

HYDROCARBON MIXTURE EQUATIONS OF STATE AND THEIR IMPACT ON GAS FLOW MEASUREMENT

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SUMMARY

Discussion is presented summarizing recently developed equations of state for hydrocarbon mixtures for use in high accuracy gas flow measurements. The accuracies of these equations of state and the ranges of their application are summarized. The impact of these equations of state on gas flow measurement also is discussed. Special attention is given to the impact of the accuracy of calculated gas densities using these equations of state on flow measurement accuracy. Another topic discussed is the impact of these equations of state on electronic flow measurement, including the computation time and resultant impact on gas volume calculation frequency. Also, the calculation of sonic velocity for use with sonic provers and meters which require sonic velocity is discussed.

1 INTRODUCTION

1.1 Background

Cooperative worldwide research has been performed in recent years to improve the accuracy of flow measurement. This research has led to numerous developments, including more accurate hydrocarbon gas mixture equations of state. Two high accuracy equations of state, the SGERG-88 equation and the AGA8-92DC equation, have been selected for implementation as standards in gas flow measurement^(1,2). The AGA8-92DC equation of state uses the molar composition for characterization of a gas mixture. The SGERG-88 equation of state uses for the characterization of a gas mixture a simplified analysis comprising superior calorific value (volumetric basis), relative density, carbon dioxide content and (if non-zero) hydrogen content. It is anticipated that ISO 12213 will utilize both of these equations of state with these two specific characterization methods⁽²⁾. A.G.A. Report No. 8 utilizes these two equations of state with these two characterization methods and also utilizes the SGERG-88 equation with natural gas characterization comprising relative density, nitrogen content and carbon dioxide content⁽¹⁾.

1.2 Previous Methods

Since 1962, when A.G.A. Report NX-19 was published,⁽³⁾ the NX-19 method and variations of this method have been used extensively for natural gas compressibility in flow measurement. The 1985 A.G.A. Report No. 8 provided much greater accuracy than the NX-19 method.⁽⁴⁾ However, the 1985 API Manual of Petroleum Measurement Standards⁽⁵⁾ did not require the use of the 1985 A.G.A. Report No. 8 and so the NX-19 method has remained in extensive use. The 1992 API Manual of Petroleum Measurement Standards⁽⁶⁾ specifies the use of the 1992 A.G.A. Report No. 8 methods. In fact, Section 2 of Chapter 14 of API MPMS⁽⁷⁾ is equivalent to the 1992 A.G.A. Report No. 8. It should also be noted that Section 3 of Chapter 14 of the API MPMS⁽⁶⁾ and A.G.A. Report No. 3 are equivalent.

1.3 Equations of State

The equations of state in the 1992 A.G.A. Report No. 8 and anticipated in ISO 12213 can be represented in the form of Equation (1).

$$Z = 1 + Bd + Cd^2 + \text{higher order terms in } d$$

(1)

In Equation (1), Z is the compressibility factor, d is the molar density (moles per unit volume) and B and C are coefficients which are functions of absolute temperature and gas characteristics. The coefficients B and C commonly are referred to as the second and third virial coefficients, respectively. The SGERG-88 equation does not have terms of higher order than d^2 , while the AGA8-92DC equation has numerous higher order terms. In the AGA8-92DC equation, the coefficients B and C and all coefficients in the higher order terms are calculated from the gas composition and absolute temperature. In the SGERG-88 equation, the coefficients B and C are calculated from absolute temperature and the gas characterization information utilized, for example, superior calorific value, relative density, carbon dioxide content and (if non-zero) hydrogen content). Both the SGERG-88 equation and the AGA8-92DC equation represent experimental natural gas density data very accurately in the range of temperatures from 263K to 338K at pressures up to 12 MPa. The AGA8-92DC equation has a more complex form to allow its use at conditions beyond the above range, usually for purposes other than flow measurement.

2 IMPACTS ON FLOW MEASUREMENT

The implementation of ISO 12213 and A.G.A. Report No. 8 will have numerous technical and economic impacts on gas flow measurement. The improved accuracy of these new methods over the A.G.A. Report NX-19 method and other methods in current use justifies the cost of implementation. A number of specific technical impacts are discussed below.

2.1 Types of Gases

The SGERG-88 and AGA8-92DC equations of state used in the new standards can be utilized for flow measurement of pipeline quality natural gases in the range from 263K to 338K at pressures up to 12 MPa with essentially equivalent absolute uncertainties which average less than 0.1%. The average absolute uncertainty for pipeline quality natural gases increases outside of this range of conditions. Although not specifically intended for manufactured (synthetic) gases, the SGERG-88 and AGA8-92DC equations can both be used (with increased uncertainties) for these gases and admixtures of these gases with natural gases. The AGA8-92DC equation can be used for wet and/or sour gases and an extension of the AGA8-92DC equation can be used for extremely rich gases.

It is anticipated that ISO 12213 will specify the allowable limits on mole fractions of components given in Table 1 for the purposes of the ISO 12213 standard. For ISO 12213 calculations using the SGERG-88 method, the anticipated ranges are 30 to 45 MJ/m³ for superior calorific value and 0.55 to 0.80 for relative density. The 1992 A.G.A. Report No. 8 defines two ranges of gas composition, the "normal" range and the "expanded" range, both of which are shown in Table 2. Although the composition limits in Table 1 and in the "normal" range in Table 2 differ, both of these ranges encompass the range of natural gas composition commonly referred to as pipeline quality gas and both ranges have an average absolute uncertainty which is less than 0.1% for 263K to 338K up to 12 MPa. In A.G.A. Report No. 8, it is recommended that calculations in the "expanded" range be performed using the AGA8-92DC equation. It should be noted that although A.G.A. Report No. 8 does not present text information regarding the use of the SGERG-88 method for gases containing hydrogen and carbon monoxide, the computer program listing does allow this computation. Calculation uncertainties using the AGA8-92DC method in the expanded range are largest for natural gases containing high concentrations of hydrocarbons heavier than pentanes (hexanes plus). An extension of the AGA8-92DC method⁽¹⁰⁾ which is not part of A.G.A. Report No. 8 has been developed for calculations when the hexanes plus content exceeds 0.2 mole percent.

Table 1

Allowable Limits on Mole Fractions of Components Consistent with ISO 12213

Component	Mole Fraction
Main Components	
Methane	≥ 0.70
Nitrogen	≤ 0.20
Carbon Dioxide	≤ 0.20
Ethane	≤ 0.10
Propane	≤ 0.035
Butanes	≤ 0.015
Pentanes	≤ 0.005
Hexanes	≤ 0.001
Heptanes	≤ 0.0005
Octanes and above	≤ 0.0005
Hydrogen	≤ 0.10
Carbon Monoxide	≤ 0.03
Helium	≤ 0.005
Minor and Trace Component	
Ethylene	≤ 0.001
Benzene	≤ 0.0005
Toluene	≤ 0.0002
Water Vapor	≤ 0.0002
Hydrogen Sulfide	≤ 0.0002
Oxygen	≤ 0.0002
Total Unspecified Components	≤ 0.0001

Table 2

Ranges of Gas Mixture Characteristics
Consistent with A.G.A. Report No. 8

Quantity	Normal Range	Expanded Range
Relative Density	.56 to .87	0.07 to 1.52
Gross Heating Value*	477 to 1150 Btu/scf	0 to 1800 Btu/scf
Gross Heating Value**	18.7 to 45.1 MJ/m ³	0 to 66 MJ/m ³
Mole Percent Methane	45.0 to 100.0	0 to 100.0
Mole Percent Nitrogen	0 to 50.0	0 to 100.0
Mole Percent Carbon Dioxide	0 to 30.0	0 to 100.0
Mole Percent Ethane	0 to 10.0	0 to 100.0
Mole Percent Propane	0 to 4.0	0 to 10.0
Mole Percent Butanes	0 to 1.0	0 to 6.0
Mole Percent Pentanes	0 to 0.3	0 to 4.0
Mole Percent Hexanes Plus	0 to 0.2	0 to Dew Point
Mole Percent Helium	0 to 0.2	0 to 3.0
Mole Percent Hydrogen	#	0 to 100.0
Mole Percent Carbon Monoxide	#	0 to 3.0
Mole Percent Argon	#	0 to 1.0
Mole Percent Oxygen	#	0 to 21.0
Mole Percent Water	0 to 0.05	0 to Dew Point
Mole Percent Hydrogen Sulfide	0 to 0.02	0 to 100.0

* Reference conditions: Combustion at 60°F, 14.73 psia; density at 60°F, 14.73 psia.

** Reference conditions: Combustion at 25°C, 0.101325 MPa; density at 0°C, 0.101325 MPa.

The normal range is considered to be zero for these compounds.

It is obvious that the differences in the SGERG-88 method and the AGA8-92DC method create important impacts on gas flow measurement decisions because of the need for selecting the appropriate computation method based on gas mixture composition and operating conditions.

2.2 Accuracy

There is ample documentation on the impact on gas flow measurement accuracy due to improved gas compressibility accuracy. ISO 12213 and A.G.A. Report No. 8 both provide summaries of expected compressibility factor uncertainties and references for detailed evaluations^(1,2). Table 3 shows comparisons of deviations of calculated compressibility factors from experimental values for the NX-19 method, the SGERG-88 method and the AGA8-92DC method. The comparisons in Table 3 are from Gas Institute Report No. GRI-91/0184 by Starling, et al.⁽⁸⁾. The experimental data are from GERG Technical Monograph 4 by Jaeschke and Humphreys⁽⁹⁾. The gas groupings in Table 3 are designated as Lean Gases (methane content greater than 94 mole percent), Rich Gases (ethane content greater than 8 mole percent), High Nitrogen Gases (nitrogen content greater than 9.5 mole percent) and High Carbon Dioxide Gases (carbon dioxide content greater than 4 mole percent).

The relative deviation of the calculated compressibility factor at the i th data point, $Z_{i \text{ calc}}$ from the experimental value $Z_{i \text{ exp}}$ is $RDEV_i$

$$RDEV_i = \frac{(Z_{i \text{ calc}} - Z_{i \text{ exp}}) \times 100\%}{Z_{i \text{ exp}}} \quad (2)$$

The maximum value of $RDEV_i$ is the MaxDev and the average absolute deviation, AAD, for N data points is

$$AAD = \frac{1}{N} \sum_{i=1}^N [(RDEV_i)^2]^{1/2} \quad (3)$$

The range of conditions for the data in Table 3 is 263 to 338K at pressures up to 12 MPa. The NX-19 method has an AAD of 0.095% for lean gases and 0.130% for high nitrogen gases and thus is reasonably accurate for these gases. For high carbon dioxide gases, the NX-19 method AAD is 0.283% and the maximum deviation is -1.043%. For high ethane content rich natural gases, the NX-19 deviations are even larger, with an AAD of 0.585% and a maximum deviation of -2.057%. Thus, the NX-19 method is badly in error for high ethane rich natural gases and has fairly large errors for high carbon dioxide natural gases. On the other hand, for the conditions of Table 3, both the SGERG-88 method and the AGA8-92DC method have average absolute deviations which are less than 0.1% and maximum deviations which are less than $\pm 0.32\%$. Thus, for the ranges of gases and conditions in Table 3, the impact of the equation of state on flow measurement uncertainty should not exceed $\pm 0.32\%$ and for orifice meters should not exceed $\pm 0.16\%$.

2.3 Computation Complexity

The complexity of calculations using either ISO 12213 or A.G.A. Report No. 8 is much greater than the computation complexity of A.G.A. Report NX-19. The accuracy improvement of the new methods over the accuracy of A.G.A. Report NX-19 justifies this increased computational overhead, but requires use of a computer, while A.G.A. Report NX-19 calculations can be performed with hand-held calculators. The fact that the new calculation methods must be programmed is having a noticeable impact on the speed of implementation of A.G.A. Report No. 8 by the U.S. gas industry. Although efficient FORTRAN language algorithms are presented in A.G.A. Report No. 8, implementation has been relatively slow.

Table 3

Summary of Deviations of Calculated Natural Gas Compressibility Factors
from Experimental Data

Gas Group	No. of Natural Gases	No. of Points	Method	AAD%	MaxDev%
Lean Gases	8	448	NX-19	0.095	-0.615
			SGERG-88	0.022	-0.137
			AGA8-92DC	0.020	-0.136
Rich Gases	23	1278	NX-19	0.585	-2.057
			SGERG-88	0.037	-0.319
			AGA8-92DC	0.031	0.253
High Nitrogen Gases	13	625	NX-19	0.130	-0.452
			SGERG-88	0.039	-0.154
			AGA8-92DC	0.059	-0.198
High Carbon Dioxide Gases	8	477	NX-19	0.283	-1.043
			SGERG-88	0.035	0.148
			AGA8-92DC	0.033	0.163

Reasons for slow implementation are numerous. One reason is the fact that source code algorithms have not been published for the orifice discharge coefficient calculations required for implementation of the 1992 API MPMS, Chapter 14, Section 3 methods. Most U.S. companies have implemented A.G.A. Report No. 8 only as a part of the implementation of new orifice meter standards. Because the new calculation methods are much more complex than earlier standards, the effort and monetary costs involved have delayed implementations in some U.S. companies.

2.4 Accounting Systems

Regardless of the source of the basic flowrate data, i.e., chart data or electronic flow meter data, the capability for calculations and/or recalculations must be incorporated in the accounting system used. Software implementing the 1992 A.G.A. Report No. 8 calculations has been installed in numerous U.S. accounting systems, including mainframe, minicomputer and PC based systems. Few quantitative problems are encountered when care is taken to properly pass the data and calculation results across computation modules, whether the modules are subroutines, libraries of subroutines or dynamic link libraries (DLLs). Checks, of course, are needed for proper variable ranges and unreasonable variable values such as negative absolute pressure.

2.5 Electronic Flow Measurement

Electronic flow measurement (EFM) software must be efficient to allow for frequent flow calculations. The algorithms in the 1992 A.G.A. Report No. 8 were designed to minimize redundant calculations with the anticipation of EFM applications. The natural gas properties depend on three quantities, (1) gas composition, (2) temperature and (3) pressure. Quantities which depend on composition but not on temperature or pressure are calculated in one computation block (a group of subroutines). Quantities which depend on temperature but not pressure are calculated in a second computation block.

Quantities which depend on pressure are calculated in a third computation block. If between two successive EFM calculations the flowing pressure changes but the temperature and composition remain unchanged, then computations of composition dependent and temperature dependent quantities are not performed as these calculations would be redundant. Most EFM applications have utilized C-language for the source code algorithms; the FORTRAN language algorithms in A.G.A. Report No. 8 can of course be used for checking the C-language algorithms.

2.6 EFM Editing

The editing of flow measurement data, especially for final accounting and monthly billings, is a necessary activity regardless of whether the flow data is from charts or electronic flow meters. However, because of the large quantity of data entries associated with EFM data, it is not feasible to edit each individual entry from a computer keyboard. It is more efficient to upload the EFM data to a computer with resident EFM editing software, enter the edit information (e.g., change of orifice diameter from first to second part of month) and allow the many recalculations of flow for the edited period. This edit can be performed while retaining the original data for archival purposes and updating the event log for the meter, so that a complete audit trail is maintained. EFM editing software using dynamic link libraries (DLLs) for the new orifice discharge coefficient and gas density calculations have been developed for PC applications, making it feasible for EFM editing as part of field or office operations. Installations also have been implemented to send the EFM data from the meter to the EFM editing in a real-time mode using dynamic data exchange (DDE).

2.7 Applications Outside Pipeline Quality Range

Both the SGERG-88 method and the AGA8-92DC method can be used outside the pipeline quality range. For many applications there is a paucity of accurate experimental gas density data for determining the uncertainties of predicted densities. Nevertheless, for many applications, the AGA8-92DC method probably is as accurate as other available methods. An exception is rich natural gases with hexanes plus content greater than 0.2 mole percent. However, an extension of the AGA8-92DC method allows calculations up to the dew point concentration for rich gases⁽¹⁰⁾. The maximum hexanes plus concentration of the data utilized in developing the extension of AGA8-92DC is 9.8 mole percent.

2.7.1 Synthetic Gases

Both the SGERG-88 method and the AGA8-92DC method have been evaluated using experimental data⁽⁹⁾ for gas mixtures containing as much as 35 mole percent hydrogen. For thirteen natural gases with more than 2 mole percent hydrogen, the average absolute deviations are 0.021% for the SGERG-88 method and 0.027% for the AGA8-92DC method⁽⁸⁾. It is clear that these equations can be used for admixtures of natural gas and manufactured gas up to at least 10 mole percent hydrogen with high accuracy and beyond 10 mole percent hydrogen at reduced accuracy.

2.7.2 Wet Gases

The AGA8-92DC method has been evaluated using natural gas compressibility factor data⁽¹¹⁾ with a maximum water content of 10 mole percent. These data cover the range 348K to 483K for pressures up to 16 MPa. Compressibility factors calculated using the AGA8-92DC method have an average absolute deviation of less than 0.1% from the experimental values. Because of this excellent agreement and the fact that the experimental data range to such high water mole fractions, it is probable that the AGA8-92DC method remains accurate for water concentrations as high as the water dew point.

2.7.3 Sour Gases

Two data sources were utilized to evaluate the AGA8-92DC method for compressibility factors of natural gas containing hydrogen sulfide. For the compressibility factor data reported by Scheloske⁽¹¹⁾,

with up to 3.0 mole percent hydrogen sulfide, the average absolute deviation is less than 0.1%. For proprietary data for a sour natural gas with 26.4 mole percent hydrogen sulfide, the average absolute deviation is 0.6%, which is probably close to the uncertainty of the experimental data. Although these deviations are much larger than for pipeline quality natural gas, it is probable that the AGA8-92DC method yields the lowest uncertainties of available correlations for high hydrogen sulfide natural gas compressibility factors at the present time.

3 EXTENSION OF AGA8-92DC FOR RICH GASES

The maximum concentration of hexanes plus for the "normal" range in Table 2 is 0.2 mole percent. An extension of the AGA8-92DC method has been developed for hexanes plus concentrations as high as the hydrocarbon dew point⁽¹⁰⁾. This extension is not a part of A.G.A. Report No. 8 but can be used conveniently as an extension of the AGA8-92DC method for rich gases. The compressibility factor data used in developing this extension to the AGA8-92DC method includes data for mixtures containing as much as 9 mole percent hexanes plus⁽¹⁰⁾. Portions of the data are for gas condensate fluids at pressures above the upper dew point. The range of conditions for the data is 273K to 409K for pressures up to 94 MPa. The average absolute deviation of calculated compressibility factors from the experimental values is 1.15%. The experimental compressibility factors probably have uncertainties near $\pm 1\%$. Therefore, this extension of the AGA8-92DC method probably is about as accurate a correlation as is possible at present for gases with more than 0.2 mole percent hexanes plus.

4 SONIC VELOCITY

Sonic velocity calculations for use with sonic nozzle provers and flow meters which require the sonic velocity can be performed using the AGA8-92DC equation of state. Although experimental sonic velocity data were used in the development of the AGA8-92DC equation, calculated sonic velocities have greater uncertainties than calculated compressibility factors, especially near dew point conditions. This fact has an impact on the choice of operating conditions for sonic provers. For conditions well away from dew points, pipeline quality natural gas sonic velocities calculated using the AGA8-92DC method generally will have uncertainties of less than $\pm 0.2\%$ in the range 250K to 350K at pressures up to 7 MPa.

5 CONCLUSIONS

It is clear that implementations of ISO 12213 and A.G.A. Report No. 8 will have decided impacts on gas flow measurements. The fact that the SGERG-88 method and the AGA8-92DC method are significantly more accurate than the A.G.A. Report NX-19 method, especially for rich gases and high carbon dioxide gases, justifies the costs of implementing ISO 12213 and A.G.A. Report No. 8. The timing for this implementation is appropriate because of coincidence with major revisions in orifice discharge coefficient equations. The fact that computer computations are required for both orifice discharge coefficients and gas densities is no longer a deterrent to implementation in light of increased usage of computers in flow measurement.

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