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Calculation of the Thermodynamic Properties of a Mixture of Gases as a Function of Temperature and Pressure

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ABSTRACT

The evaluation of the thermodynamic properties of a gas mixture can be performed using a generalized correlation which makes use of the second virial coefficient. This coefficient is based on statistical mechanics and is a function of temperature and composition, but not of pressure. The method provides results accurate to within 3 percent for gases which are nonpolar or only slightly polar. When applied to highly polar gases, errors of 5 to 10 percent may result. For gases which associate, even larger errors are possible. The sequences of calculations can be routinely programmed for a digital computer. The thermodynamic properties of a mixture of neon, argon and ethane were calculated by such a program. The result will be used for the design of the gas replenishment system for the Energetic Gamma Ray Experiment Telescope (EGRET).

NOMENCLATURE

A – Helmholtz free energy
B – Second virial coefficient
Cp – Heat capacity at constant pressure
Cv – Heat capacity at constant volume
G – Gibbs free energy
H – Enthalpy
$\Delta H'$ – Residual enthalpy
M – Extensive thermodynamic property (properties that depend on the size of the system)
MW – Molecular weight
P – Actual pressure
Pc – Critical pressure
Pr – Reduced pressure = P/Pc
R – Universal gas constant
S – Entropy
$\Delta S'$ – Residual entropy
T – Actual temperature (°K)
Tc – Critical temperature
Tr – Reduced temperature = T/Tc
U – Internal energy
V – Volume
Vc – Critical volume
Vr – Reduced volume = V/Vc
Y – Mole fraction in gas phase
Z – Compressibility factor
Zc – Critical compressibility factor
γ – Heat capacities ratio = Cp/Cv
ω – Acentric Factor = $-\log_{10}(Pr^{sat})\ Tr = 0.7^{-1.00}$
η, β, α – Constants characteristic of the gas considered for the equation $Cp = \alpha + \beta T + \eta T^2$

o, Used as a superscript, denotes a standard state.
′, The prime designates the ideal-gas state.
i, j, Used as subscript, denotes constituent in the mixture.

CALCULATION OF THE THERMODYNAMIC PROPERTIES OF A MIXTURE OF GASES AS A FUNCTION OF TEMPERATURE AND PRESSURE

INTRODUCTION

It frequently happens, in the applications of thermodynamic properties of mixtures of gases, that tabulations or diagrams do not exist or that sufficient experimental data are not available for the calculations of these properties. In such cases, one must resort to approximate methods.

The method described below is based on the use of generalized correlation and residual properties. Such properties represent the difference between the value of a thermodynamic property in the ideal-gas state and its value in the real state, at a given temperature and pressure. Thus, the residual property M is given by:

$$\Delta M' = M' - M \tag{1}$$

where M, M′ and ΔM′ represent molar values for any extensive thermodynamic property. For the calculation of values of a thermodynamic property, such as enthalpy (H) or entropy (S), Equation (1) is written:

$$H = H' - \Delta H' \tag{2}$$

$$S = S' - \Delta S' \tag{3}$$

This divides the calculation into 2 parts: first, calculation of the ideal-gas value (Ideal gas is a gas that satisfied the equation $Pv = RT$, where R is the universal gas constant, and his units depend on the units used for pressure, volume and temperature), and second, calculation of ΔM′, which has the nature of a correction to the ideal-gas state value and which depends on experimental data of pressure, volume and temperature (PVT).

ANALYSIS

A – Calculation of the Specific Heat Ratio for the Mixture (γm)

The heat capacities of real gases, in general, are directly proportional to temperature and pressure. However, at pressures below 100 psi, the effect of pressure on the specific heat of gases is relatively small, so that it can usually be disregarded. Therefore, C′p and C′v usually represent good approximations for the heat capacity of real gases at pressures below 100 psia. Heat capacities for the ideal-gas state are independent of pressure and are functions of temperature only. The temperature dependency is often given by an empirical equation of the form.

$$C'p = \alpha + \beta T + \eta T^2 \tag{4}$$

where α, β, η are constants characteristic of the gas considered. Constants for use with Equation (4) are given in Appendix A. For the ideal-gas state, we have the following relations:

$$C'p - C'v = R \tag{5}$$

$$\gamma_i = C'p/C'v \tag{6}$$

For pressures above 100 psi, it is necessary to add a correction factor to the ideal-gas state heat capacity (C'p). From Reference (3), we have that:

$$\Delta Cp = Cp + C'p \tag{7a}$$

$$\Delta C\,p = -\frac{R}{V}\left(T^2 \frac{d^2B}{dT^2}\right) \tag{7b}$$

For a mixture of gases:

$$C'pm = \sum_i Y_i \; C'p \tag{8a}$$

$$C'vm = C'pm - R \tag{8b}$$

$$\gamma m = C'pm/C'vm \tag{9}$$

where Yi represents the mole fraction of the component i in the mixture.

B – Calculation of the Thermodynamic Properties: A, G, H, S, U

The most satisfactory procedure for the calculation of the thermodynamic properties of gases requires PVT data and ideal-gas heat capacities. The equations are based on the concept of the ideal-gas state and make use of the residuals functions.

In particular, the two terms in the right side of Equations (2) and (3) are evaluated separately as follows:

a) H' and S', which are the ideal-gas value:

$$H' = H'_0 + \int_{to}^{t} C'p \; dT \tag{10}$$

$$S' = S'_0 + \int_{to}^{t} C'p \; \frac{dT}{T} - R\int_{Po}^{P} \frac{dp}{P} \tag{11}$$

The integrations are performed at constant composition from an initial (To, Po) ideal-gas reference state to the ideal-gas state at the T and P of interest. Since the equations of thermodynamics, which derive from the first and second laws, do not permit calculations of absolute values for enthalpy and entropy, and since all we need in practice are relative values, the reference state conditions To, Po may be selected for convenience and values may be assigned to H'_0 and S'_0 arbitrarily.

b) $\Delta H'$ and $\Delta S'$, which are the residual properties:

$$\frac{\Delta H'}{RT} = \frac{P}{R}\left(\frac{dB}{dT} - \frac{B}{T}\right) \tag{12}$$

$$\frac{\Delta S'}{R} = \frac{P}{R}\left(\frac{dB}{dT}\right) \tag{13}$$

In these equations, B is the second virial coefficient. (The virial equation of state $Z = 1 + B/V + C/V^2 + D/V^3 \ldots$ is based in statistical mechanics. B, C, and D are known as the second, third, fourth, etc. virial coefficients. They are functions of temperature and composition, but not of pressure.) A simple correlation was proposed by Pitzer[4] for the second virial coefficient. Pitzer proposed a correlation of the form:

$$\frac{BPc}{RTc} = B^o + \omega B \tag{14}$$

where B^o and B are functions of reduced temperature (Tr) only. Pitzer's correlation for the second virial coefficient has been extended to mixtures by Prausnitz[5], who generalized Equation (14) as follows:

$$B_{ij} = \frac{RTc_{ij}}{Pc_{ij}}\left(B^o + \omega_{ij} B^1\right) \tag{15}$$

where B^o and B^1 are defined in References (7,8) as:

$$B^o = 0.083 - \frac{0.422}{Tr^{1.6}} \tag{16}$$

$$B^1 = 0.139 - \frac{0.172}{Tr^{4.2}} \tag{17}$$

The mixing rules proposed by Prausnitz[5] for the calculation of Wij, Tcij, Pcij, Vcij and Zcij are:

$$W_{ij} = \left(\frac{W_i + W_j}{2}\right) \tag{18}$$

$$Tc_{ij} = (T_i \times T_j)^{1/2}\,(1 - K_{ij}) \tag{19}$$

$$Zc_{ij} = \left(\frac{Zc_i + Zc_j}{2}\right) \tag{20}$$

$$Vc_{ij} = \left[\left(\frac{(Vc_i)^{1/3} + (Vc_j)^{1/3}}{8}\right)\right]^3 \tag{21}$$

[illegible]$_{ij}$ $= \frac{Zc_{ij}\ R\ Tc_{ij}}{Vc_{ij}}$ (22)

where Kij (Equation 19) is a constant characteristic of the particular molecular pair ij and must be determined from experimental data. If such data is not available, Kij can be set equal to zero. When i = j, all these equations reduce to the appropriate values for single components.

When i ≠ j, these equations define pseudoparameters which have no physical significance. Reduced temperature and pressure are calculated for each pair by:

$$Tr = T/Tc_{ij} \tag{23}$$

$$Pr = P/Pc_{ij} \tag{24}$$

For a mixture of gases:

$$B = \sum_i \sum_j (Y_i \; Y_j \; B_{ij}) \tag{25}$$

Differentiations of Equations (15) and (25), with respect to temperature at constant composition and simplifying, provides the following relations:

$$\frac{dB}{dT} = \sum_i \sum_j (Y_i \; Y_j \; \frac{dB_{ij}}{dT}) \tag{26}$$

$$\frac{dB_{ij}}{dT} = \frac{R}{Pc_{ij}} (\frac{dB^o}{dTr} + \omega_{ij} \frac{dB^1}{dTr}) \tag{27}$$

where:

$$\frac{dB^o}{dTr} = \frac{0.675}{Tr^{2.6}} \tag{28}$$

$$\frac{dB^1}{dTr} = \frac{0.722}{Tr^{5.2}} \tag{29}$$

The values of Bij calculated from Equation (15) are substituted into Equation (25) yielding a value of B for the mixture. The values of dBij/dT from Equation (27) together with Equation (26) provide a value of dB/dT for the mixture. Finally, the residual functions for the mixture can be calculated using Equations (12) and (13).

Once the enthalpy and entropy are calculated using Equations (2) and (3) for a given set of PVT values, the other thermodynamic functions are evaluated by the defining equations:

$$U = H - PV \tag{30}$$

$$A = U - TS \tag{31}$$

$$G = H - TS \tag{32}$$

CALCULATIONS

The purpose of this work was to evaluate the thermodynamic properties of a mixture of neon, argon and ethane (GRO/EGRET Project). Herein is presented the method for the evaluation of such properties and a tabulation of the results of this calculation (Appendix D).

The composition (% volume) of the EGRET gas mixture is 98.5% neon, 0.75% ethane, and 0.75% argon. To find the molecular weight of the mixture, we do the following:

Base: 1 Mol of Mixture

Component	Volume	M.W.	Mass/Mol Mixture	% Mass/Mol
Neon	0.9850	20.1790	19.8763	97.4262
Ethane	0.0075	30.0680	0.2255	1.1053
Argon	0.0075	39.9440	0.2996	1.4685
			20.4014	

The Molecular Weight (M.W.) of the mixture is 20.4014.

From Appendix A, we have that:

$$C'p \text{ ethane} = 2.247 + 38.201 \times 10^{-3}\, T - 11.049 \times 10^{-6}\, T^2$$

For neon and argon:

C'p = 4.9675 for all temperatures

Using Equation (8a), we can calculate C'pm for pressures below 100 psi.

$$C'pm = (Y1 + Y3)\, 4.9675 + Y2\ (2.247 + 38.201 \times 10^{-3}\, T - 11.049 \times 10^{-6}\, T^2)$$

For pressures above 100 psia, the residual $\Delta C'p$ has to be evaluated. Taking the derivative of Equation (26), we have that:

$$\frac{d^2B}{dT^2} = \sum_i \sum_j \left(Y_i\, Y_j\, \frac{d^2B_{ij}}{dT^2}\right) \tag{33}$$

where:

$$\frac{d^2B_{ij}}{dT^2} = \frac{R}{Pc_{ij}} \left(\frac{d^2B^o}{dT^2} + \omega_{ij} \frac{d^2B^1}{dT^2}\right) \tag{34}$$

$$\frac{d^2B^o}{dT^2} = -1.755\ Tr^{-3.6} \tag{35}$$

$$\frac{d^2B^1}{dT^2} = -3.756\ Tr^{-6.2} \tag{36}$$

Therefore, the specific heat ratio of the mixture can be calculated using Equations (8a), (8b) and (9) for pressures below 100 psi, and Equations (33) thru (36), (8b) and (9) for pressures above or equal to 100 psi.

In Appendix B are found Tc, Pc, Tc, Vc, Zc and W values for neon, argon, and ethane. With that information, we can calculate the thermodynamic properties for the EGRET mixture.

DISCUSSION OF RESULTS AND CONCLUSIONS

There is no experimental data which we can use to compare the results obtained using the generalized correlation. However, because of the high percentage of neon in the mixture (98.5%), the calculated thermodynamic properties of the EGRET mixture should be similar to those of pure neon. Comparison of both values (see Table I) show that they are very close, as expected.

Table I
Thermodynamic Properties of Pure Neon
and the EGRET Mixture

P = 1 atm.	Neon (20.183 M.W.)		EGRET (20.414 M.W.)	
Temp. °K	Enthalpy CAL/MOL	Entropy CAL/MOL·°K	Enthalpy CAL/MOL	Entropy CAL/MOL·°K
100	496.80	29.5209	497.02	29.47
200	993.60	32.9646	993.60	32.92
300	1490.40	34.9790	1491.20	34.96
400	1987.20	36.4082	1989.66	36.41
500	2484.10	37.5168	2488.83	37.53
600	2980.90	38.4226	2988.54	38.46

According to Smith[7] and Prausnitz[5], this method provides results accurate within 3 percent for gases which are nonpolar (have zero dipole moment) or only slightly polar. When applied to highly polar gases (Polar compounds are characterized by a non-zero dipole moment, which express the effect of electrostatic forces between molecules. Water, alcohols, phenols, ketones, ethers are examples of polar compounds.), errors of 5 to 10 percent may result, and for gases which associate, even larger errors are possible.[5,7] For gases which reflect quantum effects (helium, hydrogen, neon), modified critical constants are recommended.[5,6] It should be emphasized that generalized correlations are not intended to be substitutes for reliable experimental PVT data and should be used only if that data is not available.

The range of reduced temperatures and reduced pressures, within which this correlation may safely be used, is represented by the area lying above the line shown in Figure 1. This line is based primarily on the criterion that $V_r \geq 2$.

The Fortran program in Appendix C was written for the Hewlett-Packard 1000 digital computer and can be used for any gas mixture, taking into consideration the limitations of the method and making the necessary changes to the input of the program.

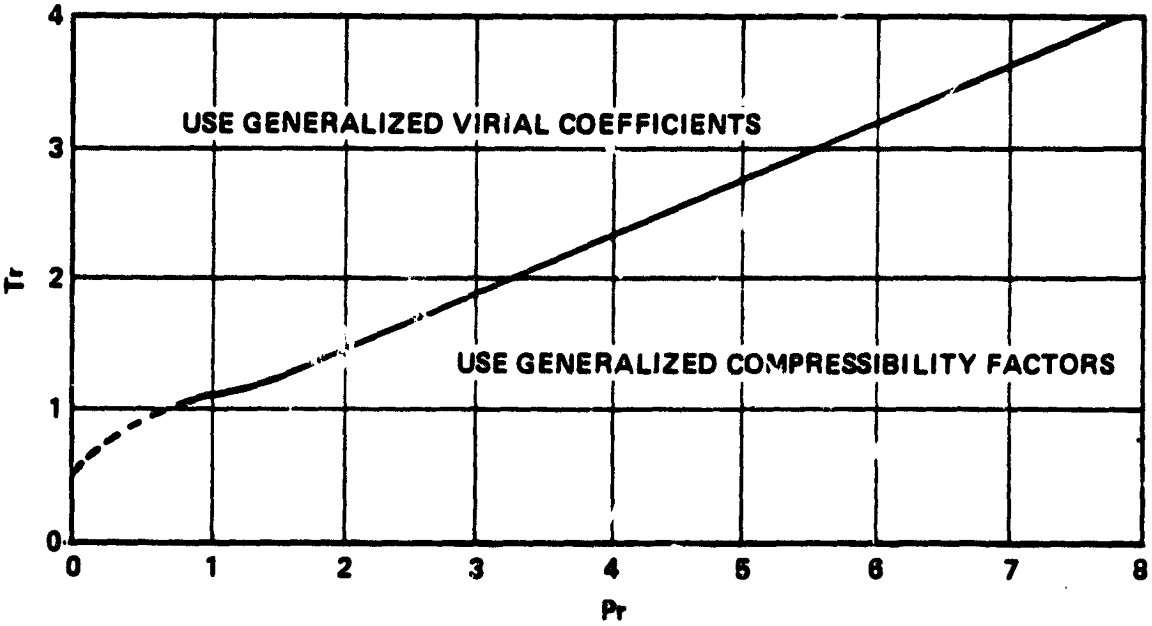

Figure 1. Line Defining Region Where Generalized Second Virial Coefficient May Be Used From Reference 7

APPENDICES

1. Appendix A – Constants for the Equation $C'p = \alpha + \beta T + \eta T^2$
2. Appendix B – Critical Constants and Acentric Factors
3. Appendix C – Fortran Program for the Evaluation of the Thermodynamic Properties of the EGRET Mixture
4. Appendix D – Tabulation of Thermodynamic Properties of EGRET Mixture

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APPENDIX A

Constants for the Equation $C'p = \alpha + \beta T + \eta T^2$
Where T is in (°K) and $C^1 p$ is in (cal)/(gm-mole) (°K)

Compound	Formula	α	$\beta \times 10^3$	$\eta \times 10^6$
Acetylene	C_2H_2	7.331	12.622	-3.889
Argon	Ar	4.969	0	0
Benzene	C_6H_6	-0.409	77.621	-26.429
Ethane	C_2H_6	2.247	38.201	-11.049
Ethanol	C_2H_6O	6.990	39.741	-11.926
Ethylene	C_2H_4	2.830	28.601	-8.726
Hydrogen	H	4.970	0	0
Methane	CH_4	3.381	18.044	-4.300
Neon	Ne	4.969	0	0
n - Butane	C_4H_{10}	3.844	73.350	-22.655
n - Pentane	C_5H_{12}	4.895	90.113	-28.039
Propane	C_3H_8	2.410	57.195	-17.533
Propylene	C_3H_6	3.253	45.116	-13.144

These values were selected from:

1 - J.M. Smith, Introduction to Chemical Engineering Thermodynamics, McGraw-Hill, NY

2 - R.H. Perry, Chemical Engineering Handbook, McGraw-Hill, NY

APPENDIX B

Critical Constants and Acentric Factors*

Compound	Tc (K)	Pc (atm)	Vc (cc/gmol)	Zc	ω
Argon	150.8	48.1	74.9	0.291	0.000
Bromine	584.0	102.0	127.0	0.270	0.132
Chlorine	417.0	76.0	124.0	0.275	0.074
Ethane	305.4	48.2	148.0	0.285	0.091
Ethanol	516.2	63.0	167.0	0.248	0.635
Helium^4	5.2	2.2	57.3	0.301	0.000
Hydrogen	43.6	12.8	51.5	0.291	0.000
Krypton	209.4	54.3	91.2	0.287	0.000
Methane	190.6	45.4	99.0	0.288	0.007
Methanol	512.6	79.9	118.0	0.224	0.556
Neon	45.5	27.2	40.3	0.291	0.000
Nitrogen	126.2	33.5	89.5	0.290	0.040
Propane	369.8	41.9	203.0	0.281	0.145
Oxygen	154.6	49.8	73.4	0.288	0.021
Water	647.1	217.6	56.0	0.230	0.348
Xenon	289.7	57.6	118.0	0.286	0.000

* Selected From:

1) J.M. Smith, "Introduction to Chemical Engineering Thermodynamics," McGraw-Hill, New York, NY, 1975.

2) J.M. Prausnitz, "Molecular Thermodynamics of Fluid-Phase Equilibrium," Prentice-Hall, Englewood Cliffs, NJ, 1969.

APPENDIX C

Computer Program Listing

The computer program, as listed in this Appendix, have the capability to calculate the following thermodynamic properties:

1. Enthalpy = H
2. Entropy = S
3. Internal Energy = $\overline{U}$
4. Gibbs Free Energy = G
5. Helmholtz Free Energy = A
6. Compressibility Ratio = Z
7. Density = φ
8. Molecular Volume = $\overline{V}$
9. Specific Heat Ratio = γ

This program was developed for the Energetic Gamma Ray Experiment Telescope (EGRET) program.

```
$EGRET T=00004 IS ON CR TC   USING 00025 BLKS R=0000

FTN4,L
      PROGRAM EGRET
C     Program to calculate the thermodynamic properties of a mixture
C     of gases (Neon,Ethene,Argon) at differents temperatures and
C     pressures.This program was developed for the ENERGETIC GAMMA RAY
C     EXPERIMENT TELESCOPE (EGRET).
C     For information please contac:Gilberto Colon, NASA/GSFC  CODE 713
C     GREENBELT,MD. 20701, TELEPHONE (301)344-6766.
C
C DEFINITION OF VARIABLES
C
C     T0 = REFERENCE TEMPERATURE       DEG.KELVIN
C     Q  = ACTUAL TEMPERATURE          DEG.KELVIN
C     H0 = REFERENCE ENTHALPY           CAL/MOL
C     P0 = REFERENCE PRESSURE           PSIA
C     PL = ACTUAL PRESSURE              PSIA
C     S0 = REFERENCE ENTROPY            CAL/MOL-DEG.KELVIN
C     R  = GAS CONSTANT                 CAL/MOL-DEG.KELVIN
C     R1 = GAS CONSTANT                 ATM-CC/MOL-DEG.KELVIN
C     Y1 = COMPOSITION OF NEON          GR/MOL
C     Y2 = COMPOSITION OF ETHANE        GR/MOL
C     Y3 = COMPOSITION OF ARGON         GR/MOL
C     TC = CRITICAL TEMPERATURE         DEG.KELVIN
C     PC = CRITICAL PRESSURE            PSIA
C     VC = CRITICAL VOLUME              CC/MOL
C     Z  = COMPRESSIBILITY FACTOR
C     W  = ACENTRIC FACTOR>
C     V  = VOLUME                       CC/MOL
C     U  = INTERNAL ENERGY              CAL/MOL
C     ENTHAL =ENTHALPY                  CAL/MOL
C     ENTRO  =ENTROPY                   CAL/MOL-DEG.KELVIN
C     GFE    =GIBBS FREE ENERGY         CAL/MOL
C     HFE    =HELMHOLTZ FREE ENERGY     CAL/MOL
C
      DOUBLE PRECISION Z(3,3),W(3,3),V(3,3),P(3,3),B(3,3),DBT(3,3),
     *TC(3),PC(3),WC(3),VC(3),ZC(3),B0(3,3),B1(3,3),DB0(3,3),DB1(3,3)
      DOUBLE PRECISION A,S,C,D,E,F,T0,R,Y1,Y2,Y3,TPC,PPC,F2,F3,X,Y,Z,
     *D2B0(3,3),D2B1(3,3),DBT1(3,3),C21,C22,D2BT,GAMMA,DENSTY,CVM,CPM,
     *TPR,PPR,TEMP,SHE,SHAN,SHM,H0,H1,T(3,3),S0,P0,A1,C1,D1,X1,S1,S2,
     *SLOP,B2,B3,B4,DB2,DB3,DB4,Q,PL,ENTHAL,H2,R1,E1,S3,CPGAS,CPREAL,
     *ENTRO,WM,TV,V1,Z1,XN,XM,V2,U,HFE,GFE
C
C The reference values are  T0=200 Deg.Kelvin, P0=14.7 psi, H0=993.6 cal/mol,
C S0=32.9646 cal/mol-deg.kelvin.This values are the same of pure Neon at the
C same temperature and pressure.
C
      F2(X,Y,Z)=Y1**2*X+2.*Y1*Y2*Y+2.*Y1*Y3*Z
      F3(X,Y,Z)=Y2**2*X+2.*Y2*Y3*Y+Y3**2*Z
C
      DATA TC/45.5D0,305.4D0,150.8D0/,PC/399.84D0,708.54D0,707.07D0/,
     *VC/40.30D0,148.0D0,74.90D0/,ZC/.291D0,.285D0,.291D0/,TV/3.278D4/,
     *WC/.0D0,.091D0,.0D0/,A/2.247D0/,C/3.683D-6/,D/.6087D0/,
     *T0/200.0D0/,H0/993.6D0/,Y1/.9850D0/,Y2/.0075D0/,Y3/.0075D0/,
     *E/.4048D0/,F/4.9675D0/,R/1.987D0/,S/.0091D0/,R1/82.10D0/,
     *S0/32.9646D0/,WM/20.4014D0/,P0/14.78D0/
C
      WRITE(1,15)
 15   FORMAT("ENTER LU NUMBER FOR OUTPUT")

      READ(1,*) LU
C
```

```
   DO 100 L=1,4500,100
   PL=L
   WRITE(LU,30)
   WRITE(LU,31)
   WRITE(LU,32)
C  WRITE(LU,33)
C
C In this section we are going to integrate the Specific Heat of the
C mixture,which are going to be used in the evaluation of the enthelpy
C and entropy.
C
   TEMP=A*T0+S*T0**2-C*T0**3
   DO 90 K=200,330,10
   Q=K
   SHE=(A*Q+S*Q**2-C*Q**3)-TEMP
   X1=DLOG (Q/T0)
   A1=F*X1
   C1=A*X1+38.201D-3*(Q-T0)-5.542D-6*(Q**2-T0**2)
   SHAN=F*(Q-T0)
   SHM=(Y1+Y3)*SHAN+Y2*SHE
   S2=(Y1+Y3)*A1+Y2*C1
C
C This section is a sentinel to verified if the method is applicable
C at a given set of temperature and pressure.
C
   TPC=Y1*TC(1)+Y2*TC(2)+Y3*TC(3)
   PPC=Y1*PC(1)+Y2*PC(2)+Y3*PC(3)
   TPR=Q/TPC
   PPR=PL/PPC
   SLOP=(TPR-D)/PPR
   IF(SLOP.LE.E) GO TO 70
C
C The calculation of the binary parameters of the mixture is done in
C this section.
C
    DO 50 I=1,3
     DO 40 J=1,3
      T(I,J)=DSQRT(TC(I)*TC(J))
      B0(I,J)=.083-.422/(Q/T(I,J))**1.6
      B1(I,J)=.139-.172/(Q/T(I,J))**4.2
      DB0(I,J)=.675/(Q/T(I,J))**2.6
      DB1(I,J)=0.722/(Q/T(I,J))**5.2
      D2B0(I,J)=-1.755/(Q/T(I,J))**3.6
      D2B1(I,J)=-3.756/(Q/T(I,J))**6.2
      Z(I,J)=(ZC(I)+ZC(J))/2.
      V(I,J)=(((VC(I))**.333333+(VC(J))**.333333)/8.)**3
      W(I,J)=(WC(I)+WC(J))/2.
      P(I,J)=(Z(I,J)*R1*T(I,J))/V(I,J)
      B(I,J)=(R1*T(I,J)/P(I,J))*(B0(I J)+W(I,J)*B1(I,J))
      DBT(I,J)=(R1/P(I,J))*(DB0(I,J)+W(I,J)*DB1(I,J))
      DBT1(I,J)=(R1/P(I,J))*(D2B0(I,J)+W(I,J)*D2B1(I,J))
40   CONTINUE
50  CONTINUE
C
C Here we evaluate the Enthalpy and Entropy of the mixture.
C
   D1=DLOG (PL/P0)
   E1=R*D1
   B2=F2(B(1,1),B(1,2),B(1,3))
   B3=F3(B(2,2),B(2,3),B(3,3))
   B4=B2+B3
   DB2=F2(DBT(1,1),DBT(1,2),DBT(1,3))
   DB3=F3(DBT(2,2),DBT(2,3),DBT(3,3))
```

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```
      DB4=DB2+DB3
      C21=F2(DBT1(1,1),DBT1(1,2),DBT1(1,3))
      C22=F3(DBT1(2,2),DBT1(2,3),DBT1(3,3))
      D2BT=C21+C22
      H1=(PL/R1)*(DB4-B4/Q)
      H2=(H1*R*Q)/14.7
      S1=(PL/R1)*DB4
      S3=(S1*R)/14.7
      ENTHAL=H0+SHM-H2
      ENTRO=S0+S2-E1-S3
C
C Evaluation of the others thermodynamics properties.
C
      Z1=1+(((B4*PL)/(Q*R1)))/14.7
      V1=((Z1*Q*R1)/PL)*14.7
      DENSTY=WM/V1
      XN=TV/V1
      XM=XN*WM
      V2=(Z1*Q*R)/PL
      U=ENTHAL-PL*V2
      HFE=U-Q*ENTRO
      GFE=ENTHAL-Q*ENTRO
      CPM=F*(Y1+Y3)+Y2*(A+38.201D-3*Q-11.049D-6*Q**2)
      IF(PL.LE.100) GO TO 110
      CPGAS=(R/V1)*(Q**2*D2BT)
      CPREAL=CPGAS+CPM
      CVM=CPREAL-R
      GAMMA=CPREAL/CVM
      GO TO 120
110   CVM=CPM-R
      GAMMA=CPM/CVM
C
C Write statements to print out the results.
C
120   WRITE(LU,60) PL,Q,ENTHAL,ENTRO,V1,XN,XM,Z1,DENSTY,GAMMA
C120  WRITE(LU,65) PL,Q,ENTHAL,ENTRO,U,HFE,GFE,GAMMA
60    FORMAT(1X,F6.1,3X,F5.1,2X,F9.3,2X,F9.3,2X,F9.4,3X,F9.4,4X,
     *F9.4,3X,F6.4,4X,F6.4,5X,F6.4)
C65   FORMAT(1X,F6.1,3X,F5.1,2X,F9.3,2X,F9.3,2X,F9.3,3X,F9.3,4X,
C    *F9.3,3X,F7.4)
30    FORMAT(1X,'PRESSURE',2X,'TEMP.',2X,'ENTHALPY',4X,'ENTROPY',
     *4X,'VOLUME',6X,'MOLES',9X,'MASS',4X,'C.FACTOR',4X,'DENSITY',
     *3X,'HEAT')
C    *3X,'INTERNAL',3X,'HELMHOLTZ',6X,'GIBBS',4X,'SPECIFIC')
31    FORMAT(1X,'PSIA',5X,'DEG-K',3X,'CAL/MOL',4X,'CAL/MOL-K',3X,
     *'CC/MOL',19X,'GRAMS',16X,'GRAMS/CC',2X,'RATIO')
C31   FORMAT(1X,39X,'ENERGY',5X,'F.ENERGY',6X,'F.ENERGY',3X,'HEAT')
C32   FORMAT(1X,'PSIA',5X,'DEG-K',3X,'CAL/MUL',4X,'CAL/MOL-K',3X,
C    *'CAL/MOL',3X,'CAL/MOL',8X,'CAL/MOL',3X,'RATIO')
32    FORMAT(85'-')
C33   FORMAT(85'-')
      GO TO 90
70    WRITE(LU,80) PL,Q,TPR,PPR
80    FORMAT(1X,F7.2,4X,F8.2,3X,'NO APPLICABLE TPR=',F6.4,3X,
     *'PPR=',F6.4)
90    CONTINUE
      WRITE(LU,32)
100   CONTINUE
      END
```

APPENDIX D

Tabulation of the Thermodynamic Properties of the EGRET Mixture

This is a sample of the data that can be obtained from this program. There is no limit for the pressure or temperature.

PRESSURE PSIA	TEMP. DEG-K	ENTHALPY CAL/MOL	ENTROPY CAL/MOL-K	INTERNAL ENERGY CAL/MOL	HELMHOLTZ F.ENERGY CAL/MOL	GIBBS F.ENERGY CAL/MOL	SPECIFIC HEAT RATIO
1.0	201.0	998.571	38.341	599.184	-7107.373	-6707.986	1.6592
1.0	206.0	1023.428	38.464	614.106	-7309.475	-6900.152	1.6589
1.0	211.0	1048.288	38.584	629.031	-7512.187	-7092.930	1.6586
1.0	216.0	1073.150	38.701	643.958	-7715.496	-7286.304	1.6584
1.0	221.0	1098.015	38.816	658.888	-7919.388	-7480.261	1.6581
1.0	226.0	1122.883	38.923	673.820	-8123.851	-7674.788	1.6578
1.0	231.0	1147.752	39.037	688.755	-8328.871	-7869.873	1.6575
1.0	236.0	1172.625	39.145	703.692	-8534.437	-8065.504	1.6573
1.0	241.0	1197.499	39.250	718.632	-8740.537	-8261.670	1.6570
1.0	246.0	1222.376	39.353	733.574	-8947.161	-8458.359	1.6567
1.0	251.0	1247.256	39.453	748.519	-9154.298	-8655.561	1.6565
1.0	256.0	1272.138	39.552	763.466	-9361.939	-8853.266	1.6562
1.0	261.0	1297.022	39.649	778.415	-9570.073	-9051.465	1.6559
1.0	266.0	1321.909	39.745	793.366	-9778.691	-9250.148	1.6557
1.0	271.0	1346.797	39.838	808.320	-9987.784	-9449.307	1.6554
1.0	276.0	1371.689	39.930	823.276	-10197.34	-9648.932	1.6552
1.0	281.0	1396.582	40.020	838.235	-10407.36	-9849.016	1.6549
1.0	286.0	1421.478	40.108	853.195	-10617.83	-10049.55	1.6546
1.0	291.0	1446.376	40.196	868.158	-10828.74	-10250.53	1.6544
1.0	296.0	1471.275	40.281	883.123	-11040.09	-10451.94	1.6541
1.0	301.0	1496.178	40.365	898.091	-11251.87	-10653.78	1.6539
1.0	306.0	1521.082	40.448	913.060	-11464.06	-10856.04	1.6536
1.0	311.0	1545.989	40.530	928.032	-11676.67	-11058.72	1.6534
1.0	316.0	1570.898	40.610	943.006	-11889.69	-11261.80	1.6531
1.0	321.0	1595.809	40.689	957.981	-12103.11	-11465.29	1.6529
1.0	326.0	1620.722	40.767	972.959	-12316.93	-11669.17	1.6526

PRESSURE PSIA	TEMP. DEG-K	ENTHALPY CAL/MOL	ENTROPY CAL/MOL-K	INTERNAL ENERGY CAL/MOL	HELMHULTZ F.ENERGY CAL/MOL	GIBBS F.ENERGY CAL/MOL	SPECIFIC HEAT RATIO
101.0	201.0	998.559	29.171	599.158	-5264.154	-4864.753	1.6636
101.0	206.0	1023.418	29.294	614.081	-5420.404	-5011.068	1.6630
101.0	211.0	1048.279	29.414	629.007	-5577.265	-5157.983	1.6625
101.0	216.0	1073.143	29.531	643.935	-5734.723	-5305.515	1.6620
101.0	221.0	1098.009	29.645	658.865	-5892.764	-5453.621	1.6615
101.0	226.0	1122.877	29.757	673.798	-6051.375	-5602.298	1.6610
101.0	231.0	1147.749	29.867	688.734	-6210.544	-5751.530	1.6606
101.0	236.0	1172.622	29.974	703.672	-6370.259	-5901.309	1.6601
101.0	241.0	1197.498	30.079	718.612	-6530.508	-6051.623	1.6597
101.0	246.0	1222.378	30.182	733.555	-6691.281	-6202.460	1.6593
101.0	251.0	1247.256	30.283	748.500	-6852.567	-6353.811	1.6589
101.0	256.0	1272.139	30.382	763.448	-7014.356	-6505.665	1.6585
101.0	261.0	1297.024	30.479	778.398	-7176.639	-6658.012	1.6581
101.0	266.0	1321.912	30.574	793.350	-7339.406	-6810.844	1.6578
101.0	271.0	1346.801	30.668	808.304	-7502.648	-6964.151	1.6574
101.0	276.0	1371.693	30.759	823.261	-7666.357	-7117.924	1.6570
101.0	281.0	1396.587	30.850	838.219	-7830.524	-7272.157	1.6567
101.0	286.0	1421.484	30.938	853.181	-7995.142	-7426.839	1.6564
101.0	291.0	1446.382	31.025	868.144	-8160.203	-7581.965	1.6560
101.0	296.0	1471.283	31.111	883.109	-8325.699	-7737.526	1.6557
101.0	301.0	1496.186	31.195	898.077	-8491.624	-7893.515	1.6554
101.0	306.0	1521.091	31.278	913.047	-8657.969	-8049.925	1.6550
101.0	311.0	1545.998	31.359	928.019	-8824.729	-8206.749	1.6547
101.0	316.0	1570.907	31.440	942.993	-8991.897	-8363.982	1.6544
101.0	321.0	1595.819	31.518	957.969	-9159.466	-8521.616	1.6541
101.0	326.0	1620.732	31.596	972.947	-9327.431	-8679.646	1.6538