Manual of Petroleum Measurement Standards Chapter 11.3.2.1

Ethylene Density

SECOND EDITION, MAY 2013

AMERICAN PETROLEUM INSTITUTE

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Introduction

The purpose of this standard is to provide an equation of state that can be used to obtain an accurate determination of ethylene density. Other thermodynamic properties can be calculated using the equation 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, published in 1974, 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.

Ethylene Density

1 Scope

This standard identifies an equation 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, an EOS 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 EOS 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.

IUPAC-88 [1], *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
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.

3.2
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.

4 Ethylene Equations of State

4.1 General

This standard provides a reference for an ethylene EOS:

— IUPAC-88, part of the *Ethylene, International Thermodynamic Tables of the Fluid State, Volume 10* (1988) publication.

IUPAC-88 is a publication that 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.

[1] International Union of Pure and Applied Chemistry, 104 T.W. Alexander Drive, Building 19, Research Triangle Park, North Carolina 27709, www.iupac.org.

The IPUAC EOS is 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 using the IUPAC EOS are not recommended in this region.

For the IUPAC-88 density prediction, the estimated uncertainty of the EOS 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.

4.2 IUPAC-88 Equation of State

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

$$A(\rho, T) = A^{\circ}(\rho, T) + \bar{A}(\rho, T) \tag{1}$$

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

The term $\bar{A}(\rho, T)$ 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 nondimensional Helmholtz energy potential function below:

$$\alpha^{\circ}(\delta, \tau) = A(\rho, T)/\mathrm{R}T = \alpha^{\circ}(\delta, \tau) + \bar{\alpha}(\delta, \tau) \tag{2}$$

where

$$\alpha^{\circ} = \frac{H^{\circ}_0 \tau}{\mathrm{R}T_c} - \frac{S^{\circ}_0}{\mathrm{R}} - 1 + \ln\frac{\delta\tau_0}{\tau\delta_0} - \frac{\tau}{\mathrm{R}}\int_{\tau_0}^{\tau}\frac{C^{\circ}_p}{\tau^2}d\tau + \frac{1}{\mathrm{R}}\int_{\tau_0}^{\tau}\frac{C^{\circ}_p}{\tau}d\tau \tag{3}$$

where

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

ρ_c is the critical density;

T_c is the critical temperature;

T_0 is the reference temperature 298.15 K;

P_0 is the reference pressure 0.101525 MPa;

ρ_0 is the ideal gas density at T_0 and P_0;

H°_0 is the reference enthalpy at T_0;

S°_0 is the reference entropy at T_0 and P_0;

R is the gas constant 0.00831434 (MPa dm^3)/(mol 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 Jahangiri et al.'s paper illustrate how density can be calculated from the methods above.

5 Implementation Procedures

To properly implement an ethylene EOS, the user should follow the implementation procedures in the IUPAC-88 publication. Through mathematical manipulation it is possible to derive a form in terms of density, pressure and temperature. However, it is recognized that tolerances for solutions and validation procedures are not provided in the publication itself. To maintain industry consistency, a technical report will be issued separate of this standard providing guidance on how to perform the calculations.

Ultimately though, the end use for an ethylene EOS 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 publication IUPAC-88.

Bibliography

[1] Majid Jahangiri, Richard T. Jacobsen, and Richard B. Stewart, “Thermodynamic Properties of Ethylene from the Freezing Line to 450 K at Pressures to 260 MPa,” *Journal of Physical and Chemical Reference Data* (1986), Vol. 15, No. 2, 1986

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