



## Full Length Article

# Application of multiparameter fundamental equations of state to predict the thermodynamic properties and phase equilibria of technological oil fractions

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## ABSTRACT

A new mixture model, explicit in the reduced Helmholtz energy, is proposed for modeling the thermodynamic properties and phase equilibria of technological oil fractions. The model covers a broad temperature and pressure range in gaseous, liquid, and supercritical regions. Based on the given hydrocarbon composition, a complex mixture is modeled by individual substances, which are identified by the acentric factor and critical parameters, while calculations of thermodynamic properties are carried out with use of individual and generalized equations of state. The generalized equation of state for normal alkanes has been used to describe the thermodynamic properties of a seven-component mixture for which there are no individual equations of state. To improve the description of the thermodynamic properties, the binary interaction parameters for ten binary systems were adjusted. The fitting procedure is based on a cubic equation of state with the group contribution and the evolutionary optimization algorithm.

The results of comparison with the experimental data on density, isobaric heat capacity, enthalpy and entropy of vaporization are presented. The comparison was performed over a temperature range 300–630 K and pressures up to 60 MPa excluding the critical region. The average absolute deviations of the properties from optimized values are the following: 0.17% for the liquid-phase density; 3.5% for the gas-phase density; 2.2% for the density in the supercritical region. The average absolute deviation of isobaric heat capacity for the liquid phase is 1.5–3.5%, for the gas phase is 2.5%, in the supercritical region is 2.1%. The average absolute deviations of the vaporization enthalpy and entropy are 1.65% and 2.23%, correspondingly.

## 1. Introduction

Mathematical models are widely used for engineering design and operation of oil and gas fields, as well as for reservoir simulation. Such models describe heat- and mass transfer, filtration through porous media and so on. Industrial and scientific applications of such models require the information on thermodynamic properties.

Oil and gas-condensate fractions are complex mixtures consisting of many hydrocarbons and non-hydrocarbon components. For such mixtures, in which the individual hydrocarbon composition is not known, there is a problem of identifying (modeling) the composition. The composition of such complex hydrocarbon mixtures is modeled by pseudo-components [1,2]. A pseudo-component is characterized by physical properties – the average boiling temperature, average molar mass, relative density, refractive index, etc. However, in practice, the information on pseudo-components is very limited and in this case it is necessary to use a data of the chromatography. In this case the oil fraction as a multicomponent mixture with the known composition can

be considered. The thermodynamic properties of such mixture can be calculated by the combining rules using the individual equations of state for the components. This approach is successfully developed by more than a hundred years in relation to cubic equations of state.

Recently there was an opportunity to use the multiparameter Helmholtz equations of state for the calculation of thermodynamic properties. Flexible functional form together with sophisticated non-linear optimization algorithms allowed the development of new multiparameter equations of state for pure fluids. These equations of state were fitted to experimental data of various thermal and caloric properties, and are able to describe the accurate measurements within their experimental uncertainty over the wide range of state parameters. A complete overview of the modern fundamental equations of state is presented in [3]. The application of multiparameter equations of state to mixtures was considered in the works of Tillner-Roth [4] and Lemmon [5]. The approach proposed in [4,5] allows the description of multi-component mixtures based on combining rules, and was developed for typical natural gas mixtures. Based on works [4,5], Kunz [6,7]

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Nomenclature		$\rho$	density (mol/l)
<i>List of symbols</i>		$\delta$	reduced density
		$\tau$	reduced temperature
		$\omega$	acentric factor
<i>Greek letters</i>		<i>Superscripts</i>	
$a$	molar Helmholtz energy	0	property in the ideal-gas state
$T$	temperature (K)	r	residual part of the thermodynamic property
$p$	pressure (MPa)	$t, d, l$	exponents in the equation of state
$R$	universal gas constant ( $\text{Jmol}^{-1}\text{K}^{-1}$ )	<i>Subscripts</i>	
$N, c$	coefficients of the equations of state	r	reduced property
$N_C$	number of carbon atoms	0	property at the reference state
$M$	molar mass (g/mol)	$i, k$	number of terms in the equation of state
$c_p$	isobaric molar heat capacity ( $\text{Jmol}^{-1}\text{K}^{-1}$ )	c	property at the critical point
$h$	molar enthalpy ( $\text{Jmol}^{-1}$ )		
$s$	molar entropy ( $\text{Jmol}^{-1}\text{K}^{-1}$ )		
$x$	mole fraction		
AAD	average absolute deviation		
<i>Greek letters</i>			
$\alpha$	reduced Helmholtz energy		

developed a mixture model for natural gas mixtures known as the GERG equation of state.

Based on the GERG model and individual hydrocarbon composition, prediction of the technological oil fraction properties has been performed in this work.

## 2. Oil fraction mixture model

The mixture model proposed in this work uses the functional form developed in the GERG equation of state [6]. The Helmholtz energy  $a$  in this mixture model for a mixture at a given mixture density  $\rho$ , temperature  $T$ , and molar composition  $x$  is the sum of two contributions, one accounting for the ideal gas  $a^0$  and the other for that of the real fluid  $a^r$

$$a(\rho, T, \bar{x}) = a^0(\rho, T, \bar{x}) + a^r(\rho, T, \bar{x}) \quad (1)$$

and can be expressed in a dimensionless form as

$$\frac{a}{RT} = \alpha(\delta, \tau, \bar{x}) = \alpha^0(\rho, T, \bar{x}) + \alpha^r(\delta, \tau, \bar{x}) \quad (2)$$

The reduced mixture density  $\delta$  and inverse reduced mixture temperature  $\tau$  are given by

$$\delta = \frac{\rho}{\rho_r(\bar{x})} \quad \text{and} \quad \tau = \frac{T_r(\bar{x})}{T} \quad (3)$$

where  $T_r(\bar{x})$  and  $\rho_r(\bar{x})$  are reducing functions for the mixture density and temperature depending on the molar composition of the mixture only.

**Table 1**  
Helmholtz equations of state used for the pure components in the mixture model.

№	Component	Pure fluid equation
1	n-Butane	Reference equation of state by Buecker and Wagner [8]
2	Isopentane	Short industrial equation of state by Lemmon and Span [9]
3	n-Pentane	Reference equation of state by Span and Wagner [10]
4	Cyclopentane	Reference equation of state by Gedanitz et al. [11]
5	n-Hexane	Reference equation of state by Span and Wagner [10]
6	Benzene	Reference equation of state by Thol et al. [12]
7	Cyclohexane	Reference equation of state by Zhou et al. [13]
8	n-Heptane	Reference equation of state by Span and Wagner [10]
9	Methylcyclopentane	Generalized equation of state for the cyclic hydrocarbons [14]
10	2,2-dimethylbutane, 3-methylpentane, 2,4-dimethylpentane, 3-methylhexane, 3-ethylpentane, 2,2,4-trimethylpentane, 2-methylpentane	Generalized equation of state for the normal alkanes, See Appendix A.

The reduced Helmholtz energy  $\alpha^0$  represents the properties of the ideal-gas mixture at a given mixture density  $\rho$ , temperature  $T$ , and molar composition  $x_i$  according to

$$\alpha^0(\rho, T, \bar{x}) = \sum_{i=1}^N x_i [\alpha_{0i}^0(\delta_{0,i}, \tau_{0,i}) + \ln x_i] \quad (4)$$

In this equation,  $\ln x_i$  is the contribution from the entropy of mixing. To indicate a pure substance as a component in a mixture, the subscript

**Table 2**  
Values of the binary parameters for the reducing functions (11), (12) fitted in this work.

№	Mixture $i-j$	$\beta_{T,ij}$	$\gamma_{T,ij}$	$\beta_{v,ij}$	$\gamma_{v,ij}$
1	n-butane – 2,2-dimethylbutane	0.998506	1.001633	1.032422	1.043088
2	n-butane – 3-methylpentane	1.002148	1.014296	0.970000	0.981212
3	n-butane – 3-methylhexane	1.002489	1.028539	0.974725	1.022894
4	n-butane – 2,2,4-trimethylpentane	1.014338	1.043948	0.822622	0.895637
5	n-butane – 2-methylpentane	1.005851	1.011118	0.955302	1.017584
6	n-butane – methylcyclopentane	1.003069	1.013318	0.975944	1.007881
7	n-pentane – 2,4-dimethylpentane	0.982517	1.009722	1.143834	0.975962
8	n-pentane – 3-methylhexane	0.995755	1.009809	1.076599	1.003131
9	n-pentane – 2,2,4-trimethylpentane	0.999654	1.004001	1.025553	1.052378
10	cyclopentane – 2,2,4-trimethylpentane	1.027847	1.010937	0.837197	1.028734

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