# Equations of State for the Thermodynamic Properties of Three Isomeric Hexanes: 3-Methylpentane, 2,2-Dimethylbutane, and 2,3-Dimethylbutane

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Equations of state for three isomeric hexanes, 3-methylpentane, 2,2-dimethylbutane, and 2,3-dimethylbutane, have been developed based on experimental thermodynamic property data from the literature. These equations are explicit in the Helmholtz energy, with independent variables of temperature and density. The ranges of validity were determined by the available measurements in temperature, pressure, and density of the equations of state for these three fluids. The uncertainties in densities, vapor pressures, saturated liquid and vapor densities, and caloric properties were estimated also from the available data. The behavior of various thermodynamic properties was analyzed to assess the quality of the equations of state. A physically correct behavior within the region of validity and beyond the validity region (at high temperatures and pressures, and at temperatures far below the triple point temperature) could be ensured.

Key words: 3-methylpentane; 2,2-dimethylbutane; 2,3-dimethylbutane; equation of state; thermodynamic property; Helmholtz energy

## 1. Introduction

3-Methylpentane (C<sub>6</sub>H<sub>14</sub>, CAS no. 96-14-0), 2,2-dimethylbutane (C<sub>6</sub>H<sub>14</sub>, CAS no. 75-83-2), and 2,3-dimethylbutane (C<sub>6</sub>H<sub>14</sub>, CAS no. 79-29-8) are isomeric hexanes. Their chemical structures are shown in Figure 1. Hexanes are raw nonprocessed organic compounds and can be used in the production of glues, and as non-polar solvents for cleansing, degreasing, and chromatography analysis. They are essential components in industrial working mixtures for the petrochemical and compressor industries. Pure fluid equations of state are needed for mixture models such as the GERG-2008 by Kunz and Wagner (2012)<sup>1</sup>. To date Helmholtz energy equations of state for isomers of hexane have been developed only for *n*-hexane form Span and Wagner (2003)<sup>2</sup> and 2-methylpentane from Lemmon and Span (2006)<sup>3</sup>. There are no Helmholtz energy

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equations of state for 3-methylpentane, 2,2-dimethylbutane, and 2,3-dimethylbutane available. In this work, equations of state, which are applicable for all liquid, gas, and supercritical states within the limits of validity, have been developed for these three fluids. They are based on experimental thermodynamic property data from the literature and multiple methods to ensure correct extrapolation behavior. These equations are explicit in the Helmholtz energy with independent variables of temperature and density. All other thermodynamic properties can be calculated with the use of this fundamental potential with uncertainties of the same magnitude as the available data. To obtain caloric properties, no integration is needed as required for a pressure explicit equation of state.

# 2. Triple and Critical Points

The critical values are important properties for the description and application of fluids. Accurate data help to ensure that the equations of state have the correct behavior in the critical region when enough data are not available. They are also used as reducing values in the development of ancillary equations and the equations of state. The physical constants and characteristic properties of 3-methylpentane, 2,2-dimethylbutane, and 2,3-dimethylbutane are shown in Table 1. All properties in this table were determined in this work except the molar gas constant *R*, the molar mass *M*, and the triple-point temperature  $T_{\rm tp}$ . Tables 2 to 4 list the published triple-point and critical-point parameters of 3-methylpentane, 2,2-dimethylbutane, and 2,3-dimethylbutane, with temperatures converted to ITS-90. For 3-methylpentane, only Finke and Messerly (1973)<sup>4</sup> published the triple-point temperature, 110.263 K, which was thus used as the triple-point temperature in this work. This value is also recommended by the Thermodynamic Data Engine (TDE) program<sup>12</sup> available from the Thermodynamic Research Center (TRC) of NIST. Tables 3 and 4 summarize the many measurements for the triple-point temperatures of 2,2-dimethylbutane and 2,3-dimethylbutane. The recommended values from TDE, 174.20 K from Kilpatrick and Pitzer (1946)<sup>28</sup> for 2,2-dimethylbutane and 145.05 K from Adachi *et al.* (1971)<sup>45</sup> for 2,3-dimethylbutane, were selected for the two equations of state.

The critical temperatures and densities given in Table 1 were determined in this work during the fitting of the equation of state, based on the experimental data and on the values that exhibit the physically correct behavior in the critical region. The critical pressures were obtained from the final equations of state as a calculated property at the critical temperature and density. As examples, Figures 2 to 4 display the behavior of temperature versus density along with the rectilinear diameter in the critical region for these three fluids. The rectilinear diameter is the average of the saturated liquid and vapor densities. Generally, it should be a straight line in the critical region. To improve the representation of both experimental data and the rectilinear diameter, we fitted the critical temperature and density within the range of published critical temperatures and densities by increasing or decreasing the value with a step size of 0.01 K and 0.001 mol·dm<sup>-3</sup> to determine the best values for each equation. The final critical-point parameters of 3-methylpentane, 2,2-dimethylbutane, and 2,3-dimethylbutane are given in Tables 1 to 4.

# 3. Ancillary Equations

Ancillary equations were developed in this work to accurately represent the vapor pressure, the saturated liquid density, and the saturated vapor density. Preliminary equations were used during the fitting process of the full equation of state to substantially decrease the time required to calculate other properties at saturation. They also provide initial values for iterative procedures to find saturation states according to the Maxwell criteria. The ancillary equations for each fluid developed in this work are given in the next section, and were compared to calculations from each equation of state developed here.

# 3.1. Vapor Pressure Equations

**3-Methylpentane.** The ancillary equation for calculating estimates of the vapor pressure that closely agree with the equation of state is

$$\ln\left(\frac{p_{\sigma}}{p_{c}}\right) = \frac{T_{c}}{T} (n_{1}\theta + n_{2}\theta^{1.5} + n_{3}\theta^{2.75} + n_{4}\theta^{4.0} + n_{5}\theta^{15.2}), \tag{1}$$

where  $\theta = (1 - T/T_c)$ , the coefficients and exponents of  $\theta$  were obtained during fitting,  $n_1 = -7.3854$ ,  $n_2 = 1.5058$ ,  $n_3 = -1.3741$ ,  $n_4 = -3.1976$ ,  $n_5 = -1.3433$ , and  $p_{\sigma}$  is the vapor pressure. The critical parameters are given in Table 1. The maximum deviation is 0.035 % between calculated values from this equation and values obtained from the full solution for the saturation properties with the use of the Maxwell criteria at temperatures from the triple-point temperature (110.263 K) to the critical-point temperature.

2,2-Dimethylbutane. As with 3-methylpentane, the vapor pressure equation developed here is

$$\ln\left(\frac{p_{\sigma}}{p_{c}}\right) = \frac{T_{c}}{T} (n_{1}\theta + n_{2}\theta^{1.5} + n_{3}\theta^{2.0} + n_{4}\theta^{3.85} + n_{5}\theta^{15.85}),$$
(2)

where  $\theta = (1 - T/T_c)$ ,  $n_1 = -7.4088$ ,  $n_2 = 2.5218$ ,  $n_3 = -1.5652$ ,  $n_4 = -3.4318$ , and  $n_5 = -1.221$ . The critical parameters are given in Table 1. The maximum deviation is 0.041 % between calculated values from this equation and values obtained from the full solution for the saturation properties with the use of the Maxwell criteria at temperatures from the triple-point temperature (174.20 K) to the critical-point temperature.

2,3-Dimethylbutane. The vapor pressure equation is

$$\ln\left(\frac{p_{\sigma}}{p_{c}}\right) = \frac{T_{c}}{T} (n_{1}\theta + n_{2}\theta^{1.5} + n_{3}\theta^{1.9} + n_{4}\theta^{3.85} + n_{5}\theta^{17.3}),$$
(3)

where  $\theta = (1 - T/T_c)$ ,  $n_1 = -7.6041$ ,  $n_2 = 3.4948$ ,  $n_3 = -2.6831$ ,  $n_4 = -3.0964$ , and  $n_5 = -1.2618$ . The maximum deviation is 0.040 % as described above at temperatures from the triple-point temperature (145.05 K) to the critical-point temperature.

#### 3.2. Saturated Liquid Density Equations

3-Methylpentane. The saturated liquid density equation can be represented as

$$\frac{\rho'}{\rho_{\rm c}} = 1 + n_1 \theta^{0.19} + n_2 \theta^{0.645} + n_3 \theta^{1.05} + n_4 \theta^{1.6} + n_5 \theta^{7.5},\tag{4}$$

where  $n_1 = 0.4911$ ,  $n_2 = 4.2494$ ,  $n_3 = -3.965$ ,  $n_4 = 2.0896$ ,  $n_5 = 0.18507$ , and  $\rho'$  is the saturated liquid density. The maximum deviation is 0.023 % between calculated values from this equation and values obtained from the full solution for the saturation properties with the use of the Maxwell criteria at temperatures from the triple-point temperature (110.263 K) to the critical-point temperature.

2,2-Dimethylbutane. The saturated liquid density equation can be represented as

$$\frac{\rho'}{\rho_{\rm c}} = 1 + n_1 \theta^{0.33} + n_2 \theta^{0.65} + n_3 \theta^{0.95} + n_4 \theta^{1.3} + n_5 \theta^{1.7},\tag{5}$$

where  $n_1 = 1.852$ ,  $n_2 = -1.405$ ,  $n_3 = 6.393$ ,  $n_4 = -7.718$ , and  $n_5 = 3.708$ . The maximum deviation is 0.032 % between the triple-point temperature (174.20 K) and the critical-point temperature.

2,3-Dimethylbutane. The saturated liquid density equation can be represented as

$$\frac{\rho'}{\rho_{\rm c}} = 1 + n_1 \theta^{0.54} + n_2 \theta^{0.818} + n_3 \theta^{1.1} + n_4 \theta^{1.4} + n_5 \theta^{1.75},\tag{6}$$

where  $n_1 = 10.132$ ,  $n_2 = -29.743$ ,  $n_3 = 49.275$ ,  $n_4 = -39.267$ , and  $n_5 = 12.406$ . The maximum deviation is 0.058 % between the triple-point temperature (145.05 K) and the critical-point temperature.

#### 3.3. Saturated Vapor Density Equations

3-Methylpentane. The saturated vapor density equation is

$$\ln\left(\frac{\rho^{\prime\prime}}{\rho_{\rm c}}\right) = n_1 \theta^{0.3} + n_2 \theta^{0.871} + n_3 \theta^{2.95} + n_4 \theta^{6.5} + n_5 \theta^{14} + n_6 \theta^{27} , \qquad (7)$$

where  $n_1 = -1.407$ ,  $n_2 = -6.4038$ ,  $n_3 = -19.274$ ,  $n_4 = -53.302$ ,  $n_5 = -108.9$ ,  $n_6 = -200.54$ , and  $\rho''$  is the saturated vapor density. The maximum deviation is 0.041 % between calculated values from this equation and values obtained from the full solution for the saturation properties with the use of the Maxwell criteria at temperatures from the triple-point temperature (110.263 K) to the critical-point temperature.

2,2-Dimethylbutane. The saturated vapor density equation is

$$\ln\left(\frac{\rho''}{\rho_c}\right) = n_1 \theta^{0.32} + n_2 \theta^{0.904} + n_3 \theta^{2.85} + n_4 \theta^{6.4} + n_5 \theta^{14.75} , \qquad (8)$$

where  $n_1 = -1.7198$ ,  $n_2 = -5.7667$ ,  $n_3 = -17.244$ ,  $n_4 = -51.992$ , and  $n_5 = -126.59$ . The maximum deviation is 0.030 % below 485 K, and 0.054 % at higher temperatures up to the critical-point temperature.

2,3-Dimethylbutane. The saturated vapor density equation is

$$\ln\left(\frac{\rho^{\prime\prime}}{\rho_{\rm c}}\right) = n_1 \theta^{0.448} + n_2 \theta^{1.55} + n_3 \theta^{3.85} + n_4 \theta^{7.85} + n_5 \theta^{17.15} , \qquad (9)$$

where  $n_1 = -3.8824$ ,  $n_2 = -8.0209$ ,  $n_3 = -25.626$ ,  $n_4 = -56.727$ , and  $n_5 = -145.5$ . The maximum deviation is 0.028 % below 430 K, and 0.30 % at higher temperatures up to the critical-point temperature.

# 4. Helmholtz Energy Equations of State

The equations of state developed in this work are explicit in the Helmholtz energy with independent variables of temperature and density. The general form is

$$a(T,\rho) = a^{0}(T,\rho) + a^{r}(T,\rho),$$
(10)

where *a* is the molar Helmholtz energy,  $a^{0}$  is the ideal-gas molar Helmholtz energy, and  $a^{r}$  is the residual molar Helmholtz energy, which corresponds to the influence of intermolecular forces as shown in Lemmon and Jacobsen (2005)<sup>49</sup>. Its dimensionless reduced form can be written as:

$$\alpha(\tau,\delta) = \frac{a(T,\rho)}{RT} = \frac{a^0(T,\rho)}{RT} + \frac{a^{\mathrm{r}}(T,\rho)}{RT} = \alpha^0(\tau,\delta) + \alpha^{\mathrm{r}}(\tau,\delta),$$
(11)

where  $\alpha$  is the dimensionless reduced Helmholtz energy, *R* the molar gas constant,  $\tau$  the reciprocal reduced temperature  $\tau = T_c/T$ , and  $\delta$  the reduced density  $\delta = \rho/\rho_c$ .  $T_c$  and  $\rho_c$  are the values of the critical temperature and density given in Table 1.

#### 4.1. Properties of the Ideal gas

The Helmholtz energy of the ideal-gas can be expressed as

$$a^{0}(T,\rho) = h^{0}(T) - RT - Ts^{0}(T,\rho).$$
<sup>(12)</sup>

The ideal-gas enthalpy in this equation is

$$h^{0} = h_{0}^{0} + \int_{T_{0}}^{T} c_{p}^{0} \mathrm{d}T.$$
<sup>(13)</sup>

The ideal-gas entropy is

$$s^{0} = s_{0}^{0} + \int_{T_{0}}^{T} \frac{c_{p}^{0}}{T} dT - R \ln\left(\frac{\rho T}{\rho_{0} T_{0}}\right), \tag{14}$$

where  $c_p^0$  is the ideal-gas isobaric heat capacity and  $\rho_0$  is the ideal-gas density at the reference state  $T_0$  and  $p_0$ , where  $\rho_0 = p_0/RT_0$ . By combining these equations and transforming the ideal-gas Helmholtz energy to a dimensionless form, the following idealgas Helmholtz energy equation is obtained

$$\alpha^{0}(\tau,\delta) = \frac{h_{0}^{0}\tau}{RT_{c}} - \frac{s_{0}^{0}}{R} - 1 + \ln\frac{\delta\tau_{0}}{\delta_{0}\tau} - \frac{\tau}{R} \int_{\tau_{0}}^{\tau} \frac{c_{p}^{0}}{\tau^{2}} d\tau + \frac{1}{R} \int_{\tau_{0}}^{\tau} \frac{c_{p}^{0}}{\tau} d\tau , \qquad (15)$$

where  $\tau_0 = T_c/T_0$  and  $\delta_0 = \rho_0/\rho_c$ . In this work, values of  $T_0 = 273.15$  K and  $p_0 = 1.0$  kPa are used as the reference state.  $T_0, p_0, h_0^0$ , and  $s_0^0$  are arbitrary constants for the enthalpy and entropy for a prescribed reference state.

In Eq 15, the ideal-gas properties require an ideal-gas isobaric heat capacity equation, which can be expressed as

$$\frac{c_p^0}{R} = c_0 + \sum_{k=1}^3 \nu_k \left(\frac{u_k}{T}\right)^2 \frac{\exp(u_k/T)}{[\exp(u_k/T) - 1]^2},\tag{16}$$

where R = 8.3144598 J·mol<sup>-1</sup>·K<sup>-1</sup> as given in Table 1. Calculated ideal-gas isobaric heat capacity values are available from the TDE program<sup>12</sup>, and their average absolute deviations (AADs) are shown in Table 5. These data were calculated from various methods and are not based on experimental data. Figures 5 to 7 display the comparisons of  $c_p^0$  values calculated with Eq 16 to those from TDE.

With Eq 16, the integration to the dimensionless ideal-gas Helmholtz energy in Eq 15 can be performed, resulting in

$$\alpha^{0}(\tau,\delta) = a_{1} + a_{2}\tau + \ln\delta + (c_{0} - 1)\ln\tau + \sum_{k=1}^{3} v_{k}\ln\left[1 - \exp\left(-\frac{u_{k}\tau}{T_{c}}\right)\right],$$
(17)

where  $a_1$  and  $a_2$  are constants. They can be calculated with the following equations,

$$a_{1} = -1 + \ln \frac{\tau_{0}}{\delta_{0}} + c_{0} - c_{0} \ln \tau_{0} - \frac{s_{0}^{0}}{R} - \sum_{k=1}^{3} v_{k} \left\{ \frac{u_{k} \tau_{0} / T_{c}}{1 - \exp(u_{k} \tau_{0} / T_{c})} + \ln \left[ 1 - \exp\left(-\frac{u_{k} \tau_{0}}{T_{c}}\right) \right] \right\}$$
(18)

and

$$a_2 = \frac{h_0^0}{RT_c} - \frac{c_0}{\tau_0} - \sum_{k=1}^3 \nu_k \frac{u_k/T_c}{\exp(u_k \tau_0/T_c) - 1}.$$
(19)

In this work, the normal-boiling point for the saturated liquid state was selected as the reference state with the values of enthalpy and entropy set to zero. The values of  $h_0^0$  and  $s_0^0$  at  $T_0 = 273.15$  K and  $p_0 = 1.0$  kPa were calculated from the final equation of this work, and  $a_1$  and  $a_2$  were obtained from Eqs 18 and 19. Their values are given in Table 1, and the other coefficients in Eqs 17 to 19 are the same as those in Eq 16.

**3-Methylpentane.** In the ideal-gas isobaric heat capacity equation of 3-methylpentane, the coefficients are  $c_0 = 7.0$ ,  $v_1 = 7.4047$ ,  $v_2 = 25.09$ ,  $v_3 = 17.741$ ,  $u_1 = 470$  K,  $u_2 = 1555$  K, and  $u_3 = 3946$  K. For the reference state described above, the enthalpy and entropy values are  $h_0^0 = 19487.5982650113$  J·mol<sup>-1</sup> and  $s_0^0 = 93.1892982505$  J·mol<sup>-1</sup>·K<sup>-1</sup>, which then gives  $a_1 = 4.64793772911$  and  $a_2 = -0.906515038458$ . The use of all digits is required to obtain values of enthalpy and entropy that are very close to zero. Although values of the ideal-gas isobaric heat capacity equation were fitted within 0.5 % to the available data in the TDE program as shown in Figure 5, the uncertainty, which is approximately 2 %, is much higher due to the calculation methods used by TDE to obtain these values.

**2,2-Dimethylbutane.** In the ideal-gas isobaric heat capacity equation of 2,2-dimethylbutane, the coefficients are  $c_0 = 7.5$ ,  $v_1 = 7.8764$ ,  $v_2 = 26.017$ ,  $v_3 = 22.147$ ,  $u_1 = 525$  K,  $u_2 = 1620$  K, and  $u_3 = 4370$  K. For the reference state described above, the enthalpy and entropy values are  $h_0^0 = 19699.8282255266$  J·mol<sup>-1</sup> and  $s_0^0 = 97.2641495983$  J·mol<sup>-1</sup>·K<sup>-1</sup>, which then gives  $a_1 = 4.07450225260$  and  $a_2 = -1.02091775242$ . Although values of the ideal-gas isobaric heat capacity equation were fitted to be within 0.5 % to the available data in the TDE program as shown in Figure 6, the uncertainty, which is approximately 2 %, is much higher due to the calculation methods used by TDE to obtain these values.

**2,3-Dimethylbutane.** In the ideal-gas isobaric heat capacity equation of 2,3-dimethylbutane, the coefficients are  $c_0 = 8.5$ ,  $v_1 = 7.2248$ ,  $v_2 = 26.48$ ,  $v_3 = 17.893$ ,  $u_1 = 535$  K,  $u_2 = 1693$  K, and  $u_3 = 4369$  K. For the reference state described above, the enthalpy and entropy values are  $h_0^0 = 19554.2027822906$  J·mol<sup>-1</sup> and  $s_0^0 = 94.7089033208$  J·mol<sup>-1</sup>·K<sup>-1</sup>, which then gives  $a_1 = 4.13396186473$  and  $a_2 = -1.39038637062$ . Although values of the ideal-gas isobaric heat capacity equation were fitted to be within 1.3 % to the available data in the TDE program as shown in Figure 7, the uncertainty, which is approximately 2 %, is much higher due to the calculation methods used by TDE to obtain these values.

## 4.2. Properties of the Real Fluid

The residual Helmholtz energy can be expressed as

$$\alpha^{r}(\tau,\delta) = \sum_{i=1}^{5} n_{i} \delta^{d_{i}} \tau^{t_{i}} + \sum_{i=6}^{10} n_{i} \delta^{d_{i}} \tau^{t_{i}} \exp(-\delta^{l_{i}})$$
$$+ \sum_{i=11}^{m} n_{i} \delta^{d_{i}} \tau^{t_{i}} \exp[-\eta_{i} (\delta - \varepsilon_{i})^{2} - \beta_{i} (\tau - \gamma_{i})^{2}], \qquad (20)$$

where the index *i* refers to each individual term, and *m* is the total number of terms in the equation of state, which is 16 for both 3-methylpentane and 2,2-dimethylbutane, and 15 for 2,3-dimethylbutane. The first two summations include five terms each, which involve polynomial-like and simple exponential terms. The third summation contains Gaussian bell-shaped terms, which are quite sensitive but powerful in modeling the properties of fluids in the critical region, especially for densities and heat capacities. The coefficients and exponents of Eq 20 for 3-methylpentane, 2,2-dimethylbutane, and 2,3-dimethylbutane are given in Table 6. When developing an equation of state, the values of  $t_i$ ,  $d_i$ , and  $l_i$  should be greater than zero. In addition,  $d_i$ and  $l_i$  should be integers. The equation of state for 3-methylpentane is valid from 110.263 K (the triple point temperature) to 550 K, with pressures up to 1200 MPa and densities up to 9.66 mol·dm<sup>-3</sup>. The equation of state for 2,2-dimethylbutane is valid from 174.2 K (the triple point temperature) to 575 K, with pressures up to 1000 MPa and densities up to 8.77 mol·dm<sup>-3</sup>. The equation of state for 2,3-dimethylbutane is valid from 145.05 K (the triple point temperature) to 550 K, with pressures up to 9.12 mol·dm<sup>-3</sup>. All thermodynamic properties can be calculated as combinations of the derivatives of the Helmholtz energy from Eqs 17 and 20 as explained by Lemmon *et al.* (2009)<sup>48</sup>.

The equations for 3-methylpentane and 2,2-dimethylbutane have one more Gaussian term than the one of 2,3dimethylbutane. As given in Table 6, the sixth term in the third summation contains large values of  $\eta_i$  and  $\beta_i$ . This term requires that the values of  $\varepsilon_i$  and  $\gamma_i$  should be close to 1, with the value of  $\varepsilon_i$  between about 0.9 and 1.0 and the value of  $\gamma_i$ between approximately 1.03 and 1.10. This term models the rapid change in ptoperties at temperatures and densities very close to the critical point and in the two-phase region, whereas other regions are insignificantly affected. The properties in the critical region are highly influenced by this term, especially the isochoric heat capacities.

Lemmon and Jacobsen  $(2005)^{49}$  pointed out that a polynomial term in the first summation with  $d_i = 4$  and  $t_i = 1$  with a small positive coefficient causes the isotherms at high temperatures and pressures to converge, without crossing each other.

In this work, we changed the value of  $d_i$  from 4 to 5, which has a stronger influence than the original term. This change helped the isotherms at high temperatures and pressures to converge faster. In addition, the term contributed more to the behavior of the equations at low temperatures in the liquid phase. Because many fluids have been developed with a polynomial term of  $d_i = 4$  and  $t_i = 1$ , there is still a need to investigate the effects of the term used in this work. It is not clear if the behavior applies in general or just for some specific fluids.

#### 5. Experimental Data and Comparisons to Equations of State

The fitting process of the equations of state for 3-methylpentane, 2,2-dimethylbutane, and 2,3-dimethylbutane include experimental saturation properties,  $p\rho T$ , heat capacities, speeds of sound, and virial coefficients. All temperatures were converted to the ITS-90 temperature scale. All of the data are summarized in Tables 7 to 9 and have been compared to the values calculated from the equations of state, including those not used in the development of the equations. In addition, the extrapolation behavior of the equations of state have been analyzed both within the region of validity and outside this region at very high temperatures and pressures, and at very low temperatures.

The goodness-of-fit of the equations of state were determined by comparisons of the calculated values of a property to the experimental data. These calculations are based on the percent deviation in any property *X*, defined as

$$\%\Delta X = 100 \left(\frac{X_{\exp} - X_{calc}}{X_{\exp}}\right). \tag{21}$$

With this definition, the average absolute deviation (AAD) can be written as

$$AAD = \frac{1}{N_{exp}} \sum_{i=1}^{N_{exp}} |\%\Delta X_i|,$$
(22)

where  $N_{exp}$  is the number of experimental data points in one dataset. The AADs between experimental data and calculated values from the equations of state are given in Tables 7 to 9.

#### 5.1. Comparisons with Saturated Data

Figures 8 and 9 compare vapor pressures and saturated liquid densities calculated from the equation of state for 3methylpentane to experimental data. There are no experimental data for the saturated vapor density of this fluid. The average absolute deviations are shown in Table 7. For vapor pressure, there are no experimental data at temperatures below 280 K and between 345 K and 420 K. However, there is a significant amount of experimental vapor pressure data at temperatures between 280 K and 340 K. Since these data are scattered and not consistent with each other, it is difficult to select the correct values. Only the two datasets of Day and Felsing (1951)<sup>6</sup> and Kay (1946)<sup>54</sup> contain vapor pressures at temperatures higher than 420 K. Only Kay (1946)<sup>54</sup> measured one data point near the critical temperature. The average absolute deviations in vapor pressure for the datasets of Day and Felsing (1951)<sup>6</sup> and Kay (1946)<sup>54</sup> are 0.16 % and 0.48 %, respectively. Much of the data provided by TRC<sup>12</sup> is a collection of many different datasets with only one or two data points. Most of them are located at temperatures near the normal-boiling temperature of 336.379 K (which was calculated from the equation of state). As shown in Figure 8, most of the vapor pressure data between 280 K and 345 K deviate within  $\pm 0.2$  %. Most of the deviations for temperatures higher than 420 K are within  $\pm 0.3$  %. The average absolute deviations in saturated liquid density for the datasets of Awwad and Pethrick (1983)<sup>58</sup>, Comelli and Francesconi (1990)<sup>59</sup>, De Vos (1950)<sup>60</sup>, and TRC<sup>12</sup> are 0.032 %, 0.007 %, 0.026 %, and 0.094 %, respectively. All of these experimental data are located in a narrow temperature range between 230 K and 330 K. Only one dataset, Awwad and Pethrick (1983)<sup>58</sup>, measured data below 270 K. Most of the other data are located at temperatures between 285 K and 305 K. As shown in Figure 9, the deviations of the experimental saturated liquid density data are within  $\pm 0.1$  % at temperatures between 230 K and 330 K.

Figures 10 to 12 compare vapor pressures, saturated liquid densities, and saturated vapor densities calculated from the equation of state for 2,2-dimethylbutane to experimental data. The average absolute deviations in these three saturation properties are shown in Table 8. The average absolute deviations in vapor pressure for the datasets of del Rio et al. (2004)<sup>69</sup>, Garriga et al. (1994)<sup>70</sup>, Hyeong et al. (2013)<sup>71</sup>, Kay (1946)<sup>54</sup>, Kilpatrick and Pitzer (1946)<sup>28</sup>, Nicolini and Laffitte (1949)<sup>72</sup>, TRC<sup>12</sup>, and Willingham et al. (1945)<sup>57</sup> are 0.21 %, 0.13 %, 0.33 %, 0.08 %, 0.82 %, 0.29 %, 0.82 %, and 0.09 %, respectively. Most of the experimental vapor pressure data are concentrated at temperatures between 230 K and 340 K. There is one data point higher than 340 K from Kay (1946)<sup>54</sup>, which is at a temperature near the critical point. Only the dataset of Kilpatrick and Pitzer (1946)<sup>28</sup> contains vapor pressure data between 210 K and 230 K, which has a discontinuity in their data at temperatures below 210 K and between 240 K and 290 K. Figure 10 shows that the deviations of most vapor pressure data are within ±0.4 % between 230 K and 340 K. The average absolute deviations in saturated liquid densities for the datasets of Polzin and Weiss (1990)<sup>73</sup> and TRC<sup>12</sup> are 0.054 % and 0.09 %, respectively. These experimental data are located at temperatures between 240 K and 320 K. The data from TRC<sup>12</sup> are from many different references with only one or two data points, and are located at temperatures between 273 K and 303 K. During the fitting process, we distributed the deviations of the data from TRC<sup>12</sup> evenly around the equation of state. As shown in Figure 11, the deviations of most saturated liquid density data are within  $\pm 0.2$  % between 240 K and 320 K. There is only one dataset with saturated vapor density data, Nicolini and Laffitte (1949)<sup>74</sup>, with an absolute average deviation of 0.69 %. Figure 12 shows that the deviations of most of the saturated vapor density points are within  $\pm 1.2$  % between 275 K and 315 K.

Figures 13 to 15 compare vapor pressures, saturated liquid densities, and saturated vapor densities calculated from the equation of state for 2,3-dimethylbutane to experimental data. The average absolute deviations in these three saturation properties are shown in Table 9. As shown in Figure 13, all of these data for the vapor pressure are located at temperatures between 260 K and 500 K. Among these datasets, only Young and Fortey (1879)<sup>47</sup> and Young and Fortey (1900)<sup>82</sup> cover the whole temperature range. The remaining data are concentrated between 280 K and 335 K, where the vapor pressure data from

all datasets are scattered and do not agree well with each other. At temperatures higher than 335 K, the datasets of Young and Fortey  $(1879)^{47}$  and Young and Fortey  $(1900)^{82}$  behave similarly, but their data at temperatures higher than 450 K show a discontinuity with their own data at temperatures under 450 K. However, one data point near the critical temperature from Kay  $(1946)^{54}$  agrees well with the value calculated from the equation of state of 2,3-dimethylbutane. The uncertainty in vapor pressure is estimated to be 0.2 % at temperatures higher than 260 K. The average absolute deviations in saturated liquid density for the datasets of De Vos  $(1950)^{60}$ , Kelso and Felsing  $(1942)^{83}$ , TRC<sup>12</sup>, and Young and Fortey  $(1879)^{47}$  are 1.18 %, 0.038 %, 0.15 %, and 0.11 %, respectively. Figure 14 shows that all of these experimental saturated liquid density data are located at temperatures between 270 K and 500 K, and that the deviations of most of these data are within ±0.15 % in this region. The average absolute deviations in saturated vapor density for the dataset of Young and Fortey  $(1879)^{47}$  are 2.21 %. Figure 15 shows that all of these data were measured at temperatures higher than 320 K, and the deviations are generally within ±3.0 % in this region.

# 5.2. $p\rho T$ Data and Virial Coefficients

The experimental  $p\rho T$  and second virial coefficient data for 3-methylpentane are summarized in Table 7. Figure 16 gives comparisons between densities calculated with the equation of state for 3-methylpentane and experimental data at different temperature intervals. From Table 7, the average absolute deviations in density for the datasets of Bridgman (1931)<sup>61</sup>, Day and Felsing (1951)<sup>6</sup>, Guerrero et al. (2013)<sup>62</sup>, Morivoshi and Aono (1988)<sup>63</sup>, and Sahli et al. (1976)<sup>64</sup> are 0.38 %, 1.31 %, 0.06 %, 0.03 %, and 0.03 %, respectively. The  $p\rho T$  data are very sparse for 3-methylpentane. There are no data at temperatures below 270 K, being far from the triple-point temperature (110.263 K), and no vapor phase data in the region below the critical temperature. Moreover, at temperatures higher than 400 K, there is only one  $p\rho T$  dataset from Day and Felsing (1951)<sup>6</sup>. At temperatures below 400 K, Bridgman (1931)<sup>61</sup> reported measurements at high pressures up to 1180 MPa. These data are in conflict with the other datasets. As shown in Figure 16, the uncertainties in density of the equation of state for 3-methylpentane are 0.2 % in the liquid phase region for temperatures between 270 K and 400 K and up to pressures of 100 MPa, 0.4 % in the liquid phase region for temperatures between 400 K and 500 K, 0.35 % in the vapor phase region at temperatures between 520 K and 550 K, and 1.0 % at pressures between 150 MPa and 1180 MPa. At temperatures below 270 K, the uncertainties increase but are unknown. An estimated value of the uncertainty in liquid density of 0.5 % at temperatures down to the triple point is plausible. The uncertainties in the critical region are higher for all properties, but unknown due to the absence of data. Figure 17 compares second virial coefficients calculated from the equation of state for 3-methylpentane to experimental data. There is only one dataset from Chun et al. (1981)68 that contains second virial coefficient data and the absolute average deviation is 32.4  $\text{cm}^3 \cdot \text{mol}^{-1}$  as shown in Table 7.

The experimental  $p\rho T$  and second virial coefficient data for 2,2-dimethylbutane are summarized in Table 8. Figure 18 shows comparisons between densities calculated with the equation of state and experimental data at different temperature intervals. From Table 8, the average absolute deviations in density for the datasets of Brazier and Freeman (1969)<sup>75</sup>, Bridgman (1931)<sup>61</sup>, Felsing and Watson (1943)<sup>76</sup>, Griskey and Canjar (1964)<sup>77</sup>, Guerrero *et al.* (2013)<sup>62</sup>, Moriyoshi and Aono (1988)<sup>63</sup>, Polzin and Weiss (1990)<sup>73</sup>, and Sahli et al. (1976)<sup>64</sup> are 1.18 %, 1.25 %, 0.20 %, 5.34 %, 0.06 %, 0.051 %, 0.064 %, and 0.059 %, respectively. As with 3-methylpentane, for 2,2-dimethylbutane the  $p\rho T$  data are very sparse. There are no data at temperatures below 240 K, which is far from the triple-point temperature (174.20 K) and no vapor phase data are available in the region below the critical temperature. Moreover, at temperatures higher than 400 K, there is only one  $p\rho T$  dataset from Felsing and Watson (1943)<sup>76</sup>. At temperatures below 400 K, Bridgman (1931)<sup>61</sup> published data at high pressures up to 980 MPa, but these data are in conflict with the other datasets. As shown in Figure 18, the uncertainties in density of the equation of state for 2,2dimethylbutane are 0.2 % in the liquid phase region for temperatures between 240 K and 475 K and up to pressures of 100 MPa, and 1.0 % in the vapor phase region at temperatures between 495 K and 575 K. At temperatures below 240 K, the uncertainties increase but are unknown. An estimated value of 0.5 % uncertainty in liquid density at the triple point is plausible. The uncertainties in the critical region are higher for all properties, but unknown due to the absence of data. Figure 19 compares second virial coefficients calculated from the equation of state for 2,2-dimethylbutane to experimental data. There is only one second virial coefficient dataset by Chun et al. (1981)<sup>68</sup> and its absolute average deviation is 16.1 cm<sup>3</sup>·mol<sup>-1</sup> as shown in Table 8.

The experimental  $\rho\rho T$  and second virial coefficient data for 2,3-dimethylbutane are summarized in Table 9. Figure 20 shows comparisons between densities calculated with the equation of state for 2,3-dimethylbutane and experimental data at different temperature intervals. From Table 7, the average absolute deviations in density for the datasets of Baonza *et al.* (1993)<sup>85</sup>, Bridgman (1931)<sup>61</sup>, Guerrero *et al.* (2013)<sup>62</sup>, Holzapfel *et al.* (1987)<sup>86</sup>, Kelso and Felsing (1942)<sup>83</sup>, Moriyoshi and Aono (1988)<sup>63</sup>, Riembauer *et al.* (1990)<sup>87</sup>, and Sahli *et al.* (1976)<sup>64</sup> are 0.28 %, 0.26 %, 0.084 %, 0.013 %, 0.23 %, 0.043 %, 0.69 %, and 0.025 %, respectively. The  $\rho\rho T$  data are very scattered for 2,3-dimethylbutane at temperatures below 300 K. Figure 20 shows that the datasets of Baonza *et al.* (1993)<sup>85</sup> and Riembauer *et al.* (1990)<sup>87</sup>, Guerrero *et al.* (2013)<sup>62</sup>, and Moriyoshi and Aono (1988)<sup>63</sup> at pressures between 10 MPa and 300 MPa, and temperatures between 260 K and 320 K. At temperatures below 260 K, there are no datasets except Baonza *et al.* (1993)<sup>85</sup> and Riembauer *et al.* (1990)<sup>87</sup>. These datasets are not used in the development of the equation of state at pressures between 10 MPa and 300 MPa. There are no vapor phase data in the region below the critical temperature. Only Kelso and Felsing (1942)<sup>83</sup> report  $\rho\rho T$  data at temperatures higher than 400 K, the same as with 3-methylpentane and 2,2-dimethylbutane. At temperatures below 400 K,

Bridgman (1931)<sup>61</sup> published density data at high pressures up to 1080 MPa. As shown in Figure 20, the uncertainties in density of the equation of state for 2,3-dimethylbutane are 0.25 % in the liquid phase region for temperatures between 205 K and 500 K and up to pressures of 150 MPa, 0.8 % in the vapor phase region at temperatures between 520 K and 550 K, and 1.0 % at pressures between 150 MPa and 1080 MPa. The uncertainties in the critical region are higher for all properties, but unknown due to the absence of data. Figure 21 compares second virial coefficients calculated from the equation of state for 2,3-dimethylbutane to experimental data. There is only one dataset, Chun *et al.* (1981)<sup>68</sup>, reporting second virial coefficient data and its absolute average deviation is 66 cm<sup>3</sup>·mol<sup>-1</sup> as shown in Table 9.

Figure 22 shows calculations of  $(Z-1)/\rho$  versus density  $\rho$  from the equation of state of 3-methylpentane along isotherms between 275 K and 800 K at intervals of 25 K in the vapor-phase region. In this plot, the interceptions of the isotherms with the *y*-axis (zero density) represent the second virial coefficients for any given temperature. The slope of each line at zero density represents the third virial coefficient at that given temperature. Figure 23 shows the behavior of *B*, *C*, and *D* (virial coefficients) from the equation of state of 2,2-dimethylbutane versus temperature with reasonable behavior from low temperatures up to extremely high temperatures, which is ensured by appropriate temperature exponents and behavior constraints. These assessments are possible for estimating the behavior of other similar fluids that have no vapor phase experimental data.

## 5.3. Caloric Data

Published caloric data for 3-methylpentane, 2,2-dimethylbutane, and 2,3-dimethylbutane are summarized in Tables 7 to 9, which include speeds of sound, heat capacities, and heats of vaporization. Figures 24 to 26 show comparisons of sound speeds, isobaric heat capacities, and saturation heat capacities calculated with the equation of state of 3-methylpentane to experimental data. There is only one dataset from Awwad and Pethrick (1983)<sup>58</sup> for the speed of sound. It contains experimental data at temperatures between 233 K and 313 K, and its absolute average deviation is 0.083 %. As shown in Figure 24, the deviations of most sound speed data are within  $\pm 0.1$  %. For the isobaric heat capacity, only Waddington *et al.* (1949)<sup>65</sup> published data that are in the vapor phase, and the other datasets all lie within the liquid phase. Table 7 gives the average absolute deviations in isobaric heat capacity of Douslin and Huffman (1946)<sup>25</sup>, Stull (1937)<sup>15</sup>, TRC<sup>12</sup>, and Waddington *et al.* (1949)<sup>65</sup>, which are 0.09 %, 3.2 %, 0.14 %, and 0.31 %, respectively. Figure 25 demonstrates that the dataset of Stull (1937)<sup>15</sup> contradicts the dataset of Douslin and Huffman (1946)<sup>25</sup> and the data compiled at TRC<sup>12</sup>. As shown in Figure 25, the uncertainty in the isobaric heat capacity is estimated to be 0.5 % in the liquid phase at temperatures between the triple-point temperature (110.263 K) and 310 K, and 1.0 % in the vapor phase at temperatures between 320 K and 480 K. The average absolute deviations in the saturation heat capacity is estimated to be 0.5 % at temperatures between the triple-point temperature 26, the uncertainty in the saturation heat capacity is estimated to be 0.5 % at temperatures between the triple-point temperature and

390 K. The values from  $TRC^{12}$  for the saturation heat capacity are theoretical calculated data. Above 340 K, the values are extrapolated and have higher uncertainties. These data were not fitted and the uncertainty in the equation of state here without connection to the deviations to these data is estimated to be 5 %.

Figures 27 and 28 show comparisons of isobaric heat capacities and saturation heat capacities calculated with the equation of state of 2,2-dimethylbutane to experimental data. For the isobaric heat capacity, only Pitzer (1941)<sup>78</sup> and Waddington and Douslin (1947)<sup>79</sup> published vapor phase data. All the other datasets published liquid phase data. In the liquid phase, the dataset by Stull (1937)<sup>15</sup> contradicts the other liquid phase datasets. The average absolute deviations in the isobaric heat capacity of Douslin and Huffman (1946)<sup>25</sup>, Kilpatrick and Pitzer (1946)<sup>28</sup>, Pitzer (1941)<sup>78</sup>, Stull (1937)<sup>15</sup>, TRC<sup>12</sup>, and Waddington and Douslin (1947)<sup>79</sup> are 0.15 %, 0.19 %, 1.28 %, 3.35 %, 0.38 %, and 0.29 %, respectively, as given in Table 8. Figure 27 shows that the uncertainty in isobaric heat capacity is estimated to be 0.5 % in the liquid phase at temperatures between 340 K and 450 K. Saturation heat capacity data are only available from TRC<sup>12</sup> with an absolute average deviation of 2.5 %. See the discussion in the previous paragraph for further information about the TRC<sup>12</sup> data. The uncertainty in the saturation heat capacity is estimated to be 0.5 % (approximately the same as that in the isobaric heat capacity) at temperatures between the triple-point temperature and 400 K.

Figures 29 and 30 show comparisons of isobaric heat capacities and saturation heat capacities calculated with the equation of state of 2,3-dimethylbutane to experimental data. For the isobaric heat capacity, only Waddington *et al.* (1949)<sup>65</sup> published vapor phase data; the others published liquid phase data. In the liquid phase, the dataset by Stull (1937)<sup>15</sup> contradicts the datasets of Douslin and Huffman (1946)<sup>25</sup> and TRC<sup>12</sup>. The average absolute deviations in the isobaric heat capacity of Douslin and Huffman (1946)<sup>25</sup>, Stull (1937)<sup>15</sup>, TRC<sup>12</sup>, and Waddington *et al.* (1949)<sup>65</sup> are 0.11 %, 3.53 %, 0.25 %, and 0.24 %, respectively, as given in Table 9. Figure 29 shows that the uncertainty in the isobaric heat capacity is estimated to be 0.5 % in the liquid phase at temperatures between the triple-point temperature (145.05 K) and 320 K, and 0.5 % in the vapor phase at temperatures between 340 K and 470 K. Saturation heat capacity data are only available from TRC<sup>12</sup>, of which the absolute average deviation is 1.2 %. See the discussion in the previous paragraph for further information about the TRC<sup>12</sup> data. The uncertainty in the saturation heat capacity is estimated to be 0.5 % (about the same as that in the isobaric heat capacity) at temperatures between the triple-point temperature and 380 K.

#### 5.4. Extrapolation Behavior

In addition to the deviations between calculated values from the equations of state and experimental data, the extrapolation behavior is another vital assessment for assessing the quality of an equation of state. Plots of constant property lines on various thermodynamic coordinates at extreme conditions (high T and p) are useful in evaluating the extrapolation

behavior. The equations for 3-methylpentane, 2,2-dimethylbutane, and 2,3-dimethylbutane developed in this work were used to calculate plots of the isochoric heat capacity versus temperature (Figure 31), the isobaric heat capacity versus temperature (Figure 32), the speed of sound versus temperature (Figure 33), temperature versus density (Figure 34), pressure versus density (Figure 35), the phase identification parameter according to Venkatarathnam and Oellrich (2011)<sup>88</sup> versus temperature and density along isobars and isotherms (Figures 36 and 37), the Gruneisen parameter versus density and temperature along isotherms and isochores (Figures 38 and 39), and the characteristic ideal curves of the equation of state (Figure 40).

Figures 31 and 32 show isochoric heat capacities calculated from the equation of state of 2,3-dimethylbutane versus temperature, and isobaric heat capacities calculated from the equation of state of 3-methylpentane versus temperature at pressures ranging from zero to very high values. For these fluids, isochoric and isobaric heat capacities should reach a local maximum along the saturation line at the critical point, and change smoothly without isobars and isochores crossing each other within the range of validity and at extrapolated states for temperatures below the triple point. These criteria are full field by the illustrated figures.

Figure 33 shows the sound speed calculated from the equation of 2,2-dimethylbutane versus the logarithm of temperature along the saturation lines and along isobars at pressures ranging from zero to 2000 MPa. In this figure it is visible that the isobars in the liquid phase are smooth with decreasing curvature at very low temperatures (even down to 0 K), meaning that the equation has a reasonable extrapolation behavior at extremely low temperatures and high pressures.

Figures 34 and 35 display the density behavior along isobars calculated from the equation of 2,3-dimethylbutane and isotherms calculated from the equation of 3-methylpentane. From these two figures, both isobars and isotherms versus density change smoothly and do not cross even at extremely high pressures and temperatures, which demonstrates that the equations of this work have reasonable  $p\rho T$  behavior not only within the region of validity, but also at extremely high pressures and temperatures.

The phase identification parameter (PIP) of a fluid is a comprehensive parameter applied to differentiate the vapor phase from the liquid phase through the use of partial derivatives of pressure, volume, and temperature, and is given by

$$\Pi = 2 - \rho \left[ \left( \frac{\partial^2 p}{\partial \rho \partial T} \right) / \left( \frac{\partial p}{\partial T} \right)_v - \left( \frac{\partial^2 p}{\partial \rho^2} \right)_T / \left( \frac{\partial p}{\partial \rho} \right)_T \right].$$
(23)

States in the liquid phase have a value greater than 1, and states in the vapor phase have a value smaller than 1. Figure 36 displays the phase identification parameter calculated from the equation of 2,2-dimethylbutane versus temperature along isobars between 0.1 MPa and 2000 MPa. In this plot, the liquid saturation line is smooth at temperatures from very low values (near 1 K) to the critical point. The isobars are flat at low and high temperatures. Figure 37 shows the phase identification parameter calculated from the equation of 2,3-dimethylbutane versus density along isotherms below 5000 K. The isotherms are smooth

at both low and high temperatures. From these two figures, the partial derivatives of pressure, volume, and temperature of the equations in this work behave reasonably within the region of validity and in the region at high temperatures and pressures.

Figure 38 shows the Gruneisen parameter calculated from the equation of 3-methylpentane versus density along isotherms between 100 K and 5000 K. The Gruneisen parameter is a property involving  $c_v$ , dp/dT at constant volume, and density, and is very sensitive to the behavior of the equation of state. This parameter is calculated as

$$\Gamma = \frac{\left(\frac{\partial p}{\partial T}\right)_{\nu}}{c_{\nu}\rho}.$$
(24)

The slope of the Gruneisen parameter with respect to density along isotherms is positive in the liquid phase, and the curvature is negative at high densities, as shown in Figure 38. Figure 39 shows the Gruneisen parameter calculated from the equation of 2,2-dimethylbutane versus temperature along isochores. In this figure, the isochores are not smooth at temperatures near but below the triple-point temperature because of the contribution from the sudden change in the isochoric heat capacity in the ideal-gas state.

Figure 40 shows the characteristic (ideal) curves of the equation of state for 2,3-dimethylbutane as a function of reduced temperature  $T/T_c$  and reduced pressure  $p/p_c$ . These ideal curves help to determine the behavior of an equation of state in regions without available experimental data. The ideal curves describe the behavior of the compressibility factor  $Z = p / \rho RT$ , and include the Boyle curve, the Joule-Thomson inversion curve, the Joule inversion curve, and the ideal curve. The ideal curve is defined as

$$Z = \frac{p}{\rho RT} = 1. \tag{25}$$

The Boyle curve is defined as

$$\left(\frac{\partial z}{\partial v}\right)_T = 0. \tag{26}$$

The Joule-Thomson inversion curve is defined as

$$\left(\frac{\partial Z}{\partial T}\right)_p = 0. \tag{27}$$

The Joule inversion curve is defined as

$$\left(\frac{\partial Z}{\partial T}\right)_{\nu} = 0.$$
<sup>(28)</sup>

As shown in this figure, these characteristic curves are smooth, indicating that the equation of state in this work has reasonable extrapolation behavior in regions without experimental data. The behavior of the lines is very similar to many other fluids that have highly-accurate data to very high temperatures, such as nitrogen<sup>89</sup> and argon<sup>90</sup>.

# 6. Conclusions

In this work, Helmholtz energy equations of state, with independent variables of temperature and density, were developed for 3-methylpentane, 2,2-dimethylbutane, and 2,3-dimethylbutane based on vapor pressures,  $p\rho T$  data, virial coefficients, and caloric properties. The equation of state for 3-methylpentane is valid from 110.263 K (the triple point temperature) to 550 K, with pressures up to 1200 MPa and densities up to 9.66 mol·dm<sup>-3</sup>. The equation of state for 2,2-dimethylbutane is valid from 174.20 K (the triple point temperature) to 575 K, with pressures up to 1000 MPa and densities up to 8.77 mol·dm<sup>-3</sup>. The equation of state for 2,3-dimethylbutane is valid from 145.05 K (the triple point temperature) to 550 K, with pressures up to 1100 MPa and densities up to 9.12 mol·dm<sup>-3</sup>. Ancillary equations for vapor pressures and saturated densities of these three fluids have been developed. These can be used for fast approximation and to provide initial values for an iterative routine to obtain the saturated states from the equations of state.

The uncertainties (k=2, indicating a level of confidence of 95 %) in density of the equation of state for 3methylpentane are 0.2 % at temperatures between 270 K and 400 K and up to pressures of 100 MPa and 0.4 % at temperatures between 400 K and 500 K in the liquid phase region, 0.35 % in the vapor phase region at temperatures between 520 K and 550 K, and 1.0 % at pressures between 150 MPa and 1200 MPa. The uncertainties in vapor pressure are 0.2 % at temperatures between 280 K and 345 K and 0.3 % at temperatures higher than 420 K. The uncertainty in saturated-liquid densities is 0.1 % at temperatures between 230 K and 330 K. The uncertainty in liquid sound speed is 0.1 % at temperatures between 230 K and 315 K. The uncertainties in isobaric heat capacity are estimated to be 0.5 % in the liquid phase at temperatures between the triple-point temperature (110.263 K) and 310 K, and 1.0 % in the vapor phase at temperatures between 320 K and 480 K. The uncertainty in saturation heat capacity is estimated to be 0.5 % at temperatures between the triple-point temperature and 390 K. The uncertainties in the critical region are higher for all properties because critical experimental data are not available.

The uncertainties in density of the equation of state for 2,2-dimethylbutane are 0.2 % in the liquid phase region for temperatures between 240 K and 475 K and up to pressures of 100 MPa, 1.0 % in the vapor phase region at temperatures between 495 K and 575 K, and are higher in the critical region due to the lack of experimental data. The uncertainty in vapor pressure is 0.4 % between 230 K and 340 K. The uncertainty in saturated-liquid density is 0.2 % between 240 K and 320 K. The uncertainty in saturated-vapor density is 1.2 % between 275 K and 315 K. The uncertainty in isobaric heat capacity is estimated to be 0.5 % in the liquid phase at temperatures between the triple-point temperature (174.20 K) and 300 K, and 0.6 % in the vapor phase at temperatures between 340 K and 450 K.

The uncertainties in density of the equation of state for 2,3-dimethylbutane are 0.25 % in the liquid phase region for temperatures between 205 K and 500 K and up to pressures of 150 MPa, 0.8 % in the vapor phase region at temperatures between 520 K and 550 K, and 1.0 % at pressures between 150 MPa and 1080 MPa. The uncertainties in the critical region are

higher for all properties, but unknown due to the absence of data. The uncertainty in vapor pressure is generally less than 0.2 % at temperatures higher than 260 K. The uncertainty in saturated-liquid density is generally less than 0.15 % between 270 K and 500 K. The uncertainty in saturated-vapor density is 3.0 % at temperatures higher than 320 K. The uncertainty in isobaric heat capacity is estimated to be 0.5 % in the liquid phase at temperatures between the triple-point temperature (145.05 K) and 320 K, and 0.5 % in the vapor phase at temperatures between 340 K and 470 K.

As shown by plots of thermodynamic properties, the equations of state for 3-methylpentane, 2,2-dimethylbutane, and 2,3-dimethylbutane have reasonable physical behavior within the region of validity and outside this region at high temperatures and pressures, and at low temperatures.

Calculated values of properties in the liquid, vapor, and supercritical regions from the equations of state for 3methylpentane, 2,2-dimethylbutane, and 2,3-dimethylbutane are given in Table 10 and can be used to validate computer code generated by the equations and parameters given in this work. The state point at zero density is given to test the ideal-gas properties. States close to the critical point are also given for these three fluids, where the properties of the fluids change rapidly. These values can be used to demonstrate the correct implementation of the equation of state.

## 7. Acknowledgement

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TABLE 1. I hysical constants and characteristic properties of 5-methylpentane, 2,2-unneuryloutane, and 2,5-unneurylouta	istic properties of 3-methylpentane, 2,2-dimethylbutane, and 2,3-dimethylbutane <sup>a</sup>
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Symbol	Property	3-Methylpentane	2.2-Dimethylbutane	2.3-Dimethylbutane
R	Molar gas constant	8.3144598 J·mol <sup>-1</sup> ·K <sup>-1</sup>	8.3144598 J·mol <sup>-1</sup> ·K <sup>-1</sup>	8.3144598 J·mol <sup>-1</sup> ·K <sup>-1</sup>
M	Molar mass	86.17536 g·mol <sup>-1</sup>	$86.17536 \text{ g} \cdot \text{mol}^{-1}$	86.17536 g·mol <sup>-1</sup>
$T_c$	Critical temperature	506.0 K	490.0 K	500.6 K
$p_c$	Critical pressure	3184.5 kPa	3138.0 kPa	3161.0 kPa
$\rho_{\rm c}$	Critical density	2.78 mol·dm <sup>-3</sup>	2.78 mol·dm <sup>-3</sup>	2.80 mol·dm <sup>-3</sup>
$T_{\rm tp}$	Triple-point temperature	110.263 K <sup>[4]</sup>	174.20 K <sup>[12]</sup>	145.05 K <sup>[12]</sup>
$p_{\rm tp}$	Triple-point pressure	1.68223×10 <sup>-10</sup> kPa	0.00488865 kPa	0.0000155898 kPa
$\rho_{ m tpv}$	Vapor density at triple point	1.8349×10 <sup>-13</sup> mol·dm <sup>-3</sup>	3.3753×10 <sup>-6</sup> mol·dm <sup>-3</sup>	1.2927×10 <sup>-8</sup> mol·dm <sup>-3</sup>
$ ho_{ m tpl}$	Liquid density at triple point	9.651 mol·dm <sup>-3</sup>	8.768 mol·dm <sup>-3</sup>	9.113 mol·dm <sup>-3</sup>
$T_{\rm nbp}$	Normal-boiling-point temperature	336.379 K	322.846 K	331.177 K
$\rho_{\rm nbpv}$	Vapor density at the normal-boiling point	0.037874 mol·dm <sup>-3</sup>	0.039354 mol·dm <sup>-3</sup>	0.038271 mol·dm <sup>-3</sup>
$ ho_{ m nbpl}$	Liquid density at the normal-boiling point	7.2398 mol·dm <sup>-3</sup>	7.2030 mol·dm <sup>-3</sup>	7.2663 mol·dm <sup>-3</sup>
ω	Acentric factor	0.268	0.230	0.247
$T_0$	Reference temperature for ideal-gas properties	273.15 K	273.15 K	273.15 K
$p_0$	Reference pressure for ideal-gas properties	1.0 kPa	1.0 kPa	1.0 kPa
$h_0^0$	Reference ideal-gas enthalpy at $T_0$	19487.5982650113 J·mol <sup>-1</sup>	19699.8282255266 J·mol <sup>-1</sup>	19554.2027822906 J·mol <sup>-1</sup>
S <sub>0</sub>	Reference ideal-gas entropy at $T_0$ and $p_0$	93.1892982505 J·mol <sup>-1</sup> ·K <sup>-1</sup>	97.2641495983 J·mol <sup>-1</sup> ·K <sup>-1</sup>	94.7089033208 J·mol <sup>-1</sup> ·K <sup>-1</sup>

<sup>*a*</sup>All properties in this table were determined in this work except R, M, and  $T_{tp}$ .

TABLE 2. Triple-point and critical-point parameters of 3-methylpentane

	Temperature T	Pressure <i>p</i>	Density $\rho$
Reference	K	MPa	mol·dm <sup>-3</sup>
	Triple-l	Point Parameters	
Finke and Messerly (1973) <sup>4</sup>	110.263		
This work	110.263		
	Critical-	Point Parameters	
Chun (1964) <sup>5</sup>	504.635	3.128	
Day and Felsing (1951) <sup>6</sup>	504.665		
Genco (1965) <sup>7</sup>	504.605	3.12443	
Genco <i>et al.</i> (1980) <sup>8</sup>	504.56	3.12442	2.712237
Kay (1946) <sup>9</sup>	504.364	3.12385	2.726998
Kay et al. (1975) <sup>10</sup>	504.55	3.124	
Young (1974) <sup>11</sup>	504.36		
This work	506.0	3.1845	2.78

 $T_{\text{ABLE 3. Triple-point and critical-point parameters of 2,2-dimethylbutane}$ 

	Temperature T	Pressure <i>p</i>	Density $\rho$
Reference	K	MPa	mol·dm <sup>-3</sup>
	Triple-Point Para	ameters	
Timmermans $(1922)^{13}$	174.986		
Van Risseghem (1922) <sup>14</sup>	174.986		
Stull (1937) <sup>15</sup>	172.164		
Smittenberg et al. (1938) <sup>16</sup>	172.685		
Hicks-Brunn et al. (1939)17	174.486		
Oberfell and Frey (1939) <sup>18</sup>	174.986		
Wibaut <i>et al.</i> (1939) <sup>19</sup>	172.685		
Brooks et al. (1940) <sup>20</sup>	173.125		
Wojciechowski (1940) <sup>21</sup>	171.183		
Glasgow and Rossini (1943) <sup>22</sup>	173.218		
Glasgow and Rossini (1943) <sup>22</sup>	173.455		
Fidler (1945) <sup>23</sup>	173.425		
Tooke and Aston (1945) <sup>24</sup>	170.773		
Douslin and Huffman (1946) <sup>25</sup>	174.316		
Forziati et al. (1946) <sup>26</sup>	173.194		
Glasgow et al. (1946) <sup>27</sup>	173.215		
Glasgow et al. (1946) <sup>27</sup>	173.455		
Kilpatrick and Pitzer (1946) <sup>28</sup>	174.196		
Fink et al. (1947) <sup>29</sup>	174.326		
Howard <i>et al.</i> (1947) <sup>30</sup>	173.125		
Denyer <i>et al.</i> $(1949)^{31}$	172.885		
Wurflinger (1975) <sup>32</sup>	173.663		
This work	174.20		

Critical-Point Parameters				
Ambrose <i>et al.</i> (1960) <sup>33</sup>	488.739			
Chun (1964) <sup>5</sup>	488.98	3.08553	2.796733	
Genco (1965) <sup>7</sup>	489.249	3.10236		
Genco <i>et al.</i> $(1980)^8$	489.21	3.10236	2.792516	
Kay (1946) <sup>9</sup>	489.3592	3.107638	2.785019	
Kay et al. (1975) <sup>10</sup>	489.2	3.102		
Rossini et al. (1953) <sup>34</sup>	489.36	3.10608	2.785127	
Young (1974) <sup>11</sup>	488.66			
This work	490.0	3.138	2.78	

TABLE 4. Triple-point and critical-point parameters of 2,3-dimethylbutane

	Temperature T	Pressure p	Density $\rho$
Reference	K	MPa	mol·dm <sup>-3</sup>
	Triple-Point Para	ameters	
Timmermans (1921) <sup>35</sup>	137.354		
Timmermans (1921) <sup>35</sup>	138.255	0.0004472	
Van Risseghem (1921) <sup>36</sup>	138.054		
Bruun and Hicks-Brunn (1930) <sup>37</sup>	138.155		
Maman (1934) <sup>38</sup>	144.159		
Kistiakowsky et al. (1936) <sup>39</sup>	144.559		
Kistiakowsky et al. (1936) <sup>39</sup>	145.36		
Brooks et al. (1937) <sup>40</sup>	127.65		
Bruun <i>et al.</i> $(1937)^{41}$	144.159		
Hoog et al. (1937) <sup>42</sup>	144.559		
Stull (1937) <sup>15</sup>	136.473		
Smittenberg et al. (1938) <sup>16</sup>	144.659		
Smittenberg et al. $(1938)^{16}$	144.96		
Wibaut <i>et al.</i> (1939) <sup>19</sup>	144.659		
Brooks et al. (1940) <sup>20</sup>	143.368		
Wojciechowski (1940) <sup>21</sup>	140.456		
Tooke and Aston (1945) <sup>24</sup>	144.93		
Douslin and Huffman (1946) <sup>25</sup>	145.2		
Forziati <i>et al.</i> (1946) <sup>26</sup>	144.361		
Glasgow et al. (1946) <sup>27</sup>	144.361		
Fink <i>et al.</i> (1947) <sup>29</sup>	145.16		
Denyer <i>et al.</i> (1949) <sup>31</sup>	144.479		
Westerdijk et al. (1950) <sup>43</sup>	144.96		
Aston <i>et al.</i> $(1956)^{44}$	145.2		
Adachi et al. (1971) <sup>45</sup>	145.054		
This work	145.05		
	Critical-Point Par	ameters	
Ambrose <i>et al.</i> $(1960)^{33}$	499.943		
Chun (1964) <sup>5</sup>	500.243	3.147	
Genco (1965) <sup>7</sup>	500.083	3.14525	
Genco <i>et al.</i> $(1980)^8$	500.04	3.14524	2.77671
Kay (1946) <sup>9</sup>	500.263	3.14006	2.796623
Kay <i>et al.</i> $(1975)^{10}$	500.03	3.145	
Quadri et al. (1992) <sup>46</sup>	499.8	3.18	
Young and Fortey (1897) <sup>47</sup>	500.563	3.11241	
Young (1974) <sup>11</sup>	499.86		
This work	500.6	3.161	2.80

TABLE 5. Summary of sources of calculated ideal-gas isobaric heat capacities for 3-methylpentane, 2,2-dimethylbutane, and 2,3-dimethylbutane including the AAD to the equation of state

Substance	Reference	No. Points	Temperature Range <i>T</i> K	AAD %
3-Methylpentane	TRC <sup>12</sup>	14	200-1500	0.5
2,2-Dimethylbutane	TRC <sup>12</sup>	14	200-1500	0.5
2,3-Dimethylbutane	TRC <sup>12</sup>	14	200-1500	1.3

i	n <sub>i</sub>	t <sub>i</sub>	$d_i$	$l_i$	$\eta_i$	$\beta_i$	$\gamma_i$	$\varepsilon_i$
			3-M	lethylpentan	9			
1	0.006178288	1.0	5					
2	0.763315017	0.16	1					
3	-0.5546657	1.0	1					
4	-1.0604327	1.0	2					
5	0.23117181	0.386	3					
6	-1.8757299	1.54	1	2				
7	-0.9327912	2.0	3	2				
8	1.0720552	1.0	2	1				
9	-0.2830806	2.5	2	2				
10	-0.024600061	1.66	8	2				
11	0.87360786	0.44	1		1.409	1.876	1.2603	0.7065
12	0.008687374	1.0	1		2.53	1.158	1.207	2.19
13	-0.27160944	0.55	3		1.781	1.808	1.045	0.244
14	-0.12365512	0.705	2		2.045	1.646	1.069	1.014
15	-0.12052593	1.5	1		0.688	1.0	0.923	0.689
16	-0.53359397	1.0	3		20.1	660.0	1.109	0.905
10	0.0000000		2.2-D	imethylbuta	ne			
1	0.00702066	1.0	5	meenyibutu				
2	0.70134226	0.156	1					
3	-0.3659372	1.0	1					
4	-1.109303	1.0	2					
5	0 22742868	0.371	3					
6	-1.8603613	1.4	1	2				
7	-0.65052551	2.0	3	2				
8	1 1465612	1.0	2	- 1				
9	-0.31514795	2.15	2	2				
10	-0.028916258	15	8	2				
10	0.9153258	0.49	1	-	1 35	1 709	1 275	0 7384
12	-0.010020802	14	1		1.33	0.218	0.91	2 063
12	-0.52208207	0.687	3		1.270	1 10	1 108	0.239
13	-0.15208042	1 275	2		1.55	0.33	1.100	1.057
14	-0.15508945	1.275	2		1.724	0.55	1.104	0.558
15	-0.21698526	1.40	1		1.042	2.10	1.1/4	0.558
16	-1.18085/3	1.0	3		27.0	1074.0	1.094	0.926
1	0.007104021	1.0	2,3-D	imethylbuta	ne			
1	0.00/194931	1.0	5 1					
2	-0.6880604	0.23	1					
3	1.02512(4	1.0	2					
4	-1.0251264	1.0	2					
5	0.203168/1	0.364	5	r				
6	-1./24/168	1.5/	1	2				
/	-0.75015882	1.//	3	2				
8	1.0/12536	1.0	2					
9	-0.301/9884	2.3	2	2				
10	-0.029150384	1.5	8	2	1.422	• •	1.1.6	0.600
11	0.69062135	0.43	1		1.432	2.3	1.16	0.689
12	-0.010365966	1.15	1		1./8/	0.46	0.91	2.139
13	-0.21028711	0.4	3		1.412	1.9	1.0	0.314
14	-0.11507614	0.8	2		1.542	1.0	1.05	0.992
15	-0.19936642	1.375	1		1.2	2.86	1.06	0.619

TABLE 6. Coefficients of the equations of state for 3-methylpentane, 2,2-dimethylbutane, and 2,3-dimethylbutane

TABLE 7. Summary of sources of experimental data for 3-methylpentane

	No.	Temperature Range T	Pressure Range p	Density Range $\rho$	$AAD^{a}$
Reference	Points	K	MPa	mol·dm <sup>-3</sup>	%
		Vapor Pressure	:		
Berro et al. (1994) <sup>50</sup>	4	308-333	0.038-0.091		0.24
Day and Felsing (1951) <sup>6</sup>	5	423-504	0.831-3.1		0.16
Funk et al. (1972) <sup>51</sup>	3	283-323	0.013-0.065		0.17
Garriga et al. (1994) <sup>52</sup>	7	283-313	0.013-0.046		0.16
Ho and Davison (1979)53	4	283-313	0.013-0.046		0.05
Kay (1946) <sup>54</sup>	3	336-503	0.101-3.07		0.48
Liu and Davison (1981)55	4	283-313	0.013-0.046		0.11
TRC <sup>12</sup>	69	298-364	0.025-0.224		0.80
Uusi-Kyyny et al. (2001)56	19	302-336	0.03-0.101		0.14

Willingham et al. (1945)57	14	288-337	0.017-0.104		0.14
		Saturated Liquid	Density		
Awwad and Pethrick (1983)58	17	233-313		7.5-8.34	0.032
Comelli and Francesconi (1990) <sup>59</sup>	10	293-303		7.6-7.71	0.007
De Vos (1950) <sup>60</sup>	5	293-324		7.37-7.71	0.026
TRC <sup>12</sup>	98	273-313		7.5-7.91	0.094
		рр Т			
Bridgman (1931) <sup>61</sup>	42	273-368	0.098-1180	6.87-10.9	0.38
Day and Felsing (1951) <sup>6</sup>	157	353-548	0.567-31.6	2.48-7.52	1.31
Guerrero <i>et al.</i> (2013) <sup>62</sup>	110	283-328	0.1-65	7.32-8.37	0.06
Moriyoshi and Aono (1988)63	62	298-313	2.4-145	7.62-8.65	0.03
Sahli et al. (1976) <sup>64</sup>	16	293-298	0.1-7	7.66-7.8	0.03
		Speed of Sou	nd		
Awwad and Pethrick (1983)58	17	233-313	Saturated		0.08
TRC <sup>12</sup>	3	298	Saturated		0.53
		Isobaric Heat Ca	pacity		
Douslin and Huffman (1946) <sup>25</sup>	49	80-302	0.101		0.09
Stull (1937) <sup>15</sup>	21	120-320	0.101		3.16
TRC <sup>12</sup>	5	298	0.101		0.14
Waddington et al. (1949)65	11	332-471	0.031-0.101		0.31
		Isochoric Heat Ca	apacity		
Ohnishi et al. (1989)66	1	298		Saturated	0.12
		Saturation Heat C	apacity		
Finke and Messerly (1973) <sup>4</sup>	24	119-327			0.14
TRC <sup>12</sup>	44	110-490			0.80
		Heat of Vaporiz	ation		
Majer et al. (1979) <sup>67</sup>	4	298-353			0.26
TRC <sup>12</sup>	4	298			0.21
Waddington et al. (1949)65	3	303-336			0.20
· ·		Second Virial Coe	fficient		
Chun et al. (1981) <sup>68</sup>	7	383-505			32.4

"The unit of average absolute deviation for the second virial coefficients is cm<sup>3</sup>·mol<sup>-1</sup>.

TABLE 8. Summary of sources of experimental data for 2,2-dimethylbutane

	No.	Temperature Range T	Pressure Range p	Density Range $\rho$	$AAD^{a}$
Reference	Points	K	MPa	mol·dm <sup>-3</sup>	%
		Vapor Pressure			
del Rio et al. (2004) <sup>69</sup>	3	298-338	0.042-0.161		0.21
Garriga et al. (1994) <sup>70</sup>	7	283-313	0.023-0.073		0.13
Hyeong <i>et al.</i> (2013) <sup>71</sup>	3	303-333	0.051-0.14		0.33
Kay (1946) <sup>54</sup>	2	323-488	0.102-3.05		0.08
Kilpatrick and Pitzer (1946) <sup>28</sup>	11	211-289	0-0.03		0.82
Nicolini and Laffitte (1949) <sup>72</sup>	19	273-318	0.015-0.088		0.29
TRC <sup>12</sup>	64	298-326	0.043-0.101		0.82
Willingham et al. (1945) <sup>64</sup>	11	289-324	0.029-0.104		0.09
C ( )		Saturated Liquid De	ensity		
Polzin and Weiss (1990) <sup>73</sup>	6	244-319		7.26-8.07	0.054
TRC <sup>12</sup>	90	273-303		7.41-7.75	0.09
		Saturated Vapor De	nsity		
Nicolini and Laffitte (1949)74	18	273-315	·	0.007-0.031	0.69
		ρρΤ			
Brazier and Freeman (1969)75	9	303	0.1-400	7.41-9.24	1.18
Bridgman (1931) <sup>61</sup>	26	273-368	49-981	7.79-9.99	1.25
Felsing and Watson (1943) <sup>76</sup>	99	373-548	1.01-30.4	1.74-7.23	0.20
Griskey and Canjar (1964) <sup>77</sup>	12	493-573	2.67-4.62	1.09-1.38	5.34
Guerrero et al. $(2013)^{62}$	109	283-328	0.1-65	7.17-8.25	0.06
Moriyoshi and Aono (1988)63	58	298-313	1.4-124	7.44-8.44	0.051
Polzin and Weiss (1990) <sup>73</sup>	78	244-319	0.1-200	7.26-9.14	0.064
Sahli et al. (1976) <sup>64</sup>	15	293-298	0.1-7	7.49-7.64	0.059
		Speed of Sound	l		
TRC <sup>12</sup>	3	298	Saturated		0.54
		Isobaric Heat Capa	ncity		
Douslin and Huffman (1946) <sup>25</sup>	30	177-300	0.101		0.15
Kilpatrick and Pitzer (1946) <sup>28</sup>	12	179-280	Saturated		0.19
Pitzer (1941) <sup>78</sup>	4	361-448	0.101		1.28
Stull (1937) <sup>15</sup>	15	180-320	0.101		3.35
TRC <sup>12</sup>	7	298	0.101		0.38
Waddington and Douslin (1947) <sup>79</sup>	9	342-449	0.039-0.101		0.29
		Isochoric Heat Cap	acity		
Ohnishi et al. (1989) <sup>66</sup>	1	298		Saturated	0.32
		Saturation Heat Cap	pacity		
TRC <sup>12</sup>	16	180-479			2.48

		Heat of Vaporization		
TRC <sup>12</sup>	8	283-323	0.37	
Second Virial Coefficient				
Chun et al. (1981) <sup>68</sup>	7	383-493	16.1	
The unit of average absolute deviation for the second virial coefficients is $cm^3 \cdot mol^{-1}$ .				

TABLE 9. Summary of sources of experimental data for 2,3-dimethylbutane

	No.	Temperature Range T	Pressure Range p	Density Range $\rho$	$AAD^{a}$
Reference	Points	K	MPa	mol·dm <sup>-3</sup>	%
		Vapor Pressure			
Ewing and Marsh (1973) <sup>80</sup>	3	288-313	0.021-0.055		0.50
Garriga et al. (1994) <sup>70</sup>	7	283-313	0.017-0.055		0.64
Hyeong et al. (2013) <sup>71</sup>	3	303-333	0.039-0.108		0.80
Kay (1946) <sup>54</sup>	2	333-498	0.108-3.05		0.40
Pavlicek et al. (2013)81	3	313-333	0.055-0.108		0.11
TRC <sup>12</sup>	83	283-332	0.016-0.101		0.56
Willingham et al. (1945) <sup>64</sup>	13	287-332	0.02-0.104		0.35
Young and Fortey (1897)47	50	260-500	0.005-3.11		0.43
Young and Fortey (1900) <sup>82</sup>	27	263-501	0.006-3.11		0.43
6 50 7		Saturated Liquid De	nsitv		
De Vos (1950) <sup>60</sup>	5	292-324		7.42-7.77	1.18
Kelso and Felsing (1942) <sup>83</sup>	7	273-303		7.57-7.89	0.038
TRC <sup>12</sup>	98	273-313		7.45-7.89	0.15
Young and Fortey (1897) <sup>47</sup>	25	273-499		3.44-7.88	0.11
		Saturated Vapor De	nsity		
Young and Fortey (1897) <sup>47</sup>	34	323-500		0.031-2.15	2.21
		роТ			
Baonza <i>et al.</i> $(1993)^{85}$	255	208-298	0.07-108	7.63-9.02	0.28
Bridgman $(1931)^{61}$	34	273-368	0.098-1080	6.85-10.5	0.26
Guerrero <i>et al.</i> $(2013)^{62}$	110	283-328	0.1-65	7.29-8.36	0.084
Holzapfel <i>et al.</i> $(1987)^{86}$	6	293	0.1-10	7 68-7 8	0.013
Kelso and Felsing $(1942)^{83}$	63	373-548	0.567-31.6	1.5-7.36	0.23
Morivoshi and Aono (1988) <sup>63</sup>	59	298-313	1.5-139	7.54-8.61	0.043
Riembauer <i>et al.</i> $(1990)^{87}$	379	173-303	0.1-300	7.57-9.93	0.69
Sahli <i>et al.</i> $(1976)^{64}$	16	293-298	0.1-7	7.63-7.77	0.025
2		Speed of Sound			
$TRC^{12}$	3	298	Saturated		0.68
	5	Isobaric Heat Cana	city		0.00
Douslin and Huffman (1946) <sup>25</sup>	38	149-306	0 101		0.11
Stull (1937) <sup>15</sup>	19	140-320	0 101		3 53
$TRC^{12}$	7	298	0 101		0.25
Waddington <i>et al.</i> $(1949)^{65}$	10	342-471	0.038-0.101		0.23
(i) (i)	10	Isochoric Heat Cana	ocity		0.21
Ohnishi <i>et al.</i> (1989) <sup>66</sup>	1	298	leny	Saturated	0.57
	1	Saturation Heat Can	acity	Suturuted	0.07
$TRC^{12}$	38	136-490	acity		1 18
	50	Heat of Vaporizati	on		1.10
Lemons and Felsing (1943) <sup>84</sup>	4	293-353	01		1 24
TRC <sup>12</sup>	2	298			0.60
Waddington <i>et al.</i> $(1949)^{65}$	4	296-331			0.89
maanigton et al. (1777)	7	Second Virial Cooffic	ciont		0.07
Chup <i>et al.</i> $(1981)^{68}$	6	403-500	ciciit.		66
Chun <i>ci ui</i> . (1901)	0	-00-000			00

<sup>*a*</sup>The unit of average absolute deviation for the second virial coefficients is cm<sup>3</sup>·mol<sup>-1</sup>.

TABLE 10. Calculated values of properties from the equations of state to verify computer code

Temperature T	Density $\rho$	Pressure p	Isochoric Heat Capacity $c_v$	Isobaric Heat Capacity $c_p$	Speed of Sound w	Enthalpy h	Entropy s		
K	mol·dm <sup>-3</sup>	MPa	$J \cdot mol^{-1} \cdot K^{-1}$	$J \cdot mol^{-1} \cdot K^{-1}$	$m \cdot s^{-1}$	kJ∙mol <sup>-1</sup>	J·mol <sup>−1</sup> ·K <sup>−1</sup>		
3-Methylpentane									
265.0	8.3	34.550	137.15	176.35	1422.0	- 10.806	- 50.641		
465.0	5.5	3.5131	208.54	278.11	394.10	30.763	75.557		
506.5	2.78	3.2077	256.17	23439.	80.181	47.393	109.62		
265.0	0.0	0.0	118.01	126.33	165.44	18.445	Infinite		
485.0	0.37	1.2155	207.56	226.94	181.49	53.556	127.17		
525.0	3.8	4.7911	230.96	395.25	165.78	49.290	112.39		
2,2-Dimethylbutane									
250.0	8.3	36.161	131.59	168.49	1433.9	- 10.345	- 52.298		
450.0	5.5	3.8486	205.79	268.04	392.06	29.468	74.872		
490.5	2.78	3.1618	246.60	19168.	82.456	45.450	108.84		
250.0	0.0	0.0	113.95	122.26	160.88	16.766	Infinite		
470.0	0.37	1.1921	204.36	222.53	180.54	51.316	126.30		

510.0	3.8	4.8161	229.28	393.39	162.78	47.551	112.05	
2,3-Dimethylbutane								
260.0	8.3	33.956	137.40	171.90	1402.5	- 10.456	- 50.036	
460.0	5.5	3.3337	205.01	274.93	394.41	30.364	75.593	
501.0	2.8	3.1802	227.24	18442.	86.224	46.717	109.37	
260.0	0.0	0.0	118.98	127.30	163.82	17.850	Infinite	
480.0	0.37	1.2234	205.93	224.34	183.06	52.986	127.31	
520.0	3.8	4.7632	229.10	402.11	161.00	48.689	112.32	



Fig. 1. The chemical structures of 3-methylpentane, 2,2-dimethylbutane, and 2,3-dimethylbutane.



Fig. 2. The behavior of the equation of state for 3-methylpentane in the vicinity of the critical region.



Fig. 3. The behavior of the equation of state for 2,2-dimethylbutane in the vicinity of the critical region.



Fig. 4. The behavior of the equation of state for 2,3-dimethylbutane in the vicinity of the critical region.



Fig. 5. Comparisons of  $c_p^0$  values calculated with Eq 16 for 3-methylpentane to estimated values from TDE.



Fig. 6. Comparisons of  $c_p^0$  values calculated with Eq 16 for 2,2-dimethylbutane to estimated values from TDE.



Fig. 7. Comparisons of  $c_p^0$  values calculated with Eq 16 for 2,3-dimethylbutane to estimated values from TDE.



FIG. 8. Comparisons of vapor pressures calculated with the equation of state for 3-methylpentane to experimental data.



FIG. 9. Comparisons of saturated liquid densities calculated with the equation of state for 3-methylpentane to experimental data.



FIG. 10. Comparisons of vapor pressures calculated with the equation of state for 2,2-dimethylbutane to experimental data.



FIG. 11. Comparisons of saturated liquid densities calculated with the equation of state for 2,2-dimethylbutane to experimental data.



+ Nicolini and Laffitte (1949)

FIG. 12. Comparisons of saturated vapor densities calculated with the equation of state for 2,2-dimethylbutane to experimental data.



Fig. 13. Comparisons of vapor pressures calculated with the equation of state for 2,3-dimethylbutane to experimental data.



FIG. 14. Comparisons of saturated liquid densities calculated with the equation of state for 2,3-dimethylbutane to experimental data.



Fig. 15. Comparisons of saturated vapor densities calculated with the equation of state for 2,3-dimethylbutane to experimental data.



FIG. 16. Comparisons of densities calculated with the equation of state for 3-methylpentane to experimental data.



FIG. 17. Comparisons of second virial coefficients calculated with the equation of state for 3-methylpentane to experimental data.



FIG. 18. Comparisons of densities calculated with the equation of state for 2,2-dimethylbutane to experimental data.



FIG. 19. Comparisons of second virial coefficients calculated with the equation of state for 2,2-dimethylbutane to experimental data.



FIG. 20. Comparisons of densities calculated with the equation of state for 2,3-dimethylbutane to experimental data.



FIG. 21. Comparisons of second virial coefficients calculated with the equation of state for 2,3-dimethylbutane to experimental data.



FIG. 22. Calculations of  $(Z - 1)/\rho$  from the equation of state for 3-methylpentane along isotherms versus density  $\rho$  in the vapor-phase region. Isotherms are drawn between 275 K and 500 K in intervals of 25 K and at 600 K, 700 K, and 800 K.



FIG. 23. The second, third, and fourth virial coefficients, *B*, *C*, and *D*, from the equation of state for 2,2-dimethylbutane versus temperature. In this plot, the values along the y-axis are equal to the value of *B*, the value of  $10 \cdot C$  (*C*\*), and the value of  $100 \cdot D$  (*D*\*). The units of the virial coefficients are dm<sup>3</sup>·mol<sup>-1</sup>, dm<sup>6</sup>·mol<sup>-2</sup>, and dm<sup>9</sup>·mol<sup>-3</sup>.



Fig. 24. Comparisons of sound speed calculated with the equation of state for 3-methylpentane to experimental data.



Fig. 25. Comparisons of isobaric heat capacities calculated with the equation of state for 3-methylpentane to experimental data.



FIG. 26. Comparisons of saturation heat capacities calculated with the equation of state for 3-methylpentane to experimental data.



FIG. 27. Comparisons of isobaric heat capacities calculated with the equation of state for 2,2-dimethylbutane to experimental data.



Fig. 28. Comparisons of saturation heat capacities calculated with the equation of state for 2,2-dimethylbutane to experimental data.



FIG. 29. Comparisons of isobaric heat capacities calculated with the equation of state for 2,3-dimethylbutane to experimental data.



FIG. 30. Comparisons of saturation heat capacities calculated with the equation of state for 2,3-dimethylbutane to experimental data.



Fig. 31. Isochoric heat capacities  $c_v$  calculated from the equation of state for 2,3-dimethylbutane versus temperature along isobars. Isobars are shown at pressures of 0, 0.1, 0.5, 1, 2,  $p_c$ , 4, 6, 8, 10, 20, 50, 100, 200, 500, 1000, 2000, 5000, and 10 000 MPa.



Fig. 32. Isobaric heat capacities  $c_p$  calculated from the equation of state for 3-methylpentane versus temperature along isobars. Isobars are shown at pressures of 0, 0.5, 1, 2,  $p_c$ , 4, 6, 8, 10, 50, 100, 500, 1000, 2000, 500 000, 50 000, and 100 000 MPa.



FIG. 33. Sound speed w calculated from the equation of state for 2,2-dimethylbutane versus the logarithm of temperature along isobars. Isobars are shown at pressures of 0, 0.5, 1, 2, pc, 4, 6, 8, 10, 20, 50, 100, 200, 500, 1000, and 2000 MPa.



Fig. 34. Temperature versus density along isobars calculated from the equation of state for 2,3-dimethylbutane. Isobars are shown at pressures of 0.1, 0.2, 0.5, 1, 2,  $p_c$ , 4, 6, 8, 10, 20, 50, 100, 200, 500, and 1000 MPa.



FIG. 35. Pressure versus density at extreme conditions of temperature and pressure along isotherms calculated from the equation of state for 3-methylpentane. Isotherms are shown at temperatures of  $T_{tp}$ ,  $T_c$ ,  $10^3$ ,  $10^4$ ,  $10^5$ ,  $10^6$ ,  $10^7$ ,  $10^8$ , and  $10^9$  K.



Fig. 36. Phase identification parameter versus temperature along isobars calculated from the equation of state for 2,2-dimethylbutane. Isobars are shown at pressures of 0.1, 0.2, 0.5, 1, 2, *p*<sub>c</sub>, 5, 10, 15, 20, 25, 30, 35, 50, 100, 200, 500, 1000, and 2000 MPa.



Fig. 37. Phase identification parameter versus density along isotherms calculated from the equation of state for 2,3-dimethylbutane. Isotherms are shown at temperatures of 50, 100, 150, 200, 250, 300, 350, 400, 450,  $T_c$ , 600, 800, 1000, 1200, 1500, 2000, 3000, and 5000 K.



Fig. 38. Gruneisen parameter versus density along isotherms calculated from the equation of state for 3-methylpentane. Isotherms are shown at temperatures of 100, 200, 300, 400, 500, 700, 1000, 1500, 2000, 2500, 3000, 4000, and 5000 K.



Fig. 39. Gruneisen parameter versus temperature along isochores calculated from the equation of state for 2,2-dimethylbutane. Isochores are shown between zero and 22 mol $dm^{-3}$  in intervals of 2 mol $dm^{-3}$ , and at densities of 0.5, 1, 25, 30, 40, 50, and 100 mol $dm^{-3}$ .



Fig. 40. Characteristic (ideal) curves of the equation of state for 2,3-dimethylbutane as a function of reduced temperature  $T/T_c$  and reduced pressure  $p/p_c$ .