



Modeling and calculation of thermodynamic properties and phase equilibria of oil and gas condensate fractions based on two generalized multiparameter equations of state



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ARTICLE INFO

Article history:

Received 14 August 2015

Received in revised form

9 January 2016

Accepted 10 January 2016

Available online 14 January 2016

Keywords:

Phase equilibria

Equation of state

Heat capacity

Density

Hydrocarbon

ABSTRACT

Based on two generalized equations of state, previously developed by the authors, describing the properties of hydrocarbon chain and cyclic structures, a method for the predictive calculation of thermodynamic properties and phase equilibria of complex hydrocarbon mixtures (petroleum and gas-condensate fractions) has been developed. The method is applicable over a temperature range from the freezing point to 700 K and at pressures up to 100 MPa, including the liquid and gas phases as well as the supercritical region.

The calculation of thermodynamic properties is made within the framework of the extended three-parameter corresponding states principle. The acentric factor was chosen as the third parameter of the corresponding states. The complex hydrocarbon mixture is treated as an individual substance, known as a “single-fluid model”. In this model, the mixture is a hypothetical individual hydrocarbon with an effective molar mass M and critical parameters, T_c , p_c and ρ_c . This “substance” is characterized by the content of paraffin and cyclic structures in an effective molecule.

For the calculation of phase equilibria, a method for modeling the composition of complex hydrocarbon mixtures using the concept of pseudo components has been developed. The method is based on the distillation curve and uses a minimum set of needed properties of mixtures, such as the average boiling temperature, relative density, and molar mass. Rules for generalization of the single-fluid model, used to calculate thermodynamic properties, to the linear model of mixtures, used for phase equilibria calculations, have been formulated.

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1. Introduction

Mathematical models are commonly used for engineering design and operation of oil and gas fields, as well as for transportation and processing of hydrocarbons. These models describe heat- and mass transfer, fluid dynamics, and filtration through porous media. Applications of such models require the information on phase equilibria, thermodynamic properties, and transport coefficients. The calculation of phase behavior and thermodynamic properties can be made in two ways:

- from empirical equations obtained by fitting of experimental data on a specific property, such as dew-point and bubble-point pressures, density, heat capacity, etc.;
- from fundamental equations of a state, enabling one to calculate all thermodynamic properties including phase behavior.

The first approach is found in numerous calculation procedures, for example in Refs. [1–3]. While this approach has certain advantages – experimental basis and relative simplicity of calculations – it has essential shortcomings. It has a limited range of applicability and commonly seen thermodynamic inconsistency of property values calculated by different techniques and authors. The main shortcoming is internal inconsistency between the calculated data. This may not be immediately seen in the analysis of the obtained values of thermodynamic properties; however, can compromise the modeling of technological processes and the

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analysis of phase behavior of the system, especially, when there is a need to consider the derivatives of thermodynamic properties.

An alternative approach – based on the fundamental equations of state – is more attractive from the scientific point of view. This approach is supported by more than a hundred years of research based on cubic equations of state. The bibliography of works in this area exceeds one thousand publications. Reviews and citations of original works can be found in Refs. [4,5]. Research in this direction still continues today and good results, especially in the prediction of phase behavior of hydrocarbon systems, are obtained. Cubic equations of state are most popular because of scientific validity, simplicity, and stability of such equations in the wide range of state parameters, as well as relative simplicity of computing procedures.

For modeling of the thermodynamic properties and phase equilibria of hydrocarbon systems and gas-condensate, the original cubic equations of Peng – Robinson [4] and Soave [5] are commonly used. In the Russian engineering practice, a generalized cubic equation of state developed by Brusilovsky [6] is widely used. This equation is based on representative experimental database on the properties of hydrocarbons and their mixtures. The equation is tested by the author in detail [6], as well as by other researchers, for example in Ref. [2]. A brief description of Brusilovsky's cubic equation of state is given in Appendix A.

However, despite the significant progress achieved in the development and application of cubic equations of state, their main shortcoming – low accuracy of calculation of thermodynamic properties in the wide range of state parameters – cannot be overcome within this class of equations. This shortcoming is a direct consequence of the simplistic structure of such equations of state.

2. Generalized fundamental equations of state

Alternative to cubic equations of state are multiparameter fundamental equations of state. Intensive research on the development of multiparameter equations of state began about 70 years ago for practically important substances, for which there were accurate experimental data on thermodynamic properties in the wide range of state parameters. Originally, the equations were developed in the form of the dependence of the compressibility factor Z on the reduced density δ and the reduced temperature τ . Furthermore, in the connection with attempts to establish a physical meaning of the terms of the equations of state, a dependence of the Helmholtz energy on density and temperature was investigated. These equations describe the liquid–gas phase transition, satisfy the critical conditions, and allow the calculation of all thermodynamic properties without additional information. An unresolved question on the structure of the equation was the number of polynomial and exponential terms and values of the temperature and density exponents. The number of coefficients in the different equations varied from 12 to 55. Thus, with the large number of coefficients in the equation, in some areas of the thermodynamic surface the equation could become unstable, which caused unphysical behavior of thermodynamic properties. The reason was an optimization procedure – the linear or linearized least-square method. It significantly complicated the development of multiparameter equations of state. A significant step forward was carried out in 1980's and 1990's due to the development of effective optimization algorithms. Optimization of the functional form of multiparameter equations of a state is discussed in the monograph of Span [7]. There are known two forms of a multiparameter equation of a state: a 12 term equation of Span [7] and a 14 term equation of Sun and Ely [8], which can be used both for nonpolar and polar substances.

Petroleum and gas-condensate systems are complex mixtures

consisting of many hydrocarbons with various structures and non-hydrocarbon components. When being modeled, such complex mixtures are divided in two parts: the gas part with known composition and the condensate part. The gas part (consisting of nitrogen, carbon dioxide, hydrogen sulfide, methane, ethane, propane, and butanes) is modeled by individual equations of a state. Information on these equations is published in the literature [7,8]. The condensate part is divided into fractions, which composition is identified by the physical properties (relative density, refractive index, molar weight, and average boiling temperature). Generalized fundamental equations of state, presented in this work, are used for the modeling of thermodynamic properties and phase behavior of the fractions.

For generalization, an equation in the form of the reduced Helmholtz energy is given as follows:

$$\frac{a(\rho, T)}{RT} = \frac{a^0(\rho, T) + a^r(\rho, T)}{RT} = \alpha^0(\delta, \tau) + \alpha^r(\delta, \tau) \quad (1)$$

where $a(\rho, T)$ is the molar Helmholtz energy, $\alpha^0(\delta, \tau)$ is the reduced Helmholtz energy of the ideal-gas state, $\alpha^r(\delta, \tau)$ is the residual part of the reduced Helmholtz energy, $\delta = \rho/\rho_c$ is the reduced density, $\tau = T_c/T$ is the inverse reduced temperature, ρ_c , T_c are reducing (critical) parameters, and R is the universal gas constant.

The ideal-gas reduced Helmholtz energy, in a dimensionless form, can be represented by

$$\alpha^0(\delta, \tau) = \frac{h_0^0 \tau}{RT_c} - \frac{s_0^0}{R} - 1 + \ln \frac{\delta \tau_0}{\delta_0 \tau} - \frac{\tau}{R} \int_{\tau_0}^{\tau} \frac{c_p^0}{\tau^2} d\tau + \frac{1}{R} \int_{\tau_0}^{\tau} \frac{c_p^0}{\tau} d\tau \quad (2)$$

where $\delta_0 = \rho_0/\rho_c$ and $\tau_0 = T_c/T_0$. T_0 and p_0 are arbitrary constants, and ρ_0 is the ideal gas density at T_0 and p_0 ($\rho_0 = p_0/(T_0 R)$). h_0^0 is the ideal-gas enthalpy of the reference state, and s_0^0 is the ideal-gas entropy of the reference state.

To describe the residual part of the reduced Helmholtz energy, an optimized functional form developed by Sun and Ely [8] has been used. This form of the equation can be further extended to a broader class of substances:

$$\alpha^r(\delta, \tau) = \sum_{k=1}^6 N_k \delta^{d_k} \tau^{l_k} + \sum_{k=7}^{14} N_k \delta^{d_k} \tau^{l_k} \exp(-\delta^{l_k}) \quad (3)$$

The exponents in Eq. (3) are given in Table 1. Eq. (1) takes the reduced density, reduced temperature, and acentric factor as variables. Therefore, the critical constants and the acentric factor are necessary for calculation of thermodynamic properties by Eq. (1).

Table 1
Exponents in Eq. (3).

k	(n-alkanes) t_k	(Cyclic) t_k	d_k	l_k
1	0.686	0.511	1	0
2	1.118	1.136	1	0
3	0.857	0.771	1	0
4	0.559	0.942	3	0
5	0.442	0.274	7	0
6	0.831	1.903	2	0
7	0.484	1.304	1	1
8	2.527	2.774	1	1
9	1.549	2.614	2	1
10	0.757	0.185	5	1
11	3.355	3.071	1	2
12	1.905	2.4	1	2
13	4.941	0.475	4	2
14	12.805	20.215	2	3

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