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Calculation of the Compressibility Factor of Natural Gases Based on the Calorific Value and the Specific Gravity[1]

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The measurement of large volume flows of natural gas in transmission lines requires an accurate equation of state for pressures up to about 12 MPa and in the temperature range from 265 to 335 K. If a detailed analysis of the gas mixture is available, one of the possibilities is to use the virial equation of state. However, such a gas analysis is time-consuming and expensive and, therefore, not always practical. We have developed a new equation which is based on the virial equation but requires limited input data. In general, for any given natural gas, the gross calorific value, the specific gravity, and the mole fractions of nitrogen and carbon dioxide are known. It will be shown that a knowledge of three of these four quantities is sufficient for an accurate prediction of the compressibility factor of the natural gas.

KEY WORDS: calorific value; compressibility factor; equation of state; natural gas; mixtures; specific gravity.

1. INTRODUCTION

The relation among the pressure, volume, and temperature of a system is of fundamental importance from both a theoretical and a practical point of view. Since the pioneering work of Van der Waals, numerous investigators have developed several equations of state based mainly on his ideas. In order to obtain better quantitative agreement with experiment, the number of adjustable parameters was increased. These equations can also be used

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for the description of the p–V–T–x behavior of mixtures, if suitable mixing and combining rules are applied. Generally speaking, however, a particular equation is applicable only for a certain class of systems in a limited temperature and pressure range.

In the natural gas industry, the measurement of large volume flows of gas requires an accurate knowledge of the compressibility factor in the temperature range from 265 to 335 K and pressures up to 12 MPa. Recently, a virial equation of state was developed at the Van der Waals Laboratory [1] to predict the compressibility factor of natural gases in this temperature and pressure range. The parameters were determined from data on pure and binary systems provided by the GERG (Groupe Européen de Recherche Gazière) and from open literature. The accuracy of the equation, which has been tested for 84 natural gases, is approximately 0.1%. Since an equation of state represents the effect of the mutual interactions between the molecules of the species composing the mixture, the detailed composition of the natural gas must, in principle, be known.

It is obvious that in many situations the composition of the natural gases is not always available; besides, it is both time-consuming and expensive to obtain a gas analysis. It would, therefore, be favorable to have an equation of state based on a restricted number of parameters which are directly available to the gas industry.

Such a simplified equation is presented in this paper. For the application of the equation, three of the four following quantities should be known:

the gross calorific value H_S,
the specific gravity d,
the mole fraction of nitrogen, and
the mole fraction of carbon dioxide.

If, for example, H_S, d, and the mole fraction of CO_2 are given, apart from the compressibility factor the mole fraction of N_2 is also calculated. It is possible to use the equation for hydrogen containing natural gases but in that case the mole fraction of hydrogen should also be given.

2. MODEL

The virial equation for a multicomponent mixture can be written as follows:

$$Z = \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \cdots \quad (1)$$

with the mixing rules

$$B = \sum_{i=1}^{n} \sum_{j=1}^{n} B_{ij} x_i x_j \tag{2}$$

$$C = \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{k=1}^{n} C_{ijk} x_i x_j x_k \tag{3}$$

where V is the molar volume of the system and n the number of components. B_{ij} and C_{ijk} are the contributions to the second and third virial coefficients from interactions among molecules indicated by the subscripts, respectively, and x_i is the mole fraction of component i in the mixture. In Ref. 1 it is assumed that the natural gases consist of 13 different components. A large amount of data concerning the volumetric behavior of pure gases and their binary mixtures had, therefore, to be taken into account for Eq. (2) and approximations to Eq. (3). It turned out that, up to 12MPa, sufficient accuracy could be obtained by the full equation if fourth and higher virial coefficients were omitted. For the development of the simplified equation, we make use of the results obtained for the full equation.

In the new approach we consider the natural gas as a three-component system consisting of nitrogen, carbon dioxide, and an "equivalent hydrocarbon," since only three input data are available. This equivalent hydrocarbon (abbreviated CH) represents all hydrocarbons present in the natural gas. Two of the components (N_2 and CO_2) are specified in the usual way. The three-component model is valid only if the data (gross calorific value, specific gravity) which specify the third component, i.e., the equivalent hydrocarbon, characterize the volumetric behavior of that component with sufficient accuracy. Since the application of Eqs. (1)–(3) requires a knowledge of the virial coefficients, we have to establish a relation between gross calorific value (or specific gravity) and the virial coefficients of the equivalent hydrocarbon.

It should first be pointed out that the gross calorific value H_S and the specific gravity d are primarily properties of the natural gas, not of the equivalent hydrocarbon. Therefore, a method has been developed to convert H_S and d to H_{CH} and M_{CH}, respectively. H_{CH} is defined as the molar heating value of the equivalent hydrocarbon and M_{CH} as its molar mass. This method is described later.

It is also worht mentioning that, although a particular natural gas is described as a three-component system, this third component is different for distinct natural gases. For example, two natural gases may have the same mole fractions of N_2, CO_2, and equivalent hydrocarbon but because of differences in the amounts of higher hydrocarbons present, the composition of the equivalent hydrocarbon may be different and therefore H_{CH}.

3. VIRIAL COEFFICIENTS FOR THE EQUIVALENT HYDROCARBON

Bronsted and Koefoed [2] developed the principle of congruence for a mixture of *n*-alkanes. According to this principle, the excess thermodynamic functions of a liquid mixture of *n*-alkanes depend only on the average chain length, which is defined as $\sum x_i n_i$ (x_i the mole fraction of the *i*th alkane and n_i the number of carbon atoms). Longuet-Higgins [3] proposed the following generalization: if two mixtures, both containing chain molecules, are such that these molecules can be divided into identical sets of fragments by cutting the chain in suitable places, than these mixtures will have identical equations of state and identical solvent properties.

Barker and Linton [4] applied this principle to gaseous mixtures and showed its usefulness for the calculation of the second virial coefficient B of mixed *n*-alkane vapors at high temperature. For an equimolar mixture of CH_4 and C_3H_8 the principle of congruence predicts that B is equal to that of C_2H_6. The same holds for a mixture of 75 mol %. CH_4 and 25 mol % $n-C_5H_{12}$. In Table I, B calculated from the data in Ref. 1 is given for C_2H_6 and the two mixtures. This table shows that the principle gives a good first approximation but is not accurate enough for the calculation of the compressibility factor of natural gases with an accuracy of about 0.1%. Another problem is that the average chain length is, in general, not an integer. Since this value is between 1 and 2 for a natural gas, a pure hydrocarbon with the same chain length is not available, and therefore, no values for the virial coefficients are available either. Interpolation between the pure hydrocarbons is not very accurate.

On the other hand, it is well known that the principle of congruence predicts the molar heating value (H) reasonably well. For example, for C_2H_6 $H = 1560.7\ \mathrm{kJ \cdot mol^{-1}}$, while for CH_4–C_3H_8 (50–50) $H = 1554.9\ \mathrm{kJ \cdot mol^{-1}}$, and for CH_4–C_5H_{12} (75–25) $H = 1551.9\ \mathrm{kJ \cdot mol^{-1}}$.

Table I. Second Virial Coefficients (in $cm^3 \cdot mol^{-1}$) for C_2H_6 and Mixtures of CH_4 with C_3H_8 and n-C_5H_{12}

	Temperature (°C)			
	0	20	40	60
C_2H_6	−221.8	−192.3	−167.3	−146.8
CH_4–C_3H_8 (50–50)	−209.6	−180.7	−156.3	−134.8
CH_4–n-C_5H_{12} (75–25)	−240.0	−199.5	−163.8	−132.0

The above results suggest a relation between the molar heating value and the virial coefficients. The examples given above show that this relation will probably not be very accurate if large amounts of higher hydrocarbons are mixed with CH_4. It appears, however, that for natural gases of pipeline quality the average chain length is restricted to the range 1–1.25 and the molar heating value H to $890\,\mathrm{kJ \cdot mol^{-1}} < H < 1030\,\mathrm{kJ \cdot mol^{-1}}$. In this limited range the principle may work out much better. Moreover, the mole fractions of the higher hydrocarbons are not arbitrary but are related to each other. The amount of C_4H_{10} is approximately one-third that of C_3H_8, the amount of C_5H_{12} roughly one-third that of C_4H_{10}, etc. [7]. These two aspects favor the applicability of a general relation between the heating value and the virial coefficients.

Here, we develop only the relation between the molar heating value of the equivalent hydrocarbon H_{CH} and the virial coefficients. The relation between the molecular weight M_{CH} and these coefficients is obtained along the same lines.

The second virial coefficient of the equivalent hydrocarbon in an arbitrary hydrocarbon mixture of known composition can be obtained from Eq. (2) using the data of Ref. 1. The molar heating value of the equivalent hydrocarbon, H_{CH}, can be calculated using the calorific values of the pure hydrocarbons taken from the literature [5]. In Fig. 1, the second virial coefficient is plotted as a function of H_{CH} for seven temperatures in the range from -5 to 60°C. The composition of the equivalent hydrocarbon is taken to be the same as in the 84 natural gases of the GERG file. Figure 2 shows the third virial coefficient for the same set of gases at the same temperatures. It turns out that in both cases the virial coefficient is a quadratic function of H_{CH} at constant temperature,

$$B_{CH}(T) = B_0(T) + B_1(T) H_{CH} + B_2(T) H_{CH}^2 \tag{4}$$

and

$$C_{CH}(T) = C_0(T) + C_1(T) H_{CH} + C_2(T) H_{CH}^2 \tag{5}$$

The temperature dependence of the coefficients can be described by

$$B_i(T) = B_{i0} + B_{i1} T + B_{i2} T^2, \qquad i = 0, 1, 2 \tag{6}$$

and

$$C_i(T) = C_{i0} + C_{i1} T + C_{i2} T^2, \qquad i = 0, 1, 2 \tag{7}$$

with T the temperature in K.

The values for B_{00}, ..., C_{22} are reported in the Appendix. It should be pointed out that no volumetric data of the natural gases have been used to

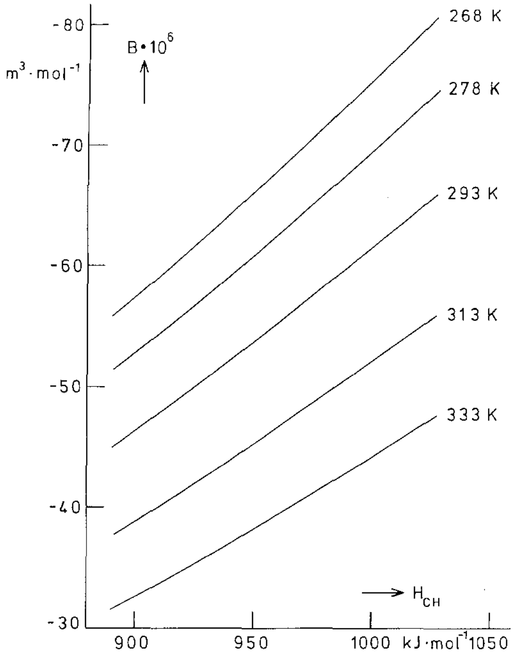

Fig. 1. The second virial coefficient of a hydrocarbon mixture as a function of calorific value at five different temperatures.

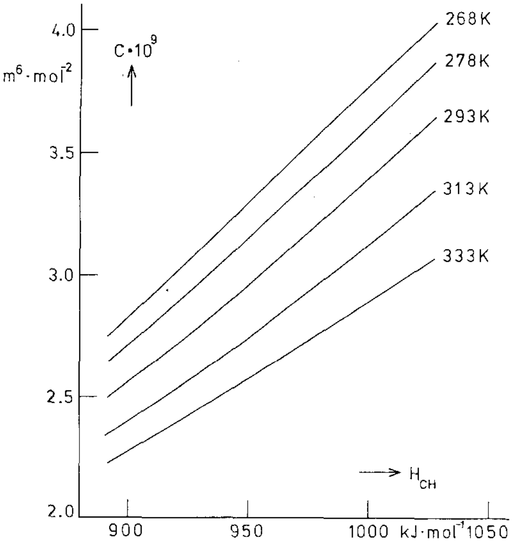

Fig. 2. The third virial coefficient of a hydrocarbon mixture as a function of calorific value at five different temperatures.

establish the relations (4) and (5). We have calculated these relations only for hydrocarbon mixtures of the same character as those present in natural gases.

4. UNLIKE INTERACTION VIRIAL COEFFICIENTS

The unlike interaction virial coefficients for the system N_2–CO_2 are already known from the full equation [1]. The unlike interaction coefficients between the equivalent hydrocarbon and both nitrogen and carbon dioxide have still to be determined. As usual, these coefficients depend upon temperature but in this case also on the composition of the hydrocarbon (or the molar heating value or the molecular weight). The coefficients can be calculated from the full equation and fitted with a power series in temperature and H_{CH}. This results in a complicated expression. Another approach is to write the second unlike interaction virial coefficient for CO_2–CH without loss of generality as

$$B_{\mathrm{CO_2,CH}} = \zeta_{\mathrm{CO_2,CH}}(B_{\mathrm{CO_2}} B_{\mathrm{CH}})^{1/2} \tag{8}$$

where ζ is an arbitrary function of T and composition. Even if $\zeta_{\mathrm{CO_2,CH}}$ is taken to be a constant, $B_{\mathrm{CO_2,CH}}$ is still dependent on temperature and composition via $B_{\mathrm{CO_2}}$ and B_{CH}. A comparison with the coefficients calculated from the full equation shows that the agreement is within experimental error with the following expression for ζ

$$\zeta_{\mathrm{CO_2,CH}} = -0.865 \tag{9}$$

Equation (9) has been tested for gases containing up to 9% ethane.

Since the second virial coefficient for nitrogen is small and changes sign in the temperature range under consideration, the coefficient for N_2–CH is expressed as

$$B_{\mathrm{N_2,CH}} = \zeta_{\mathrm{N_2,CH}} \frac{(B_{\mathrm{N_2}} + B_{\mathrm{CH}})}{2} \tag{10}$$

with

$$\zeta_{\mathrm{N_2,CH}} = 0.72 + 1.875 \times 10^{-5}(320 - T)^2 \tag{11}$$

One might have anticipated the simple expression (9) for ζ. The equivalent hydrocarbon consists mainly of CH_4 and C_2H_6 and if, e.g., Eq. (8) had been applied to $B_{\mathrm{CO_2,CH_4}}$ and $B_{\mathrm{CO_2,C_2H_6}}$, the resulting values for ζ would have been nearly independent of temperature and approximately equal for both systems.

The third unlike interaction virial coefficients can be described by

$$C_{iij} = \zeta_{iij}(C_{iii}^2 C_{jjj})^{1/3} \tag{12}$$

and

$$C_{ijj} = \zeta_{ijj}(C_{iii} C_{jjj}^2)^{1/3} \tag{13}$$

The unlike interaction coefficient of N_2 (or CO_2) with all the individual hydrocarbons can be calculated and summed up. Since it is not very clear which terms contribute to C_{iij} and which to C_{ijj}, we have assumed that $\zeta_{iij} = \zeta_{ijj}$. It can be shown that this is a good approximation for N_2–CH_4 and CO_2–CH_4. The result is

$$\zeta_{\mathrm{CH,CH,CO_2}} = \zeta_{\mathrm{CH,CO_2,CO_2}} = 0.92$$

and

$$\zeta_{\mathrm{CH,CH,N_2}} = \zeta_{\mathrm{CH,N_2,N_2}} = 0.92 + 0.0013(T - 270).$$

Finally, for the ternary interaction coefficient, we have taken

$$C_{\mathrm{CH,N_2,CO_2}} = 1.10(C_{\mathrm{CH}} C_{\mathrm{N_2}} C_{\mathrm{CO_2}})^{1/3}.$$

5. CALCULATION OF H_{CH} AND M_{CH} FROM THE INPUT DATA

It has been shown that the relevant data are the molar heating value H_{CH} and molar mass M_{CH}, not the gross calorific value H_{S} and specific gravity d. We now derive the relation between H_{CH}, M_{CH}, H_{S}, and d. Let us first assume that H_{S} and the mole fractions of N_2 and CO_2 are known. The grass calorific value is given in $\mathrm{kJ \cdot m^{-1}}$, while H_{CH} should preferably be obtained in $\mathrm{kJ \cdot mol^{-1}}$. The number of moles in $1\mathrm{m}^3$ gas at normal conditions (0°C and 1.01325 bar) is

$$n = \frac{1000}{22.413828 + B} \tag{14}$$

where 22.413828 is the ideal gas molar volume (in $\mathrm{m^3 \cdot kmol^{-1}}$) and B the second virial coefficient of the natural gas. Since the number of moles of CH is nx_{CH} (x_{CH} is the mole fraction of CH), the following equation can now be written:

$$H_{\mathrm{CH}} = \frac{H_{\mathrm{S}}(22.413828 + B)}{x_{\mathrm{CH}} 1000} \tag{15}$$

As a first estimate for B we take $B = -0.065\ \mathrm{m^3 \cdot kmol^{-1}}$. Equation (15) then gives a first approximation for H_{CH}. Substitution of this value in Eq. (4) results in a better value for B_{CH} and therefore for B, using Eq. (2) for the three-component system N_2, CO_2, and equivalent hydrocarbon. An accurate value for H_{CH} is obtained via an iteration procedure. The final value for H_{CH} is substituted in Eqs. (4) and (5). Using Eqs. (2), (3), and (1), the compressibility factor of the gas is calculated.

Since the most practical application of the model is probably in those cases where the gross calorific value H_S, the specific gravity d, and the mole fraction of CO_2 are known, a detailed elaboration for this situation is given.

The density ρ of the natural gas at normal conditions is

$$\rho = n \sum_{i=1}^{3} x_i M_i \tag{16}$$

where M_i is the molar mass of N_2, CO_2, or CH. Equation (16) contains three independent unknown quantities: n, x_{CH}, and M_{CH}. Two other equations are, therefore, needed. It can be shown easily that the following relation exists between M_{CH} and H_{CH}:

$$M_{CH} = -2.709328 + 0.0210622 H_{CH} \tag{17}$$

The mole fraction of CH is

$$x_{CH} = \frac{H_S}{n \cdot H_{CH}} \tag{18}$$

Since we have introduced another variable, H_{CH}, we need a fourth equation, Eq. (14). From Eqs. (14), (16), (17), and (18), n, x_{CH}, M_{CH}, and H_{CH} can be solved easily in the following way. As a first approximation $B = -0.065\ \mathrm{m^3 \cdot kmol^{-1}}$ and $H_{CH} = 970\ \mathrm{kJ \cdot mol^{-1}}$ are taken, which are both in the middle of the range of interest. Substitution of B in (14) and, subsequently, H_{CH} and n in (18) gives the mole fraction CH. The density at normal conditions is then calculated from (16) and compared with the experimental density given by $d\rho_{air}$ (where $\rho_{air} = 1.2929\ \mathrm{kg \cdot m^{-3}}$ is the density of air at normal conditions and d the specific gravity). If the calculated density is too low, H_{CH} is increased, and vice versa. The value for H_{CH} is adjusted using a convergence technique until the difference between calculated and experimental density is less than 10^{-5}. Subsequently, a more accurate value for B is calculated. The procedure is repeated until sufficient convergence is obtained for H_{CH} and x_{CH}. The compressibility factor can then be calculated using Eqs. (4), (5), (2), (3), and (1).

The procedure for the other combinations of the input data is similar to those described above. The method can also be used for hydrogen-containing gases if the mole fraction of H_2 is known. In this case the gross calorific value should be corrected for the hydrogen contribution.

6. COMPARISON BETWEEN EXPERIMENTAL AND PREDICTED RESULTS

The data bank of the GERG contains the experimental values for the compressibility factor of a large number of natural gases in the pressure and temperature range under investigation. These measurements were carried out mainly by Gasunie and Ruhrgas. Different types of gases are included in this data set: natural gases containing considerable amount of nitrogen, ethane, carbon dioxide, or hydrogen. The total number of experimental points is about 4,500. The relative percentage deviation between the calculated and the experimental compressibility factor is given by

$$\varepsilon_i = \frac{Z_{i,\text{calc.}} - Z_{i,\text{exp}}}{Z_{i,\text{exp}}} 100 \tag{19}$$

In Fig. 3, the number of experimental points in a given range of ε_i is plotted as a function of ε_i. The distribution shows a somewhat larger tail

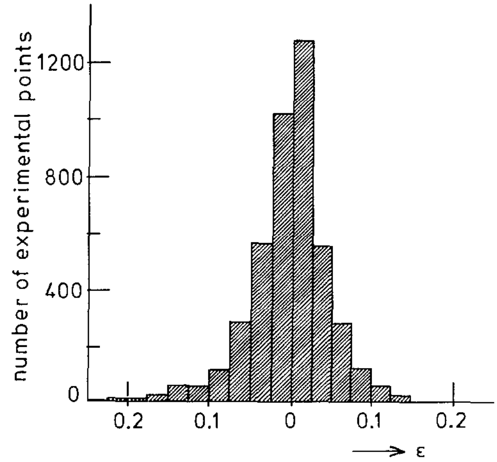

Fig. 3. The number of experimental points as a function of the relative percentage deviation between calculated and experimental compressibility factors for the data in the GERG data bank.

at the negative side. For less than 6% of the points, the deviation is more than 0.1%. The root mean square error (RMS) defined by

$$\mathrm{RMS} = \left[\frac{1}{N}\sum_{i=i}^{N}\left(\frac{Z_{i,\mathrm{calc}} - Z_{i,\mathrm{exp}}}{Z_{i,\mathrm{exp}}}\right)^2\right]^{1/2} \tag{20}$$

is well within 0.1% for all these data. Generally speaking, the deviations have the same tendency as for the full equation. The largest deviations occur mostly at low temperatures and pressures above 100 bar. A more elaborate comparison between experimental and calculated results is given in Ref. 6.

APPENDIX

Numerical values for the coefficients in Eqs. (6) and (7) are as follows.

$$B_0(T) = -0.425468 + 0.286500\ 10^{-2}T - 0.462073\ 10^{-5}T^2$$

$$B_1(T) = 0.877118\ 10^{-3} - 0.556281\ 10^{-5}T + 0.881510\ 10^{-8}T^2$$

$$B_2(T) = -0.824747\ 10^{-6} + 0.431436\ 10^{-8}T - 0.608319\ 10^{-11}T^2$$

and

$$C_0(T) = -0.302488 + 0.195861\ 10^{-2}T - 0.316302\ 10^{-5}T^2$$

$$C_1(T) = 0.646422\ 10^{-3} - 0.422876\ 10^{-5}T + 0.688157\ 10^{-8}T^2$$

$$C_2(T) = -0.332805\ 10^{-6} + 0.223160\ 10^{-8}T - 0.367713\ 10^{-11}T^2$$

The like and unlike virial coefficients for N_2 (component 2) and CO_2 (component 3) are the following:

$$B_{22} = -0.144600 + 0.740910\ 10^{-3}T - 0.911950\ 10^{-6}T^2\ \mathrm{m}^3 \cdot \mathrm{kmol}^{-1}$$

$$B_{33} = -0.868340 + 0.403760\ 10^{-2}T - 0.516570\ 10^{-5}T^2\ \mathrm{m}^3 \cdot \mathrm{kmol}^{-1}$$

$$B_{23} = -0.339693 + 0.161176\ 10^{-2}T - 0.204429\ 10^{-5}T^2\ \mathrm{m}^3 \cdot \mathrm{kmol}^{-1}$$

and

$$C_{222} = 0.784980\ 10^{-2} - 0.398950\ 10^{-4}T + 0.611870\ 10^{-7}T^2\ \mathrm{m}^6 \cdot \mathrm{kmol}^{-2}$$

$$C_{333} = 0.205130\ 10^{-2} + 0.348880\ 10^{-4}T - 0.837030\ 10^{-7}T^2\ \mathrm{m}^6 \cdot \mathrm{kmol}^{-2}$$

$$C_{223} = 0.552066\ 10^{-2} - 0.168609\ 10^{-4}T + 0.157169\ 10^{-7}T^2\ \mathrm{m}^6 \cdot \mathrm{kmol}^{-2}$$

$$C_{233} = 0.358783\ 10^{-2} + 0.806674\ 10^{-5}T - 0.325798\ 10^{-7}T^2\ \mathrm{m}^6 \cdot \mathrm{kmol}^{-2}$$

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REFERENCES

1. J. A. Schouten, J. P. J. Michels, and C. A. ten Seldam, An Equation of State for Natural Gases, GERG Report No. 8410 (Van der Waals laboratory, University of Amsterdam, Valckenierstr. 67, 1018 XE Amsterdam, The Netherlands, Oct. 1984); J. A. Schouten, J. P. J. Michels, and C. A. ten Seldam, Updating the GERG-Equation Based on Full Gas Analysis, GERG Report No. 8709 (Van der Waals laboratory, University of Amsterdam, Amsterdam, The Netherlands, Oct. 1987).
2. N. Bronsted and J. Koefoed, *Dan. Mat. Fys. Medd.* **XXII**:No. 17 (1946).
3. H. C. Longuet-Higgens, *Disc. Faraday Soc.* **15**:73 (1953).
4. J. A. Barker and M. Linton, *J. Chem. Phys.* **38**:1853 (1963).
5. A. E. Humphreys, GERG Technical Monograph No. TPC/1, International Gas Research Conference Toronto (British Gas Corporation, London Research Station, Michael Road, London SW6, U.K., 1986).
6. M. Jaeschke, S. Audibert, P. v. Caneghem, A. E. Humphreys, R. Janssen, Q. Pellei, J. A. Schouten, and J. P. J. Michels, Proceedings of the Gas Technology Symposium Dallas, Society of Petroleum Engineers (SPE), Inc. (1988).
7. This is valid for the 70 natural gases collected in the GERG data bank.