Chapter 11.3.2.1—Ethylene Density

INTRODUCTION

The purpose of this standard is to provide equations of state that can be used to obtain an accurate determination of ethylene density. Other thermodynamic properties can be calculated using the equations of state, but this standard is primarily concerned with the determination of ethylene density. Temperature and pressure can have significant effects on the accurate determination of ethylene density, and as a result, the means for temperature and pressure determination have to be assessed appropriately for these applications.

The previous edition of this standard was in the form of a measurement manual and was not confined to calculating the physical properties of ethylene. The previous edition included orifice and turbine metering calculations, as well as data that were not in agreement with the current API Manual of Petroleum Measurement Standards (MPMS) that cover these metering devices. The original density lookup tables were based on FORTRAN code originally published in the mid-1960s as API 2565 Subroutine Ethyl. This second edition of API MPMS Chapter 11.3.2.1 is intended to replace the 30+ year old equations with references to more modern equations of state, limited to the physical properties of ethylene.

Typically, ethylene equations of state are used in custody transfer metering applications. Such is the case with modern flow computers, which have various options for selecting which equation of state is utilized in determining flowing ethylene density.

1 SCOPE

This standard identifies equations of state (EOS) suitable for use in custody transfer measurement of pure ethylene (>99 %) in the gaseous, liquid, and super critical phases. Given flowing temperature and pressure, each equation of state identified in this document is capable of calculating density, and other thermodynamic properties used to calculate mass and volumetric flow of ethylene to custody transfer accuracy. All accuracy and uncertainty statements in this standard are limited to the equation of state results, and do not include the uncertainty added by the primary and secondary measuring equipment.

2 NORMATIVE REFERENCES

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

NIST Standard Reference Database 23

IUPAC-88 Ethylene (Ethene), International Thermodynamic Tables of the Fluid State Volume 10 (1988)

3 TERMS AND DEFINITIONS

For the purposes of this document, the following definitions apply:

3.1 equation of state

EOS

Thermodynamic equation describing the state of matter under a given set of physical conditions.

NOTE An EOS provides a mathematical relationship between two or more state functions associated with the material, such as its temperature or pressure.

1 National Institute of Standards and Technology, 100 Bureau Drive, Stop 1070, Gaithersburg, MD 20899, USA.
2 International Union of Pure and Applied Chemistry, 104 T.W. Alexander Drive, Building 19, Research Triangle Park, NC 27709, USA.
3.2 critical region
Thermodynamic state of a fluid in which phase boundaries cease to exist.

NOTE In the case of ethylene, a vapour-liquid critical region exists. Density determination is extremely sensitive in the critical region, as minor changes in flowing pressure can bring about significant changes in density for a given temperature.

4 ETHYLENE EQUATIONS OF STATE

4.1 General
This standard provides two references for ethylene equations of state:

- NIST 23, part of the “NIST Standard Reference Database 23” publication

IUPAC-88 is a publication which incorporates the work carried out by Jahangiri et al[1] on ethylene. The paper “Thermodynamic Properties of Ethylene from the Freezing Line to 450 K at Pressures to 260 MPa” was published a year or so before IUPAC published lookup tables in 1988. NIST 23 is a multi-component property database which incorporates the work performed by Wagner et al[2], in their paper “New Equation of State for Ethylene Covering the Fluid Region for Temperatures From the Melting Line to 450 K at Pressures up to 300 MPa.”

Both equations of state are acceptable for use in custody transfer applications. However, the user should be aware that a critical region for ethylene exists across pressures ranging approximately from 5171.1 kPa to 5860.5 kPa (750 psig to 850 psig) and temperatures ranging approximately from 10 °C to 21.1 °C (50 °F to 70 °F). Density predictions with either equation of state are not recommended in this region.

For the NIST 23 density prediction, the estimated uncertainty of the equation of state is less than ±0.02 % for pressures up to 12 MPa (10,152.6 psig) and temperatures up to 66.85 °C (152.3 °F), with the exception of the critical region. For the IUPAC-88 density prediction, the estimated uncertainty of the equation of state is less than ±0.08 % for pressures up to 260 MPa (65,266.9 psig) and temperatures up to 176.85 °C (350.3 °F), with the exception of the critical region.

Density calculation differences between IUPAC-88 and NIST 23, especially in the critical region, are discussed in Annex A.

4.2 IUPAC-88 Equation of State
The paper by Jahangiri et al[1] is the basis for the IUPAC-88 equation of state. According to the paper, the Helmholtz energy for ethylene is given below by the fundamental equation:

\[ A(\rho, T) = A^\circ(\rho, T) + \overline{A}(\rho, T) \]

where \( A^\circ(\rho, T) \) is the ideal gas contribution to the Helmholtz energy of any state.

The term \( \overline{A}(\rho, T) \) is the contribution represented by the compressibility of the real gas. After additional manipulation, the functional form used for the fundamental equation for ethylene is a non-dimensional Helmholtz energy potential function below:

\[ \alpha^\circ(\delta, \tau) = A(\rho, T)/RT = \alpha^\circ(\delta, \tau) + \overline{\alpha}(\delta, \tau) \]

where

\[ \alpha^\circ = \frac{H^\circ}{RT_c} - \frac{S^\circ}{R} - 1 + \ln \frac{\delta T_0}{\tau \delta_0} - \frac{\tau}{R} \int_{T_0}^{T_c} \frac{C_p}{T^2} dT + \frac{1}{R} \int_{T_0}^{T_c} \frac{C_p}{T} dT \]

where

\[ \tau = T_c/T, \tau_0 = T_c/T_0, \delta = \rho/\rho_c, \delta_0 = \rho_0/\rho_c \]

\( \rho_c \) is the critical density;

\( T_c \) is the critical temperature;

\( T_0 \) is the reference temperature 298.15 K;
Given the equations above, it is possible to derive functions for calculating properties of ethylene such as density. The equations and procedures described in Section 5.4 of the Jahangiri et al’s paper illustrate how density can be calculated from the methods above.

### 4.3 NIST-23 Equation of State

The paper by Wagner et al[2] is the basis for the NIST 23 equation of state. According to the paper, the equation of state described is explicit in the Helmholtz energy ‘a’ with the independent variables density $\rho$ and temperature $T$. The dimensionless Helmholtz energy $\alpha = a/(RT)$ is commonly split into a part $\alpha^o$, which represents the properties of the ideal gas at given $T$ and $\rho$, $\alpha^o$ and a part $\alpha^r$, which takes into account the residual fluid behavior. This convention can be written as:

$$\alpha(\delta, \tau) = \alpha^o(\delta, \tau) + \alpha^r(\delta, \tau)$$

where $\tau = T_c/T$, $\delta = \rho/\rho_c$.

Both the density and the temperature are reduced with their critical values $\rho_c$ and $T_c$, respectively.

Since the Helmholtz energy as a function of density and temperature is one of the four fundamental forms of an equation of state, all thermodynamic properties of a pure substance can be obtained by combining derivatives of the equation above. In the Wagner ethylene paper, Table 26 gives the relations between the equation above and its derivatives and the thermodynamic properties considered. Illustrations and calculations for the properties of ethylene follow thereafter.

### 5 IMPLEMENTATION PROCEDURES

To properly implement an ethylene EOS, the user should follow the implementation procedures in the IUPAC-88/NIST 23 publications, respectively. For example, at the time of publication of this document, a purchased copy of NIST 23 provides the right to use both the FORTRAN code and Excel DLL for use in users own applications. If the user wishes to use the EOS in another manner, additional processing could be required.

Ultimately though, the end use for an ethylene equation of state will determine the procedures of implementation. In some custody transfer applications, programming support could be required to implement the proper code for each EOS. In other custody transfer applications, the EOS could already be in a compiled form and available for use. An example of this would be the use of an ethylene EOS in flow computing applications to determine mass flow rate.

Example and auxiliary calculations are presented in the individual publications for both IUPAC-88 and NIST 23.
ANNEX A
(informative)

Differences between IUPAC-88 and NIST 23

IUPAC-88 and NIST 23 both provide an ethylene equation of state that can be utilized to calculate density if flowing pressure and temperature are known. Based on actual ethylene laboratory data, both equations of state predict density below 0.1% uncertainty across pressures and temperatures outside the critical zone. However, the user should be aware that a critical region for ethylene exists across pressures ranging approximately from 5171.1 kPa to 5860.5 kPa (750 psig to 850 psig) and temperatures ranging approximately from 10 °C to 21.1 °C (50 °F to 70 °F). Density predictions with either equation of state are not recommended in this region.

This phenomenon can be visually represented as shown in Figure 1. The figure depicts the percent agreement between density calculated by NIST 23 and IUPAC-88’s equations of state. For example, the ethylene density difference between NIST 23’s prediction and IUPAC-88’s prediction is approximately 0.01% at a temperature of 4.44 °C (40 °F) and a pressure of 2757.9 kPa (400 psig).

The percent agreement is between 0.00% and 0.05% for approximately 70% of the pressures and temperatures covered by the figure, with the percent agreement between 0.05% and 0.1% for approximately 29% of the pressures and temperatures covered by the figure. Less than 1% of the pressures and temperature data points covered by the figure have a percent agreement value above 0.1%. It is obvious from the figure that the large spiked region represents the critical region for ethylene.

![Figure 1—NIST versus IUPAC-88 Density Prediction (Percent Agreement)](image-url)
Bibliography
