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Standard for LNG Density Calculation Models¹

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INTRODUCTION

This standard is a description of four mathematical models of the equation of state for LNG-like mixtures that were adopted in 1988. The four models include an extended corresponding states model, a cell model, a hard sphere model, and a revised Klosek and McKinley model. Each of the models has been optimized to the same experimental data set which included data for pure nitrogen, methane, ethane, propane, iso and normal butane, iso and normal pentane, and mixtures thereof. For LNG-like mixtures (mixtures of the orthobaric liquid state at temperatures of 120K or less and containing at least 60 % methane, less than 4 % nitrogen, less than 4 % each of iso and normal butane, and less than 2 % total of iso and normal pentane), all of the models are estimated to predict densities to within 0.1 % of the true value. These models were developed by the National Institute of Standards and Technology (formerly the Bureau of Standards) upon culmination of seven years of effort in acquiring physical properties data, performing extensive experimental measurements using specially developed equipment, and in using these data to develop predictive models for use in density calculations.

1. Scope

1.1 This standard covers LNG density calculation models² for use in the calculation or prediction of the densities of saturated LNG mixtures from 90 to 120K to within 0.1 % of true values given the pressure, temperature, and composition of the mixture.

1.2 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Significance and Use

2.1 The models in this standard can be used to calculate the density of saturated liquid natural gas in the temperature range 90 to 120K. The estimated uncertainty for the density calculations is $\pm 0.1\%$. The restrictions on composition of the liquefied natural gas are:

methane	60 % or greater
nitrogen	less than 4 %
<i>n</i> -butane	less than 4 %
<i>i</i> -butane	less than 4 %
pentanes	less than 2 %

It is assumed that hydrocarbons with carbon numbers of six or greater are not present in the LNG solution.

3. Models

3.1 *Extended Corresponding States*—The extended corresponding states method is defined by the following equations:

$$Z[P,T] = Z_o[P h_{ii,o}/f_{ii,o}, T/f_{ii,o}] \quad (1)$$

$$G[P,T] = f_{ii,o} G_o[P h_{ii,o}/f_{ii,o}, T/f_{ii,o}] - RT \ln(h_{ii,o}) \quad (2)$$

where:

Z = compressibility factor,

G = Gibbs free energy,

P = pressure,

T = temperature,

o = reference fluid, and

i = fluid for which properties are to be obtained via the equation of state for the reference fluid and the transformation functions $f_{ii,o}$ and $h_{ii,o}$ are introduced to allow extension of the method to mixtures.

The two defining Eq 1 and Eq 2 are necessary since there are two transformation functions. In this case, an equation of state for methane was chosen for the reference fluid. During the course of the study it was necessary to modify the equation of state to give a realistic vapor liquid phase boundary down to a temperature of 43K. This modification was necessary to

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² The formulation of the models and the supporting work was done by the National Bureau of Standards under the sponsorship of British Gas Corp., Chicago Bridge and Iron Co., Columbia Gas Service Corp., Distrigas Corp., Easco Gas LNG, Inc., El Paso Natural Gas, Gaz de France, Marathon Oil Co., Mobil Oil Corp., Natural Gas Pipeline Co., Phillips Petroleum Co., Shell International Gas, Ltd., Sonatrach, Southern California Gas Co., Tennessee Gas Pipeline, Texas Eastern Transmission Co., Tokyo Gas Co., Ltd., and Transcontinental Gas Pipe Line Corp., through a grant administered by the American Gas Association, Inc.



accommodate the very low reduced temperatures of the heavier hydrocarbons and was accomplished without changing the performance of the equation of state above the triple point of methane. The $f_{ii,o}$ and $h_{ii,o}$ are defined as

$$f_{ii,o} = (T_{ii}^c/T_o^c) \theta_{ii,o}(T_{ri}, V_{ri}) \quad (3)$$

and

$$h_{ii,o} = (V_{ii,o}^c/V_o^c) \phi_{ii,o}(T_{ri}, V_{ri}) \quad (4)$$

where:

$$\theta_{ii,o} = 1 + (w_i - w_o) [n_1 - n_2 \ell n T_{ri} + (n_3 - n_4/T_{ri})(V_{ri} - n_5)] \quad (5)$$

and

$$\phi_{ii,o} = \frac{Z_o^c}{Z_i^c} [1 + (w_i - w_o) [n_6(V_{ri} - n_7) - n_8(V_{ri} - n_9) \ell n T_{ri}]] \quad (6)$$

The V_{ri} and T_{ri} are reduced temperature and volume (that is, $T_{ri} = T/T_{ii}^c$ and $V_{ri} = V/V_{ii}^c$); each fluid requires a unique w_i which was estimated using pure fluid experimental data. A single set of the n 's is used for all fluids. The n 's were estimated using all of the pure fluid experimental data from the NBS Boulder Study. The Z^c/Z_i^c is the ratio of the compressibility factors ($Z^c = P_c V_c/RT_c$) at the critical point. The parameters n 's and w_i were estimated using the experimental PVT data set from NBS measurements and least squares estimation techniques.

3.1.1 The extension of the above to mixtures is now accomplished by the application of the following combining rules:

$$h_{x,o} = \sum_i \sum_j x_i x_j h_{ij,o} \quad (7)$$

$$f_{x,o} h_{x,o} = \sum_i \sum_j x_i x_j f_{ij,o} h_{ij,o} \quad (8)$$

$$f_{ij,o} = \epsilon_{ij} (f_{ii,o} f_{jj,o})^{1/2} \quad (9)$$

$$h_{ij,o} = \eta_{ij} \left(\frac{1}{2} h_{ii,o}^{1/3} + \frac{1}{2} h_{jj,o}^{1/3} \right)^3 \quad (10)$$

The ϵ_{ij} and the η_{ij} are binary interaction parameters determined by least squares from the PVT_x data for binary mixtures. Values for the coefficients and other adjustable parameters are given in the Research Report.³

3.2 *Hard Sphere*—The hard sphere model equation of state:

$$\frac{PV}{RT} = c \frac{1 + y + y^2}{(1 - y)^3} - \frac{a}{RTV} \quad (11)$$

where:

- $y = b/4V$ and $a, b,$ and c are adjustable parameters,
- P = pressure,
- V = specific volume,
- T = temperature, and
- R = the gas constant.

The equation is applied to mixtures by assuming the one-fluid theory and applying the following combining rules.

$$a_m = \sum_i \sum_j a_{ij} x_i x_j \quad (12)$$

$$b_m = \sum_i \sum_j b_{ij} x_i x_j \quad (13)$$

$$c_m = \sum_i \sum_j c_{ij} x_i x_j \quad (14)$$

The mixing rules are:

$$b_{ij} = \left[\frac{b_{ii}^{1/3} + b_{jj}^{1/3}}{2} (1 - j_{ij}) \right]^3 \quad (15)$$

$$a_{ij} = (a_i a_j)^{1/2} \left[\frac{b_{ij}^2}{b_{ii} b_{jj}} \right]^{1/2} (1 - k_{ij}) \quad (16)$$

$$c_{ij} = \frac{c_{ii} + c_{jj}}{2} \quad (17)$$

The parameters j_{ij} and k_{ij} are in this case the binary interaction parameters. The excess volume is now calculated using the equation of state and

$$V_E = V_m - V_i x_i \quad (18)$$

where \bar{V}_m and \bar{V}_i are calculated via Eq 11-17. The calculated value of V_E can now be used with measured values $V_i x_i$ to give an actual volume of the mixture. Then:

$$V_m = \sum_i V_i x_i + V_E \quad (19)$$

where the V_E is from Eq 18 and the V_i is from experimental data. Values for the coefficients and other adjustable parameters are given in the Research Report.³

3.3 *Revised Klosek and McKinley*—The revised Klosek and McKinley model equation is:

$$V_{\text{mix}} = \sum x_i V_i - [k_1 + (k_2 - k_1) x_{N_2}/0.0425] x_{CH_4} \quad (20)$$

where:

- V_{mix} = volume of the mixture,
- X_i and V_i = mole fraction and volume of the i^{th} component,
- X_{CH_4} = mole fraction of methane, and
- k_1 and k_2 = correction factors.

Tables of values for the correction factors are given in the Research Report.

3.4 *The Cell Model*⁴—Comparisons of NBS measured data with the cell model were made during the course of the NBS study, but the details of the model have not been reported. Additional information is available in NBS Monograph 172.⁵

4. Additional Information

4.1 These models were originally published in NBS Monograph 172, which also contains the following:

4.1.1 Descriptions of the experimental apparatus developed, constructed, and proven for use in taking the necessary LNG data points,

4.1.2 Descriptions of the operational procedures used with the special apparatus in obtaining the required data point measurements,

⁴ The Cell Model was developed by M. A. Albright of Phillips Petroleum Co. from a correlation published by Renon, Eckert, and Prausnitz, but a paper documenting its formulation and performance was never published.

⁵ NBS Monograph 172, Liquefied Natural Gas Densities: Summary of Research Program at the National Bureau of Standards, is available from the Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

³ Available from ASTM Headquarters. Request RR: D03-1006.



4.1.3 Descriptions of the data point measurement programs,
4.1.4 Descriptions of the development of the various models, and

4.1.5 Basic publications resulting from the extensive LNG Density Research project.

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