Speed of Sound and Related Thermodynamic Properties Calculated from the AGA Report No. 8 Detail Characterization Method Using a Helmholtz Energy Formulation

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Abstract

The AGA Report No. 8 Detail Characterization Method allows for the calculation of the compressibility factor (or pressure) for a natural gas mixture given known conditions of temperature, density, and composition. Iterative procedures can be used to calculate the density when the pressure and temperature are known. Other thermodynamic properties such as the speed of sound, heat capacities, enthalpies, or entropies can be calculated from the AGA8 model if the equation of state is rewritten in a form explicit in the Helmholtz energy. In addition, equations for the ideal gas heat capacity are required for each of the constituents in the mixture. All required equations and coefficients are outlined here.

Introduction

The DETAIL characterization method of AGA Report No. 8 (Starling and Savidge, 1994) allows for the calculation of the compressibility factor and density of natural gas mixtures. Computations can be made over the range from –8 to 62 °C and pressures to 12 MPa with uncertainties in density of 0.1%. Calculations outside this region will have greater uncertainties, reaching up to 0.5% between –130 and 200 °C at pressures to 70 MPa. Liquid states within this region are not included in these uncertainty estimates (AGA8 is not valid in the liquid) and the uncertainties in density increase near the critical region. In the normal calculation of properties from AGA8, the compositions of the constituents are limited, *e.g.*, methane ranges from 45 to 100% (on a molar basis), nitrogen from 0 to 50%, carbon dioxide from 0 to 30%, and ethane from 0 to 10%. These limits can be exceeded (resulting in higher uncertainties in an "extended" approach) for gas mixtures in which the compositions can be varied from 0 to 100% for the components methane, nitrogen, carbon dioxide, ethane, hydrogen, and hydrogen sulfide. Mixtures with propane up to 12%, the butanes up to 6%, and the pentanes up to 4% are also allowed in the extended approach.

Although the published equation of state for AGA8 is explicit in the compressibility factor (Z), the formulation was originally developed using an equation of state explicit in the Helmholtz energy (a) with independent variables of molar density (ρ) and temperature (T). The Helmholtz energy equation is not given in the AGA8 documentation, where equations explicit in pressure and compressibility factor are reported. Formulations explicit in the Helmholtz energy have been used heavily during the last several years to represent the properties of pure fluids and mixtures because of the ease of calculating all other thermodynamic properties by mathematical differentiation (*e.g.*, Span and Wagner, 1996, 2003). The Helmholtz energy is a fundamental thermodynamic property from which all other thermodynamic properties can be calculated as derivatives with respect to molar density or temperature. For example, the expression for calculating pressure is

$$p = \rho^2 \left(\frac{\partial a}{\partial \rho} \right)_T . \tag{1}$$

On the other hand, starting from the pressure explicit equation in AGA8, the calculation of other properties, including the speed of sound, requires not only derivatives of the pressure (or compressibility factor) with respect to molar density and temperature, but also requires integrations over molar density which can be quite complicated. For further information on this technique, refer to the documentation for AGA Report No. 10 (Peterson, 2003). The equations presented here show the AGA8 equation in its Helmholtz energy form, and allow access to other thermodynamic properties such as heat capacities, enthalpies, entropies, and sound speeds by differentiation of the Helmholtz energy.

The AGA Report No. 8 Equation for the Compressibility Factor

The equation of state for the DETAIL characterization method in AGA8, given in terms of the compressibility factor, is

$$Z = 1 + \rho B - D \sum_{n=13}^{18} C_n^* T^{-u_n} + \sum_{n=13}^{58} C_n^* T^{-u_n} \left(b_n - c_n k_n D^{k_n} \right) D^{b_n} \exp\left(-c_n D^{k_n} \right), \tag{2}$$

where B is the second virial coefficient, D is the reduced density ($K^3 \rho$), K is the mixture size parameter, and u_n, b_n, c_n, and k_n are coefficients and exponents given in Table 1. The units for temperature and molar density are kelvins and moles per cubic decimeter. The mixture size parameter K for a mixture of N components is

$$K^5 = \left[\sum_{i=1}^{N} x_i K_i^{5/2} \right]^2 + 2 \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} x_i x_j \left(K_{ij}^5 - 1 \right) \left(K_i K_j \right)^{5/2} \tag{3}$$

and the second virial coefficient is

$$B = \sum_{n=1}^{18} a_n T^{-u_n} B^*, \text{ with} \tag{4}$$

$$B^* = \sum_{i=1}^{N} \sum_{j=1}^{N} x_i x_j \left[E_{ij} \left(E_i E_j \right)^{1/2} \right]^{u_n} \left(K_i K_j \right)^{3/2} B_{nij}^* \text{ and} \tag{5}$$

$$B_{nij}^* = \left[G_{ij} \left(G_i + G_j \right) / 2 + 1 - g_n \right]^{g_n} \left(Q_i Q_j + 1 - q_n \right)^{q_n} \left(F_i^{1/2} F_j^{1/2} + 1 - f_n \right)^{f_n}$$
$$\left(S_i S_j + 1 - s_n \right)^{s_n} \left(W_i W_j + 1 - w_n \right)^{w_n}. \tag{6}$$

The coefficients C_n^* in Eq. (2) are

$$C_n^* = a_n \left(G + 1 - g_n \right)^{g_n} \left(Q^2 + 1 - q_n \right)^{q_n} \left(F + 1 - f_n \right)^{f_n} U^{u_n}, \tag{7}$$

where G, Q, F, and U are

$$U^5 = \left[\sum_{i=1}^{N} x_i E_i^{5/2} \right]^2 + 2 \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} x_i x_j \left(U_{ij}^5 - 1 \right) \left(E_i E_j \right)^{5/2}, \tag{8}$$

$$G = \sum_{i=1}^{N} x_i G_i + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} x_i x_j \left(G_{ij} - 1 \right)\left(G_i + G_j \right),$$ (9)

$$Q = \sum_{i=1}^{N} x_i Q_i , \text{ and}$$ (10)

$$F = \sum_{i=1}^{N} x_i^2 F_i .$$ (11)

Values of E_i, K_i, G_i, Q_i, F_i, S_i, and W_i are given in Table 2. The binary interaction parameters E_{ij}, U_{ij}, K_{ij}, and G_{ij} are given in Table 3.

The integration of Eq. (1) with the pressure taken from Eq. (2) results in the original formulation expressed in terms of the Helmholtz energy,

$$\frac{a^r}{RT} = B\rho - D \sum_{n=13}^{18} C_n^* T^{-u_n} + \sum_{n=13}^{58} C_n^* T^{-u_n} D^{b_n} \exp\left(-c_n D^{k_n} \right),$$ (12)

where the superscript r indicates a residual property, or the contribution from the interaction of molecules in a nonideal gas. The equations used for calculating compressibility factor, pressure, and the derivatives of pressure with respect to density and temperature are given below.

$$Z = \frac{p}{\rho RT}$$ (13)

$$p = \rho^2 \left(\frac{\partial a}{\partial \rho} \right)_T = \rho RT + \rho^2 \left(\frac{\partial a^r}{\partial \rho} \right)_T$$ (14)

$$\left(\frac{\partial p}{\partial \rho} \right)_T = RT + 2\rho \left(\frac{\partial a^r}{\partial \rho} \right)_T + \rho^2 \left(\frac{\partial^2 a^r}{\partial \rho^2} \right)_T$$ (15)

$$\left(\frac{\partial^2 p}{\partial \rho^2} \right)_T = 2 \left(\frac{\partial a^r}{\partial \rho} \right)_T + 4\rho \left(\frac{\partial^2 a^r}{\partial \rho^2} \right)_T + \rho^2 \left(\frac{\partial^3 a^r}{\partial \rho^3} \right)_T$$ (16)

$$\left(\frac{\partial p}{\partial T} \right)_\rho = \rho R + \rho^2 \left(\frac{\partial^2 a^r}{\partial \rho \partial T} \right)$$ (17)

Speed of Sound and Other Thermodynamic Properties

The Helmholtz energy can be separated into two parts accounting for the ideal gas (superscript 0) and the real fluid (superscript r),

$$a = a^0 + a^r .$$ (18)

The real gas contribution a^r is given in Eq. (12), which is fundamentally part of AGA8. The contribution to the ideal gas is commonly expressed as a summation involving the ideal gas enthalpy (h^0) and entropy (s^0),

$$a^0 = h^0 - RT - Ts^0 .$$

(19)

If an expression for the ideal gas heat capacity is available, the ideal gas enthalpy can be derived from the relation

$$c_p = \left(\frac{\partial h}{\partial T} \right)_p ,$$

(20)

resulting in

$$h^0 = \int_0^T c_p^0 dT ,$$

(21)

where c_p^0 is the ideal gas heat capacity and the enthalpy at zero temperature is assumed to be zero. Likewise, the ideal gas entropy can be derived from the fundamental relation given by

$$Tds = du + pdv - \sum_{i=1}^{N} \mu_i dN_i ,$$

(22)

resulting in

$$s^0 = s_0^0 + \int_{T_0}^{T} \frac{c_p^0}{T} dT - R\ln\left(\frac{T\rho}{T_0\rho_0} \right) - R\sum_{i=1}^{N} x_i \ln(x_i),$$

(23)

where ρ_0 is the ideal gas density at T_0 and p_0 ($\rho_0 = p_0/T_0R$), and T_0 and p_0 are arbitrary constants. Because of the divergence of $\ln(T)$ at zero temperature, reference states of $T_0 = 1$ K and $p_0 = 101.325$ kPa can be used in Eq. (23). The molar gas constant, R, is 8.31451 J/(mol·K) (as given in AGA Report No. 8). The last part of this term, summed over the number of components N in the mixture, accounts for the entropy of mixing of ideal gas components. Combining these equations results in the following practical expression for the Helmholtz energy of the ideal gas,

$$a^0 = \int_0^T c_p^0 dT - RT - Ts_0^0 - T\int_{T_0}^{T} \frac{c_p^0}{T} dT + RT\ln\left(\frac{\rho T}{\rho_0 T_0} \right) + RT\sum_{i=1}^{N} x_i \ln(x_i).$$

(24)

Expressions for the ideal gas heat capacity, c_p^0, were taken from Aly and Lee (1981) and the thesis of McFall (1984) identical to that done in AGA Report No. 10,

$$c_p^0 = \sum_{i=1}^{N} x_i \left\{ B_i + C_i \left[\frac{D_i/T}{\sinh(D_i/T)} \right]^2 + E_i \left[\frac{F_i/T}{\cosh(F_i/T)} \right]^2 \right.$$
$$\left. + G_i \left[\frac{H_i/T}{\sinh(H_i/T)} \right]^2 + I_i \left[\frac{J_i/T}{\cosh(J_i/T)} \right]^2 \right\}.$$

(25)

The coefficients are given in Table 4. The integration of the ideal gas heat capacity required in Eq. (24) results in the following:

$$\int_0^T c_p^0 dT = \sum_{i=1}^{N} x_i \left\{ A_i + B_i T + C_i D_i \coth(D_i/T) - E_i F_i \tanh(F_i/T) \right.$$
$$\left. + G_i H_i \coth(H_i/T) - I_i J_i \tanh(J_i/T) \right\}$$

(26)

$$\int_{T_0}^{T} \frac{c_p^0}{T} dT = \sum_{i=1}^{N} x_i \left\{ K_i + B_i \ln(T) + C_i \left[\frac{D_i}{T} \coth \frac{D_i}{T} - \ln\left(\sinh \frac{D_i}{T} \right) \right] \right.$$
$$- E_i \left[\frac{F_i}{T} \tanh \frac{F_i}{T} - \ln\left(\cosh \frac{F_i}{T} \right) \right] + G_i \left[\frac{H_i}{T} \coth \frac{H_i}{T} - \ln\left(\sinh \frac{H_i}{T} \right) \right]$$
$$\left. - I_i \left[\frac{J_i}{T} \tanh \frac{J_i}{T} - \ln\left(\cosh \frac{J_i}{T} \right) \right] \right\}$$

(27)

where A_i and K_i are integration constants, with K_i including s_0^0 in Eq. (23). The resulting equation for the ideal gas Helmholtz energy is then

$$\frac{a^0}{RT} = -1 + \ln\frac{\rho RT}{p_0} + \frac{1}{R} \sum_{i=1}^{N} x_i \left\{ \frac{A_i}{T} - K_i + B_i - B_i \ln(T) + C_i \ln\left(\sinh \frac{D_i}{T} \right) \right.$$
$$\left. - E_i \ln\left(\cosh \frac{F_i}{T} \right) + G_i \ln\left(\sinh \frac{H_i}{T} \right) - I_i \ln\left(\cosh \frac{J_i}{T} \right) \right\} + \sum_{i=1}^{N} x_i \ln(x_i)$$

(28)

with p_0 equal to 101.325 kPa. The equations for calculating entropy (s), energy (u), enthalpy (h), Gibbs energy (g), isochoric heat capacity (c_v), isobaric heat capacity (c_p), and the speed of sound (w) are given below, where M_r is the molar mass of the mixture. Additional equations for other properties and alternative methods for expressing Helmholtz energy equations are given in Lemmon *et al.* (2000).

$$s = -\left(\frac{\partial a}{\partial T} \right)_\rho$$

(29)

$$u = a + Ts$$

(30)

$$h = u + \frac{p}{\rho}$$

(31)

$$g = a + \frac{p}{\rho} \tag{32}$$

$$c_v = \left(\frac{\partial u}{\partial T}\right)_\rho = T\left(\frac{\partial s}{\partial T}\right)_\rho = -T\left(\frac{\partial^2 a}{\partial T^2}\right)_\rho \tag{33}$$

$$c_p = c_v + \frac{T}{\rho^2}\left(\frac{\partial p}{\partial T}\right)_\rho^2\left(\frac{\partial \rho}{\partial p}\right)_T = c_v + R\frac{\left[1 + \dfrac{\rho}{R}\left(\dfrac{\partial^2 a^r}{\partial \rho \partial T}\right)\right]^2}{\left[1 + \dfrac{2\rho}{RT}\left(\dfrac{\partial a^r}{\partial \rho}\right)_T + \dfrac{\rho^2}{RT}\left(\dfrac{\partial^2 a^r}{\partial \rho^2}\right)_T\right]} \tag{34}$$

$$w^2 = \frac{c_p}{M_r c_v}\left(\frac{\partial p}{\partial \rho}\right)_T = \frac{c_p}{M_r c_v}\left[RT + 2\rho\left(\frac{\partial a^r}{\partial \rho}\right)_T + \rho^2\left(\frac{\partial^2 a^r}{\partial \rho^2}\right)_T\right] \tag{35}$$

The derivatives of the Helmholtz energy required in these equations are:

$$
\begin{aligned}
\frac{\partial a^0}{\partial T} = {}& R\ln\left(\frac{\rho RT}{p_0}\right) - \sum_{i=1}^{N} x_i\left\{B_i\ln(T) + K_i + C_i\left[\frac{D_i}{T}\coth\frac{D_i}{T} - \ln\left(\sinh\frac{D_i}{T}\right)\right]\right.\\
& - E_i\left[\frac{F_i}{T}\tanh\frac{F_i}{T} - \ln\left(\cosh\frac{F_i}{T}\right)\right] + G_i\left[\frac{H_i}{T}\coth\frac{H_i}{T} - \ln\left(\sinh\frac{H_i}{T}\right)\right]\\
& \left. - I_i\left[\frac{J_i}{T}\tanh\frac{J_i}{T} - \ln\left(\cosh\frac{J_i}{T}\right)\right]\right\} + R\sum_{i=1}^{N} x_i\ln(x_i)
\end{aligned}
\tag{36}
$$

$$
\begin{aligned}
T\frac{\partial^2 a^0}{\partial T^2} = {}& R - \sum_{i=1}^{N} x_i\left\{B_i + C_i\left[\frac{D_i/T}{\sinh(D_i/T)}\right]^2 + E_i\left[\frac{F_i/T}{\cosh(F_i/T)}\right]^2\right.\\
& \left. + G_i\left[\frac{H_i/T}{\sinh(H_i/T)}\right]^2 + I_i\left[\frac{J_i/T}{\cosh(J_i/T)}\right]^2\right\}
\end{aligned}
\tag{37}
$$

$$\frac{\rho}{RT}\frac{\partial a^r}{\partial \rho} = B\rho - D\sum_{n=13}^{18} C_n^* T^{-u_n} + \sum_{n=13}^{58} C_n^* T^{-u_n} D^{b_n}\exp\left(-c_n D^{k_n}\right)\left[b_n - c_n k_n D^{k_n}\right] \tag{38}$$

$$\frac{\rho^2}{RT}\frac{\partial^2 a^r}{\partial \rho^2} = \sum_{n=13}^{58} C_n^* T^{-u_n} D^{b_n}\exp\left(-c_n D^{k_n}\right)\left[\left(b_n - c_n k_n D^{k_n}\right)\left(b_n - 1 - c_n k_n D^{k_n}\right) - c_n k_n^2 D^{k_n}\right] \tag{39}$$

$$
\begin{aligned}
\frac{\rho^3}{RT}\frac{\partial^3 a^r}{\partial \rho^3} = {}& \sum_{n=13}^{58} C_n^* T^{-u_n} D^{b_n}\exp\left(-c_n D^{k_n}\right)\left\{b_n(b_n - 1)(b_n - 2)\right.\\
& + c_n D^{k_n}\left[-2k_n + 6b_n k_n - 3b_n^2 k_n - 3b_n k_n^2 + 3k_n^2 - k_n^3\right]\\
& \left. + \left(c_n D^{k_n}\right)^2\left[3b_n k_n^2 - 3k_n^2 + 3k_n^3\right] - \left(c_n k_n D^{k_n}\right)^3\right\}
\end{aligned}
\tag{40}
$$

$$\frac{1}{R}\frac{\partial a^r}{\partial T} = B\rho + \rho T\frac{\partial B}{\partial T} + (u_n - 1)D\sum_{n=13}^{18}C_n^*T^{-u_n} - (u_n - 1)\sum_{n=13}^{58}C_n^*T^{-u_n}D^{b_n}\exp(-c_nD^{k_n}) \tag{41}$$

$$\frac{1}{R}\frac{\partial^2 a^r}{\partial T^2} = 2\rho\frac{\partial B}{\partial T} + \rho T\frac{\partial^2 B}{\partial T^2} - u_n(u_n - 1)D\sum_{n=13}^{18}C_n^*T^{-u_n-1}$$
$$+ u_n(u_n - 1)\sum_{n=13}^{58}C_n^*T^{-u_n-1}D^{b_n}\exp(-c_nD^{k_n}) \tag{42}$$

$$\frac{\rho}{R}\frac{\partial^2 a^r}{\partial\rho\partial T} = B\rho + \rho T\frac{\partial B}{\partial T} + (u_n - 1)D\sum_{n=13}^{18}C_n^*T^{-u_n}$$
$$- (u_n - 1)\sum_{n=13}^{58}C_n^*T^{-u_n}D^{b_n}\exp(-c_nD^{k_n})[b_n - c_nk_nD^{k_n}] \tag{43}$$

$$\frac{\partial B}{\partial T} = \sum_{n=1}^{18} -u_na_nT^{-u_n-1}B^* \tag{44}$$

$$\frac{\partial^2 B}{\partial T^2} = \sum_{n=1}^{18}u_n(u_n + 1)a_nT^{-u_n-2}B^* \tag{45}$$

Uncertainties in calculated values of the speed of sound are outlined in AGA Report No. 10 (Peterson, 2003) by comparing calculated values to experimental measurements available in NIST Monograph 178 (Younglove *et al.*, 1993). Comparisons of calculated values with experimental data between 250 and 350 K with pressures to 12 MPa for 17 gravimetrically prepared mixtures showed that the uncertainty in the AGA8 equation was within 0.1% in the speed of sound for the specified blends.

Conclusions

Starting with the AGA Report No. 8 Detail Characterization Method equation in its original Helmholtz energy form, the equations presented here show that other thermodynamic properties such as heat capacities, enthalpies, entropies, and sound speeds can be obtained by differentiation of the Helmholtz energy equation. This methodology avoids the necessity of numerical integration, which is used in AGA Report No. 10. The method described here may lead to fewer complications in calculating the derived properties. Both methods require a numerical technique to calculate the density for a fixed temperature and pressure and the details of the density calculation technique used are given in AGA8.

Without compromising accuracy and traceability, the highest design priority for AGA Report No. 10 was compatibility with existing implementations of Report No. 8. The resulting solution method extends rather than replaces AGA8, minimizing cost and effort for natural gas industry users. AGA10 acknowledges the fact that other solution methods are possible by specifying calculation compliance targets, rather than design targets.

Although calculations of dew and bubble point properties are not possible with the AGA8 equation, existing models are being updated which have similar accuracies to those reported in AGA8, but are capable of liquid phase calculations, including near the critical point. The original model was reported for light natural gases by Lemmon and Jacobsen (1999) and is currently being modified to include heavier hydrocarbons as well as the components hydrogen sulfide, carbon monoxide, hydrogen, and

helium. Future work will include water as well. Parts of the original model are available as a computer database and is distributed by NIST (Lemmon *et al.*, 2002) and work is ongoing to improve the model. In the next release of the database, we anticipate the inclusion of the AGA8 equation as an option, with calculations of the dew and bubble points coming from the full mixture model described by Lemmon and Jacobsen. Additionally, in situations where it is not required to use AGA8 for thermodynamic property calculations, use of the new models for all computations will ensure consistency across the full spectrum of state conditions, including phase equilibrium, along with the capability to add additional fluids that are not available in AGA8.

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Table 1. Equation of State Coefficients and Exponents

n	a_n	b_n	c_n	k_n	u_n	g_n	q_n	f_n	s_n	w_n
1	0.1538326	1	0	0	0.	0	0	0	0	0
2	1.341953	1	0	0	0.5	0	0	0	0	0
3	-2.998583	1	0	0	1.	0	0	0	0	0
4	-0.04831228	1	0	0	3.5	0	0	0	0	0
5	0.3757965	1	0	0	-0.5	1	0	0	0	0
6	-1.589575	1	0	0	4.5	1	0	0	0	0
7	-0.05358847	1	0	0	0.5	0	1	0	0	0
8	0.88659463	1	0	0	7.5	0	0	0	1	0
9	-0.71023704	1	0	0	9.5	0	0	0	1	0
10	-1.471722	1	0	0	6.	0	0	0	0	1
11	1.32185035	1	0	0	12.	0	0	0	0	1
12	-0.78665925	1	0	0	12.5	0	0	0	0	1
13	2.29129d-9	1	1	3	-6.	0	0	1	0	0
14	0.1576724	1	1	2	2.	0	0	0	0	0
15	-0.4363864	1	1	2	3.	0	0	0	0	0
16	-0.04408159	1	1	2	2.	0	1	0	0	0
17	-0.003433888	1	1	4	2.	0	0	0	0	0
18	0.03205905	1	1	4	11.	0	0	0	0	0
19	0.02487355	2	0	0	-0.5	0	0	0	0	0
20	0.07332279	2	0	0	0.5	0	0	0	0	0
21	-0.001600573	2	1	2	0.	0	0	0	0	0
22	0.6424706	2	1	2	4.	0	0	0	0	0
23	-0.4162601	2	1	2	6.	0	0	0	0	0
24	-0.06689957	2	1	4	21.	0	0	0	0	0
25	0.2791795	2	1	4	23.	1	0	0	0	0
26	-0.6966051	2	1	4	22.	0	1	0	0	0
27	-0.002860589	2	1	4	-1.	0	0	1	0	0
28	-0.008098836	3	0	0	-0.5	0	1	0	0	0
29	3.150547	3	1	1	7.	1	0	0	0	0
30	0.007224479	3	1	1	-1.	0	0	1	0	0
31	-0.7057529	3	1	2	6.	0	0	0	0	0
32	0.5349792	3	1	2	4.	1	0	0	0	0
33	-0.07931491	3	1	3	1.	1	0	0	0	0
34	-1.418465	3	1	3	9.	1	0	0	0	0
35	-5.99905d-17	3	1	4	-13.	0	0	1	0	0
36	0.1058402	3	1	4	21.	0	0	0	0	0
37	0.03431729	3	1	4	8.	0	1	0	0	0
38	-0.007022847	4	0	0	-0.5	0	0	0	0	0
39	0.02495587	4	0	0	0.	0	0	0	0	0
40	0.04296818	4	1	2	2.	0	0	0	0	0
41	0.7465453	4	1	2	7.	0	0	0	0	0
42	-0.2919613	4	1	2	9.	0	1	0	0	0
43	7.294616	4	1	4	22.	0	0	0	0	0
44	-9.936757	4	1	4	23.	0	0	0	0	0
45	-0.005399808	5	0	0	1.	0	0	0	0	0
46	-0.2432567	5	1	2	9.	0	0	0	0	0
47	0.04987016	5	1	2	3.	0	1	0	0	0
48	0.003733797	5	1	4	8.	0	0	0	0	0
49	1.874951	5	1	4	23.	0	1	0	0	0
50	0.002168144	6	0	0	1.5	0	0	0	0	0
51	-0.6587164	6	1	2	5.	1	0	0	0	0

Table 1. Equation of State Coefficients and Exponents (continued)

n	a_n	b_n	c_n	k_n	u_n	g_n	q_n	f_n	s_n	w_n
52	0.000205518	7	0	0	-0.5	0	1	0	0	0
53	0.009776195	7	1	2	4.	0	0	0	0	0
54	-0.02048708	8	1	1	7.	1	0	0	0	0
55	0.01557322	8	1	2	3.	0	0	0	0	0
56	0.006862415	8	1	2	0.	1	0	0	0	0
57	-0.001226752	9	1	2	1.	0	0	0	0	0
58	0.002850908	9	1	2	0.	0	1	0	0	0

Table 2. Characterization Parameters

Component	M_r (g/mol)	E_i (K)	K_i $(dm^3/mol)^{1/3}$	G_i	Q_i	F_i	S_i	W_i
Methane	16.043	151.3183	0.4619255	0.	0.	0.	0.	0.
Nitrogen	28.0135	99.73778	0.4479153	0.027815	0.	0.	0.	0.
Carbon Dioxide	44.01	241.9606	0.4557489	0.189065	0.69	0.	0.	0.
Ethane	30.07	244.1667	0.5279209	0.0793	0.	0.	0.	0.
Propane	44.097	298.1183	0.583749	0.141239	0.	0.	0.	0.
Water	18.0153	514.0156	0.3825868	0.3325	1.06775	0.	1.5822	1.
Hydrogen Sulfide	34.082	296.355	0.4618263	0.0885	0.633276	0.	0.39	0.
Hydrogen	2.0159	26.95794	0.3514916	0.034369	0.	1.	0.	0.
Carbon Monoxide	28.01	105.5348	0.4533894	0.038953	0.	0.	0.	0.
Oxygen	31.9988	122.7667	0.4186954	0.021	0.	0.	0.	0.
Isobutane	58.123	324.0689	0.6406937	0.256692	0.	0.	0.	0.
n-Butane	58.123	337.6389	0.6341423	0.281835	0.	0.	0.	0.
Isopentane	72.15	365.5999	0.6738577	0.332267	0.	0.	0.	0.
n-Pentane	72.15	370.6823	0.6798307	0.366911	0.	0.	0.	0.
n-Hexane	86.177	402.636293	0.7175118	0.289731	0.	0.	0.	0.
n-Heptane	100.204	427.72263	0.7525189	0.337542	0.	0.	0.	0.
n-Octane	114.231	450.325022	0.784955	0.383381	0.	0.	0.	0.
n-Nonane	128.258	470.840891	0.8152731	0.427354	0.	0.	0.	0.
n-Decane	142.285	489.558373	0.8437826	0.469659	0.	0.	0.	0.
Helium	4.0026	2.610111	0.3589888	0.	0.	0.	0.	0.
Argon	39.948	119.6299	0.4216551	0.	0.	0.	0.	0.

Table 3. Binary Interaction Parameters[a]

	Methane	Nitrogen	CO_2	Ethane	H_2S
K_{ij}					
Nitrogen	1.00363				
Carbon Dioxide	0.995933	0.982361			
Ethane		1.00796	1.00851		
Propane	1.007619			0.986893	
Hydrogen Sulfide	1.00008	0.942596	1.00779	0.999969	
Hydrogen	1.02326	1.03227		1.02034	
n-Butane	0.997596				
n-Pentane	1.002529				
n-Hexane	0.982962		0.910183		0.96813
n-Heptane	0.983565		0.895362		0.96287
n-Octane	0.982707		0.881152		0.957828
n-Nonane	0.981849		0.86752		0.952441
n-Decane	0.980991		0.854406		0.948338

Table 3. Binary Interaction Parameters (continued)

	Methane	Nitrogen	CO$_2$	Ethane	Propane	H$_2$S	Hydrogen
E_{ij}							
Nitrogen	0.97164						
Carbon Dioxide	0.960644	1.02274					
Ethane		0.97012	0.925053				
Propane	0.994635	0.945939	0.960237	1.02256			
Water	0.708218	0.746954	0.849408	0.693168			
Hydrogen Sulfide	0.931484	0.902271	0.955052	0.946871			
Hydrogen	1.17052	1.08632	1.28179	1.16446	1.034787		
Carbon Monoxide	0.990126	1.00571	1.5				1.1
Oxygen		1.021					
Isobutane	1.01953	0.946914	0.906849				1.3
n-Butane	0.989844	0.973384	0.897362	1.01306	1.0049		1.3
Isopentane	1.00235	0.95934	0.726255				
n-Pentane	0.999268	0.94552	0.859764	1.00532			
n-Hexane	1.107274		0.855134			1.008692	
n-Heptane	0.88088		0.831229			1.010126	
n-Octane	0.880973		0.80831			1.011501	
n-Nonane	0.881067		0.786323			1.012821	
n-Decane	0.881161		0.765171			1.014089	
U_{ij}							
Nitrogen	0.886106						
Carbon Dioxide	0.963827	0.835058					
Ethane		0.816431	0.96987				
Propane	0.990877	0.915502		1.065173			
Hydrogen Sulfide	0.736833	0.993476	1.04529	0.971926			
Hydrogen	1.15639	0.408838		1.61666			
Carbon Monoxide			0.9				
Isobutane				1.25			
n-Butane	0.992291	0.993556		1.25			
Isopentane				1.25			
n-Pentane	1.00367			1.25			
n-Hexane	1.302576		1.066638			1.028973	
n-Heptane	1.191904		1.077634			1.033754	
n-Octane	1.205769		1.088178			1.038338	
n-Nonane	1.219634		1.098291			1.042735	
n-Decane	1.233498		1.108021			1.046966	
G_{ij}							
Carbon Dioxide	0.807653	0.982746					
Ethane			0.370296				
Water			1.67309				
Hydrogen	1.95731						

[a]The binary interaction parameters for all binary pairs are 1 except for those listed above.

Table 4. Coefficients and Exponents of the Ideal Gas Heat Capacity Equations[a]

Component	A_i (cal/mol)	B_i (cal/mol-K)	C_i (cal/mol-K)	D_i (K)	E_i (cal/mol-K)	F_i (K)	G_i (cal/mol-K)	H_i (K)	I_i (cal/mol-K)	J_i (K)	K_i (cal/mol-K)
Methane	-29776.4	7.95454	43.9417	1037.09	1.56373	813.205	-24.9027	1019.98	-10.1601	1070.14	-20.0615
Nitrogen	-3495.34	6.95587	0.272892	662.738	-0.291318	-680.562	1.7898	1740.06	0.	100.	4.49823
CO_2	20.7307	6.96237	2.68645	500.371	-2.56429	-530.443	3.91921	500.198	2.1329	2197.22	5.81381
Ethane	-37524.4	7.98139	24.3668	752.32	3.5399	272.846	8.44724	1020.13	-13.2732	869.51	-22.401
Propane	-56072.1	8.14319	37.0629	735.402	9.38159	247.19	13.4556	1454.78	-11.7342	984.518	-24.0426
Water	-13773.1	7.97183	6.27078	2572.63	2.0501	1156.72	0.	100.	0.	100.	-3.24989
H_2S	-10085.4	7.9468	-0.0838	433.801	2.85539	843.792	6.31595	1481.43	-2.88457	1102.23	-0.51551
Hydrogen	-5565.6	6.66789	2.33458	2584.98	0.749019	559.656	0.	100.	0.	100.	-7.94821
CO	-2753.49	6.95854	2.02441	1541.22	0.096774	3674.81	0.	100.	0.	100.	6.23387
Oxygen	-3497.45	6.96302	2.40013	2522.05	2.21752	1154.15	0.	100.	0.	100.	9.19749
Isobutane	-72387.	17.8143	58.2062	1787.39	40.7621	808.645	0.	100.	0.	100.	-44.1341
n-Butane	-72674.8	18.6383	57.4178	1792.73	38.6599	814.151	0.	100.	0.	100.	-46.1938
Isopentane	-91505.5	21.3861	74.341	1701.58	47.0587	775.899	0.	100.	0.	100.	-60.2474
n-Pentane	-83845.2	22.5012	69.5789	1719.58	46.2164	802.174	0.	100.	0.	100.	-62.2197
n-Hexane	-94982.5	26.6225	80.3819	1718.49	55.6598	802.069	0.	100.	0.	100.	-77.5366
n-Heptane	-103353.	30.4029	90.6941	1669.32	63.2028	786.001	0.	100.	0.	100.	-92.0164
n-Octane	-109674.	34.0847	100.253	1611.55	69.7675	768.847	0.	100.	0.	100.	-106.149
n-Nonane	-122599.	38.5014	111.446	1646.48	80.5015	781.588	0.	100.	0.	100.	-122.444
n-Decane	-133564.	42.7143	122.173	1654.85	90.2255	785.564	0.	100.	0.	100.	-138.006
Helium	0.	4.968	0.	100.	0.	100.	0.	100.	0.	100.	1.8198
Argon	0.	4.968	0.	100.	0.	100.	0.	100.	0.	100.	8.6776

[a]Units of calories are given to be consistent with the original work. Conversions to joules should use the multiplier: 1 cal = 4.184 J.