STATTHERM:
A Statistical Thermodynamics Program for Calculating Thermochemical Information

Nick M. Marinov

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STATTHERM: A Statistical Thermodynamics Program For Calculating Thermochemical Information

Nick M. Marinov

Lawrence Livermore National Laboratory
P.O. Box 808
Livermore, CA 94550
Abstract

A statistical thermodynamics program is presented which computes the thermochemical properties of a polyatomic molecule using statistical thermodynamic formulas. Thermodynamic data for substances involving C, H, O, N, and CL elements are fitted into NASA polynomial form for use in combustion research or research where thermodynamical information is important.

Introduction

The thermochemical properties of molecules, radicals, ions, and atoms are involved in almost every computational aspect of combustion science. In most chemical kinetics and equilibrium calculations, such as kinetics of reactions in shock waves, nozzle flow, detonation processes, combustion bombs, rapid compression machines, diffusion flames, adiabatic flame calculations, stirred and plug flow reactors, and supercritical oxidation processes, these thermochemical properties must be found at a number of temperatures.

There are two ways to handle the task of representing properties of individual species. In the first one, the properties of the species in question are provided in a tabular form at predetermined temperature intervals and the values needed are calculated by interpolation. This method gives a very accurate determination of the species thermochemical values but at the expense requiring large memory storage, handling potentially of millions of thermodynamic values, and does not permit use beyond the temperature limits of the table. A second and more commonly used technique is representation of the species thermochemical properties by polynomials that allows for direct calculation of the thermodynamic properties at any temperature, including limited extrapolation beyond the fitted temperature range of the polynomial. The polynomial approach can accurately fit the thermodynamic properties of a molecule to within an error band of 0.5%.  

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The Statistical Thermodynamic Equations

Thermodynamics and quantum mechanics provide a framework for studying the macroscopic and molecular properties of matter. The link between quantum mechanics and thermodynamics is provided by statistical mechanics, whose aim is to deduce the macroscopic properties of matter from the properties of the molecules composing the system. Typical macroscopic properties are entropy, internal energy, heat capacity, enthalpy, and the Gibbs free energy. Molecular properties typically include molecular masses, molecular geometries, and intramolecular forces which determine the molecular vibration frequencies. The statistical thermodynamic equations developed from statistical mechanics provide a vital link between the macroscopic properties that we seek in defining the thermodynamic state of a system and the molecular properties of the molecules that make up that system.

The molar partition function \( Q \) is defined as an assembly of identical molecules by the equation:

\[
Q = \sum p_i e^{-E_i/RT}
\]

where \( p_i \) is the number of discrete states of the molecules which have the energy \( E_i \) in a system at thermal equilibrium \( T \) and volume \( V \). It can then be shown that the familiar thermodynamic properties are related to \( Q \) as follows:

- **Gibbs Free Energy:**
  \[
  G = -RT \ln Q + PV
  \]

- **Internal Energy:**
  \[
  U = RT(\Delta \ln Q/\Delta \ln T)_V = -R(\Delta \ln Q / \Delta(1/T))_V
  \]

- **Enthalpy:**
  \[
  H = U + PV
  \]

- **Entropy:**
  \[
  S = U/T + R \ln Q
  \]

- **Molar Heat Capacity at constant volume:**
  \[
  C_V = (\Delta U / \Delta T)_V = R(\Delta \ln Q / \Delta \ln T)_V + R(\Delta^2 \ln Q / \Delta(1/T)^2)_V
  \]

- **Molar Heat Capacity at constant pressure:**
  \[
  C_p = C_V + R \text{ (for ideal gases)}
  \]
For ideal gases the partition function $Q$ can be factored into a product of partition functions for each of the degrees of freedom of the system. These will be $3N$ in number, where $N$ is the number of atoms in the molecule, ion, or radical; 3 translational degrees of freedom; 0 for atoms, 2 for linear molecules, or 3 rotational degrees of freedom for nonlinear molecules, and the remainder internal vibrational degrees of freedom. If we have low-lying electronic states or a nonzero spin then an additional factor $Q_{\text{elec}}$ for the electronic degrees of freedom is included.

$$Q = Q_{\text{tran}}Q_{\text{rot}}Q_{\text{vibration}}Q_{\text{elec}}$$

Each of the thermodynamic functions depends on the logarithm or logarithmic derivative of $Q$ and will thus receive additive contributions from each of the degrees of freedom. For example, we have as follows:

$$S = S_{\text{tran}} + S_{\text{rot}} + S_{\text{vib}} + S_{\text{elec}}$$

The translational partition function is rigorously known and only the result will be shown. For one mole of ideal gas, we have the following:

$$Q_{\text{trans}} = (2\pi M kT/h^2)^{1.5V}$$

$$H^0(T) - H^0(0K)_{\text{trans}} = 5/2RT$$

$$C_v^0_{\text{trans}} = 3/2 R$$

$$S^0_{\text{trans}} = R(3/2 \ln M + 5/2 \ln T + 5/2 + \ln k/P_0 (2\pi k/Vn^2)^{1.5} + \ln n)$$

where $M$ is the molecular weight, $k$ is the Boltzmann constant, $T$ is temperature, $h$ is Planck's constant, $V$ is volume, $R$ is the gas constant, $P_0$ is the reference pressure (typically at one atmosphere), $N$ is the number of atoms in a molecule (Avogadro's constant), and $n$ is the number of optical isomers.

For rotational degrees of freedom we have the following:

1. Linear molecule (2 degrees of freedom)

$$Q_{\text{rot-2D}} = (8\pi^2 kT/h^2) / \sigma_e$$
H^0(T) - H^0(OK) \text{rot-2D} = RT
Cv^0 \text{rot-2D} = R
S_0^{\text{rot-2D}} = R + R \ln \left(8\pi^2 kT/h^2 / \sigma_e\right)

2. Nonlinear molecule (3 degrees of freedom)

Q_{\text{rot-3D}} = \pi^{0.5} (8\pi^2 I_{x,y} I_{z} kT/h^2)^{3/2} / \sigma_e
H^0(T) - H^0(OK) \text{rot-3D} = 3/2RT
Cv^0 \text{rot-3D} = 3/2R
S_0^{\text{rot-3D}} = 1.5R + R \ln \left[\left(\pi^{0.5} (8\pi^2 kT/h^2)^{1.5} / \sigma_e\right) (I_{x,y} I_{z})^{0.5}\right]

where \(I\) is the moment of inertia [rotational constant \(B\) is related to the moment of inertia \(I\) by the equation \(B(\text{cm}^{-1}) = 16.85 / I(\text{amu} \cdot \text{Å}^2)\)] for a linear molecule about its center of mass, \(I_{x,y} I_{z}\) is the product of the three principal moments of inertia for a nonlinear molecule around its center of gravity, and \(\sigma_e\) is the external rotation symmetry number of the molecule.

In complex molecules, one or more of the internal degrees of freedom may become a simple, one-dimensional, free rotation. In that case its properties are described by:

3. One-dimensional rotor

Q_{\text{rot-1D}} = \pi^{0.5} (8\pi^2 I_{r} kT/h^2)^{0.5} / \sigma_i
H^0(T) - H^0(OK) \text{rot-1D} = RT/2
Cv^0 \text{rot-1D} = R/2
S_0^{\text{rot-1D}} = 0.5R + R \ln \left(8\pi^3 I_{r} kT/h^2)^{0.5} / \sigma_i\right)

where \(\sigma_i\) is the symmetry of the internal rotation, and \(I_r\) is the reduced moment of inertia for the internal rotation of a nonlinear polyatomic molecule.

For each vibrational degree of freedom we have the following:

Q_{\text{vib}} = (1 - e^{-h\nu / kT})^{-1}
H^0(T) - H^0(OK) \text{vib} = RT e^{-\nu} / (1 - e^{-\nu})
Cp^0_{\text{vib}} = R x^2 e^{-\nu} / (1 - e^{-\nu})^2
S_0^{\text{vib}} = R x e^{-\nu} / (1 - e^{-\nu}) - R \ln (1 - e^{-\nu})
where \( x \) equals \( h \nu c / kT \), \( \nu \) is the fundamental frequency of a harmonic oscillator, and \( c \) is the velocity of light.

The STATHERM code does not correct the thermodynamic properties for anharmonic vibrations nor does it correct for hindered internal rotation. In a future version of this statistical thermodynamic program, corrections for hindered internal rotation using the Pitzer and Gwinn Tables \([1,2]\) will be implemented into the STATHERM code.

The statistical thermodynamic formulas presented above can be used to generate thermochemical information from spectroscopic data \([3-6]\), semi-empirical calculations via the MOPAC program \([7]\), and high quality \textit{ab initio} electronic structure calculations from programs such as GAUSSIAN \([8]\) or GAMESS \([9]\). The STATHERM program can also calculate the enthalpy of formation, entropy of formation, the gibbs free energy of formation, and the logarithm of the standard equilibrium constant (\( \log_{10} K_p \)) at any temperature from the formulas listed below:

\[
\Delta H_f^o(T) = \Delta H_f^o(298K) + \{ H^o(T) - H^o(298K) \} \text{compound} - \sum \{ H^o(T) - H^o(298K) \} \text{elements}
\]

\[
\Delta S_f^o(T) = S^o(T) \text{compound} - \sum S^o(T) \text{elements}
\]

\[
\Delta G_f^o(T) = \Delta H_f^o(T) - T \Delta S_f^o(T)
\]

\[
\log K_p = - \Delta G_f^o(T) / RT
\]

The reference elements presently hardwired into the STATHERM program are C, H, O, N, and Cl. In a future version of STATHERM, the inclusion of reference elements such as Al, Ar, Ba, Be, Ca, Cs, Cr, Cb, e\(^-\), F, Ga, Hf, I, Fe, Kr, Pb, Li, Mg, Mn, Hg, Mo, Ne, Ni, Nb, P, K, Rn, Rb, Si, Sr, S, Ta, Ti, W, V, Xe, and Zn will be considered. For further inquiries about STATHERM, please contact Nick Marinov (marinov@llnl.gov) at (510) 424-5463.

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The Fitting Procedure

The thermodynamic data are stored as polynomial fits to the specific heat (Cp°/R), enthalpy (H°/RT), and entropy (S°/R). There are seven coefficients for each of the two temperature ranges.

\[
\begin{align*}
Cp°/R &= a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4 \\
H°/RT &= a_1 + a_2 T/2 + a_3 T^2/3 + a_4 T^3/4 + a_5 T^4/5 + a_6/T \\
S°/R &= a_1 \ln T + a_2 T + a_3 T^2/2 + a_4 T^3/3 + a_5 T^4/4 + a_7
\end{align*}
\]

Thus for each species there are 14 coefficients in all. The temperature range for a valid data fit typically range from 300K to 5000K. However, the user may modified the temperature range depending on the problem in question.

The essential input to the data fitting procedure is a table of specific heat, enthalpy, and entropy as a function of temperature. The STATTHERM program provides a JANAF [10] thermochemical table-like output prior to the generation of the thermochemical coefficients. The STATTHERM program provides a high (1000K - 5000K) and low (298K - 1000K) temperature polynomial fit to the thermodynamic properties whereupon the common temperature connecting the two temperature ranges has been arbitrarily selected at 1000K. The STATTHERM program will print out the thermochemical coefficients separately for each temperature range, as well as a combined coefficient listing in accordance to the standard format found in thermodynamic databases which employ the use of NASA polynomial coefficient data [11,12].

The STATTHERM program fits the three properties, Cp°, S°, and H°-H°ref by a simultaneous least square fitting procedure. This approach generally gives better reproducibility of all properties and low deviation of ≥ ±0.5%. The polynomials obtained from simultaneous equation fitting are known as the NASA thermodynamic polynomials because of their use in a variety of NASA computer programs [13,14]. In Appendix A, the STATTHERM program is shown that uses the simultaneous least square fitting approach of Zeleznik and Gordon [15].
An Example Problem: Methyl Chloride (CH3CL)

An example problem is given to indicate the required inputs needed to run the STATATHERM program. Page 8 shows a typical data input file (data.inp) required. The data input follows a strict formatting requirement which is explained in Table 1.

The following data were obtained from JANAF Thermochemical Tables [10] for the methyl chloride molecule in order to test the STATATHERM program.

Methyl Chloride or Chloromethane
Chemical Formula : CH3CL
Element Composition: 1 C (Carbon), 3 H (Hydrogen), 1 Cl (Chlorine)
Number of atoms: 1 (C) + 3 (H) + 1 (Cl) = 5 atoms
Molecular Weight: 50.48 g/gmol
External Rotation Symmetry Number: 3
Heat of Formation at 298.15K ($\Delta H_f^0(298.15K)$): -20.0 kcal/mol
Statistical Weight of the Ground Level: 1
Optical Isomers: 1
Internal Rotation Symmetry Number: 1
One-Dimensional Active Rotors: 0
Moments of Inertia: 3.17 amu-Å, 38.47978 amu-Å, and 38.47978 amu-Å.
Fundamental Vibrational Frequencies: 732 cm$^{-1}$, 1017 cm$^{-1}$, 1017 cm$^{-1}$, 1355 cm$^{-1}$, 1455 cm$^{-1}$, 1455 cm$^{-1}$, 2968 cm$^{-1}$, 3054 cm$^{-1}$, and 3054 cm$^{-1}$

This information is the required input to the STATATHERM program. The data input file is opened by the STATATHERM program, and the results are written to a file called results.out. A sample results.out output file for the methyl chloride (CH3CL) test problem is shown in Appendix B.

The output information found from running the STATATHERM program while utilizing the data.inp file gives an array of information typically found in the JANAF Thermochemical Tables and standard thermodynamic databases [11,12] which store thermodynamic data in NASA polynomial coefficient form. The STATATHERM program writes out the data input as specified by the user as.
CH3Cl

C   1
H   3
O   0
N   0
CL  1
N
5   50.48
3   -20.0
1.  1  0
M
3.17  38.47978  38.47978
0.   0.        0.
0.   0.        0.
732.
1017.
1017.
2968.
3054.
3054.
1355.
1455.
1455.
Table 1: The Input Cards to the DATA.INP file for the STATTHERM code

<table>
<thead>
<tr>
<th>Order</th>
<th>Contents</th>
<th>Format</th>
<th>Card Columns</th>
</tr>
</thead>
<tbody>
<tr>
<td>First</td>
<td>Chemical formula</td>
<td>25A1</td>
<td>1 to 25</td>
</tr>
<tr>
<td>Second</td>
<td>Read the constituent elements of the molecule and the number elements that make up the molecule. Only five elements (C,H,O,N,CL) can be read. Elements may be read in any order. One element per card (i.e., line).</td>
<td>A2</td>
<td>1 to 2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>I5</td>
<td>4 to 8</td>
</tr>
<tr>
<td>Third</td>
<td>Is the molecule linear or nonlinear?</td>
<td>A1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>L signifies a linear molecule, and N signifies a nonlinear molecule</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fourth</td>
<td>Read the number of atoms and molecular weight</td>
<td>I4</td>
<td>1 to 4</td>
</tr>
<tr>
<td>Fifth</td>
<td>Read the symmetry number of external rotation and the heat of formation in kcal/mol at 298.15K</td>
<td>F15.7</td>
<td>6 to 20</td>
</tr>
<tr>
<td>Sixth</td>
<td>Read the statistical weight of the ground level (electronic degeneracy), number of optical isomers, and the number of one dimensional active rotors</td>
<td>F4.0</td>
<td>1 to 4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>F4.0</td>
<td>6 to 9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>I5</td>
<td>11 to 15</td>
</tr>
<tr>
<td>Seventh</td>
<td>Are rotational constants or moments of inertia data to be entered?</td>
<td>A1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>M signifies moments of inertia</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>R signifies rotational constants</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eighth</td>
<td>Read moments of inertia or rotational constants</td>
<td>3(F14.4,1X)</td>
<td>1 to 44</td>
</tr>
<tr>
<td>Ninth</td>
<td>Read moments of inertia or rotational constants for a complex molecule that exhibits one-dimensional free rotation in one or more of its internal degrees of freedom</td>
<td>3(F14.4,1X)</td>
<td>1 to 44</td>
</tr>
<tr>
<td>Tenth</td>
<td>Read internal rotation symmetry number associated with each one dimensional rotor</td>
<td>3(F4.0,1X)</td>
<td>1 to 14</td>
</tr>
<tr>
<td>Eleventh</td>
<td>Read vibrational frequencies (cm(^{-1})). One vibrational frequency per line.</td>
<td>F11.4</td>
<td>1 to 11</td>
</tr>
<tr>
<td>Last</td>
<td>Blank Card</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a double check to the entries made. The program then calculates and lists in tabular form the standard state heat capacities (Cp\(^{0}\)), entropies (S\(^{0}\)), and enthalpies [(H\(^{0}\)-H\(^{0}\)(298K))] followed by the enthalpy of formation (\(\Delta\text{H}_{\text{f}}^{0}\)), the gibbs free energy of formation (\(\Delta\text{G}_{\text{f}}^{0}\)), and the logarithm of the standard
equilibrium constant ($\log_{10} K_p$) for the 0K - 5000K temperature range. The thermodynamic properties are then fitted by a simultaneous least squares equation fitting scheme to obtain the NASA polynomial coefficients for high (1000K - 5000K) and low (298K - 1000K) temperature ranges. The STATTHERM program also computes the predicted thermodynamic quantities from the polynomial fitted equations and compares those predicted values to the actual (or correct) values (PRED/CORRECT). Those values when subtracted by 1 and multiplied by 100% reflect the relative error involved in the data fit with respect to the actual value. Prior to the close of the program, the STATTHERM program prints the combined thermochemical coefficients for both the high and low temperature ranges as typically found in thermodynamic data bases that store thermodynamic information in NASA polynomial coefficient form.
References

7. MOPAC 93.00, J.J.P. Stewart et al., Fujitsu Limited, Tokyo, Japan (1993).
PROGRAM STATTHERM computes the thermochemical properties of a polyatomic molecule using statistical thermodynamic formulas. The data are fitted into the NASA polynomial form for use in combustion codes.

This program does not calculate thermochemical information for hindered internal rotation. Please consult Pitzer and Gwynn tables. If there is a need within the LLNL combustion group to include this additional information for thermochemical data fitting, please contact N.M. Marinov for inclusion of this calculation in program STATTHERM.

This program does not make corrections for anharmonic vibrations.

Required input:

1. Molecular name
2. Molecular weight
3. Heat of formation at 298K
4. Vibrational frequencies (cm⁻¹)
5. Symmetry numbers for internal and external rotation
6. Electronic degeneracy and number of optical isomers
7. Rotational constants (cm⁻¹) or moments of inertia (amu·Å²)

Program written and modified for use by N.M. Marinov (1997)

Version 1.0

Program written and modified for use by N.M. Marinov (1997)

Version 1.0

```plaintext
PARAMETER (NTEMP=40, NCHAR=35, NUMB=65, NELEM=5)

DOUBLE PRECISION SE(NELEM,NTEMP), HE(NELEM,NTEMP)
DOUBLE PRECISION DELGFA(NTEMP), TLOGKP (NTEMP)
DOUBLE PRECISION DELGF(NTEMP), DELSF(NTEMP), DELHF(NTEMP)
DOUBLE PRECISION CP(NTEMP), DELTAH(NTEMP), S(NTEMP), T(NTEMP)
DOUBLE PRECISION EQLBRMK(NTEMP)
DOUBLE PRECISION MU(100), BX(10), SYM(10), DIM1(10), SYMINT(10)
DOUBLE PRECISION MW, HF298, IROT, R, H, K, PI, SIGMA, C2, ZR, THETA, IE, X, N
DOUBLE PRECISION SYMEXT, SNO
DIMENSION CPA(50), DELHA(50), SA(50), TA(50), NLABEL(NELEM), YE(NUMB)
COMMON /PAss/M,KK,TA,cPA,sA,DELHA, cpoATo, sToATo,DELHTo,HFF298
LOGICAL LINEAR

CHARACTER*1 NAME(NCHAR), AA, AAA
CHARACTER*2 LABEL(5), SELEMENT, HELEMENT
```

Data T/0.0D0,1.0D2,2.5D2,2.9815D2,3.0D2,4.0D2,4.5D2,5.0D2,
1 5.5D2,6.0D2,6.5D2,7.0D2,7.5D2,8.0D2,8.5D2,9.0D2,
2 9.5D2,1.0D3,1.1D3,1.2D3,1.3D3,1.4D3,1.5D3,1.6D3,1.7D3,
3 1.8D3,1.9D3,2.0D3,2.1D3,2.2D3,2.3D3,2.4D3,2.5D3,2.6D3,
4 2.7D3,2.8D3,2.9D3,3.0D3,4.0D3,5.0D3/

Data R/1.987D0/,H/6.62617636D-34/,K/l.38066244D–23/
Data N/6.02204531D+23/,PI/3.14159260/,C2/1.438786654D-02/
OPEN (unit=8, FILE='entropy.dat', STATUS='OLD')
OPEN (unit=9, FILE='enthalpy.dat', STATUS='OLD')
OPEN (unit=5, FILE='data.inp', STATUS='OLD')
OPEN (unit=6, FILE='results.out', STATUS='OLD')

LINEAR=.TRUE.

READ IN THE NAME OF THE MOLECULE
READ(5, '(35A1)') (NAME(I), I=1,NCHAR)

READ IN THE CONSTITUENT ELEMENTS AND THE NUMBER OF ATOMS THAT
MAKE UP THE MOLECULE. ONLY 5 CONSTITUENT ELEMENTS ARE
TABULATED AS REFERENCES IN THE "STATTHERM" PROGRAM. THE
CONSTITUENT ELEMENTS ARE C, H, O, N, and CL.

DO 11 I=1,5
    READ(5, '(A2,1X,I5)') LABEL(I), NLABEL(I)
    CONTINUE

READ LABEL OF MOLECULE.
"L" EQUALS LINEAR AND "N" EQUALS NONLINEAR.

READ(5, '(A)') AA

IF (AA.NE. 'L'.AND.AA.NE. '1') LINEAR=.FALSE.

READ IN THE NUMBER OF ATOMS AND MOLECULAR WEIGHT
READ(5, '(I4,1X,F15.7)') NATOM, MW
NVIB=3*NATOM-6
IF(LINEAR) NVIB=NVIB+1

READ IN THE SYMMETRY NUMBER OF EXTERNAL ROTATION AND THE
HEAT OF FORMATION (IN KCAL/MOL) AT 298K
READ(5, '(F4.0,1X,F10.4)') SYMEXT, HF298

HF298=HF298*1.0D3

READ IN STATISTICAL WEIGHT OF THE GROUND LEVEL (ELECTRONIC
DEGENERACY), NUMBER OF OPTICAL ISOMERS, AND THE NUMBER
OF ONE-DIMENSIONAL ACTIVE ROTORS
READ(5, '(F4.0,1X,F4.0,1X,15)') STAT, SNOI, NROTOR

NVIB=NVIB-NROTOR

READ IN THE ROTATIONAL CONSTANTS (CM-1) OR MOMENT OF INERTIAS (AMU-A**2)
FOR 2 ROTATIONAL DEGREES OR 3 ROTATIONAL DEGREES OF FREEDOM IN THE
THE (LINEAR OR NONLINEAR) MOLECULE.

READ LABEL OF VALUES. "M" EQUALS MOMENT OF INERTIA IN AMU-A**2 UNITS USED
AND "R" EQUALS ROTATIONAL CONSTANTS IN CM-1 UNITS USED.

READ(5, '(A)') AAA

IF (AAA.NE. 'M'.AND.AAA.NE. 'm') THEN
    READ(5, '(F14.4,1X,F14.4,1X,F14.4)') (BX(I), I=1,3)
    KKOUNT=1
ELSE
    READ(5, '(F14.4,1X,F14.4,1X,F14.4)') (BX(I), I=1,3)
    KKOUNT=0
ENDIF
READ IN THE ROTATIONAL CONSTANTS (cm⁻¹) OR MOMENTS OF INERTIA (AMU·Å²)
FOR A COMPLEX MOLECULE THAT EXHIBITS ONE-DIMENSIONAL, FREE ROTATION
IN ONE OR MORE OF ITS INTERNAL DEGREES OF FREEDOM

IF (AAA.NE.'M' .AND.AAA.NE.'m') THEN
READ(5,'(F14.4,1X,F14.4,1X,F14.4)') (BX(I),I=4,6)
KKOUNT=1
ELSE
READ(5,'(F14.4,1X,F14.4,1X,F14.4)') (BX(I),I=4,6)
KKOUNT=0
ENDIF

READ IN THE INTERNAL ROTATION SYMMETRY NUMBER ASSOCIATED WITH
EACH ONE-DIMENSIONAL ROTOR

READ(5,'(F4.0, 1X,F4.0,1X,F4.0)') (SYMINT(I),I=1,3)

READ IN THE VIBRATIONAL FREQUENCIES

DO 777 I=1,NVIB
   READ(5, '(F11.4,1X)') MU(I)
CONTINUE

INITIALIZE HEAT CAPACITY AND ENTROPY AT 0K

CP(1)=0.0D0
S(1)=0.0D0
DELTAH(1)=0.0D0

TRANSLATIONAL CONTRIBUTION

DO 20 I=2,NTEMP
   CP(I)=2.5D0*R
   DELTAH(I)=2.5D0*R*T(I)
   ZR=(2.0D0*PI*MW*1.0D-3/N/H**2)**(1.5D0)*(K*T(I))**2.5D0/
    1 1.01325D5
   S(I)=R*(DLOG(ZR)+2.5D0+DLOG(SNOI))
CONTINUE

ROTATIONAL CONTRIBUTION

IF(BX(1).LE.0.0) GOTO 747
IF(LINEAR) THEN
   DO 30 I=2,NTEMP
      CP(I)=CP(I)+R*(1.0D0)
      DELTAH(I)=DELTAH(I)+R*T(I)*(1.0D0)
      IF(KKOUNT.EQ.0) THEN
         S(I)=S(I)+4.5758*(DLOG10(BX(I)/6.0231)+DLOG10(T(I))-
         1 1 DLOG10(SYMEXT))-0.7804
      ELSE
         S(I)=S(I)+4.5758*(DLOG10(21.543931D0/(BX(I)*BX(2)*BX(3))))-
         1 1 DLOG10(SYMEXT))-0.7804
      ENDIF
   CONTINUE
ELSE
   DO 40 I=2,NTEMP
      CP(I)=CP(I)+R*(1.5D0)
      DELTAH(I)=DELTAH(I)+(1.5D0)*R*T(I)
      IF(KKOUNT.EQ.0) THEN
         S(I)=S(I)+2.2879D0*DLOG10(BX(1)*BX(2)*BX(3)/218.504D0)-
         1 4.5758D0*DLOG10(SYMEXT)+6.8637D0*DLOG10(T(I))-0.0332D0
      ELSE
         S(I)=S(I)+2.2879D0*DLOG10(21.543931D0/(BX(1)*BX(2)*BX(3)))-
         1 4.5758D0*DLOG10(SYMEXT)+6.8637D0*DLOG10(T(I))-0.0332D0
   ENDIF
   ELSE
ENDIF
40 CONTINUE
ENDIF

C C VIBRATIONAL CONTRIBUTION
C
747 DO 50 I=2,NTEMP
   DO 60 J=1,NVIB
      THETAV=C2*1.0D2*MU(J)
      X=THETAV/T(I)
      CP(I)=CP(I)+R*(X**2)*DEXP(X)/(DEXP(X)-1.0D0)**2
      DELTAH(I)=DELTAH(I)+R*THETAV/(DEXP(X)-1.0D0)
      S(I)=S(I)+R*(-DLOG(1.0D0-EXP(-X))+X/(DEXP(X)-1.0D0))
   60 CONTINUE
      50 CONTINUE
C C ELECTRONIC CONTRIBUTION
C
DO 65 I=2,NTEMP
   S(I)=S(I)+ALOG(STAT)*R
   65 CONTINUE
C C INTERNAL ROTATION CONTRIBUTION
C
IF(NROTOR.EQ.0) GOTO 121
DO 70 J=1,NROTOR
   DO 75 I=2,NTEMP
      IF(BX(J+3).LE.0.0) GOTO 121
      IF(KKOUNT.EQ.0) BX(J+3)=16.85/BX(J+3)
      Q=SQRT(3.1415926)/SMINT(J)*SQRT(0.695104D0*T(I)/BX(J+3))
      DELTAH(I)=DELTAH(I)+1.5D0*R*T(I)
      CP(I)=CP(I)+R/2.0
      S(I)=S(I)+R*0.5+ALOG(Q))
   75 CONTINUE
      70 CONTINUE
C 121 CP(1)=0.0D0
      S(I)=0.0D0
C C COMPUTE THE ENTHALPIES OF FORMATION, GIBBS FREE ENERGIES, AND C
LOG Kp's AT ALL TEMPERATURES OF INTEREST
C
DO 307 J=1,NELEM
   DO 308 K=1,NTEMP
      SE(J,K)=0.0D0
      HE(J,K)=0.0D0
   308 CONTINUE
      307 CONTINUE
C
DO 600 J=1,NELEM
   IF(NLABEL(J).EQ.0) GOTO 600
   IF(NLABEL(J).NE.0) THEN
      READ(8,'(A)',IOSTAT=ICODE) SELEMENT
      IF(ICODE.LE.0) GOTO 401
      IF(SELEMENT.NE.LABEL(J)) GOTO 601
      READ(8,'(8F8.3)',END=502) (YE(K),K=1,NUMB)
   ELSE
      WRITE(6,402)
      FORMAT(/1X,'Element specified can not be found in
1STATTHERM...Please select C,H,O,N,CL elements only')
      PAUSE
      ENDIF
   601 READ(8,'(A)',IOSTAT=ICODE) SELEMENT
   IF(ICODE.LE.0) GOTO 401
   401 IF(SELEMENT.NE.LABEL(J)) GOTO 601
      READ(8,'(8F8.3)',END=502) (YE(K),K=1,NUMB)
      ELSE
      WRITE(6,402)
      402 FORMAT(/1X,'Element specified can not be found in
1STATTHERM...Please select C,H,O,N,CL elements only')
      PAUSE
      ENDIF
C
502 DO 602 K=1,NUMB
      YE(K)=YE(K)*(R/8.314D0)
CONTINUE

DO 603 K=1, NTEMP
   TK=T(K)
   CALL POLINT(YE, NUMB, TK, Y, DY)
   SE(J, K)=Y
CONTINUE

IF (NLABEL(J).NE.0) THEN
   READ(9,'(A)', IOSTAT=ICODE) HELEMENT
   IF (ICODE.LE.0) GOTO 404
   IF (HELEMENT.NE.LABEL(J)) GOTO 604
   READ(9,'(8F8.3)', END=505) (YE(K), K=1, NUMB)
ELSE
   WRITE(6,402)
   GOTO 891
ENDIF

DO 605 K=1, NUMB
   YE(K)=YE(K)*(R/8.314DO)
CONTINUE

DO 606 K=1, NTEMP
   TK=T(K)
   CALL POLINT(YE, NUMB, TK, Y, DY)
   HE(J, K)=Y
CONTINUE

DO 116 K=1, NTEMP
   DELHF(K)=0.0
   DELSF(K)=0.0
   DELGF(K)=0.0
CONTINUE

DO 117 J=1, NELEM
   DO 118 K=1, NTEMP
      IF (LABEL(J).EQ.'C') THEN
         DELSF(K)=DELSF(K)+FLOAT(NLABEL(J))*SE(J, K)
         DELHF(K)=DELHF(K)+FLOAT(NLABEL(J))*HE(J, K)
      ELSEIF (LABEL(J).EQ.'H') THEN
         DELSF(K)=DELSF(K)+0.5D0*FLOAT(NLABEL(J))*SE(J, K)
         DELHF(K)=DELHF(K)+0.5D0*FLOAT(NLABEL(J))*HE(J, K)
      ELSEIF (LABEL(J).EQ.'O') THEN
         DELSF(K)=DELSF(K)+(0.5D0*FLOAT(NLABEL(J))*SE(J, K))
         DELHF(K)=DELHF(K)+(0.5D0*FLOAT(NLABEL(J))*HE(J, K))
      ELSEIF (LABEL(J).EQ.'N') THEN
         DELSF(K)=DELSF(K)+(0.5D0*FLOAT(NLABEL(J))*SE(J, K))
         DELHF(K)=DELHF(K)+(0.5D0*FLOAT(NLABEL(J))*HE(J, K))
      ELSEIF (LABEL(J).EQ.'CL') THEN
         DELSF(K)=DELSF(K)+(0.5D0*FLOAT(NLABEL(J))*SE(J, K))
         DELHF(K)=DELHF(K)+(0.5D0*FLOAT(NLABEL(J))*HE(J, K))
      ELSE
         WRITE(6,402)
         GOTO 891
      ENDIF
   CONTINUE

DO 219 J=1, NTEMP
   DELHF(J)=(HF298/1.0D3)+((DELTAH(J)-DELTAH(4))/1.0D3)-DELHF(J)
   DELSF(J)=S(J)-DELSF(J)
   DELGF(J)=(DELHF(J)*1.0D3)-T(J)*DELSF(J)
CONTINUE
PRINT TABLE

\texttt{H298=Deltah(4)}
\texttt{WRITE(6,122) (NAME(I),I=1,NCHAR),MW,HFH298,INT(SYMEXT+0.01)}

\texttt{122 FORMAT(1X,35A1,1X,'MOLECULAR WEIGHT =',F7.3//1X,'HEAT OF FORMATION 1'\,' AT 298K =',F15.5,1X,'(CAL/MOL)'/1X,\,'EXTERNAL SYMMETRY NUMBER =',13/)}

\texttt{WRITE(6,120)}
\texttt{120 FORMAT(1X,'MOLECULAR MAKE-UP')}  

\texttt{DO 73 I=1,5}
\texttt{WRITE(6,123) LABEL(I),NLABEL(I)}
\texttt{123 FORMAT(1X, A2, 1X, 15)}
\texttt{73 CONTINUE}

\texttt{IF (LINEAR) THEN}
\texttt{WRITE(6,124)}
\texttt{124 FORMAT(/1X,'MOLECULE IS LINEAR',/)}
\texttt{ELSE}
\texttt{WRITE(6,125)}
\texttt{125 FORMAT(/1X,'MOLECULE IS NONLINEAR',/)}
\texttt{ENDIF}

\texttt{WRITE(6,126) INT(STAT+0.01)}
\texttt{126 FORMAT(1X,'ELECTRONIC DEGENERACY = ',14/)}

\texttt{WRITE(6,127) INT(SNOI+0.01)}
\texttt{127 FORMAT(1X,'NUMBER OF OPTICAL ISOMERS = ',14/)}

\texttt{IF (AAA.NE.' M'.AND.AAA.NE.' m') THEN}
\texttt{WRITE(6,128)}
\texttt{128 FORMAT(/1X,'ROTATIONAL CONSTANTS (UNITS: CM-1) ARE:')}
\texttt{WRITE(6,129) (BX(I), I=1,3)}
\texttt{129 FORMAT(3(1 X, F14.4))}
\texttt{WRITE(6,130) (BX(I), I=4,6)}
\texttt{130 FORMAT(3(1 X, F14.4),/)}
\texttt{ELSE}
\texttt{WRITE(6,131)}
\texttt{131 FORMAT(/1X,'MOMENTS OF INERTIA (UNITS: AMU-A**2) ARE:')}
\texttt{WRITE(6,132) (BX(I), I=1,3)}
\texttt{132 FORMAT(3(1 X, F14.4))}
\texttt{WRITE(6,133) (BX(I), I=4,6)}
\texttt{133 FORMAT(3(1 X, F14.4),/)}
\texttt{ENDIF}

\texttt{WRITE(6,98)}
\texttt{98 FORMAT(1X,'INTERNAL SYMMETRY NUMBER(S)')}  
\texttt{WRITE(6,99) (INT(SYMINT(I)),I=1,3)}
\texttt{99 FORMAT(3(1X,I4),/)}

\texttt{WRITE(6,134)}
\texttt{134 FORMAT(1X,'VIBRATIONAL FREQUENCIES (CM-1)'/1X,'-------------------------------'//1X)}
\texttt{WRITE(6,135) (MU(I), I=1,NVIB)}
\texttt{135 FORMAT(F11.1)}
\texttt{WRITE(6,136)}
\texttt{136 FORMAT(1X,'-------------------------------'//1X)}
\texttt{WRITE(6,137)}
\texttt{137 FORMAT(3X,'T(K)',7X,'CP (CAL/MOL/K)',3X,'S(CAL/MOL/K)',12X,'[H(T)-H(298K)] (KCAL/MOL)'/1X,65(' '))}
\texttt{DO 138 I=1,NTEMP}
\texttt{DELHA(I)=(DELTAH(I)-H298)/1000.0}
\texttt{WRITE(6,139) T(I),CP(I),S(I),DELHA(I)}
\texttt{138 CONTINUE}

\textit{A-6}
WRITE (6, 140)
140 FORMAT (1X, 65 ('-') / 1H1)
WRITE (6, 141)
141 FORMAT (3X, 'T (K)', 7X, 'DELHF (KCAL/MOL)', 3X, 'DELGF (KCAL/MOL)',
1      2X, 'LOG10KP' / 1X, 65 ('-'))
DELGFA (1) = DELGF (1) / 1000.
EQLBRMK (1) = 1000000000.
TLOGKP (1) = 1000000000.
DO 242 I = 2, NTEMP
   DELGFA (I) = DELGF (I) / 1000.0
   EQLBRMK (I) = EXP (-DELGF (I) / (R*T (I)))
   TLOGKP (I) = DLOG10 (EQLBRMK (I))
242 CONTINUE
DO 142 I = 1, NTEMP
   WRITE (6, 143) T(I), DELHF(I), DELGFA(I), TLOGKP(I)
   FORMAT (1X, F7.2, F15.3, 1X, F14.3, 1X, F17.3)
CONTINUE
WRITE (6, 144)
144 FORMAT (1X, 65 ('-') / 1H1)
CALL SUBROUTINE FIT TO COMPUTE THE NASA POLYNOMIAL
H298 = SNGL (DELTAH (4))
HFF298 = SNGL (HF298) / 1000.0
DELHT0 = SNGL (DELTAH (18) - H298) / 1000.0
CPOATO = SNGL (CP (18))
STOATO = SNGL (S (18))
DO 300 I = 18, NTEMP
   TA(I-17) = SNGL (T(I))
   CPA(I-17) = SNGL (CP (I))
   SA(I-17) = SNGL (S (I))
   DELHA(I-17) = SNGL (DELTAH (I) - H298) / 1000.0
300 CONTINUE
WRITE (6, 310)
310 FORMAT (1X, 'HIGH TEMPERATURE')
M = NTEMP - 18 + 1
KK = 1
CALL FIT (M, KK, TA, CPA, SA, DELHA, CPOATO, STOATO, DELHT0, HFF298)
H298 = SNGL (DELTAH (4))
HFF298 = SNGL (HF298) / 1000.0
DELHT0 = SNGL (DELTAH (18) - H298) / 1000.0
CPOATO = SNGL (CP (18))
STOATO = SNGL (S (18))
DO 200 I = 3, 19
   TA(I-2) = SNGL (T(I))
   CPA(I-2) = SNGL (CP (I))
   SA(I-2) = SNGL (S (I))
   DELHA(I-2) = (SNGL (DELTAH (I) - H298)) / 1000.0
200 CONTINUE
WRITE (6, 210)
210 FORMAT (1X, '/1X, 'LOW TEMPERATURE'/)
M = 17
KK = 2
CALL FIT (M, KK, TA, CPA, SA, DELHA, CPOATO, STOATO, DELHT0, HFF298)
CLOSE (UNIT = 8)
CLOSE (UNIT = 9)
CLOSE (UNIT=5)
CLOSE (UNIT=6)
STOP
END

SUBROUTINE FIT (M, KK, T, CPO, STO, DELH, CPOATO, STOATO, DELHTO, HF2 98)

DIMENSION T(50), DELH(50), STO(50), CPO(50), X(10), XH(14), BB(50), CC(50), DD(50)

COMMON /PASS1/X, R

TO=1000.
TSCALE=5000.
R=1.987
TO=1000./TSCALE
DELHTO=DELHTO*1000./TSCALE
DO 48 I=1,M
   T(I)=T(I)/TSCALE
48
DO 21 I=1,10
   C(I)=0.0
   DO 21 J=1,10
      A(I, J)=0.0
   DO 22 I=1, M
      ARG1=ALOG (T(I) )
      A(1, 1)=A(1, 1)+2.+ARG1*ARG1
      A(1, 2)=A(1, 2)+(3./2.+ARG1) * T(I)
      T2=T(I) * T(I)
      A(1, 3)=A(1, 3)+(4./3.+0.5*ARG1) * T2
      T3=T(I) * T2
      A(1, 4)=A(1, 4)+(5./4.+1./3.)*ARG1 * T3
      T4=T(I) * T3
      A(1, 5)=A(1, 5)+(6./5.+1./4.)*ARG1 * T4
      TINV=1./T(I)
      A(1, 6)=A(1, 6)+TINV
      A(1, 7)=A(1, 7)+ARG1
      A(2, 2)=A(2, 2)+T2
      A(2, 3)=A(2, 3)+T3
      A(2, 4)=A(2, 4)+T4
      T5=T(I) * T4
      A(2, 5)=A(2, 5)+T5
      A(2, 7)=A(2, 7)+T(I)
      T6=T(I) * T5
      A(3, 5)=A(3, 5)+T6
      T7=T(I) * T6
      A(4, 5)=A(4, 5)+T7
      T8=T(I) * T7
      A(5, 5)=A(5, 5)+T8
      A(6, 6)=A(6, 6)+1./T2
SS1=CPO(I)/R
SS2=(DELH(I))/(R*T(I))
SS3=STO(I)/R
C(1)=C(1)+SS1+SS2+SS3*ARG1
C(2)=C(2)+(T(I))*(SS1+0.5*SS2+SS3)
C(3)=C(3)+T2*(SS1+1./3.)*SS2+0.5*SS3
C(4)=C(4)+T3*(SS1+0.25*SS2+(1./3.))*SS3
C(5)=C(5)+T4*(SS1+0.2*SS2+0.25*SS3)
C(6)=C(6)+TINV*SS2
C(7)=C(7)+SS3
CONTINUE

A(1,8)=1.0
A(1,9)=1.0
A(1,10)=ALOG(T0)
SUM22=A(2,2)
A(2,2)=(9./4.)*SUM22
SUM23=A(2,3)
A(2,3)=(5./3.)*SUM23
SUM24=A(2,4)
A(2,4)=(35./24.)*SUM24
SUM25=A(2,5)
A(2,5)=(27./20.)*SUM25
P=FLOAT(M)
A(2,6)=P/2.
A(2,8)=T0
A(2,9)=T0/2.
A(2,10)=T0
A(3,3)=(49./36.)*SUM24
A(3,4)=(5./4.)*SUM25
SUM35=A(3,5)
A(3,5)=(143./120.)*SUM35
A(3,6)=(1./3.)*A(2,7)
A(3,7)=0.5*SUM22
TOSQ=T0*T0
A(3,8)=TOSQ
A(3,9)=TOSQ/3.
A(3,10)=TOSQ/2.
A(4,4)=(169./144.)*SUM35
A(4,5)=(17./15.)*A(4,5)
A(4,6)=(1./4.)*SUM22
A(4,7)=(1./3.)*SUM23
TOQUB=T0*TOSQ
A(4,8)=TOQUB
A(4,9)=TOQUB/4.
A(4,10)=TOQUB/3.
A(5,5)=(441./400.)*A(5,5)
A(5,6)=0.2*SUM23
A(5,7)=0.25*SUM24
TOFORT=TOSQ*TOSQ
A(5,8)=TOFORT
A(5,9)=TOFORT/5.
A(5,10)=TOFORT/4.
A(6,9)=1./T0
A(7,7)=P
A(7,10)=1.0
C(8)=CPOATO/R
C(9)=(DELEHT0)/(R*T0)
C(10)=STOATO/R
DO 70 I=1,10
  DO 60 J=1,10
    A(J,I)=A(I,J)
60    CONTINUE
70  CONTINUE
91  A(I,11)=C(I)
N=10
EPS=1.E-10
CALL SIMUL(N,A,X,EPS,NER)
TO=TSCLAE*T0
DELEHT0=TSCLAE*DELEHT0
WRITE (6,1010)
1010 FORMAT('/5X,'"INPUT VALUES"','/5X,12(-')")
WRITE (6,45) M,R,HF298,CPOATO,DELEHT0,STOATO
45 FORMAT('/1X,"NO. POINTS =",I5,4X,"GAS CONSTANT=",F12.4,5X,
1  "ENTHALPY OF FORMATION=",F11.4//1X,"Cpo AT To=",F14.3,
2 5X,"H-H298 AT To=",F14.3,5X,"Sto AT To=",F14.3////)
IF(NER.EQ.0) GO TO 222
WRITE(6,100)
100 FORMAT(/5X,'TEMP.',10X,'H-H298',10X,'PRED/CORRECT',
       1 10X,'STO',10X,'PRED/CORRECT',10X,'Cpo',10X,'PRED/CORRECT'
       1 '/5X,5(',5X,10X,6(',5X,10X,
       2 12(',5X,10X,3(',5X,10X,12(',5X,10X,3(',5X,10X,12(',5X)
30 DO 8 I=1,M
     T(I)=TSCALE*T(I)
     DELH(I)=DELH(I)*TSCALE
8 CONTINUE
   X(2)=X(2)/TSCALE
   X(3)=X(3)/(TSCALE**2)
   X(4)=X(4)/(TSCALE**3)
   X(5)=X(5)/(TSCALE**4)
   X(6)=TSCALE*X(6)+1000.*HF298/R
   X(7)=X(7)-X(1)*ALOG(TSCALE)
   DO 9 I=1,M
      ER1(I)=CSUPO(T(I))/CPO(I)
      ER2(I)=(DELHso(T(I))-HF298*1000.0)/DELH(I)
      ER3(I)=STSUPO(T(I))/STO(I)
9 CONTINUE
   WRITE(6,101) (T(I), DELH(I), ER2(I), STO(I), ER3(I), CPO(I), ER1(I),
       1 =1,M)
101 FORMAT((1X,F12.1,3X,F13.4,7X,F12.4,5X,F13.4,5X,F12.4,5X,
       1 F13.4,5X,F12.4))
   WRITE(6,102)
102 FORMAT(5X,113('-'))
   WRITE(6,110)
110 FORMAT(/5X,'LEAST SQUARE COEFFICIENTS',/5X,25('-'))
   WRITE(6,112) (I,X(I),I=1,5)
112 FORMAT(5X,'A(',I1,')=',E16.8/
   WRITE(6,113) (X(I),I=6,10)
113 FORMAT(5X,'A(6)=',E16.8//5X,'A(7)=',E16.8//5X,
       1 'LAMBDA0=',E15.8//5X,'LAMBDAL=',E15.8//5X,'LAMBDAA2=',E15.8//)
222 WRITE(6,102)
   WRITE(6,221) NER
221 FORMAT(5X,'NER=',12)
   WRITE(6,102)
222 FORMAT(5X,'NER=',12)
   WRITE(6,223)
   WRITE(6,102)
223 FORMAT(1H1)
   WRITE(6,224) T(1),T(M)
   WRITE(6,226) (X(I),I=1,7)
   WRITE(6,225) (X(I),I=1,3)
   WRITE(6,226) (X(I),I=4,7)
224 FORMAT(F10.0, ' K TO',F10.0, ' K')
225 FORMAT(30X,3E15.8)
226 FORMAT(5E15.8)
   IF (KK.EQ.1) THEN
      DO 227 I=1,7
         XH(I)=X(I)
227 CONTINUE
   ENDIF
   IF (KK.EQ.2) THEN
      DO 228 I=1,7
         XH(I+7)=X(I)
228 CONTINUE
   WRITE(6,229) TO
229 FORMAT(/2X,'PINNING TEMPERATURE IS ',F7.1,'K',/)
   WRITE(6,230)
230 FORMAT(/2X,' THERMOCHEMICAL COEFFICIENTS')
   WRITE(6,231) (XH(I),I=1,5)
   WRITE(6,231) (XH(I),I=1,5)
   WRITE(6,232) (XH(I),I=6,10)
   WRITE(6,232) (XH(I),I=11,14)
231 FORMAT(1P,5E15.8)
232 FORMAT(1P,4E15.8,/)
SUBROUTINE SIMUL(N, A, X, EPS, NER)
DIMENSION IROW(10), JCOL(10), JORD(10), Y(10), A(11, 11), X(10)

MAX=N+1
DETER=1.
DO 18 K=1, N
KM1=K-1
PIVOT=0.
DO 11 I=1, N
DO 11 J=1, N
IF(K.EQ.1) GOTO 9
DO 8 ISCAN=1, KM1
DO 8 JSCAN=1, KM1
IF(I.EQ.IROW(ISCAN)) GOTO 11
IF(J.EQ.JCOL(JSCAN)) GOTO 11
8 CONTINUE
9 IF(ABS(A(I, J)).LE.ABS(PIVOT)) GOTO 11
PIVOT=A(I, J)
IROW(K)=I
JCOL(K)=J
CONTINUE
10 IF(ABS(PIVOT).GT.EPS) GOTO 13
NER=0
RETURN
11 IROWK=IROW(K)
NER=1
JCOLK=JCOL(K)
DO 14 J=1, MAX
A(IROWK, J)=A(IROWK, J)/PIVOT
A(IROWK, JCOLK)=1./PIVOT
DO 18 I=1, N
AIJCK=A(I, JCOLK)
IF(I.EQ.IROWK) GOTO 18
A(I, JCOLK)=-AIJCK/PIVOT
DO 17 J=1, MAX
17 IF(J.NE.JCOLK) A(I, J)=A(I, J)-AIJCK*A(IROWK, J)
CONTINUE
10 IROWI=IROW(I)
JCOLI=JCOL(I)
JORD(IROWI)=JCOLI
X(JCOLI)=A(IROWI, MAX)
RETURN
END

SUBROUTINE POLINT(YA, N, X, Y, DY)
PARAMETER (NMAX=100)
DIMENSION XA(NMAX), YA(N), C(NMAX), D(NMAX)

C INITIALIZE THE TEMPERATURE ARRAY XA

XA(1)=0.0E0
XA(2)=1.0E2
XA(3)=2.0E2
XA(4)=2.5E2
XA(5)=2.9815E2
XA(6)=3.0E2
XA(7)=3.5E2
XA(8)=4.0E2
XA(9)=4.5E2
XA(10)=5.0E2
DO 9 I=11, N
XA(I)=XA(I-1)+100.
9 CONTINUE
C
NS=1
DIF=ABS(X-XA(I))
DO 11 I=1,N
   DIFT=ABS(X-XA(I))
   IF (DIFT.LT.DIF) THEN
      NS=I
      DIF=DIFT
   ENDIF
   C(I)=YA(I)
   D(I)=YA(I)
11 CONTINUE
Y=YA(NS)
NS=NS-1
DO 13 M=1,N-1
   DO 12 I=1,N-M
      HO=XA(I)-X
      HP=XA(I+M)-X
      W=C(I+1)-D(I)
      DEN=HO-HP
      IF (DEN.EQ.0.) PAUSE
      DEN=W/DEN
      D(I)=HP*DEN
      C(I)=HO*DEN
12 CONTINUE
   IF (2*NS.LT.N-M) THEN
      DY=C(NS+1)
   ELSE
      DY=D(NS)
      NS=NS-1
   ENDIF
   Y=Y+DY
13 CONTINUE
RETURN
END

C
REAL FUNCTION CSUPO(T)
COMMON /PASS1/X,R
DIMENSION X(10)
CSUPO=R*(X(1)+X(2)*T+X(3)*(T**2)+X(4)*(T**3)+X(5)*(T**4))
RETURN
END

C
REAL FUNCTION DEHSO(T)
COMMON /PASS1/X,R
DIMENSION X(10)
DEHSO=R*T*(X(1)+X(2)*T/2.+X(3)*(T**2)/3.+X(4)*(T**3)/4.
      +X(5)*(T**4)/5.+X(6)/T)
RETURN
END

C
REAL FUNCTION STSUPO(T)
COMMON /PASS1/X,R
DIMENSION X(10)
STSUPO=R*(X(1)*ALOG(T)+X(2)*T+X(3)*(T*T/2.)+(X(4)*(T**3)/3.)+
      X(5)*((T**4)/4.))
RETURN
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A-16
APPENDIX B.

Results output (RESULTS.OUT) from the STATTHERM program
CH3Cl

MOLECULAR WEIGHT = 50.480

HEAT OF FORMATION AT 298K = -20000.00000 (CAL/MOL)

EXTERNAL SYMMETRY NUMBER = 3

MOLECULAR MAKE-UP
C 1
H 3
O 0
N 0
Cl 1

MOLECULE IS NONLINEAR

ELECTRONIC DEGENERACY = 1

NUMBER OF OPTICAL ISOMERS = 1

MOMENTS OF INERTIA (UNITS: AMU-A**2) ARE:
3.1700 38.4798 38.4798
0.0000 0.0000 0.0000

INTERNAL SYMMETRY NUMBER(S)
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250.00 8.993        54.341        -0.450
298.15 9.734        55.987         0.000
300.00 9.765        56.047         0.018
400.00 11.508       59.093         1.081
450.00 12.366       60.498         1.678
500.00 13.179       61.844         2.317
550.00 13.939       63.136         2.995
600.00 14.646       64.380         3.710
650.00 15.304       65.578         4.459
700.00 15.917       66.735         5.239
750.00 16.490       67.853         6.050
800.00 17.025       68.935         6.888
850.00 17.526       69.982         7.752
900.00 17.994       70.997         8.640
950.00 18.432       71.982         9.551
1000.00 18.843       72.938        10.483
1100.00 19.585       74.769        12.405
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NER = 1

LOW TEMPERATURE

INPUT VALUES

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A(3) = 0.83700689E-05
\[ A(4) = -0.12837361 \times 10^{-7} \]
\[ A(5) = 0.47679022 \times 10^{-11} \]
\[ A(6) = -0.11154073 \times 10^{5} \]
\[ A(7) = 0.11789707 \times 10^{2} \]
\[ \lambda_0 = -0.50071675 \times 10^{-1} \]
\[ \lambda_1 = 0.48962392 \times 10^{-1} \]
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\[
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1 & 250. K & 1100. K \\
0.24777012 \times 10^{1} & 0.67045814 \times 10^{-2} & 0.83700688 \times 10^{-5} & -0.12837361 \times 10^{-7} & 0.47679022 \times 10^{-11} & -0.11154073 \times 10^{5} & 0.11789707 \times 10^{2} \\
-0.11154073 \times 10^{5} & 0.11789707 \times 10^{2} & 0.24777012 \times 10^{1} & 0.67045814 \times 10^{-2} & 0.83700688 \times 10^{-5} & -0.12837361 \times 10^{-7} & 0.47679022 \times 10^{-11} & -0.11154073 \times 10^{5} & 0.11789707 \times 10^{2} \\
\end{array}
\]

PINNING TEMPERATURE IS 1000.0 K

THERMOCHEMICAL COEFFICIENTS
\[
\begin{array}{cccccccc}
3.12318063 \times 10^{0} & 9.56861395 \times 10^{-3} & -3.88244143 \times 10^{-6} & 7.24232785 \times 10^{-10} & -5.06910798 \times 10^{-14} \\
-1.15740752 \times 10^{4} & 7.27722931 \times 10^{0} & 2.47770119 \times 10^{0} & 6.70458144 \times 10^{-3} & 8.37006883 \times 10^{-6} \\
-1.28373605 \times 10^{-8} & 4.76790222 \times 10^{-2} & 1.11540732 \times 10^{4} & 1.17897072 \times 10^{0} \\
\end{array}
\]