Fluid Phase Equilibria 334 (2012) 128–136

Contents lists available at SciVerse ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Pure saturated gases with predicted negative fundamental derivative of gas dynamics

Marcelo Castier [a,*,1], Vladimir F. Cabral [b]

[a] Chemical Engineering Program, Texas A&M University at Qatar, P.O. Box 23874, Doha, Qatar
[b] Departamento de Engenharia Química, Universidade Estadual de Maringá, Av. Colombo 5790, Maringá 87020-900, Brazil

ARTICLE INFO

Article history:
Received 19 January 2012
Received in revised form 10 June 2012
Accepted 26 June 2012
Available online 23 August 2012

Keywords:
Gas dynamics
Sound speed
Equations of state
Dew point
Isentropic processes

ABSTRACT

The fundamental derivative of gas dynamics is a purely thermodynamic property associated with the analysis of detonation processes and shock waves. A fluid with negative value of this derivative, called a BZT (Bethe, Zel'dovich, and Thompson) fluid, would present rarefaction shock waves. Also, close to conditions in which in the fundamental derivative of gas dynamics is equal to zero, entropy losses are small, potentially leading to improved efficiency in turbomachinery. The experimental evidence that BZT fluids exist is disputed, but published calculations based on equations of state (EOS) predict their existence. Here, calculations with more than 1800 pure substances using the original Peng–Robinson EOS, in its modified form known as PR78, and the Patel–Teja–Valderrama EOS have initially identified 185 organic substances with negative or near-zero, positive minimum value of the fundamental derivative of gas dynamics. The effect of uncertainties in critical properties and acentric factors on the predicted fundamental derivative of gas dynamics has also been evaluated.

1. Introduction

Water is possibly the working fluid most commonly used in industrial power cycles. It is widely available, inexpensive, and chemically stable at the conditions of typical cycles. Besides, its properties are suitable for operations between the combustion temperature of common fuels and usual ambient temperatures. However, there is great interest in consolidating methods to recover waste, low-temperature heat from industrial activities and convert it to mechanical power. To run these cycles, it is necessary to find working fluids suitable for operations at such conditions. Some organic substances and their mixtures may be fit for the task and there has been much work to identify candidate working fluids for the so-called organic Rankine cycles (ORCs). The recent work of Desai and Bandyopadhyay [1] discusses the fundamentals of ORCs and their integration into process plants.

Deciding on the fitness of a fluid for an ORC depends on the joint analysis of transport properties, such as viscosities and thermal conductivities and of thermodynamic properties, such as vapor pressures, enthalpies of vaporization, heat capacities, densities, and the characteristics of the temperature–entropy (TS) diagram [2]. Also, chemical stability is essential because of the drastic state changes the fluid undergoes during the many hours of uninterrupted cycle operation in an industrial environment. Further, the fluid should be safe, inexpensive, and noncorrosive. However, this paper focuses on a different property, potentially relevant for analyzing candidate working fluids for ORCs: the fundamental derivative of gas dynamics (Γ).

The fundamental derivative of gas dynamics is associated with the analysis of detonation processes and shock waves and an interesting historical perspective about the study of shock waves is available in the work of Heuzé [3]. Thompson [4] introduced this parameter in a general way, giving examples of its relevance to the analysis of the dynamic behavior of gas flows, including transonic flows through nozzles and supersonic flows around airfoils. After suitable manipulations, it is possible to identify a purely thermodynamic property, named fundamental derivative of gas dynamics, given as the combination of several derivatives obtained from an equation of state (EOS), capable of distinguishing different flow behaviors. Fluids with $\Gamma < 0$ in at least one state are called BZT (Bethe, Zel'dovich, and Thompson) fluids in honor of the first researchers that discussed them. In such fluids, it is theoretically possible to have rarefaction shock waves [4]. Also, close to conditions in which in the fundamental derivative of gas dynamics is equal to zero, entropy losses are small, potentially leading to improved efficiency in turbomachinery [5–8].

Experimental evidence that BZT fluids exist is under dispute [9], but there is at least one group engaged in an experimental program whose goal is to settle this issue [10]. Calculations reported in the literature have identified some candidate BZT fluids in certain

* Corresponding author. Tel.: +974 44230534; fax: +974 44230065.
E-mail addresses: mcastier@gmail.com, marcelo.castier@qatar.tamu.edu (M. Castier), vladimir@deq.uem.br (V.F. Cabral).
[1] On leave from the Federal University of Rio de Janeiro, Brazil.

0378-3812/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.fluid.2012.06.032

List of symbols

Roman letters

A, B, C, D, E	parameters of molar heat capacity correlation
c	thermodynamic speed of sound
c_P	molar heat capacity at constant pressure
c_v	molar heat capacity at constant volume
M	molar mass
P	absolute pressure
P_c	critical pressure
R	universal gas constant
s	molar entropy
T	absolute temperature
T_c	critical temperature
T_R	reduced temperature
v	molar volume
V	volume
X	generic property
Z_c	critical compressibility factor

Greek letters

Γ	fundamental derivative of gas dynamics
$\Gamma^{v,sat}$	fundamental derivative of gas dynamics of saturated vapor
$\Gamma^{v,sat}_{min}$	minimum value of the fundamental derivative of gas dynamics
$\overline{\Gamma^{v,sat}_{min}}$	average of the minimum value of the fundamental derivative of gas dynamics
σ_X	standard deviation of a generic property X
σ_Γ	standard deviation in $\Gamma^{v,sat}_{min}$ for a given substance
ω	acentric factor

Superscripts

ig	ideal gas
R	residual property

regions. These calculations are based either on tabulated data or on different EOS, some of them accurate models for reference fluids, which are typically available only for a few substances of relatively simple molecular structure. A recent comparison [9] of the results for these reference fluids using these accurate models and a cubic EOS (the Stryjek–Vera [11] version of the Peng–Robinson EOS [12]) has shown the reference EOS and the cubic EOS predict similar Γ values. BZT fluids are expected to be composed of complex molecules [13] for which accurate, tailor-made EOS are generally unavailable. In a recent paper, Colonna et al. [9] have summarized information about 50 BZT fluids whose existence has been theoretically predicted. Among these substances, 31 are fluorinated, 34 have 10 or more carbon atoms in their structure, and 5 are siloxanes.

Based on the apparent suitability of cubic EOS as tools to identify possible BZT fluids, this paper reports the result of a thorough search of possible BZT pure fluids among the substances available in the DIPPR database [14]. The critical temperature (T_c), critical pressure (P_c), critical compressibility factor (Z_c), acentric factor (ω), and coefficients for an ideal gas heat capacity correlation are available for most substances in the database. Therefore, the EOS adopted in this study only use $\{T_c,P_c,\omega\}$ or $\{T_c,P_c,Z_c,\omega\}$ as parameters to characterize a pure substance. Results are reported for the original Peng–Robinson EOS [12], its modified version known as PR78 for substances whose acentric factor is greater than 0.491 [15], and the Patel–Teja–Valderrama (PTV) EOS [16]. For most of the substances identified as possible BZT fluids, the critical properties and acentric factor available in the DIPPR database are the results of correlations and not experimental values. Therefore, their uncertainties may be large: in some cases, as much as 50% according to the DIPPR documentation. For this reason, the effect of these uncertainties on the predicted Γ-values is also evaluated.

2. Fundamental derivative of gas dynamics (Γ)

Γ is a dimensionless property given by [4]:

$$\Gamma = \frac{v^3}{2c^2M}\left(\frac{\partial^2 P}{\partial v^2}\right)_s \tag{1}$$

where v and s are the molar volume and molar entropy, c is the thermodynamic sound speed, and M is the molar mass. By using standard techniques of classical thermodynamics, such as Jacobian transformations and Maxwell relations, it is possible to rewrite Γ as [17]:

$$\Gamma = \frac{v^3}{2c^2M}(\Gamma_1 + \Gamma_2 + \Gamma_3) \tag{2}$$

The expressions for Γ_1, Γ_2, and Γ_3 are:

$$\Gamma_1 = \left(\frac{\partial^2 P}{\partial v^2}\right)_T \tag{3}$$

$$\Gamma_2 = -\frac{3T}{c_v}\left(\frac{\partial P}{\partial T}\right)_v\left(\frac{\partial}{\partial v}\left(\frac{\partial P}{\partial T}\right)_v\right)_T \tag{4}$$

$$\Gamma_3 = \left(\frac{T}{c_v}\left(\frac{\partial P}{\partial T}\right)_v\right)^2\left(3\left(\frac{\partial^2 P}{\partial T^2}\right)_v + \frac{1}{T}\left(\frac{\partial P}{\partial T}\right)_v\left(1-\frac{T}{c_v}\left(\frac{\partial c_v}{\partial T}\right)_v\right)\right) \tag{5}$$

In these expressions, T, P, and c_v are the absolute temperature, absolute pressure, and molar heat capacity at constant volume, respectively. The pressure derivatives in Eqs. (3)–(5) can be obtained directly from an EOS explicit in temperature and volume, as most used for chemical process design and those utilized in this work. The molar heat capacity at constant volume is given by:

$$c_v = c_v^{ig} + c_v^R \tag{6}$$

where c_v^{ig} and c_v^R are the ideal gas and residual contributions. The ideal gas heat capacities at constant volume and at constant pressure are related by:

$$c_v^{ig} = c_P^{ig} - R \tag{7}$$

where R is the universal gas constant and c_P^{ig} is the ideal gas molar heat capacity at constant pressure, which is only a function of temperature for a pure substance. Several expressions are available to describe the dependence of c_P^{ig} on temperature. In the DIPPR database [14] used in this work, c_P^{ig} for some substances is given as a fourth-degree temperature polynomial whereas, for others, it is given by an expression in terms of hyperbolic functions:

$$c_P^{ig} = A + B\left(\frac{(C/T)}{\sinh(C/T)}\right)^2 + D\left(\frac{(E/T)}{\cosh(E/T)}\right)^2 \tag{8}$$

where A, B, C, D, and E are tabulated parameters characteristic of each substance.

The value of c_v^R is found from the EOS used to model the fluid, for instance, by obtaining the expression for the molar residual internal energy and differentiating it with respect to temperature at constant molar volume.