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MONAT: A FORTRAN 63 PROGRAM FOR COMPUTING THERMODYNAMIC PROPERTIES OF MONATOMIC IDEAL GASES

M. H. Fontana

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SEPTEMBER 1968

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M. H. Fontana

ABSTRACT

A computer program was written in Fortran 63 for generating tables of thermodynamic properties of monatomic ideal gases, given the spectroscopic constants. The properties computed and presented are the specific heat at constant pressure, entropy, enthalpy referred to $0^{\circ}K$, and free energy functions. This is done for temperatures from 100 to $6000^{\circ}K$ in $100^{\circ}K$ increments.

A sample calculation is presented for monatomic chromium ideal gas, extended to $6000^{\circ}K$. This is compared with separately published data to $3000^{\circ}K$.

MONAT: A FORTRAN 63 PROGRAM FOR COMPUTING THERMODYNAMIC PROPERTIES OF MONATOMIC IDEAL GASES

INTRODUCTION

The program described in this report is a by-product of a larger effort aimed at determining thermochemical equilibrium concentrations of various compounds formed from fission products and the materials existing in nuclear reactor fuels during a major loss-of-coolant accident. The object is to present one computational tool developed to extend thermodynamic data of monatomic gaseous elements into temperature ranges of interest, given some spectroscopic information.

The data is computed and presented for each element in a table giving specific heat at constant pressure, entropy, enthalpy difference of the ideal gas in going from zero to the temperature of interest, and the free energy function for temperatures ranging from 100 to 6000°K.

Description of Computations Performed by the Program

The program computes the thermodynamic functions given the electronic energy levels and degeneracies of the atom, and the molecular weight.

Specific Heat*

The equation used to compute the specific heat is

$$C_p = C_{p,tr} + C_{eL}. \tag{1}$$

*For a complete discussion of these methods, see, for example, references (1) and (2).

where C_p is the specific heat, $C_{p,tr}$ is the translational contribution and C_{eL} is the electronic contribution. The translational contribution to the specific heat is

$$C_{p,tr} = \frac{5}{2} R = 4.96815 \text{ cal/g-mole-}^{o}\text{K} \tag{2}$$

The electronic contribution is most easily compiled by

$$C_{eL} = R \left[\frac{Q''}{Q} - \left(\frac{Q'}{Q}\right)^2\right] \tag{3}$$

where the electronic partition function, Q, is given by

$$Q = \sum_i g_i e^{-\epsilon_i/kT}. \tag{4}$$

The function, Q', by

$$Q' = \sum_i g_i \left(\frac{\epsilon_i}{kT}\right) e^{-\epsilon_i/kT}, \tag{5}$$

and the function, Q", by

$$Q'' = \sum_i g_i \left(\frac{\epsilon_i}{kT}\right)^2 e^{-\epsilon_i/kT}. \tag{6}$$

Actually, computer programming was somewhat simpler if the temperature was taken outside the series, giving

$$C_{eL} = \frac{R}{k^2T^2}\left[\frac{\sum g_i \epsilon_i^2 e^{-\epsilon_i/kT}}{\sum g_i e^{-\epsilon_i/kT}} - \left(\frac{\sum g_i \epsilon e^{-\epsilon_i/kT}}{\sum g_i e^{-\epsilon_i/kT}}\right)^2\right] \tag{7}$$

If ϵ is given in wave numbers (cm^{-1}), the units of k must be consistent.

Enthalpy

The enthalpy difference between the temperature of interest and absolute zero is given by

$$H^o - H^o_o = H_{tr} - H^o_{tro} + (E^o - E^o_o)_{int} \tag{8}$$

where H^o is the standard state enthlpy, H^o_o is the enthalpy at 0^oK, and $(E^o - E^o_o)_{int}$ is the internal energy at T minus that at 0^oK.

$$H^o_{tr} - H^o_{tro} = \int_o^T C_{p,tr}\, dT = C_{p,tr}T \tag{9}$$

since the translational specific heat is constant.

The electronic term is best given by

$$(E^o - E^o_o)_{int} = RT\left(\frac{Q'}{Q}\right), \tag{10}$$

where the function Q' and Q are defined previously. As with the case of specific heat, it is more convenient for computer purposes to extract the temperature and Boltzman constant from the sum, resulting in

$$(E^o - E^o_o)_{int} = \frac{R}{k}\left(\frac{\sum \epsilon_i g_i e^{-\epsilon_i/kT}}{\sum g_i e^{-\epsilon_i/kT}}\right). \tag{11}$$

Entropy

The standard entropy is given by

$$S^o = S^o_{tr} + S^o_{int} \tag{12}$$

the translational contribution by

$$S^o_{tr} = R\left(\frac{3}{2}\ln M + \frac{5}{2}\ln T\right) - 2.315 \tag{13}$$

where M is the molecular weight, and the internal contribution by

$$S^o_{int} = R\left(\ln Q + \frac{Q'}{Q}\right). \tag{14}$$

Again for ease of computation:

$$S^o_{int} = \frac{R}{kT}\left(\frac{\sum \epsilon_i g_i e^{-\epsilon_i/kT}}{\sum g_i e^{-\epsilon_i/kT}}\right) + R\ln \sum g_i e^{-\epsilon_i/kT} \tag{15}$$

Free Energy Function

The standard free energy function was computed by

$$\frac{F^o - H^o_o}{T} = \left(\frac{F^o - H^o_o}{T}\right)_{tr} + \left(\frac{F^o - H^o_o}{T}\right)_{int} \tag{16}$$

where F^o is the free energy in the standard state. The translational contribution:

$$-\left(\frac{F^o - H^o_o}{T}\right) = R\left(\frac{3}{2}\ln M + \frac{5}{2}\ln T\right) - 7.283 \ (\text{cal}/^oK), \tag{17}$$

and the internal contribution:

$$-\left(\frac{F^o - H^o_o}{T}\right) = R \ln Q \tag{18}$$

DESCRIPTION OF THE PROGRAM AND ITS USE

As presently written, the program can allow for thirty electronic energy levels and degeneracies. There is no reason why this could not be expanded to more, but averaging the known levels into thirty groups gives adequate accuracy for our purposes.

The program requires a seven card data input. The first three cards contain the energy levels in the format 8F10.0 (three cards must be provided even if not all used). The next three cards contain the degeneracies of each state, again in the format 8F10.0. The seventh and final card must contain the molecular weight with format F10.0.

As presently written, the program will automatically start at a temperature of 100°K and compute thermodynamic values at 100°K increments up to 6000°K, including the value at 298°K to give values of $H^o_{298} - H^o_o$

if required to convert the calculated values to a system based at 298°K. Although the program is presently written in Fortran 63 for the CDC 1604A computer which has a limit on the number size of e^{208}, the program is written so that values larger than e^{87} will be truncated. Thus if one wishes to convert the program for use with the IBM system 360, the number size limit will not be exceeded.

DICTIONARY OF COMPUTER TERMS

E = electronic energy levels (cm^{-1})

G = degeneracy of each electronic energy level (dimensionless)

M = molecular weight (gms/g-mole)

T = absolute temperature (^{o}K)

CPT = translational contribution to the specific heat (cal/g-mole^{o}K)

HT = translational contribution to the enthalpy (cal/g-mole)

FT = translational contribution to the free energy function (cal/g-mole^{o}K)

ST = translational contribution to the entropy (e.u.)

SUM 1 = $\sum_i \epsilon_i^2 g_i \exp(-\epsilon_i/kT)$ (cm^{-2})

I = counter

EØT = ϵ_i/kT (dimensionless)

EX = $\exp(\epsilon_i/kT)$ (dimensionless)

AD1 = $\epsilon_i^2 g_i \exp(-\epsilon_i/kT)$ (cm^{-2})

SUM 2 = $\sum_i g_i \exp(-\epsilon_i/kT)$ (dimensionless)

AD2 = $g_i \exp(-\epsilon_i/kT)$ (dimensionless)

SUM 3 = $\sum_i \epsilon_i g_i \exp(-\epsilon_i/kT)$ (cm^{-1})

AD3 = $\epsilon_i g_i \exp(-\epsilon_i/kT)$ (cm^{-1})

CPE = electronic contribution to the specific heat (cal/g-mole^{o}K)

HTMO = $H_T - H_o$, enthalpy (cal/g-mole)

FMHOT = $(F - H_o)/T$, free energy function (cal/g-mole)

S = entropy (e.u.)

LISTING OF THE PROGRAM

Table 1 gives a listing of program MØNAT.

Table 1. Listing of Program MØNAT

```
      PROGRAM MONAT
      DIMENSION E(30),G(30)
      READ 16,E
      READ 16,G
      READ 80,M
   80 FORMAT (F10.0)
      T=100.
   16 FORMAT (10F8.0)
      PRINT 74
      PRINT 75
   17 CPT=4.96815
      HT=CPT*T
      FT=2.98035*LOGF(M)+4.96725*LOGF(T)-7.28374
      ST=2.98035*LOGF(M)+4.96725*LOGF(T)-2.315589
      SUM1=0.
      I=1
      DO 5 I=1,30
      EOT=1.43884*E(I)/T
      IF(EOT-87.)3,3,2
    2 EOT=87.
    3 EX=EXPF(EOT)
      AD1=F(I)**2*G(I)*1./EX
      SUM1=SUM1+AD1
    5 CONTINUE
      I=1
      SUM2=0.
      DO 10 I=1,30
      EOT=1.43884*E(I)/T
      IF(EOT-87.)7,7,6
    6 EOT=87.
    7 EX=EXPF(EOT)
      AD2=G(I)*1./EX
      SUM2=SUM2+AD2
   10 CONTINUE
      I=1
      SUM3=0.
      DO 15 I=1,30
      EOT=1.43884*E(I)/T
      IF(EOT-87.)9,9,8
    8 EOT=87.
    9 EX=EXPF(EOT)
      AD3=E(I)*G(I)*1./EX
      SUM3=SUM3+AD3
   15 CONTINUE
      CPE=4.11414/T**2*(SUM1/SUM2-(SUM3/SUM2)**2)
      HTM0=2.85935*(SUM3/SUM2)
      FMH0T=4.57584/2.303*LOGF(SUM2)
      S=2.85935/T*SUM3/SUM2+4.57584/2.303*LOGF(SUM2)
      CPE=CPE+CPT
      S=S+ST
      HTM0=HTM0+HT
      FMH0T=FMH0T+FT
      PRINT 76,T,CPE,S,HTM0,FMH0T,
   72 IF(T-150.)73,73,12
   12 IF(T-298.15)13,81,73
   13 T=298.15
```

Table 1 (con't)

```
14 GO TO 17
81 T=300.
   GO TO 17
73 T=T+100.
   IF(T-6000.)17,17,20
74 FORMAT(1H1,47HTOTAL THERMODYNAMIC VALUES MONATOMIC IDEAL GAS,///)
75 FORMAT(3HT,R,12X,2HCP,13X,1HS,14X,4HH-H0,11X,
  19H-(F-H0)/T,6X,//)
76 FORMAT(5E15.7)
20 END
```

SAMPLE OUTPUT

Table 1 shows a table of properties as produced by program MØNAT. This case is for monatomic, gaseous chromium. Comparison with Stull and Sinke[3] shows agreement to the fourth significant figure at 2000°K. Stull and Sinke's tables extend only to 3000°K whereas MØNAT can go to 6000°K, to be consistent with work requiring the JANAF[4] format.

ELECTRONIC ENERGY LEVELS USED FOR CHROMIUM

The electronic energy levels used in program MØNAT were obtained from Moore[5]. All levels up to the series I limit of 54565 cm^{-1} were used and averaged into thirty groups, the summary of which is shown in Table 3.

Table 2. Thermodynamic Properties Produced by Program MØNAT for Chromium Monatomic Gas

TOTAL THERMODYNAMIC VALUES MONATOMIC IDEAL GAS, Cr

T, K	CP	S	H-H0	-(F-H0)/T
1.0000000E+02	4.9681500E+00	3.6225275E+01	4.9681500E+02	3.1257124E+01
2.0000000E+02	4.9681500E+00	3.9668311E+01	9.9363000E+02	3.4700160E+01
2.9815000E+02	4.9681500E+00	4.1651631E+01	1.4812539E+03	3.6683480E+01
3.0000000E+02	4.9681500E+00	4.1682357E+01	1.4904450E+03	3.6714206E+01
4.0000000E+02	4.9681500E+00	4.3111346E+01	1.9872600E+03	3.8143195E+01
5.0000000E+02	4.9681506E+00	4.4219756E+01	2.4840750E+03	3.9251605E+01
6.0000000E+02	4.9681667E+00	4.5125393E+01	2.9808905E+03	4.0157242E+01
7.0000000E+02	4.9683325E+00	4.5891109E+01	3.4777129E+03	4.0922947E+01
8.0000000E+02	4.9692127E+00	4.6554461E+01	3.9745799E+03	4.1586236E+01
9.0000000E+02	4.9722308E+00	4.7139787E+01	4.4716254E+03	4.2171314E+01
1.0000000E+03	4.9798809E+00	4.7663911E+01	4.9691794E+03	4.2694731E+01
1.1000000E+03	4.9955110E+00	4.8139114E+01	5.4678673E+03	4.3168324E+01
1.2000000E+03	5.0227671E+00	4.8574773E+01	5.9686696E+03	4.3600881E+01
1.3000000E+03	5.0649520E+00	4.8978294E+01	6.4729193E+03	4.3999124E+01
1.4000000E+03	5.1245089E+00	4.9355647E+01	6.9822404E+03	4.4368331E+01
1.5000000E+03	5.2027280E+00	4.9711698E+01	7.4984446E+03	4.4712734E+01
1.6000000E+03	5.2996739E+00	5.0050412E+01	8.0234116E+03	4.5035778E+01
1.7000000E+03	5.4142833E+00	5.0375001E+01	8.5589693E+03	4.5340312E+01
1.8000000E+03	5.5445697E+00	5.0688040E+01	9.1067917E+03	4.5628710E+01
1.9000000E+03	5.6878819E+00	5.0991557E+01	9.6683181E+03	4.5902968E+01
2.0000000E+03	5.8411733E+00	5.1287122E+01	1.0244701E+04	4.6164770E+01
2.1000000E+03	6.0012550E+00	5.1575921E+01	1.0836779E+04	4.6415549E+01
2.2000000E+03	6.1650143E+00	5.1858827E+01	1.1445075E+04	4.6656519E+01
2.3000000E+03	6.3295913E+00	5.2136463E+01	1.2069809E+04	4.6888719E+01
2.4000000E+03	6.4925070E+00	5.2409259E+01	1.2710938E+04	4.7113034E+01
2.5000000E+03	6.6517475E+00	5.2677501E+01	1.3368188E+04	4.7330225E+01
2.6000000E+03	6.8058049E+00	5.2941369E+01	1.4041114E+04	4.7540940E+01
2.7000000E+03	6.9536826E+00	5.3200979E+01	1.4729143E+04	4.7745740E+01
2.8000000E+03	7.0948715E+00	5.3456405E+01	1.5431628E+04	4.7945108E+01
2.9000000E+03	7.2293040E+00	5.3707702E+01	1.6147893E+04	4.8139462E+01
3.0000000E+03	7.3572934E+00	5.3954928E+01	1.6877275E+04	4.8329168E+01
3.1000000E+03	7.4794650E+00	5.4198145E+01	1.7619158E+04	4.8514545E+01
3.2000000E+03	7.5966839E+00	5.4437439E+01	1.8373003E+04	4.8695874E+01
3.3000000E+03	7.7099850E+00	5.4672912E+01	1.9138365E+04	4.8873407E+01
3.4000000E+03	7.8205063E+00	5.4904694E+01	1.9914908E+04	4.9047367E+01
3.5000000E+03	7.9294302E+00	5.5132934E+01	2.0702414E+04	4.9217957E+01
3.6000000E+03	8.0379322E+00	5.5357803E+01	2.1500781E+04	4.9385363E+01
3.7000000E+03	8.1471381E+00	5.5579491E+01	2.2310025E+04	4.9549754E+01
3.8000000E+03	8.2580899E+00	5.5798200E+01	2.3130269E+04	4.9711286E+01
3.9000000E+03	8.3717197E+00	5.6014142E+01	2.3961734E+04	4.9870107E+01
4.0000000E+03	8.4888312E+00	5.6227536E+01	2.4804730E+04	5.0026352E+01
4.1000000E+03	8.6100872E+00	5.6438601E+01	2.5659639E+04	5.0180152E+01
4.2000000E+03	8.7360029E+00	5.6647557E+01	2.6526904E+04	5.0331627E+01
4.3000000E+03	8.8669446E+00	5.6854617E+01	2.7407009E+04	5.0480893E+01
4.4000000E+03	9.0031314E+00	5.7059987E+01	2.8300469E+04	5.0628061E+01
4.5000000E+03	9.1446403E+00	5.7263861E+01	2.9207814E+04	5.0773235E+01
4.6000000E+03	9.2914142E+00	5.7466422E+01	3.0129574E+04	5.0916513E+01
4.7000000E+03	9.4432711E+00	5.7667838E+01	3.1066268E+04	5.1057993E+01
4.8000000E+03	9.5999153E+00	5.7868261E+01	3.2018390E+04	5.1197762E+01
4.9000000E+03	9.7609491E+00	5.8067827E+01	3.2986399E+04	5.1335908E+01
5.0000000E+03	9.9258852E+00	5.8266654E+01	3.3970712E+04	5.1472511E+01
5.1000000E+03	1.0094160E+01	5.8464844E+01	3.4971689E+04	5.1607649E+01
5.2000000E+03	1.0265145E+01	5.8662480E+01	3.5989636E+04	5.1741396E+01

Table 2 (con't)

5.3000000E+03	1.0438162E+01	5.8859629E+01	3.7024788E+04	5.1873819E+01
5.4000000E+03	1.0612492E+01	5.9056340E+01	3.8077314E+04	5.2004984E+01
5.5000000E+03	1.0787392E+01	5.9252646E+01	3.9147307E+04	5.2134953E+01
5.6000000E+03	1.0962100E+01	5.9448566E+01	4.0234708E+04	5.2263781E+01
5.7000000E+03	1.1135851E+01	5.9644102E+01	4.1339698E+04	5.2391523E+01
5.8000000E+03	1.1307885E+01	5.9839246E+01	4.2461903E+04	5.2518228E+01
5.9000000E+03	1.1477455E+01	6.0033975E+01	4.3601195E+04	5.2643941E+01
6.0000000E+03	1.1643838E+01	6.0228255E+01	4.4757290E+04	5.2768705E+01

Table 3. Electronic Energy Levels of Chromium (Grouped and Averaged for Use with Program MØNAT)

g = 2J + 1	Level (cm^{-1})	J
3	0.00	7
2	7593.16	5
0	7750.78	1
1	7810.82	3
2	7927.47	5
3	8095.21	7
4	8307.57	9

The following are grouped and averaged values.

g = 2J + 1	Level (cm^{-1})	Number of Levels Included
45	20,520.80	5
15	21,848.00	3
88	23,899.64	14
97	25,149.92	13
15	26,795.00	3
65	27,558.35	14
65	29,983.81	11
111	31,320.15	13
193	34,670.03	29
88	37,699.30	13
261	41,978.32	37
304	44,887.26	38
163	46,456.88	25

Table 3 (con't)

g = 2J + 1	Level (cm^{-1})	Number of Levels Included
335	47,572.69	43
284	49,027.73	42
257	51,548.43	37
265	53,908.09	33

NOMENCLATURE

C_p = heat capacity at constant pressure (cal/mole-^oK)

E^o = internal energy at standard state (cal/mole)

F^o = Gibbs free energy at standard state (cal/mole)

g_i = degeneracy of a given level (dimensionless)

H^o = standard enthalpy (cal/mole)

J = electronic quantum numbers related to the total angular momentum of an atom (dimensionless)

k = Boltzmann's constant = 1.3805×10^{-16} (erg/^oK)

M = molecular weight (gm/mole)

Q = partition function (dimensionless)

Q' = grouping of terms defined in text (dimensionless)

Q" = grouping of terms defined in text (dimensionless)

R = universal gas constant = 1.987 (cal/mole-^oK)

S^o = standard entropy (e.u.)

T = absolute temperature (^oK)

ϵ_i = electronic energy levels (cm^{-1})

<u>Subscripts</u>

tr = translational contribution to specified property

eL = electronic contribution

int = internal contribution

o = value of specified property at 0^oK

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