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Thermodynamic properties of the butenes[☆]
Part II. Short fundamental equations of state

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Abstract

Experimental measurements of density, vapor pressure, and the critical point for 1-butene, isobutene, *cis*-2-butene, and *trans*-2-butene were discussed in Part I of this work. The equations of state presented in this work were developed from these measurements and other information from the literature using a short functional form explicit in the Helmholtz energy. The functional form is based on temperature and density polynomial terms used in previous work, with both the coefficients of the equations of state and the exponents on temperature polynomial terms fitted to substance-specific data sets. Uncertainties of properties calculated using the new equations are typically 0.1% in density in the liquid phase, 0.5% in heat capacities for the saturated liquid, and 0.25–0.5% in vapor pressure. Deviations in the critical region are higher for all properties except vapor pressure. The equations are valid from the triple points of the fluids to temperatures of 525 K, with pressures to 50 MPa.
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Keywords: 1-Butene; Caloric properties; *cis*-2-Butene; Density; Equation of state; Fundamental equation; Isobutene; Thermodynamic properties; *trans*-2-Butene; Vapor pressure

1. Introduction

This work is the second part of a project between the Laboratory for Thermophysical Properties in Oldenburg, Germany, and the National Institute of Standards and Technology in Boulder, CO, USA, to characterize the properties of 1-butene (CAS-RN 106-98-9), isobutene (2-methylpropene, CAS-RN 115-11-7), *cis*-2-butene ((*Z*)-but-2-ene, CAS-RN 590-18-1), and *trans*-2-butene ((*E*)-but-2-ene, CAS-RN 624-64-6). Part I of this work [1] described the measurement of densities, vapor pressures, and the critical points of each of the four compounds. Part II, this work, describes the collection of additional experimental data and the development of the equations of state, and compares properties calculated with the equations to all available measurements for each fluid.

Most modern, high-accuracy equations of state for pure fluid properties are fundamental equations explicit in the Helmholtz energy as a function of density and temperature. All single-phase thermodynamic properties can be calculated as derivatives of the Helmholtz energy. The location of the saturation boundaries requires an iterative solution of the physical constraints on saturation (the Maxwell criterion, i.e., equal pressures and Gibbs energies at constant temperature during phase changes).

Recently, Span and Wagner [2] developed two 12-term fundamental equations with fixed functional forms; one equation focused on nonpolar or slightly polar substances, while the other focused on polar fluids. Their work concentrated on representing fluid properties for substances already described with high-accuracy equations. Although the new technical equations suffer from a slight loss in accuracy, their shorter form allows faster computations and better extrapolation into areas with few or no data. The technical equations of Span and Wagner were developed with much insight into the proper behavior of an equation of state. This includes the proper extrapolation of the equa-

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Table 1
Critical point values for the butenes taken from the literature

Reference	Critical temperature (K)	Critical density (mol/dm^3)	Critical pressure (MPa)
1-Butene			
Coffin and Maass [22]	417.1		
Olds et al. [47]	420.4	4.16	4.05
Beattie and Marple [14]	419.5	4.15	4.02
Tsonopoulos and Ambrose [62][a]	419.5 ± 0.5	4.15 ± 0.21	4.02 ± 0.05
Ihmels et al. [1]	419.29 ± 0.1	4.240 ± 0.04	4.0051 ± 0.005
Isobutene			
Coffin and Maass [22]	416.6		
Scheeline and Gilliland [53]	422.0		4.02
Beattie et al. [16]	417.9	4.17	4.00
Tsonopoulos and Ambrose [62][a]	417.9 ± 0.1	4.19 ± 0.07	4.00 ± 0.01
Ihmels et al. [1]	418.09 ± 0.1	4.170 ± 0.04	4.0098 ± 0.005
cis-2-Butene			
Ambrose et al. [9]	435.5		
Tsonopoulos and Ambrose [62][a]	435.5 ± 0.1	4.28 ± 0.18	4.21 ± 0.05
Ihmels et al. [1]	435.75 ± 0.1	4.244 ± 0.04	4.2255 ± 0.005
trans-2-Butene			
Ambrose et al. [9]	428.6		
Tsonopoulos and Ambrose [62][a]	428.6 ± 0.1	4.21 ± 0.09	4.10 ± 0.02
Ihmels et al. [1]	428.61 ± 0.1	4.213 ± 0.04	4.0273 ± 0.005

[a] Review article reporting recommended values.

tion at low temperatures (as demonstrated by the curvature of the isobaric and isochoric heat capacities, and the speed of sound) and at high temperatures (as demonstrated by the ideal curves). In addition, the number of terms in the equations (12 each) was kept to a minimum, thus decreasing the intercorrelation between terms and the likelihood of "overfitting", or representing spurious or inaccurate data. Although the smaller number of terms decreases the flexibility of the equation, and thus its ability to represent a fluid's properties, its rigid shape is more applicable to substances with limited data, where both interpolation and extrapolation are needed to accurately represent the thermodynamic surface.

2. Functional form of the equation of state

The functional form of the equation of state uses reduced values of temperature and density as independent properties. The reducing values are the critical temperature and density of the specific fluid. Table 1 summarizes the available measured and evaluated critical point values taken from the literature. The values of the critical parameters reported in Table 2 and taken from Part I of this work [1] should be used for all property calculations from the equations of state reported here. The selected triple-point temperatures and calculated normal boiling point temperatures are also reported in Table 2. The molecular weight of the butenes is 56.10632 g/mol.

The functional form of the Helmholtz energy can be expressed using the dimensionless variable α with independent variables of dimensionless density, δ, and temperature, τ,

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

where a is the Helmholtz energy, $\alpha^0(\delta, \tau)$ the ideal gas contribution to the Helmholtz energy, $\alpha^{\mathrm{r}}(\delta, \tau)$ the residual Helmholtz energy that corresponds to the influence of

Table 2
Critical points (reducing parameters) and other fixed points used in this work

Fluid	Critical temperature[a] (K)	Critical density[a] (mol/dm^3)	Critical pressure[a] (MPa)	Triple-point temperature (K)	Boiling point temperature[b] (K)
1-Butene	419.29	4.24	4.0051	87.8[c]	266.84
Isobutene	418.09	4.17	4.0098	132.4[d]	266.15
cis-2-Butene	435.75	4.244	4.2255	134.3[e]	276.87
trans-2-Butene	428.61	4.213	4.0273	167.6[f]	274.03

[a] Ihmels et al. [1].
[b] Calculated from the equation of state at 1 atm.
[c] Takeda et al. [59].
[d] Todd and Parks [61].
[e] Scott et al. [57].
[f] Guttman and Pitzer [27].

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