.+EXP F(XZ231))
      GO TO 18
 17   TZ23=0.0
```

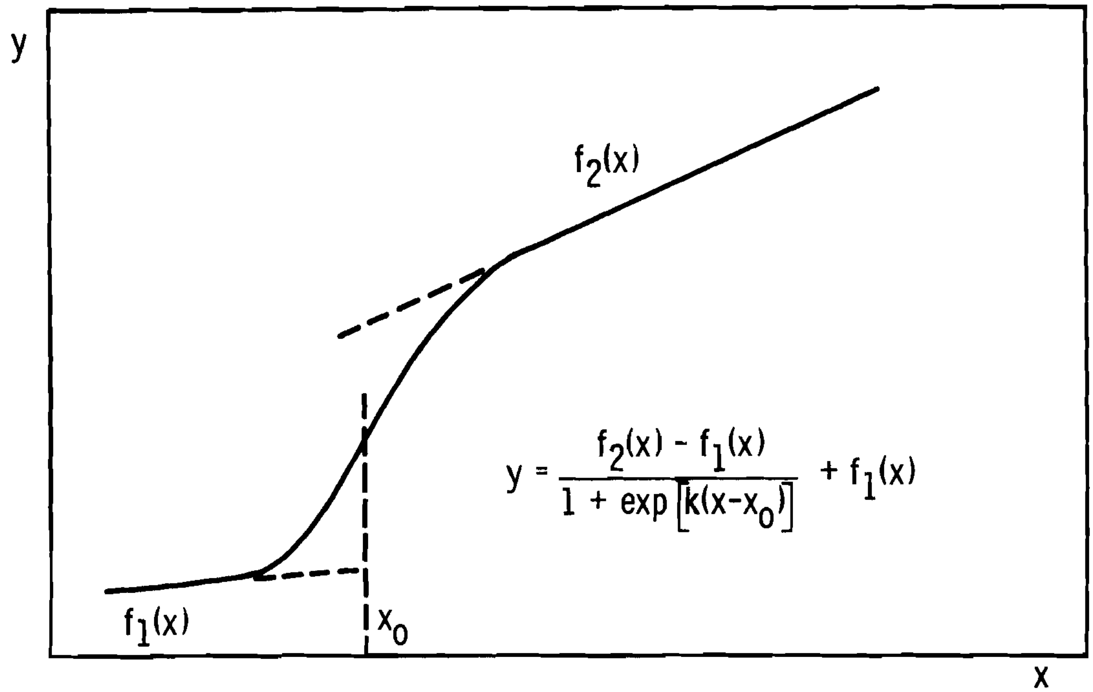
```
   18   ZCAL=1.+(ZCAL2-1.)*TZ12+(ZCAL3-ZCAL2)*TZ23
        ZHRT=ZCAL
        GO TO (300,300,300,211),I
C       LOG(H/R)=F(LOG(P),LOG(S/R))
  181   IF(SRLOG-1.67)19,19,20
   19   HRCAL=489.55741-55.049214*PLOG-1216.5424*SRLOG+1.5942474*A
      1 +108.02105*PLOG*SRLOG+1117.1136*B-.017158685*C-2.095931*A*SRLOG
      2 -69.772324*PLOG*B-446.31509*D+.000081375758*C*PLOG+.011380104*C
      3 *SRLOG+.6840628*A*B+14.889246*PLOG*D+65.601564*D*SRLOG
        GO TO 21
   20   HRCAL=-521.74875+41.654096*PLOG+1179.5552*SRLOG-.99243287*A
      1 -70.12461*PLOG*SRLOG-995.19092*B+.0064153564*C+1.1103749*A*SRLOG
      2 +39.413318*PLOG*B+374.20789*D+.0000149833*PLOG*C -.0033178953*
      3 C*SRLOG-.30857129*A*B-7.3757847*PLOG*D-52.774942*D*SRLOG
   21   ZHRT=HRCAL
        GO TO 300
C       LOG(RHO/RHOA)=F(LOG(P),LOG(S/R))
  211   XR12=219.6-122.5*SRLOG
        XR23=-23.2167+79.1667*SRLOG-41.6667*B
        XR121= -30.*(PLOG-XR12)
        XR231= -30.*(PLOG-XR23)
```

```
      RHCL1=  (32.641296-.38756741*PLOG-52.217392*SRLOG-.0075626552*A
     1 +.90033723*PLOG*SRLOG+27.205865*B+.00015729175*C-.0051697773*A*
     2 SRLOG-.34481455*B*PLOG-4.6250012*D)/(1.0-.020398785*PLOG-.50736384
     3 *SRLOG )
      RHCL2=1880.1145-122.3931*PLOG-4430.137*SRLOG+3.209142*A
     1 +219.61577*PLOG*SRLOG+3908.248*B-.036075276*C-3.8264955*A*SRLOG
     2 -130.12534*PLOG*B-1530.282*D+.00018329152*C*PLOG+.021413897*C*
     3 SRLOG+1.1360325*A*B+25.639507*PLOG*D+224.23844*D*SRLOG
      RHCL3=2.872289-1.6432766*PLOG+7.368364*SRLOG+.091353715*A
     1 +2.7334952*PLOG*SRLOG-10.340992*B-.0007031218*C-.056173475*A*SRLOG
     2 -.74623782*PLOG*B+2.4727295*D
      IF  (XR121-40.)22,23,23
   22 IF (XR121+40.)221,222,222
  221 TR12=1.
      GO TO 24
  222 TR12=1./(1.+EXP F(XR121))
      GO TO 24
   23 TR12=0.0
   24 IF (XR231-40.)25,26,26
   25 IF (XR231+40.)251,252,252
  251 TR23=1.
```

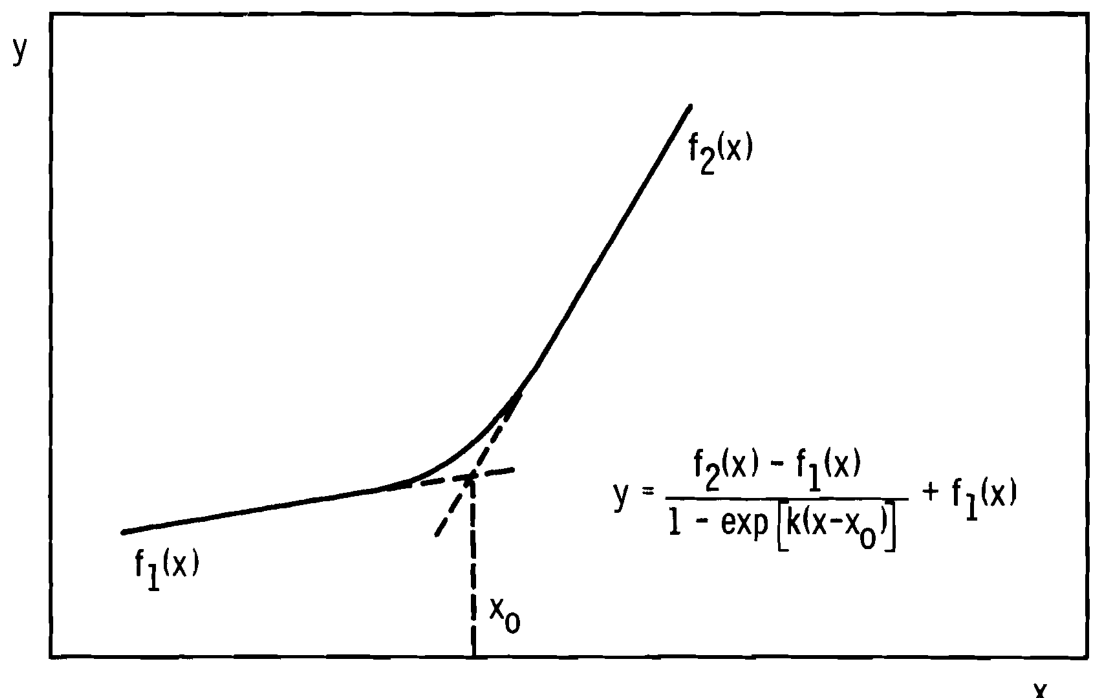
```
      GO TO 27
252   TR23=1./(1.+EXP F(XR231))
      GO TO 27
 26   TR23=0.0
 27   RHCAL=RHCL3+(RHCL2-RHCL3)*TR23+(RHCL1-RHCL2)*TR12
      ZHRT=RHCAL
      GO TO (300,300,300,500),I
500   T= (EXPXF(PLOG)*273.15)/(ZCAL*EXPXF(RHCAL))
      ZHRT=T
      IF (T-2000.)501,400,400
501   CON1=SQRTF(T)
      CON2=CON1-254.2+125.*SRLOG
      CON3=1.- EXPF(-1.62*CON2)
      AOA0=.0566*CON1+.0748-  (.0338*CON2/CON3)
      GO TO 300
C     A/A0=F(LOG(P),LOG(S/R))   TEMP. IN DEG. KELVIN  2000-15000
400   XA12=-90.3953+153.064*SRLOG-61.657*B
      XA23= 318.959-562.976*SRLOG+346.466*B-73.7847*D
      XA34=1391.18-2145.3*SRLOG+1111.12*B-193.399*D
      XA121=-10.*(PLOG-XA12)
      XA231=-10.*(PLOG-XA23)
```

```
      XA341=-10.*(PLOG-XA34)
      A1=154.02215-4.9427938*PLOG-226.16395*SRLOG+.06434176*A
     1 +3.8196588*PLOG*SRLOG+83.667474*B
      A2=-1160.0377+56.321429*PLOG+2166.1955*SRLOG-1.2476059*A
     1 -72.070582*PLOG*SRLOG-1351.0662*B+.012951044*C+.83628876*A*SRLOG
     2 +23.292021*PLOG*B+282.61871*D
      A3=-1334.5733+82.105159*PLOG+2227.5893*SRLOG-1.9854366*A
     1 -95.040801*PLOG*SRLOG-1247.3112*B+.020908233*C+1.2247047*A*SRLOG
     2 +27.960659*PLOG*B+235.86875*D
      A4=5392.7139-155.01043*PLOG-5636.037*SRLOG+1.1554369*A
     1 +82.033548*PLOG*SRLOG+1476.3358*B
      IF (XA121-40.)402,401,401
  401 TA12=0.0
      GO TO 405
  402 IF (XA121+40.)403,403,404
  403 TA12=1.0
      GO TO 405
  404 TA12=1./(1.+EXPF(XA121))
  405 IF (XA231-40.)407,406,406
  406 TA23=0.0
      GO TO 410
```

```
407   IF (XA231+40.)408,408,409
408   TA23=1.0
      GO TO 410
409   TA23=1./(1.+EXPF(XA231))
410   IF (XA341-40.)412,411,411
411   TA34=0.0
      GO TO 415
412   IF (XA341+40.)413,413,414
413   TA34=1.0
      GO TO 415
414   TA34=1./(1.+EXPF(XA341))
415   AOAO=A1+(A2-A1)*TA12+(A3-A2)*TA23+(A4-A3)*TA34
300   RETURN
      END
```



a. A Transition with a Point of Inflection



b. A Transition without Inflection

Fig. 1 Grabau-type Transition Function

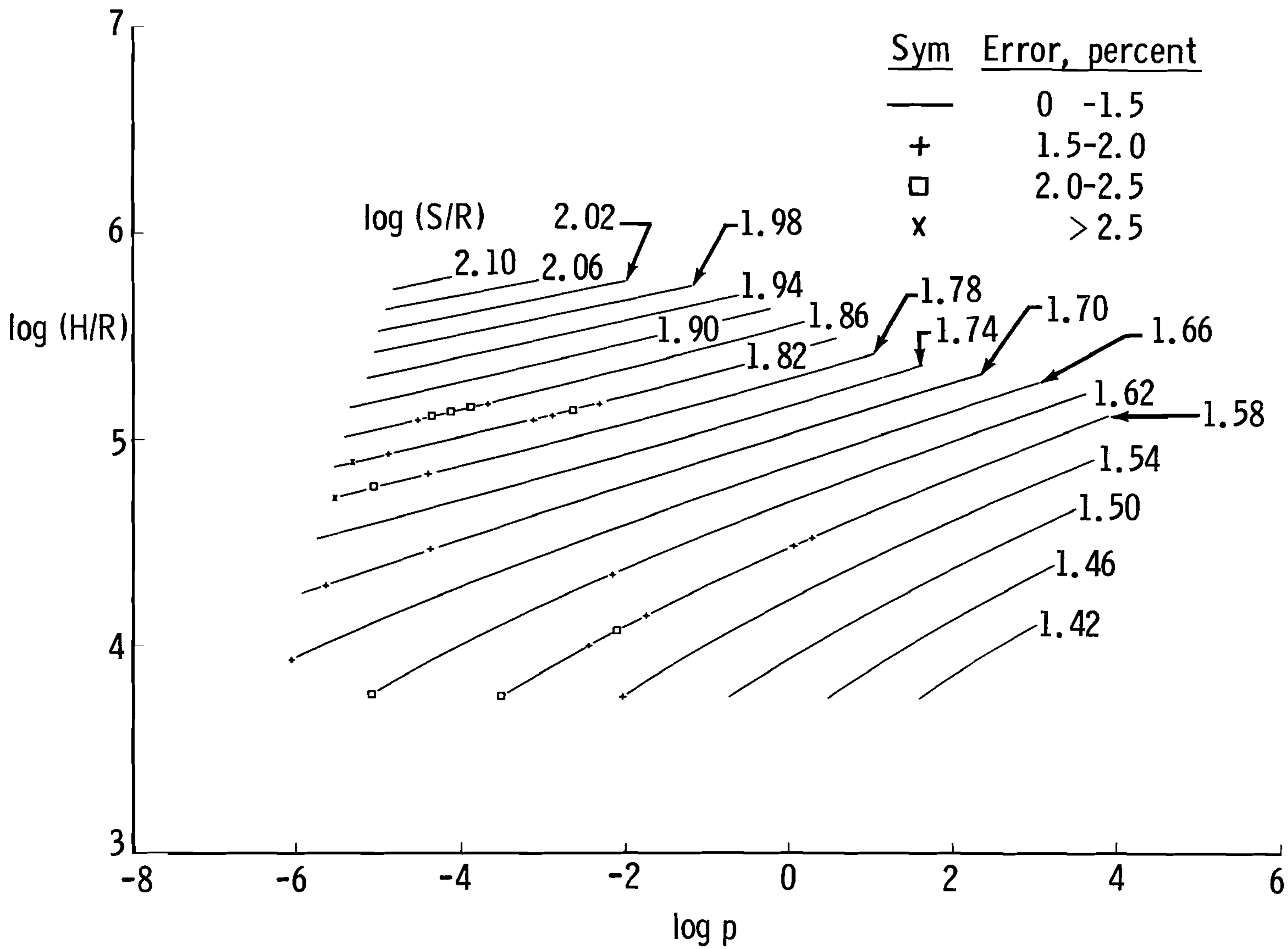


Fig. 2 Enthalpy of Air

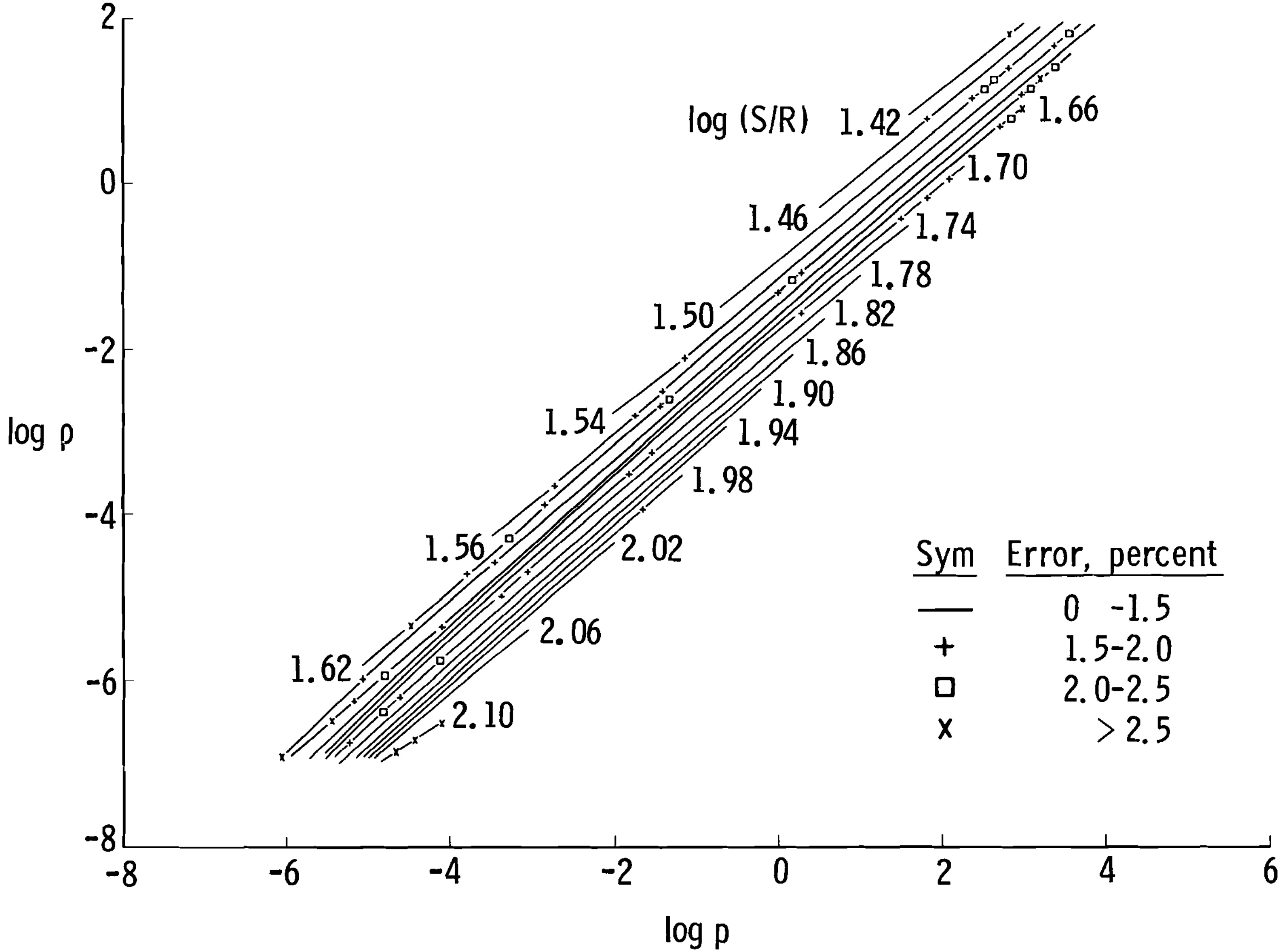


Fig. 3 Density of Air

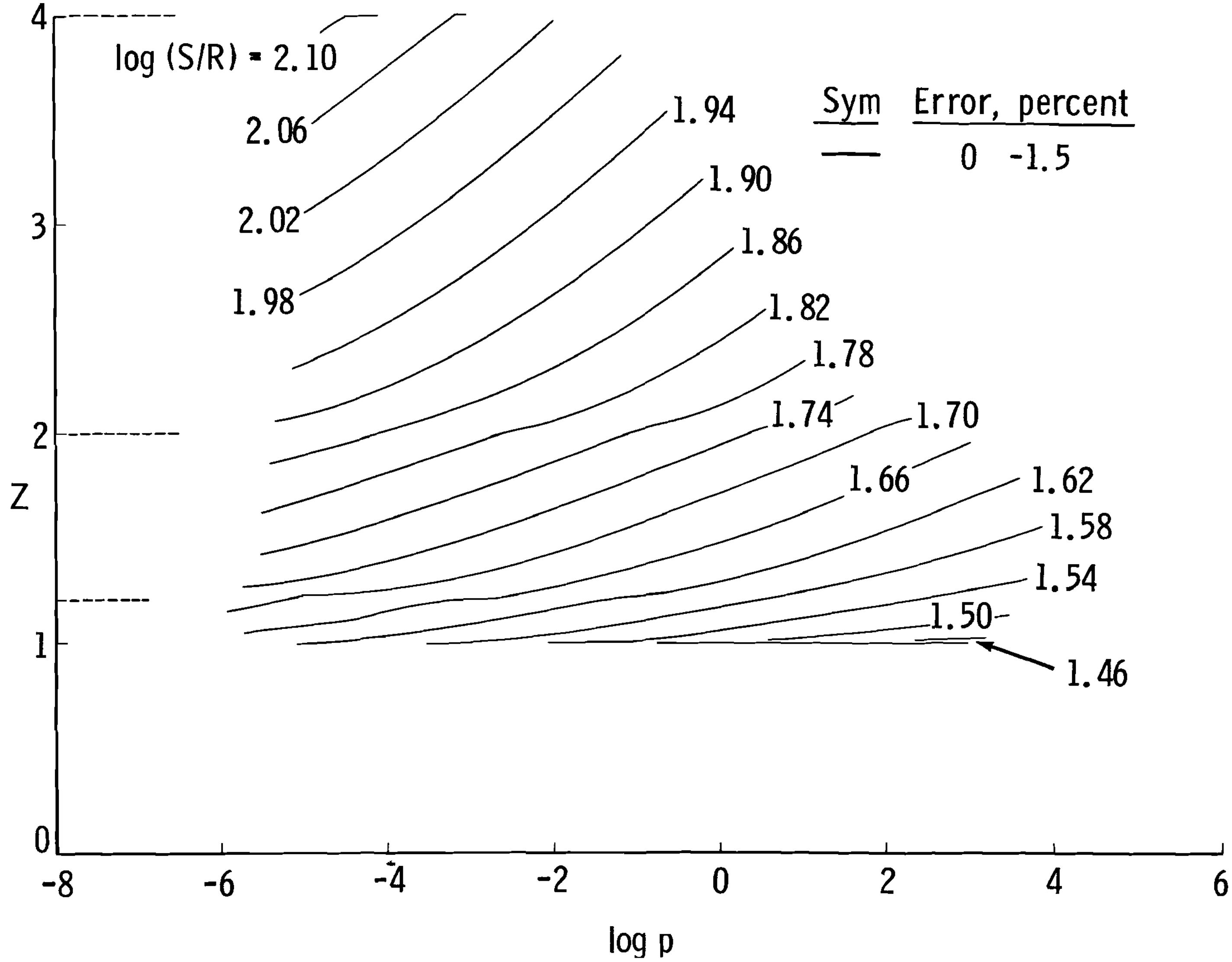


Fig. 4 Compressibility Factor for Air

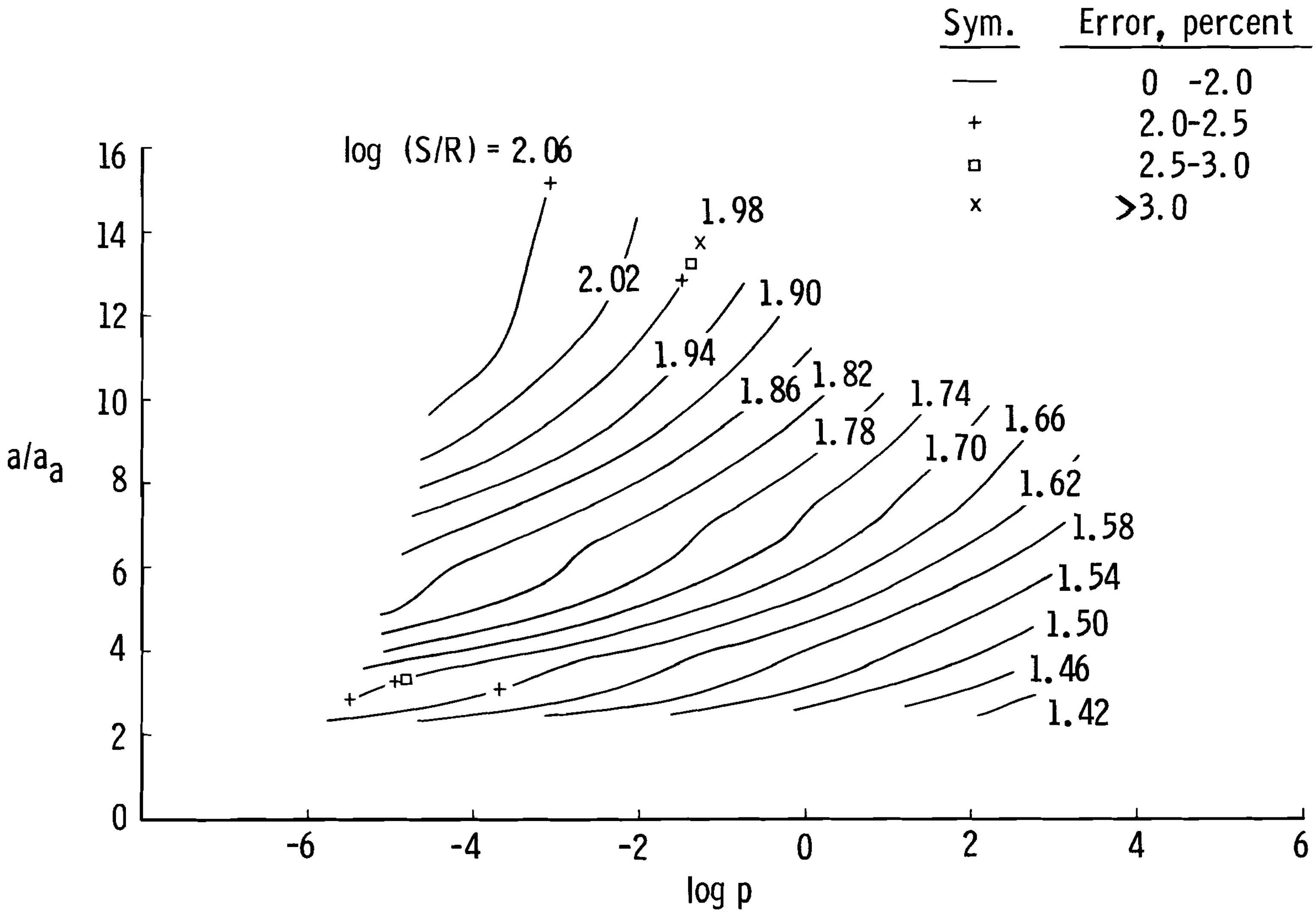


Fig. 5 Speed of Sound Ratio in Air for T ≥ 1800°K

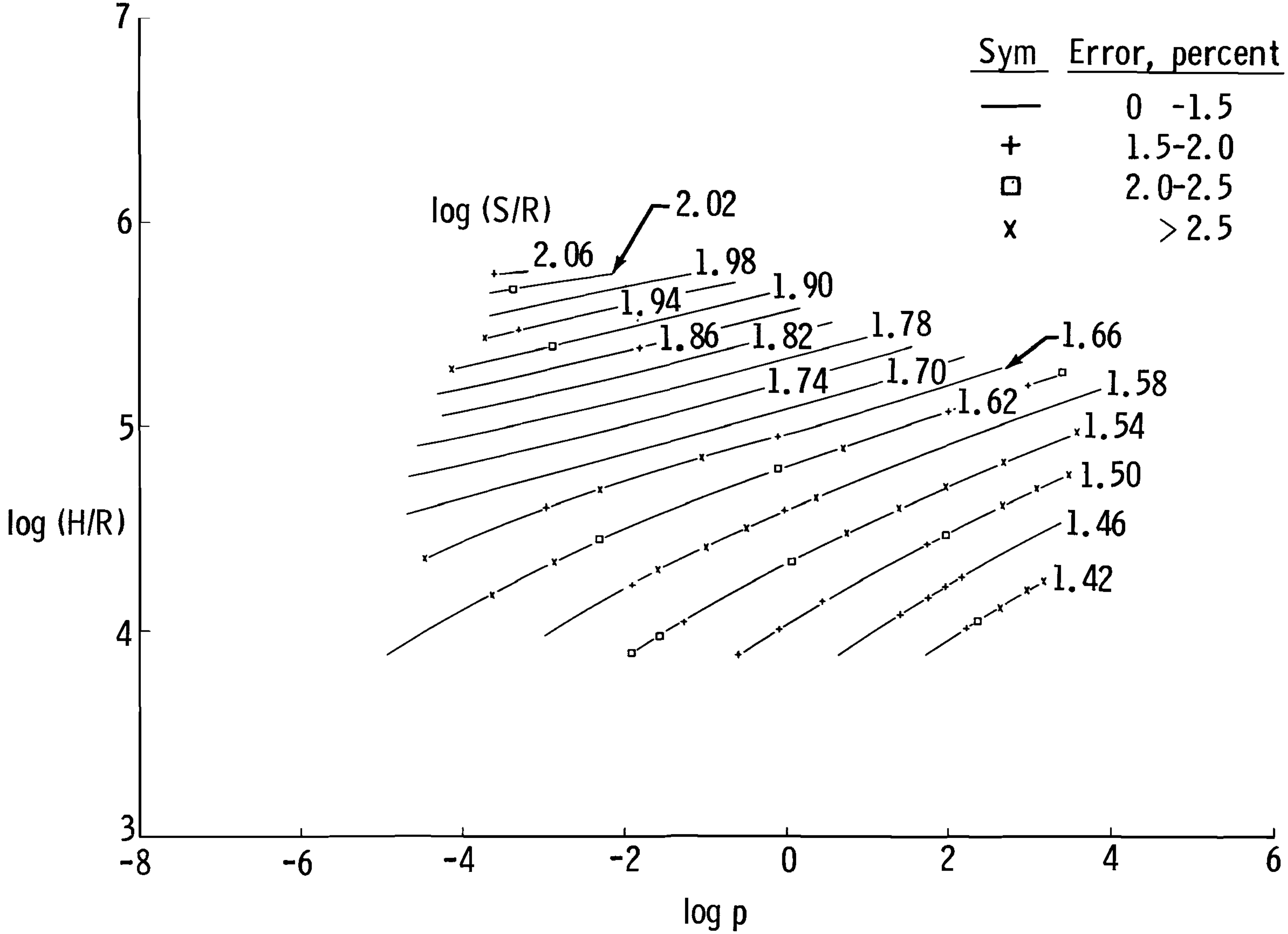


Fig. 6 Enthalpy of Nitrogen

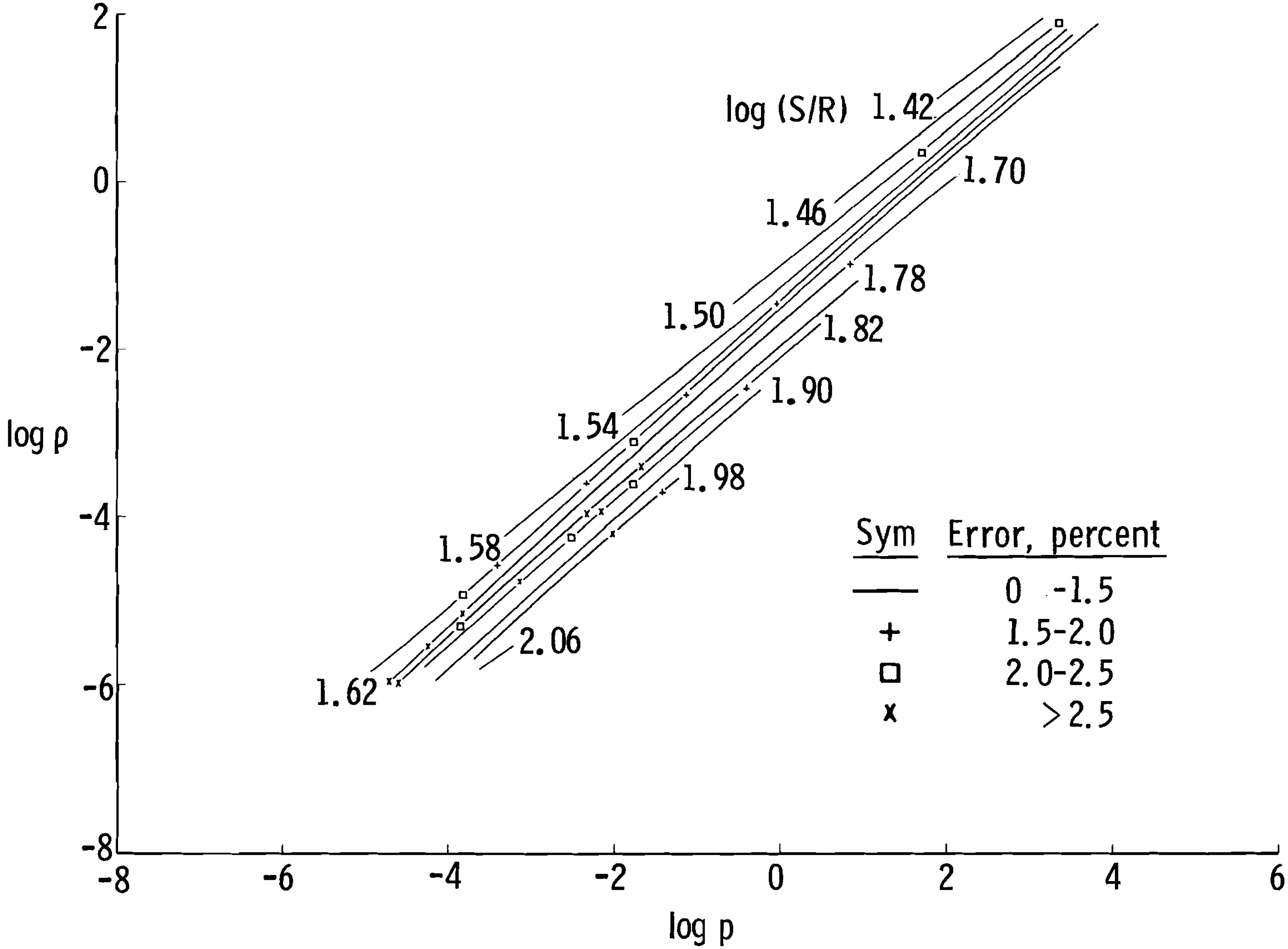


Fig. 7 Density of Nitrogen

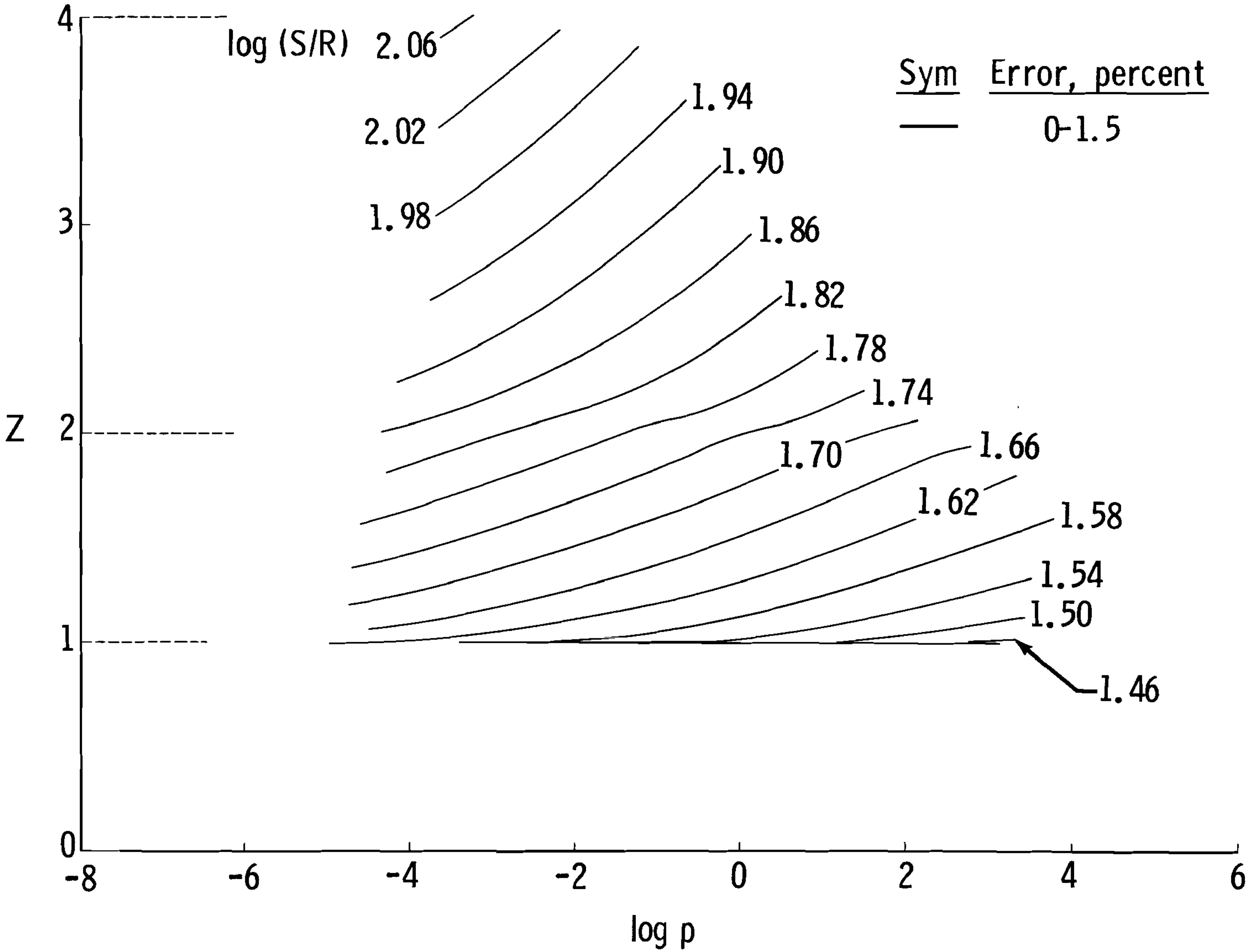


Fig. 8 Compressibility Factor for Nitrogen

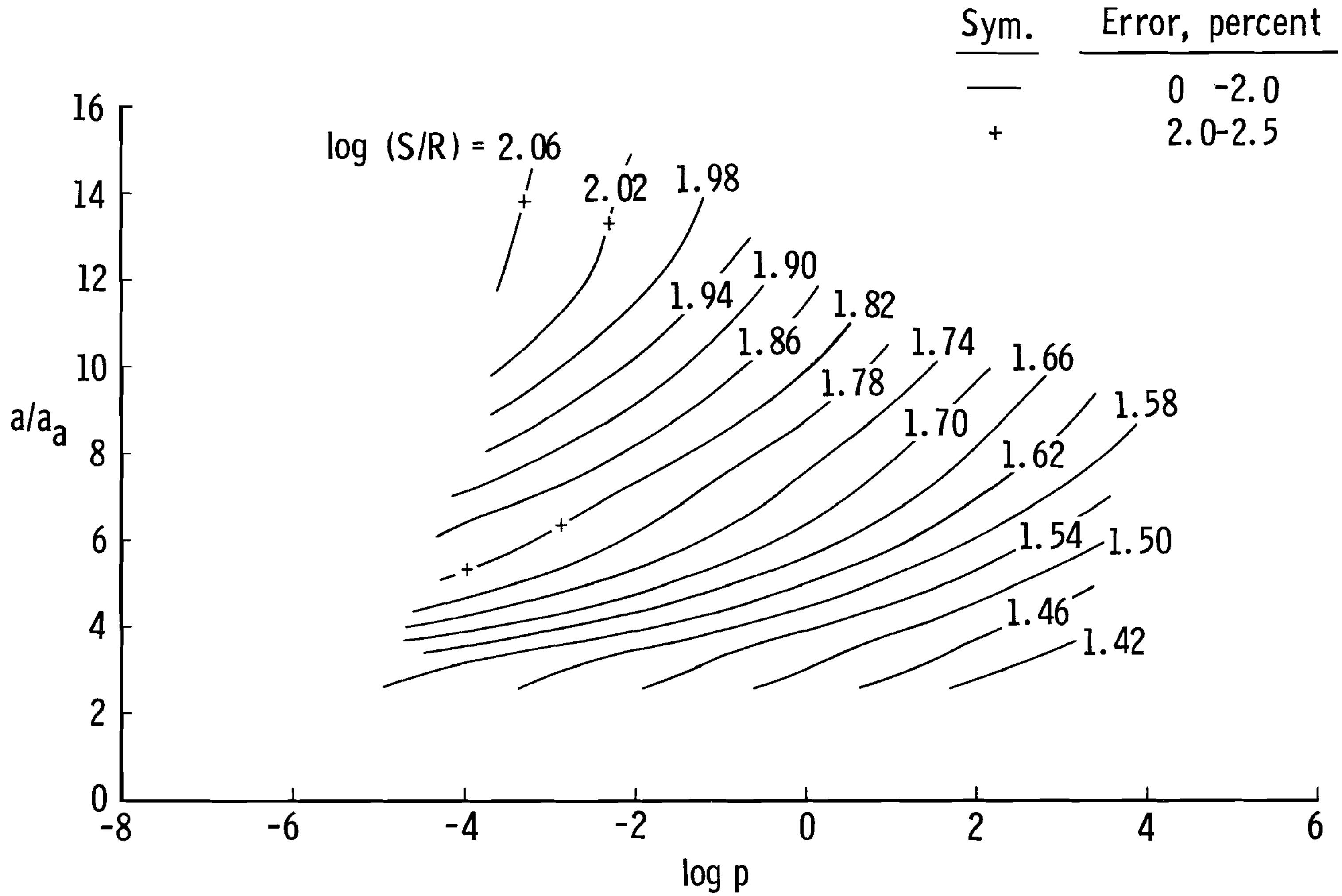


Fig. 9 Speed of Sound Ratio in Nitrogen for T $\geq$ 2000°K