STATTHERM: A Statistical Thermodynamics Program for Calculating Thermochemical Information

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**STATTHERM: A Statistical Thermodynamics Program For
Calculating Thermochemical Information**

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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%.

The Statistical Thermodynamic Equations

Thermodynamics and quantum mechanics provides 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:	$C_V = (\Delta U / \Delta T)_V = R(\Delta \ln Q / \Delta \ln T)_V + R(\Delta^2 \ln Q / \Delta(\ln T)^2)_V$ $= R/T^2(\Delta^2 \ln Q / \Delta(1/T)^2)_V$
Molar Heat Capacity at constant pressure:	$C_p = C_V + R$ (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_{elec} for the electronic degrees of freedom is included.

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

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:

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

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

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

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

$$C_{v,0}^{trans} = 3/2 R$$

$$S_{0,trans}^0 = R(3/2 \ln M + 5/2 \ln T + 5/2 + \ln k/P^0 (2\pi k/Nh^2)^{1.5} + \ln n)$$

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)

$$Q_{rot-2D} = (8\pi^2 I k T / h^2) / \sigma_e$$

$$H^0(T) - H^0(0K)_{\text{rot-2D}} = RT$$

$$C_v^0_{\text{rot-2D}} = R$$

$$S^0_{\text{rot-2D}} = R + R \ln (8\pi^2 I k T / h^2 / \sigma_e)$$

2. Nonlinear molecule (3 degrees of freedom)

$$Q_{\text{rot-3D}} = \pi^{0.5} (8\pi^2 I_x I_y I_z k T / h^2)^{3/2} / \sigma_e$$

$$H^0(T) - H^0(0K)_{\text{rot-3D}} = 3/2 RT$$

$$C_v^0_{\text{rot-3D}} = 3/2 R$$

$$S^0_{\text{rot-3D}} = 1.5R + R \ln [(\pi^{0.5} (8\pi^2 k T / h^2)^{1.5} / \sigma_e) (I_x I_y I_z)]^{0.5}$$

where I is the moment of inertia [rotational constant B is related to the moment of inertia I by the equation $B(\text{cm}^{-1}) = 16.85 / I(\text{amu-}\text{\AA}^2)$] for a linear molecule about its center of mass, $I_x I_y I_z$ is the product of the three principal moments of inertia for a nonlinear molecule around its center of gravity, and σ_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

$$Q_{\text{rot-1D}} = \pi^{0.5} (8\pi^2 I_r k T / h^2)^{0.5} / \sigma_i$$

$$H^0(T) - H^0(0K)_{\text{rot-1D}} = RT/2$$

$$C_v^0_{\text{rot-1D}} = R/2$$

$$S^0_{\text{rot-1D}} = 0.5R + R \ln (8\pi^3 I_r k T / h^2)^{0.5} / \sigma_i$$

where σ_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:

$$Q_{\text{vib}} = (1 - e^{-h\nu / kT})^{-1}$$

$$H^0(T) - H^0(0K)_{\text{vib}} = RT e^{-x} / (1 - e^{-x})$$

$$C_p^0_{\text{vib}} = R x^2 e^{-x} / (1 - e^{-x})^2$$

$$S^0_{\text{vib}} = R x e^{-x} / (1 - e^{-x}) - R \ln (1 - e^{-x})$$

where x equals $h\nu/kT$, ν is the fundamental frequency of a harmonic oscillator, and c is the velocity of light.

The STATTHERM 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 STATTHERM 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 *ab initio* electronic structure calculations from programs such as GAUSSIAN [8] or GAMESS [9]. The STATTHERM 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 ($\text{Log}_{10} K_p$) at any temperature from the formulas listed below:

$$\Delta H_f^0(T) = \Delta H_f^0(298K) + [H^0(T) - H^0(298K)]_{\text{compound}} - \sum [H^0(T) - H^0(298K)]_{\text{elements}}$$

$$\Delta S_f^0(T) = S^0(T)_{\text{compound}} - \sum S^0(T)_{\text{elements}}$$

$$\Delta G_f^0(T) = \Delta H_f^0(T) - T \Delta S_f^0(T)$$

$$\text{Log } K_p = - \Delta G_f^0(T) / RT$$

The reference elements presently hardwired into the STATTHERM program are C, H, O, N, and Cl. In a future version of STATTHERM, 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 STATTHERM, please contact Nick Marinov (marinov@llnl.gov) at (510) 424-5463.

The Fitting Procedure

The thermodynamic data are stored as polynomial fits to the specific heat (C_p^0/R), enthalpy (H^0/RT), and entropy (S^0/R). There are seven coefficients for each of the two temperature ranges.

$$\begin{aligned}C_p^0/R &= a_1 + a_2T + a_3T^2 + a_4T^3 + a_5T^4 \\H^0/RT &= a_1 + a_2T/2 + a_3T^2/3 + a_4T^3/4 + a_5T^4/5 + a_6/T \\S^0/R &= a_1 \ln T + a_2T + a_3T^2/2 + a_4T^3/3 + a_5T^4/4 + a_7\end{aligned}$$

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, C_p^0 , S^0 , and $H_T^0 - H_{ref}^0$ by a simultaneous least square fitting procedure. This approach generally gives better reproducibility of all properties and low deviation of $\geq \pm 0.5\%$. 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 STATTHERM 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 STATTHERM 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 ($\Delta H_f^0(298.15K)$): -20.0kcal/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-Å², 38.47978 amu-Å², and 38.47978 amu-Å².

Fundamental Vibrational Frequencies: 732cm⁻¹, 1017cm⁻¹, 1017cm⁻¹, 1355cm⁻¹, 1455cm⁻¹, 1455cm⁻¹, 2968cm⁻¹, 3054cm⁻¹, and 3054cm⁻¹

This information is the required input to the STATTHERM program. The data input file is opened by the STATTHERM 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 STATTHERM 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 STATTHERM 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

Order	Contents	Format	Card Columns
First	Chemical formula	25A1	1 to 25
Second	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).	A2 I5	1 to 2 4 to 8
Third	Is the molecule linear or nonlinear? L signifies a linear molecule, and N signifies a nonlinear molecule	A1	1
Fourth	Read the number of atoms and molecular weight	I4 F15.7	1 to 4 6 to 20
Fifth	Read the symmetry number of external rotation and the heat of formation in kcal/mol at 298.15K	F4.0 F10.4	1 to 4 6 to 15
Sixth	Read the statistical weight of the ground level (electronic degeneracy), number of optica isomers, and the number of one dimensional active rotors	F4.0 F4.0 I5	1 to 4 6 to 9 11 to 15
Seventh	Are rotational constants or moments of inertia data to be entered? M signifies moments of inertia R signifies rotational constants	A1	1
Eighth	Read moments of inertia or rotational constants	3(F14.4,1X)	1 to 44
Ninth	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	3(F14.4,1X)	1 to 44
Tenth	Read internal rotation symmetry number associated with each one dimensional rotor	3(F4.0,1X)	1 to 14
Eleventh	Read vibrational frequencies (cm ⁻¹). One vibrational frequency per line.	F11.4	1 to 11
Last	Blank Card		

a double check to the entries made. The program then calculates and lists in tabular form the standard state heat capacities (C_p^0), entropies (S^0), and enthalpies $[(H^0T)-H^0(298K)]$ followed by the enthalpy of formation (ΔH_f^0), the gibbs free energy of formation (ΔG_f^0), and the logarithm of the standard

equilibrium constant ($\text{Log}_{10} K_p$) 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

1. K.S. Pitzer, and W.D. Gwinn, J. Chem. Phys., 10, pp.428-440, (1942).
2. K.S. Pitzer, J. Chem. Phys., 14, pp.239-243, (1946).
3. G. Herzberg, *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules* (Van Nostrand, New York, 1950).
4. G. Herzberg, *Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules* (Van Nostrand, New York, 1955).
5. G. Herzberg, *Molecular Spectra and Molecular Structure. III. Electronic Spectra of Polyatomic Molecules* (Van Nostrand, New York, 1966).
6. K.P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules* (Van Nostrand, New York, 1979).
7. MOPAC 93.00, J.J.P. Stewart et al., Fujitsu Limited, Tokyo, Japan (1993).
8. GAUSSIAN 94 (Rev B), M.J. Frisch et al., Gaussian Inc., Pittsburgh, PA, (1995).
9. GAMESS, M.W. Schmidt et al., QPCE Bulletin, 10, 52-54, (1990).
10. JANAF Thermochemical Tables, Natl. Stand. Ref. Data Ser. NSRDS-NBS 37, (1971); also Dow Chemical Company, distributed by Clearinghouse for Federal Scientific and Technical Information, PB168370 (1965) and subsequent updates.
11. R.J. Kee, F.M. Rupley, and J.A. Miller, (1987), "The Chemkin Thermodynamic Database", Sandia Report #SAND86-8246, Sandia National Laboratory
12. A. Burcat and B. McBride, (1993), "1994 Ideal Gas Thermodynamic Data for Combustion and Air-Pollution Use", Technion Report #TAE 697.
13. S. Gordon and B.J. McBride, (1991), "A Computer Program for Complex Chemical Equilibrium Compositions - Incident and Reflected Shocks and Chapman Jouget Detonations", NASA SP-273.
14. A.G. McLain and C.S.R. Rao, (1976), "A Hybrid Computer Program for Rapidly Solving Flowing or Static Chemical Kinetic Problems Involving Many Chemical Species", NASA TM-X-3403.
15. F.J. Zeleznik, and S. Gordon, (1961), "Simultaneous Least-Square Approximation of a Function and its First Integrals with Application to Thermodynamic Data", NASA TN D-767.

APPENDIX A.
STATTHERM PROGRAM

```

C
C*****
C*****
C PROGRAM STATTHERM COMPUTES THE THERMOCHEMICAL PROPERTIES OF A
C POLYATOMIC MOLECULE USING STATISTICAL THERMODYNAMIC FORMULAS.
C THE DATA ARE FITTED INTO THE NASA POLYNOMIAL FORM FOR USE IN
C COMBUSTION CODES.
C
C THIS PROGRAM DOES NOT CALCULATE THERMOCHEMICAL INFORMATION
C FOR HINDERED INTERNAL ROTATION. PLEASE CONSULT PITZER AND
C GWINN TABLES. IF THERE IS A NEED WITHIN THE LLNL COMBUSTION
C GROUP TO INCLUDE THIS ADDITIONAL INFORMATION FOR THERMOCHEMICAL
C DATA FITTING, PLEASE CONTACT N.M. MARINOV FOR INCLUSION OF
C THIS CALCULATION IN PROGRAM STATTHERM.
C
C THIS PROGRAM DOES NOT MAKE CORRECTIONS FOR ANHARMONIC
C VIBRATIONS.
C
C
C REQUIRED INPUT:      (1) MOLECULAR NAME
C                    (2) MOLECULAR WEIGHT
C                    (3) HEAT OF FORMATION AT 298K
C                    (4) VIBRATIONAL FREQUENCIES (CM-1)
C                    (5) SYMMETRY NUMBERS FOR INTERNAL AND
C                        EXTERNAL ROTATION
C                    (6) ELECTRONIC DEGENERACY AND
C                        NUMBER OF OPTICAL ISOMERS
C                    (7) ROTATIONAL CONSTANTS (CM-1)
C                        OR MOMENTS OF INERTIA (AMU-A**2)
C
C PROGRAM WRITTEN AND MODIFIED FOR USE BY N.M. MARINOV (1997)
C
C Version 1.0
C
C*****
C*****
C
C PROGRAM STATTHERM
C
C PARAMETER (NTEMP=40, NCHAR=35, NUMB=65, NELEM=5)
C
C DOUBLE PRECISION SE (NELEM,NTEMP), HE (NELEM,NTEMP)
C DOUBLE PRECISION DELGFA (NTEMP), TLOGKP (NTEMP)
C DOUBLE PRECISION DELGF (NTEMP), DELSF (NTEMP), DELHF (NTEMP)
C DOUBLE PRECISION CP (NTEMP), DELTAH (NTEMP), S (NTEMP), T (NTEMP)
C DOUBLE PRECISION EQLBRMK (NTEMP)
C DOUBLE PRECISION MU (100), BX (10), SYM (10), DIM1 (10), SYMINT (10)
C DOUBLE PRECISION MW, HF298, IROT, R, H, K, PI, SIGMA, C2, ZR, THETA, IE, X, N
C DOUBLE PRECISION SYMEXT, SNOI
C DIMENSION CPA (50), DELHA (50), SA (50), TA (50), NLABEL (NELEM), YE (NUMB)
C COMMON /PASS/M, KK, TA, CPA, SA, DELHA, CPOATO, STOATO, DELHTO, HFF298
C
C LOGICAL LINEAR
C
C CHARACTER*1 NAME (NCHAR), AA, AAA
C CHARACTER*2 LABEL (5), SELEMENT, HELEMENT
C
C 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/
C
C DATA R/1.987D0/,H/6.62617636D-34/,K/1.38066244D-23/
C DATA N/6.02204531D+23/,PI/3.1415926D0/,C2/1.43878645D-02/

```

A-1


```

C      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')

C
C      LINEAR=.TRUE.

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

C
C      READ IN THE CONSTITUENT ELEMENTS AND THE NUMBER OF ATOMS THAT
C      MAKE UP THE MOLECULE. ONLY 5 CONSTITUENT ELEMENTS ARE
C      TABULATED AS REFERENCES IN THE "STATTHERM" PROGRAM. THE
C      CONSTITUENT ELEMENTS ARE C,H,O,N, and CL.
C
      DO 11 I=1,5
        READ(5,'(A2,1X,I5)') LABEL(I),NLABEL(I)
11     CONTINUE

C
C      READ LABEL OF MOLECULE.
C      "L" EQUALS LINEAR AND "N" EQUALS NONLINEAR.
C
      READ(5,'(A)') AA

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

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

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

C
      HF298=HF298*1.0D3

C
C      READ IN STATISTICAL WEIGHT OF THE GROUND LEVEL (ELECTRONIC
C      DEGENERACY), NUMBER OF OPTICAL ISOMERS, AND THE NUMBER
C      OF ONE-DIMENSIONAL ACTIVE ROTORS
C
      READ(5,'(F4.0,1X,F4.0,1X,I5)') STAT,SNOI,NROTOR

C
      NVIB=NVIB-NROTOR

C
C      READ IN THE ROTATIONAL CONSTANTS (CM-1) OR MOMENT OF INERTIAS (AMU-A**2)
C      FOR 2 ROTATIONAL DEGREES OR 3 ROTATIONAL DEGREES OF FREEDOM IN THE
C      THE (LINEAR OR NONLINEAR) MOLECULE.
C
C      READ LABEL OF VALUES. "M" EQUALS MOMENT OF INERTIA IN AMU-A**2 UNITS USED
C      AND "R" EQUALS ROTATIONAL CONSTANTS IN CM-1 UNITS USED.
C
      READ(5,'(A)') AAA

C
      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

```

A-2

```

C      READ IN THE ROTATIONAL CONSTANTS (CM-1) OR MOMENTS OF INERTIA (AMU-A**2)
C      FOR A COMPLEX MOLECULE THAT EXHIBITS ONE-DIMENSIONAL, FREE ROTATION
C      IN ONE OR MORE OF ITS INTERNAL DEGREES OF FREEDOM
C
      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
C
C      READ IN THE INTERNAL ROTATION SYMMETRY NUMBER ASSOCIATED WITH
C      EACH ONE-DIMENSIONAL ROTOR
C
      READ(5,'(F4.0,1X,F4.0,1X,F4.0)') (SYMINT(I),I=1,3)
C
C      READ IN THE VIBRATIONAL FREQUENCIES
C
      DO 777 I=1,NVIB
        READ(5,'(F11.4,1X)') MU(I)
777    CONTINUE
C
C      INITIALIZE HEAT CAPACITY AND ENTROPY AT 0K
C
      CP(1)=0.0D0
      S(1)=0.0D0
      DELTAH(1)=0.0D0
C
C      TRANSLATIONAL CONTRIBUTION
C
      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))
20    CONTINUE
C
C      ROTATIONAL CONTRIBUTION
C
      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(1)/6.0231)+DLOG10(T(I))-
1            DLOG10(SYMEXT))-0.7804
          ELSE
            S(I)=S(I)+4.5758*(DLOG10(2.797563/BX(1))+DLOG10(T(I))-
1            DLOG10(SYMEXT))-0.7804
          ENDIF
30    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
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)/SYMINT(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(1)=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
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
1STATTERM...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)

```

A-4

```

602      CONTINUE
C
        DO 603 K=1,NTEMP
            TK=T(K)
            CALL POLINT(YE,NUMB,TK,Y,DY)
            SE(J,K)=Y
603      CONTINUE
C
        IF(NLABEL(J).NE.0) THEN
604          READ(9,'(A)',IOSTAT=ICODE) HELEMENT
            IF(ICODE.LE.0) GOTO 404
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
C
C
605      DO 605 K=1,NUMB
            YE(K)=YE(K)*(R/8.314D0)
605      CONTINUE
C
        DO 606 K=1,NTEMP
            TK=T(K)
            CALL POLINT(YE,NUMB,TK,Y,DY)
            HE(J,K)=Y
606      CONTINUE
600      CONTINUE
C
        DO 116 K=1,NTEMP
            DELHF(K)=0.0
            DELSF(K)=0.0
            DELGF(K)=0.0
116      CONTINUE
C
        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
118          CONTINUE
117      CONTINUE
C
        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)
219      CONTINUE
C

```

A-5

```

C      PRINT TABLE
C
      H298=DELTAH(4)
      WRITE(6,122) (NAME(I),I=1,NCHAR),MW,HF298,INT(SYMEXT+0.01)
122    FORMAT(1X,35A1,1X,'MOLECULAR WEIGHT =',F7.3//1X,'HEAT OF FORMATION
1    ' , ' AT 298K =',F15.5,1X, '(CAL/MOL)'/1X,
2      'EXTERNAL SYMMETRY NUMBER =',I3/)
C
      WRITE(6,120)
120    FORMAT(1X,'MOLECULAR MAKE-UP')
C
      DO 73 I=1,5
        WRITE(6,123) LABEL(I),NLABEL(I)
123      FORMAT(1X,A2,1X,I5)
73      CONTINUE
C
      IF (LINEAR) THEN
        WRITE(6,124)
124      FORMAT(/1X,'MOLECULE IS LINEAR',/)
      ELSE
        WRITE(6,125)
125      FORMAT(/1X,'MOLECULE IS NONLINEAR',/)
      ENDIF
C
      WRITE(6,126) INT(STAT+0.01)
126    FORMAT (1X,'ELECTRONIC DEGENERACY = ',I4/)
C
      WRITE(6,127) INT(SNOI+0.01)
127    FORMAT (1X,'NUMBER OF OPTICAL ISOMERS = ',I4/)
C
      IF (AAA.NE.'M'.AND.AAA.NE.'m') THEN
        WRITE(6,128)
128      FORMAT(/1X,'ROTATIONAL CONSTANTS (UNITS: CM-1) ARE:')
        WRITE(6,129) (BX(I),I=1,3)
129      FORMAT(3(1X,F14.4))
        WRITE(6,130) (BX(I),I=4,6)
130      FORMAT(3(1X,F14.4),/)
      ELSE
        WRITE(6,131)
131      FORMAT(/1X,'MOMENTS OF INERTIA (UNITS: AMU-A**2) ARE:')
        WRITE(6,132) (BX(I),I=1,3)
132      FORMAT(3(1X,F14.4))
        WRITE(6,133) (BX(I),I=4,6)
133      FORMAT(3(1X,F14.4),/)
      ENDIF
C
      WRITE(6,98)
98      FORMAT(1X,'INTERNAL SYMMETRY NUMBER(S)')
      WRITE(6,99) (INT(SYMINT(I)),I=1,3)
99      FORMAT(3(1X,I4),/)
C
      WRITE(6,134)
134    FORMAT(1X,'VIBRATIONAL FREQUENCIES (CM-1)'/
1      1X,'-----')
      WRITE(6,135) (MU(I),I=1,NVIB)
135    FORMAT(F11.1)
      WRITE(6,136)
136    FORMAT(1X,'-----'///1H1)
      WRITE(6,137)
137    FORMAT(3X,'T(K)',7X,'CP (CAL/MOL/K)',3X,'S (CAL/MOL/K)',
1      2X,' [H(T)-H(298K)] (KCAL/MOL)'/1X,65(' -'))
      DO 138 I=1,NTEMP
        DELHA(I)=(DELTAH(I)-H298)/1000.0
        WRITE(6,139) T(I),CP(I),S(I),DELHA(I)
139      FORMAT(1X,F7.2,F15.3,1X,F14.3,1X,F17.3)
138    CONTINUE

```

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```

      WRITE(6,140)
140  FORMAT(1X,65('-')/1H1)
C
      WRITE(6,141)
141  FORMAT(3X,' T(K)',7X,' DELHF (KCAL/MOL)',3X,' DELGF (KCAL/MOL)',
1    2X,' LOG10KP'/1X,65('-'))
C
      DELGFA(1)=DELGF(1)/1000.
      EQLBRMK(1)=1000000000.
      TLOGKP(1)=10000000000.
C
      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
C
      DO 142 I=1,NTEMP
          WRITE(6,143) T(I),DELHF(I),DELGFA(I),TLOGKP(I)
143  FORMAT(1X,F7.2,F15.3,1X,F14.3,1X,F17.3)
142  CONTINUE
      WRITE(6,144)
144  FORMAT(1X,65('-')/1H1)
C
C      CALL SUBROUTINE FIT TO COMPUTE THE NASA POLYNOMIAL
C
      H298=SNGL(DELTAH(4))
      HFF298=SNGL(HF298)/1000.0
      DELHTO=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
C
      CALL FIT(M,KK,TA,CPA,SA,DELHA,CPOATO,STOATO,DELHTO,HFF298)
C
      H298=SNGL(DELTAH(4))
      HFF298=SNGL(HF298)/1000.0
      DELHTO=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,' LOW TEMPERATURE' /)
      M=17
      KK=2
C
C      CALL FIT(M,KK,TA,CPA,SA,DELHA,CPOATO,STOATO,DELHTO,HFF298)
C
891  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,HF298)

```

```

DIMENSION T(50),DELH(50),STO(50),CPO(50),KP(10),ARG(50)
DIMENSION A(11,11),C(10),X(10),XH(14),BB(50),CC(50),DD(50)
DIMENSION ER1(50),ER2(50),ER3(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  DELH(I)=DELH(I)*1000./TSCALE

```

```

    DO 21 I=1,10

```

```

        C(I)=0.0

```

```

    DO 21 J=1,10

```

```

21  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

```

A-8

```

22  CONTINUE
    A(1,8)=1.0
    A(1,9)=1.0
    A(1,10)=ALOG(TO)
    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)=TO
    A(2,9)=TO/2.
    A(2,10)=TO
    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=TO*TO
    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=TO*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./TO
    A(7,7)=P
    A(7,10)=1.0
    C(8)=CPOATO/R
    C(9)=(DELHTO)/(R*TO)
    C(10)=STOATO/R
    DO 70 I=1,10
        DO 60 J=1,10
60      A(J,I)=A(I,J)
70      CONTINUE
    DO 91 I=1,10
91      A(I,11)=C(I)
    N=10
    EPS=1.E-10
    CALL SIMUL(N,A,X,EPS,NER)
    TO=TSCALE*TO
    DELHTO=TSCALE*DELHTO
    WRITE(6,1010)
1010  FORMAT(/5X,' INPUT VALUES',/5X,12('-'))
    WRITE(6,45) M,R,HF298,CPOATO,DELHTO,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

```

A-9


```

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(' '),10X,6(' '),10X,
2    12(' '),10X,3(' '),10X,12(' '),10X,3(' '),10X,12(' '))
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)=(DEHSO(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        I=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,' LAMBDA1=' ,E15.8//5X,' LAMBDA2=' ,E15.8//)
222  WRITE(6,102)
      WRITE(6,221) NER
221  FORMAT(5X,'NER=' ,I2)
      WRITE(6,102)
      WRITE(6,223)
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=6,10)
          WRITE(6,232) (XH(I),I=11,14)
231  FORMAT(1P,5E15.8)
232  FORMAT(1P,4E15.8,/)
      ENDIF
      RETURN

```

A-10

```

      END
C
      SUBROUTINE SIMUL(N,A,X,EPS,NER)
      DIMENSION IROW(10),JCOL(10),JORD(10),Y(10),A(11,11),X(10)
C
      MAX=N+1
      DETER=1.
5     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
11        CONTINUE
         IF (ABS(PIVOT).GT.EPS) GOTO 13
         NER=0
         RETURN
13        IROWK=IROW(K)
15        NER=1
         JCOLK=JCOL(K)
         DO 14 J=1,MAX
14         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)
18        CONTINUE
         DO 20 I=1,N
            IROWI=IROW(I)
            JCOLI=JCOL(I)
            JORD(IROWI)=JCOLI
20         X(JCOLI)=A(IROWI,MAX)
      RETURN
      END
C
      SUBROUTINE POLINT(YA,N,X,Y,DY)
      PARAMETER (NMAX=100)
      DIMENSION XA(NMAX),YA(N),C(NMAX),D(NMAX)
C
C  INITIALIZE THE TEMPERATURE ARRAY XA
C
      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

```

A-11

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.
1      +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.)+
1      X(5)*((T**4)/4.)+X(7))
RETURN
END

```

Enthalpy Data File

C

-1.0510	-0.9910	-0.6650	-0.3690	0.00000	0.01600	0.48700	1.03900
1.66700	2.36500	3.94300	5.71600	7.63700	9.67200	11.7950	13.9890
16.2400	18.5390	20.8790	23.2530	25.6580	28.0900	30.5470	33.0260
35.5250	38.0440	40.5810	43.1340	45.7040	48.2890	50.8890	53.5030
56.1310	58.7730	61.4270	64.0950	66.7750	69.4670	72.1720	74.8890
77.6170	80.3570	83.1090	85.8720	88.6460	91.4320	94.2290	97.0370
99.8560	102.685	105.526	108.378	111.240	114.114	116.997	119.892
122.797	125.713	128.640	131.577	134.524	137.482	140.451	143.429
146.419							

H

-8.4670	-5.4680	-2.7740	-1.3780	0.00000	0.05300	1.50200	2.95900
4.42000	5.88200	8.81100	11.7490	14.7020	17.6760	20.6800	23.7190
26.7970	29.9180	33.0820	36.2900	39.5410	42.8350	46.1690	49.5410
52.9510	56.3970	59.8760	63.3870	66.9280	70.4980	74.0960	77.7200
81.3690	85.0430	88.7400	92.4600	96.2020	99.9660	103.750	107.555
111.380	115.224	119.089	122.972	126.874	130.795	134.734	138.692
142.667	146.660	150.670	154.698	158.741	162.801	166.876	170.967
175.071	179.190	183.322	187.465	191.621	195.787	199.963	204.148
208.341							

O

-8.6830	-5.7790	-2.8680	-1.4100	0.00000	0.05400	1.53100	3.02500
4.54300	6.08400	9.24400	12.4990	15.8350	19.2410	22.7030	26.2120
29.7610	33.3440	36.9570	40.5990	44.2660	47.9580	51.6730	55.4130
59.1750	62.9610	66.7690	70.6000	74.4530	78.3280	82.2240	86.1410
90.0790	94.0360	98.0130	102.009	106.023	110.054	114.102	118.165
122.245	126.339	130.447	134.569	138.705	142.854	147.015	151.188
155.374	159.572	163.783	168.005	172.240	176.488	180.749	185.023
189.311	193.614	197.933	202.267	206.618	210.987	215.375	219.782
224.210							

N

-8.6700	-5.7680	-2.8570	-1.4020	0.00000	0.05400	1.51100	2.97100
4.4370	5.91100	8.89400	11.9370	15.0460	18.2230	21.4630	24.7600
28.1090	31.5030	34.9360	38.4050	41.9040	45.4290	48.9780	52.5480
56.1370	59.7420	63.3610	66.9950	70.6400	74.2960	77.9630	81.6390
85.3230	89.0150	92.7150	96.4210	100.134	103.852	107.577	111.306
115.041	118.781	122.525	126.274	130.027	133.784	137.545	141.309
145.078	148.850	152.625	156.405	160.187	163.973	167.763	171.556
175.352	179.152	182.955	186.761	190.571	194.384	198.201	202.023
205.848							

CL

-9.1810	-6.2690	-3.2310	-1.6130	0.00000	0.06300	1.78200	3.53300
5.30900	7.10400	10.7360	14.4080	18.1080	21.8280	25.5650	29.3150
33.0770	36.8490	40.6310	44.4220	48.2210	52.0300	55.8480	59.6750
63.5120	67.3610	71.2220	75.0960	78.9850	82.8890	86.8110	90.7510
94.7100	98.6880	102.686	106.703	110.739	114.793	118.864	122.949
127.048	131.158	135.277	139.402	143.532	147.663	151.792	155.918
160.037	164.147	168.246	172.332	176.402	180.454	184.487	188.499
192.488	196.454	200.394	204.307	208.194	212.053	215.883	219.685
223.456							

BR

Entropy Data File

C

0.00000	000.952	3.08200	4.39400	5.74000	5.79300	7.24200	8.71300
10.1910	11.6620	14.5330	17.2630	19.8260	22.2210	24.4570	26.5480
28.5060	30.3460	32.0800	33.7180	35.2700	36.7440	38.1490	39.4890
40.7710	42.0000	43.1800	44.3150	45.4080	46.4640	47.4830	48.4700
49.4260	50.3530	51.2530	52.1270	52.9780	53.8070	54.6140	55.4010
56.1700	56.9210	57.6550	58.3720	59.0750	59.7630	60.4370	61.0970
61.7450	62.3810	63.0060	63.6190	64.2220	64.8140	65.3970	65.9700
66.5340	67.0890	67.6360	68.1750	68.7060	69.2300	69.7460	70.2550
70.7580							

H

0.00000	100.727	119.412	125.640	130.680	130.858	135.325	139.216
142.656	145.737	151.077	155.606	159.548	163.051	166.216	169.112
171.790	174.288	176.633	178.846	180.944	182.940	184.846	186.669
188.418	190.099	191.718	193.278	194.785	196.243	197.654	199.021
200.349	201.638	202.891	204.111	205.299	206.457	207.587	208.690
209.767	210.821	211.851	212.860	213.848	214.816	215.765	216.696
217.610	218.508	219.389	220.255	221.106	221.943	222.767	223.577
224.374	225.158	225.931	226.691	227.440	228.177	228.903	229.619
230.323							

O

0.00000	173.307	193.485	199.990	205.147	205.329	209.880	213.871
217.445	220.693	226.451	231.466	235.921	239.931	243.578	246.922
250.010	252.878	255.556	258.068	260.434	262.672	264.796	266.818
268.748	270.595	272.366	274.069	275.709	277.290	278.819	280.297
281.729	283.118	284.466	285.776	287.050	288.291	289.499	290.677
291.826	292.948	294.044	295.115	296.162	297.186	298.189	299.171
300.133	301.076	302.002	302.910	303.801	304.677	305.538	306.385
307.217	308.037	308.844	309.639	310.424	311.197	311.960	312.713
313.457							

N

0.00000	159.811	179.985	186.481	191.609	191.789	196.281	200.181
203.633	206.739	212.176	216.866	221.017	224.757	228.170	231.313
234.226	236.943	239.487	241.880	244.138	246.275	248.304	250.234
252.074	253.833	255.517	257.132	258.684	260.176	261.614	263.001
264.341	265.637	266.891	268.106	269.285	270.429	271.541	272.622
273.675	274.699	275.698	276.671	277.622	278.549	279.456	280.341
281.208	282.056	282.885	283.698	284.494	285.275	286.041	286.792
287.529	288.253	288.964	289.662	290.348	291.023	291.687	292.341
292.984							

CL

0.00000	189.007	209.964	217.183	223.079	223.289	228.586	233.263
237.446	241.228	247.849	253.509	258.449	262.831	266.767	270.342
273.615	276.634	279.437	282.052	284.504	286.813	288.995	291.065
293.033	294.911	296.707	298.429	300.084	301.678	303.216	304.703
306.143	307.539	308.894	310.211	311.492	312.740	313.955	315.139
316.294	317.420	318.518	319.590	320.636	321.656	322.651	323.621
324.568	325.492	326.393	327.272	328.129	328.964	329.779	330.573
331.348	332.103	332.840	333.558	334.258	334.941	335.608	336.257
336.891							

BR

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)

0 0 0

VIBRATIONAL FREQUENCIES (CM-1)

732.0
1017.0
1017.0
2968.0
3054.0
3054.0
1355.0
1455.0
1455.0

1

T (K)	CP (CAL/MOL/K)	S (CAL/MOL/K)	[H (T) - H (298K)] (KCAL/MOL)
0.00	0.000	0.000	-2.489
100.00	7.954	46.809	-1.694
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
1200.00	20.234	76.502	14.397
1300.00	20.802	78.145	16.449
1400.00	21.298	79.705	18.555

B-1

1500.00	21.732	81.189	20.707
1600.00	22.113	82.604	22.899
1700.00	22.447	83.955	25.128
1800.00	22.742	85.247	27.387
1900.00	23.003	86.484	29.675
2000.00	23.234	87.669	31.987
2100.00	23.439	88.808	34.321
2200.00	23.622	89.903	36.674
2300.00	23.786	90.957	39.045
2400.00	23.933	91.972	41.431
2500.00	24.066	92.952	43.831
2600.00	24.185	93.898	46.243
2700.00	24.294	94.813	48.667
2800.00	24.392	95.698	51.102
2900.00	24.481	96.556	53.545
3000.00	24.563	97.387	55.998
4000.00	25.092	104.536	80.860
5000.00	25.350	110.166	106.095

1

T (K)	DELHF (KCAL/MOL)	DELGF (KCAL/MOL)	LOG10KP
0.00	-18.105	-18.105	1000000000.000
100.00	-18.748	-17.537	38.329
250.00	-19.675	-15.250	13.332
298.15	-20.000	-14.368	10.533
300.00	-20.012	-14.333	10.442
400.00	-20.650	-12.342	6.744
450.00	-20.939	-11.286	5.482
500.00	-21.206	-10.198	4.458
550.00	-21.105	-8.603	3.419
600.00	-21.674	-7.952	2.897
650.00	-22.036	-6.936	2.332
700.00	-22.060	-5.633	1.759
750.00	-22.107	-4.327	1.261
800.00	-22.372	-3.264	0.892
850.00	-22.554	-2.126	0.547
900.00	-22.617	-0.861	0.209
950.00	-22.697	0.376	-0.087
1000.00	-22.805	1.567	-0.343
1100.00	-22.945	4.012	-0.797
1200.00	-23.044	6.467	-1.178
1300.00	-23.110	8.929	-1.501
1400.00	-23.150	11.395	-1.779
1500.00	-23.169	13.864	-2.020
1600.00	-23.170	16.333	-2.231
1700.00	-23.159	18.801	-2.417
1800.00	-23.138	21.269	-2.583
1900.00	-23.109	23.735	-2.730
2000.00	-23.075	26.200	-2.863
2100.00	-23.039	28.662	-2.983
2200.00	-23.001	31.124	-3.092
2300.00	-22.962	33.583	-3.191
2400.00	-22.924	36.040	-3.282
2500.00	-22.888	38.497	-3.366
2600.00	-22.855	40.951	-3.443
2700.00	-22.826	43.404	-3.514
2800.00	-22.801	45.858	-3.580
2900.00	-22.781	48.309	-3.641
3000.00	-22.766	50.760	-3.698
4000.00	-22.961	75.281	-4.113
5000.00	-23.736	99.920	-4.368

1

HIGH TEMPERATURE

B-2

LAMBDA2= 0.74013412E-01

NER= 1

1

1000.K TO 5000. K

0.31231806E+01 0.95686140E-02-0.38824414E-05 0.72423278E-09-0.50691080E-13
-0.11574075E+05 0.72772293E+01

0.31231806E+01 0.95686140E-02-0.38824414E-05
0.72423278E-09-0.50691080E-13-0.11574075E+05 0.72772293E+01

LOW TEMPERATURE

INPUT VALUES

NO. POINTS = 17 GAS CONSTANT= 1.9870 ENTHALPY OF FORMATION= -20.0000

Cpo AT To= 18.843 H-H298 AT To= 10482.633 Sto AT To= 72.938

TEMP.	H-H298	PRED/CORRECT	STO	PRED/CORRECT
250.0	-450.3520	1.0047	54.3411	0.9999
298.1	0.0001	-26773.1875	55.9867	0.9999
300.0	18.0363	0.8836	56.0470	0.9999
400.0	1081.0044	1.0017	59.0930	1.0001
450.0	1678.0266	1.0011	60.4984	1.0001
500.0	2316.8633	1.0002	61.8439	1.0001
550.0	2995.0171	0.9996	63.1360	1.0000
600.0	3709.8374	0.9993	64.3796	1.0000
650.0	4458.7783	0.9992	65.5782	0.9999
700.0	5239.4917	0.9993	66.7351	0.9999
750.0	6049.8350	0.9995	67.8530	0.9999
800.0	6887.8555	0.9997	68.9346	1.0000
850.0	7751.7559	0.9999	69.9819	1.0000
900.0	8639.8711	1.0000	70.9971	1.0000
950.0	9550.6484	1.0000	71.9818	1.0000
1000.0	10482.6328	1.0000	72.9379	1.0000
1100.0	12404.8428	1.0001	74.7694	1.0000

LEAST SQUARE COEFFICIENTS

A(1)= 0.24777012E+01

A(2)= 0.67045814E-02

A(3)= 0.83700688E-05

B-4

A(4)= -0.12837361E-07
A(5)= 0.47679022E-11
A(6)= -0.11154073E+05
A(7)= 0.11789707E+02
LAMBDA0=-0.50071675E-01
LAMBDA1= 0.48962392E-01
LAMBDA2= 0.97828573E-02

NER= 1

1
250.K TO 1100. K
0.24777012E+01 0.67045814E-02 0.83700688E-05-0.12837361E-07 0.47679022E-11
-0.11154073E+05 0.11789707E+02
0.24777012E+01 0.67045814E-02 0.83700688E-05
-0.12837361E-07 0.47679022E-11-0.11154073E+05 0.11789707E+02

PINNING TEMPERATURE IS 1000.OK

THERMOCHEMICAL COEFFICIENTS

3.12318063E+00 9.56861395E-03-3.88244143E-06 7.24232785E-10-5.06910798E-14
-1.15740752E+04 7.27722931E+00 2.47770119E+00 6.70458144E-03 8.37006883E-06
-1.28373605E-08 4.76790222E-12-1.11540732E+04 1.17897072E+01

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