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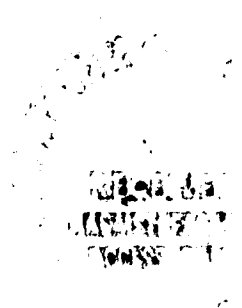
Calculation of the Thermodynamic Properties of a Mixture of Gases as a Function of Temperature and Pressure

Gilberto Colon

DECEMBER 1981

National Aeronautics and
Space Administration

Goddard Space Flight Center
Greenbelt, Maryland 20771



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OF A MIXTURE OF GASES AS A FUNCTION
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**CALCULATION OF THE THERMODYNAMIC PROPERTIES
OF A MIXTURE OF GASES AS A FUNCTION
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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
- C_p – Heat capacity at constant pressure
- C_v – Heat capacity at constant volume
- G – Gibbs free energy
- H – Enthalpy
- ΔH' – Residual enthalpy
- M – Extensive thermodynamic property (properties that depend on the size of the system)
- MW – Molecular weight
- P – Actual pressure
- P_c – Critical pressure
- P_r – Reduced pressure = P/P_c
- R – Universal gas constant
- S – Entropy
- ΔS' – Residual entropy
- T – Actual temperature (°K)
- T_c – Critical temperature
- T_r – Reduced temperature = T/T_c
- U – Internal energy
- V – Volume
- V_c – Critical volume
- V_r – Reduced volume = V/V_c
- Y – Mole fraction in gas phase
- Z – Compressibility factor
- Z_c – Critical compressibility factor
- γ – Heat capacities ratio = C_p/C_v
- ω – Acentric Factor = -log₁₀ (P_r^{sat}) T_r = 0.7-1.00
- η, β, α – Constants characteristic of the gas considered for the equation C_p = α + βT + ηT²

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:

$$\Delta M' = M' - M \quad (1)$$

where M , M' and $\Delta M'$ 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:

$$H = H' - \Delta H' \quad (2)$$

$$S = S' - \Delta S' \quad (3)$$

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 $\Delta M'$, 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 (γ_m)

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.

$$C'_p = \alpha + \beta T + \eta T^2 \quad (4)$$

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:

$$C'_p - C'_v = R \quad (5)$$

$$\gamma_i = C'_p / C'_v \quad (6)$$

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:

$$\Delta C_p = C_p + C'_p \quad (7a)$$

$$\Delta C_p = - \frac{R}{V} \left(T^2 \frac{d^2 B}{dT^2} \right) \quad (7b)$$

For a mixture of gases:

$$C'_{pm} = \sum_i Y_i C'_p \quad (8a)$$

$$C'_{vm} = C'_{pm} - R \quad (8b)$$

$$\gamma_m = C'_{pm} / C'_{vm} \quad (9)$$

where Y_i 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:

$$H' = H'_0 + \int_{T_0}^T C'_p dT \quad (10)$$

$$S' = S'_0 + \int_{T_0}^T C'_p \frac{dT}{T} - R \int_{P_0}^P \frac{dp}{P} \quad (11)$$

The integrations are performed at constant composition from an initial (T_0, P_0) 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 T_0, P_0 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:

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

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

In these equations, B is the second virial coefficient. (The virial equation of state $Z = 1 + B/V + C/V^2 + D/V^3 \dots$ 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 Pitzer⁴ for the second virial coefficient. Pitzer proposed a correlation of the form:

$$\frac{BP_c}{RT_c} = B^0 + \omega B \quad (14)$$

where B^0 and B are functions of reduced temperature (T_r) only. Pitzer's correlation for the second virial coefficient has been extended to mixtures by Prausnitz⁵, who generalized Equation (14) as follows:

$$B_{ij} = \frac{RT_{cij}}{P_{cij}} (B^0 + \omega_{ij} B^1) \quad (15)$$

where B^0 and B^1 are defined in References (7,8) as:

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} \quad (16)$$

$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}} \quad (17)$$

The mixing rules proposed by Prausnitz⁵ for the calculation of W_{ij} , T_{cij} , P_{cij} , V_{cij} and Z_{cij} are:

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

$$T_{cij} = (T_i \times T_j)^{1/2} (1 - K_{ij}) \quad (19)$$

$$Z_{cij} = \left(\frac{Z_{ci} + Z_{cj}}{2} \right) \quad (20)$$

$$V_{cij} = \left[\frac{(V_{ci})^{1/3} + (V_{cj})^{1/3}}{2} \right]^3 \quad (21)$$

$$P_{cij} = \frac{Z_{cij} R T_{cij}}{V_{cij}} \quad (22)$$

where K_{ij} (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, K_{ij} can be set equal to zero. When $i = j$, all these equations reduce to the appropriate values for single components.

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

$$T_r = T/T_{c,ij} \quad (23)$$

$$P_r = P/P_{c,ij} \quad (24)$$

For a mixture of gases:

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

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

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

$$\frac{dB_{ij}}{dT} = \frac{R}{P_{c,ij}} \left(\frac{dB_{ij}^0}{dT_r} + \omega_{ij} \frac{dB_{ij}^1}{dT_r} \right) \quad (27)$$

where:

$$\frac{dB_{ij}^0}{dT_r} = \frac{0.675}{T_r^{2.6}} \quad (28)$$

$$\frac{dB_{ij}^1}{dT_r} = \frac{0.722}{T_r^{3.2}} \quad (29)$$

The values of B_{ij} calculated from Equation (15) are substituted into Equation (25) yielding a value of B for the mixture. The values of dB_{ij}/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:

$$U = H - PV \quad (30)$$

$$A = U - TS \quad (31)$$

$$G = H - TS \quad (32)$$

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

<u>Component</u>	<u>Volume</u>	<u>M.W.</u>	<u>Mass/Mol Mixture</u>	<u>% Mass/Mol</u>
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
			<u>20.4014</u>	

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:

$$C'_p = 4.9675 \text{ for all temperatures}$$

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

$$C'_{pm} = (Y_1 + Y_3) 4.9675 + Y_2 (2.247 + 38.201 \times 10^{-3} T - 11.049 \times 10^{-6} T^2)$$

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

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

where:

$$\frac{d^2 B_{ij}}{dT^2} = \frac{R}{P c_{ij}} \left(\frac{d^2 B^0}{dT^2} + w_{ij} \frac{d^2 B^1}{dT^2} \right) \quad (34)$$

$$\frac{d^2 B^0}{dT^2} = -1.755 T_r^{-3.6} \quad (35)$$

$$\frac{d^2 B^1}{dT^2} = -3.756 T_r^{-6.2} \quad (36)$$

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 T_c , P_c , T_c , V_c , Z_c 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

<u>P = 1 atm.</u>	<u>Neon (20.183 M.W.)</u>		<u>EGRET (20.414 M.W.)</u>	
<u>Temp.</u> °K	<u>Enthalpy</u> CAL/MOL	<u>Entropy</u> CAL/MOL·°K	<u>Enthalpy</u> CAL/MOL	<u>Entropy</u> 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	36.4087	1989.66	36.41
500	2484.10	37.5168	2488.83	37.53
600	2980.90	38.4226	2988.54	38.46

According to Smith⁷ and Prausnitz⁵, 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.

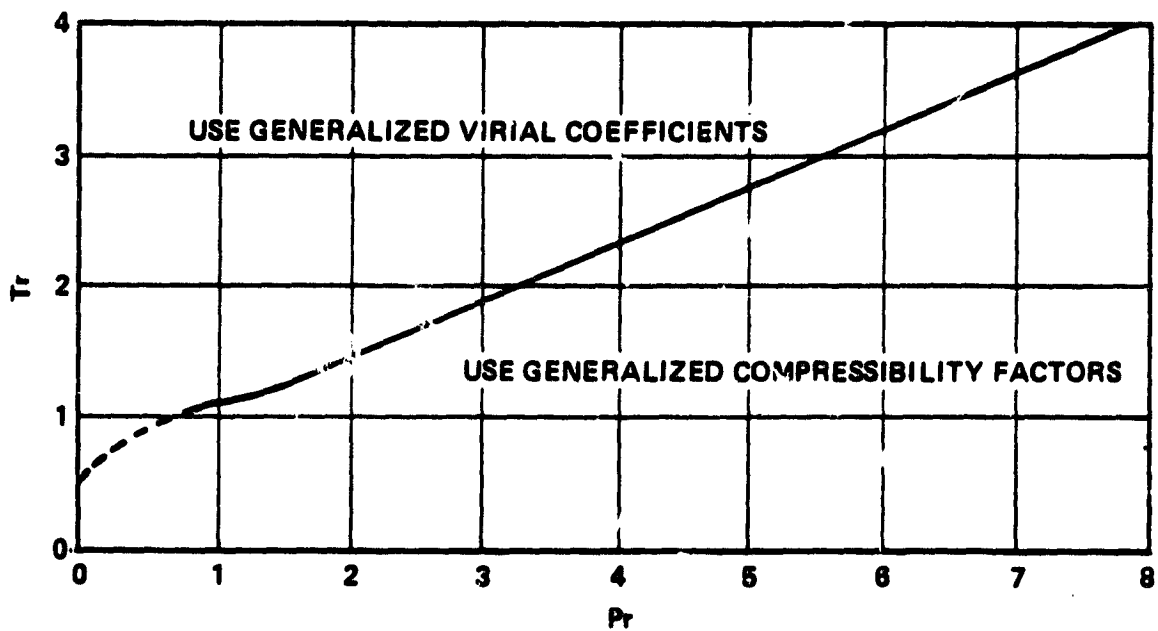


Figure 1. Line Defining Region Where Generalized Second Virial Coefficient May Be Used From Reference 7

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**

REFERENCES

1. Cambel, A. B. and Jennings, B. H., "Gas Dynamics," McGraw-Hill Company, New York, NY, 1958.
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4. Lewis, G. N. and Randall, M., "Thermodynamics," Second Edition, revised by K. S. Pitzer and L. Brewer, Appendix 1, McGraw-Hill, New York, 1961.
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8. Tsonopoulos, C., "An Empirical Correlation of Second Virial Coefficient," AIChE Journal, Volume 20, #2, March 1974, p. 263.

APPENDIX A

Constants for the Equation $C_p = \alpha + \beta T + \eta T^2$
 Where T is in ($^{\circ}$ K) and C_p is in (cal)/(gm-mole) ($^{\circ}$ 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	90.115	-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	T _c (K)	P _c (atm)	V _c (cc/gmol)	Z _c	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
Propene	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 = \bar{U}
4. Gibbs Free Energy = G
5. Helmholtz Free Energy = A
6. Compressibility Ratio = Z
7. Density = ρ
8. Molecular Volume = \bar{V}
9. Specific Heat Ratio = γ

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

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0001 FTN4,L
0002 PROGRAM EGRET
0003 C Program to calculate the thermodynamic properties of a mixture
0004 C of gases (Neon,Ethane,Argon) at different temperatures and
0005 C pressures.This program was developed for the ENERGETIC GAMMA RAY
0006 C EXPERIMENT TELESCOPE (EGRET).
0007 C For information please contact:Gilberto Colon, NASA/GSFC CODE 713
0008 C GREENBELT,MD. 20701, TELEPHONE (301)344-6766.
0009 C
0010 C DEFINITION OF VARIABLES
0011 C
0012 C T0 = REFERENCE TEMPERATURE DEG.KELVIN
0013 C Q = ACTUAL TEMPERATURE DEG.KELVIN
0014 C H0 = REFERENCE ENTHALPY CAL/MOL
0015 C P0 = REFERENCE PRESSURE PSIA
0016 C PL = ACTUAL PRESSURE PSIA
0017 C S0 = REFERENCE ENTROPY CAL/MOL-DEG.KELVIN
0018 C R = GAS CONSTANT CAL/MOL-DEG.KELVIN
0019 C R1 = GAS CONSTANT ATM-CC/MOL-DEG.KELVIN
0020 C Y1 = COMPOSITION OF NEON GR/MOL
0021 C Y2 = COMPOSITION OF ETHANE GR/MOL
0022 C Y3 = COMPOSITION OF ARGON GR/MOL
0023 C TC = CRITICAL TEMPERATURE DEG.KELVIN
0024 C PC = CRITICAL PRESSURE PSIA
0025 C VC = CRITICAL VOLUME CC/MOL
0026 C Z = COMPRESSIBILITY FACTOR
0027 C W = ACENTRIC FACTOR
0028 C V = VOLUME CC/MOL
0029 C U = INTERNAL ENERGY CAL/MOL
0030 C ENTHAL -ENTHALPY CAL/MOL
0031 C ENTRO -ENTROPY CAL/MOL-DEG.KELVIN
0032 C GFE =GIBBS FREE ENERGY CAL/MOL
0033 C HFE =HELMHOLTZ FREE ENERGY CAL/MOL
0034 C
0035 C DOUBLE PRECISION Z(3,3),W(3,3),V(3,3),P(3,3),B(3,3),DBT(3,3),
0036 C #TC(3),PC(3),WC(3),VC(3),ZC(3),H0(3,3),B1(3,3),DB0(3,3),DB1(3,3)
0037 C DOUBLE PRECISION A,S,C,D,E,F,T0,R,Y1,Y2,Y3,TPC,PPC,F2,F3,X,Y,Z,
0038 C #D2B0(3,3),D2B1(3,3),DBT1(3,3),C21,C22,D2BT,GAMMA,DENSTY,CVM,CPM,
0039 C #TPR,PPR,TEMP,SHE,SHAN,SHM,H0,H1,I(3,3),S0,P0,A1,C1,D1,X1,S1,S2,
0040 C #SLOP,B2,B3,B4,DB2,DB3,DB4,Q,PL,ENTHAL,H2,R1,E1,S3,CPGAS,CPREAL,
0041 C #ENTRO,WM,TV,V1,Z1,XN,XM,V2,U,HFE,GFE
0042 C
0043 C The reference values are T0=200 Deg.Kelvin, P0=14.7 psi, H0=993.6 cal/mol,
0044 C S0=32.9646 cal/mol-deg.kelvin.This values are the same of pure Neon at the
0045 C same temperature and pressure.
0046 C
0047 C F2(X,Y,Z)=Y1**2*X+2.*Y1*Y2*Y+2.*Y1*Y3**2
0048 C F3(X,Y,Z)=Y2**2*X+2.*Y2*Y3*Y+Y3**2*Z
0049 C
0050 C DATA TC/45.500,305.400,150.800/,PC/399.8400,708.5400,707.0700/,
0051 C #VC/40.3000,148.000,74.9000/,ZC/.29100,.29500,.29100/,TV/3.27804/,
0052 C #WC/.000,.09100,.000/,A/2.24700/,C/3.6830-b/,D/.608700/,
0053 C #T0/200.000/,H0/993.600/,Y1/.985000/,Y2/.007500/,Y3/.007500/,
0054 C #E/.454800/,F/4.967500/,R/1.98700/,S/.009100/,R1/82.1000/,
0055 C #S0/32.964600/,WM/20.401400/,P0/14.7800/
0056 C
0057 C WRITE(1,15)
0058 C 15 FORMAT('ENTER LU NUMBER FOR OUTPUT')
0059 C
0060 C READ(1,*) LU
0061 C

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0062      DO 100 L=1,4500,100
0063      PL=L
0064      WRITE(LU,30)
0065      WRITE(LU,31)
0066      WRITE(LU,32)
0067      C      WRITE(LU,33)
0068      C
0069      C In this section we are going to integrate the Specific Heat of the
0070      C mixture, which are going to be used in the evaluation of the enthalpy
0071      C and entropy.
0072      C
0073      TEMP=AMT0+SMT0##2-CMT0##3
0074      DO 90 K=200,330,10
0075      Q=K
0076      SHE=(AMQ+SMQ##2-CMQ##3)-TEMP
0077      X1=DLOG (Q/T0)
0078      A1=FMX1
0079      C1=A#X1+.30.201D-3#(Q-T0)-5.542D-6#(Q##2-T0##2)
0080      SHAN=FM(Q-T0)
0081      SHM=(Y1+Y3)#SHAN+Y2#SHF.
0082      S2=(Y1+Y3)#A1+Y2#C1
0083      C
0084      C This section is a sentinel to verified if the method is applicable
0085      C at a given set of temperature and pressure.
0086      C
0087      TPC=Y1#TC(1)+Y2#TC(2)+Y3#TC(3)
0088      PPC=Y1#PC(1)+Y2#PC(2)+Y3#PC(3)
0089      TPR=Q/TPC
0090      PPR=PL/PPC
0091      SLOP=(TPR-D)/PPR
0092      IF(SLOP.LE.E) GO TO 70
0093      C
0094      C The calculation of the binary parameters of the mixture is done in
0095      C this section.
0096      C
0097      DO 50 I=1,3
0098      DO 40 J=1,3
0099      T(I,J)=DSQRT(TC(I)#TC(J))
0100      B0(I,J)=.083-.422/(Q/T(I,J))##1.6
0101      B1(I,J)=.139-.172/(Q/T(I,J))##4.2
0102      B00(I,J)=.675/(Q/T(I,J))##2.6
0103      B01(I,J)=0.722/(Q/T(I,J))##5.2
0104      B2B0(I,J)=-1.755/(Q/T(I,J))##3.6
0105      B2B1(I,J)=-3.756/(Q/T(I,J))##6.2
0106      Z(I,J)=(ZC(I)+ZC(J))/2.
0107      VC(I,J)=(((VC(I))##.333333+(VC(J))##.333333)/8.)##3
0108      W(I,J)=(WC(I)+WC(J))/2.
0109      P(I,J)=(Z(I,J)#R1#T(I,J))/V(I,J)
0110      B(I,J)=(R1#T(I,J)/P(I,J))#(B0(I,J)+W(I,J)#B1(I,J))
0111      DBT(I,J)=(R1/P(I,J))#(B00(I,J)+W(I,J)#B01(I,J))
0112      DBT1(I,J)=(R1/P(I,J))#(B2B0(I,J)+W(I,J)#B2B1(I,J))
0113      40      CONTINUE
0114      50      CONTINUE
0115      C
0116      C Here we evaluate the Enthalpy and Entropy of the mixture.
0117      C
0118      D1=DLOG (PL/P0)
0119      E1=RND1
0120      B2=F2(B(1,1),B(1,2),B(1,3))
0121      B3=F3(B(2,2),B(2,3),B(3,3))
0122      B4=C2+B3
0123      DB2=F2(DBT(1,1),DBT(1,2),DBT(1,3))
0124      DB3=F3(DBT(2,2),DBT(2,3),DBT(3,3))

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0125      DB4=DB2+DB3
0126      C21=F2(DBT1(1,1),DBT1(1,2),DBT1(1,3))
0127      C22=F3(DBT1(2,2),DBT1(2,3),DBT1(3,3))
0128      D2BT=C21+C22
0129      M1=(PL/R1)=(DB4-B4/Q)
0130      M2=(M1*RWQ)/14.7
0131      S1=(PL/R1)*DB4
0132      S3=(S1*W)/14.7
0133      ENTHAL=M0+SMM-M2
0134      ENTRO=S0+S2-E1-S3
0135      C
0136      C Evaluation of the others thermodynamics properties.
0137      C
0138      Z1=1+(((B4*PL)/(QMR1)))/14.7
0139      V1=(Z1*QMR1)/PL#14.7
0140      DENSTY=M/V1
0141      XM=TV/V1
0142      XM=XN*MM
0143      V2=(Z1*QMR)/PL
0144      U=ENTHAL-PL*V2
0145      HFE=U-Q*ENTRO
0146      GFE=ENTHAL-Q*ENTRO
0147      CPM=F*(Y1+Y3)+Y2*(A+38.2010-3*Q-11.0490-6*Q**2)
0148      IF(PL.L.E.100) GO TO 110
0149      CPGAS=(R/V1)*(Q**2*D2BT)
0150      CPREAL=CPGAS+CPM
0151      CVM=CPREAL-R
0152      GAMMA=CPREAL/CVM
0153      GO TO 120
0154      110  CVM=CPM-R
0155      GAMMA=CPM/CVM
0156      C
0157      C Write statements to print out the results.
0158      C
0159      120  WRITE(LU,60) PL,Q,ENTHAL,ENTRO,V1,XN,XM,Z1,DENSTY,GAMMA
0160      C120 WRITE(LU,65) PL,Q,ENTHAL,ENTRO,U,HFE,GFE,GAMMA
0161      60   FORMAT(1X,F6.1,3X,F5.1,2X,F9.3,2X,F9.3,2X,F9.4,3X,F9.4,4X,
0162      #F9.4,3X,F6.4,4X,F6.4,5X,F6.4)
0163      C65  FORMAT(1X,F6.1,3X,F5.1,2X,F9.3,2X,F9.3,2X,F9.3,3X,F9.3,4X,
0164      #F9.3,3X,F7.4)
0165      30   FORMAT(1X,'PRESSURE',2X,'TEMP.',2X,'ENTHALPY',4X,'ENTROPY',
0166      #4X,'VOLUME',6X,'MOLES',9X,'MASS',4X,'C.FACTOR',4X,'DENSITY',
0167      #3X,'HEAT')
0168      C    #3X,'INTERNAL',3X,'HELMHOLTZ',6X,'GIBBS',4X,'SPECIFIC')
0169      31   FORMAT(1X,'PSIA',5X,'DEG-K',3X,'CAL/MOL',4X,'CAL/MOL-K',3X,
0170      # 'CC/MOL',19X,'GRAMS',16X,'GRAMS/CC',2X,'RATIO')
0171      C31  FORMAT(1X,39X,'ENERGY',5X,'F.ENERGY',6X,'F.ENERGY',3X,'HEAT')
0172      C32  FORMAT(1X,'PSIA',5X,'DEG-K',3X,'CAL/MOL',4X,'CAL/MOL-K',3X,
0173      # 'CAL/MOL',3X,'CAL/MOL',6X,'CAL/MOL',3X,'RATIO')
0174      32   FORMAT(85'-')
0175      C33  FORMAT(85'-')
0176      GO TO 90
0177      70   WRITE(LU,80) PL,Q,TPR,PPR
0178      80   FORMAT(1X,F7.2,4X,F8.2,3X,'NO APPLICABLE TPR-',F6.4,3X,
0179      # 'PPR-',F6.4)
0180      90   CONTINUE
0181      WRITE(LU,32)
0182      100  CONTINUE
0183      END
0184

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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.

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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	-7092.830	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	38.929	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	1371.688	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	HELMHOLTZ 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	673.799	-6051.375	-5602.296	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	1222.376	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