

# An Equation of State for the Thermodynamic Properties of Cyclohexane

Yong Zhou, Jun Liu, Steven G. Penoncello, and Eric W. Lemmon

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# An Equation of State for the Thermodynamic Properties of Cyclohexane

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An equation of state for cyclohexane has been developed using the Helmholtz energy as the fundamental property with independent variables of density and temperature. Multi-property fitting technology was used to fit the equation of state to data for  $p\rho T$ , heat capacities, sound speeds, virial coefficients, vapor pressures, and saturated densities. The equation of state was developed to conform to the Maxwell criteria for two-phase vapor-liquid equilibrium states, and is valid from the triple-point temperature to 700 K, with pressures up to 250 MPa and densities up to  $10.3 \text{ mol dm}^{-3}$ . In general, the uncertainties ( $k = 2$ , indicating a level of confidence of 95%) in density for the equation of state are 0.1% (liquid and vapor) up to 500 K, and 0.2% above 500 K, with higher uncertainties within the critical region. Between 283 and 473 K with pressures lower than 30 MPa, the uncertainty is as low as 0.03% in density in the liquid phase. The uncertainties in the speed of sound are 0.2% between 283 and 323 K in the liquid, and 1% elsewhere. Other uncertainties are 0.05% in vapor pressure and 2% in heat capacities. The behavior of the equation of state is reasonable within the region of validity and at higher and lower temperatures and pressures. A detailed analysis has been performed in this article. © 2014 by the U.S. Secretary of Commerce on behalf of the United States. All rights reserved. [<http://dx.doi.org/10.1063/1.4900538>]

Key words: cyclohexane; equation of state; thermodynamic properties.

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### Greek Letters

$\Delta$	Deviation
$\delta$	Reduced density
$\phi$	Dimensionless Helmholtz energy
$\rho$	Density
$\tau$	Inverse reduced temperature
$\omega$	Acentric factor

### Superscripts

0	Ideal gas
r	Residual
'	Saturated-liquid state
"	Saturated-vapor state

### Subscripts

0	Reference-state property
c	Critical
calc	Calculated
exp	Experimental
l	Liquid property
nbp	Normal-boiling-point property
tp	Triple-point property
v	Vapor property
$\sigma$	Saturation property

## 1. Introduction

Cyclohexane ( $\text{C}_6\text{H}_{12}$ , CAS No. 110-82-7) is an important industrial cycloalkane, which is used as a nonpolar solvent for the chemical industry, and also as a raw material for the production of adipic acid and caprolactam, both of which are intermediates used in the production of nylon.<sup>1</sup> Cyclohexane is

### List of Symbols

$a, n, v, u$	Coefficients
$B$	Second virial coefficient

also used in labs and as a standard due to its unique chemical and conformational properties.<sup>2</sup> Hence a high-precision equation of state is required to calculate accurate thermodynamic properties of cyclohexane to satisfy the needs of scientific research and engineering applications.

High-accuracy ( $p, \rho, T$ ) measurements on cyclohexane have been carried out,<sup>3</sup> which makes it possible to develop a high-precision equation of state. This article describes a new equation of state for cyclohexane developed for the replacement of the existing equations.<sup>4,5</sup> With the Helmholtz energy as the fundamental property, and temperature and density as the independent variables, this equation of state is valid from the triple-point temperature to 700 K, with pressures up to 250 MPa. The Helmholtz energy equation of state has the advantage that all thermodynamic properties can be calculated as derivatives of it,<sup>6</sup> as given in many publications such as those of Wagner and Pruß,<sup>7</sup> Span,<sup>8</sup> and Lemmon *et al.*<sup>9</sup> A detailed analysis is given in Sec. 6, which shows that the extrapolation behavior of the equation of state is reasonable at higher temperatures and pressures.

There are two Helmholtz equations of state for cyclohexane available.<sup>4,5</sup> The equation of state reported by Span and Wagner<sup>4</sup> was developed for technical applications; the uncertainties are approximately 0.2% (to 0.5% at high pressures) in density, 1% (in the vapor phase) to 2% in heat capacity, 1% (in the vapor phase) to 2% in sound speed, and 0.2% in vapor pressure. The upper limits in temperature and pressure of the equation of state are 600 K and 100 MPa. The equation of state reported by Penoncello *et al.*<sup>5</sup> is more accurate; the uncertainties are 0.1% in density, 2% in heat capacity, and 1% in sound

speed, except in the critical region. The upper limits in temperature and pressure of the equation of state are 700 K and 80 MPa. The uncertainties of the equation of state of this work are 0.1% in density in the compressed liquid region, 0.2% in the vapor and critical regions, 2% in heat capacities, and 0.2% in sound speed. Detailed comparisons of values calculated with the equation of state developed in this work to available experimental data and the equations by Span and Wagner<sup>4</sup> and Penoncello *et al.*<sup>5</sup> are given to evaluate the accuracy of the equation of state in this work.

## 2. The Critical and Triple Points

The critical point is one of the most important properties for a fluid in the development of the equation of state and other equations for thermophysical properties. It is the reducing parameter for the equations and the upper limit for vapor-liquid equilibrium calculations. Critical points have been reported by numerous authors and are listed in Table 1 (temperatures are given on ITS-90). Figures 1–3 show critical temperatures, pressures, and densities as a function of the year published. As shown in the figures, there are considerable differences among the results reported by different authors due to the difficulties in the experimental determination of the critical parameters and impurities in the samples; the differences between the reported values and the true critical point cannot be described as a function of the year published. We fitted the reducing parameters (critical temperature and density) of the equation of state simultaneously with the other

TABLE 1. Summary of critical point parameters for cyclohexane

Author	$T_c$ (K)	$p_c$ (MPa)	$\rho_c$ (mol dm <sup>-3</sup> )
Young and Fortey (1899) <sup>15</sup>	553.18 ± 0.60	4.0333 ± 0.054	3.247 ± 0.06
Young (1910) <sup>16</sup>	553.13 ± 0.61	4.03434 ± 0.016	
Rotinyantz and Nagornov (1934) <sup>17</sup>	554.18 ± 1.0	4.11076 ± 0.060	3.238 ± 0.06
Fischer and Reichel (1944) <sup>18</sup>	553.88 ± 0.20		
Kay and Albert (1956) <sup>19</sup>	553.00 ± 0.10	4.07823 ± 0.030	
Ambrose and Grant (1957) <sup>20</sup>	553.48 ± 0.15		
Glaser and Ruland (1957) <sup>21</sup>	554.13 ± 10		
Simon (1957) <sup>22</sup>	553.38 ± 0.60		3.23 ± 0.036
Reamer <i>et al.</i> (1958) <sup>23</sup>	553.23 ± 0.10	4.11107	
Richardson and Rowlinson (1959) <sup>24</sup>	553.38 ± 0.60		
Krichevskii and Sorina (1960) <sup>25</sup>	553.13	4.053	
Partington <i>et al.</i> (1960) <sup>26</sup>	553.38 ± 0.20		
Cheng (1963) <sup>27</sup>	553.38 ± 0.20		3.25 ± 0.33
Kay and Hissong (1967) <sup>28</sup>	554.08 ± 2.0	4.09478 ± 0.047	
Plenkina <i>et al.</i> (1971) <sup>29</sup>	554.21		3.39
Raetzsch and Strauch (1972) <sup>30</sup>	555.061 ± 0.50		
Young (1972) <sup>31</sup>		4.036 ± 0.061	3.236 ± 0.031
Naziev <i>et al.</i> (1974) <sup>32</sup>	553.011	4.030	
Hugill and McGlashan (1978) <sup>12</sup>	553.601 ± 0.080	4.075	
Christou (1988) <sup>33</sup>	553.461 ± 0.1		
Teja and Anselme (1990) <sup>34</sup>	553.9 ± 0.40		3.256 ± 0.071
Teja and Rosenthal (1990) <sup>35</sup>	553.7 ± 0.60	4.071 ± 0.020	
Nikitin <i>et al.</i> (2003) <sup>36</sup>	551 ± 6.0	4.060 ± 0.120	
Morton <i>et al.</i> (2004) <sup>11</sup>	553.6 ± 1.1		
Zhang <i>et al.</i> (2005) <sup>37</sup>	556.35 ± 0.60	4.200 ± 0.120	3.327 ± 0.071
<b>This work</b>	<b>553.6 ± 0.3</b>	<b>4.0805 ± 0.04</b>	<b>3.224 ± 0.025</b>

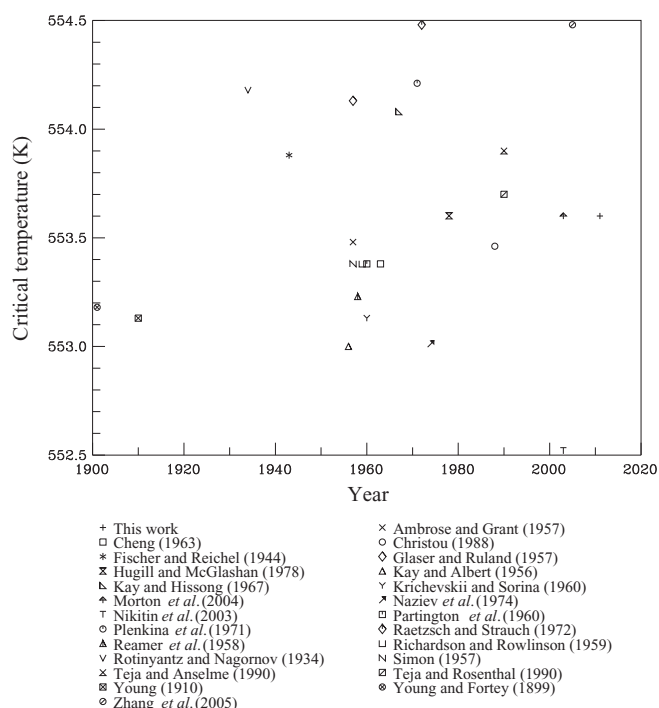


FIG. 1. Reported critical temperatures of cyclohexane as a function of the year published.

coefficients and exponents in the equation at first. The reader can access other publications for more information.<sup>9,10</sup> It is interesting that the final temperature from fitting was around  $(553.6 \pm 0.3)$  K, which is the same value reported by Morton *et al.*<sup>11</sup> and Hugill and McGlashan;<sup>12</sup> hence we chose this value as the final critical temperature. The critical density, taken as the final fitted value, is  $(3.224 \pm 0.025)$  mol dm<sup>-3</sup>. The critical pressure,  $p_c = (4.0805 \pm 0.04)$  MPa, was determined from the

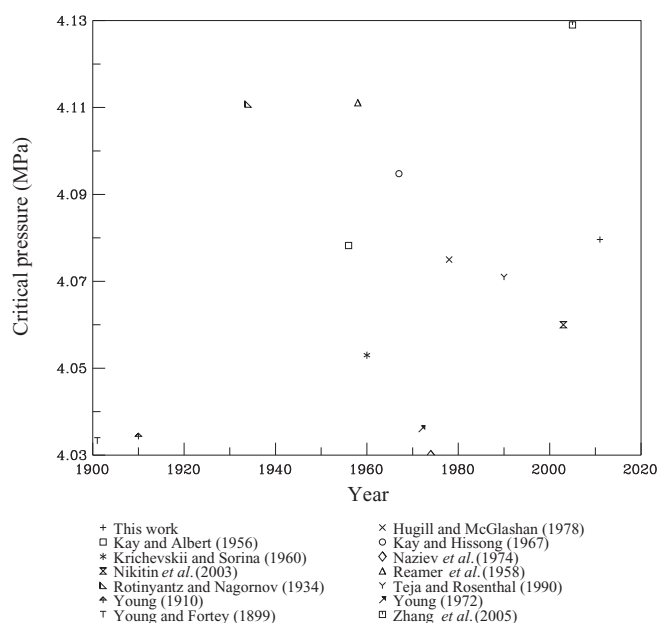


FIG. 2. Reported critical pressures of cyclohexane as a function of the year published.

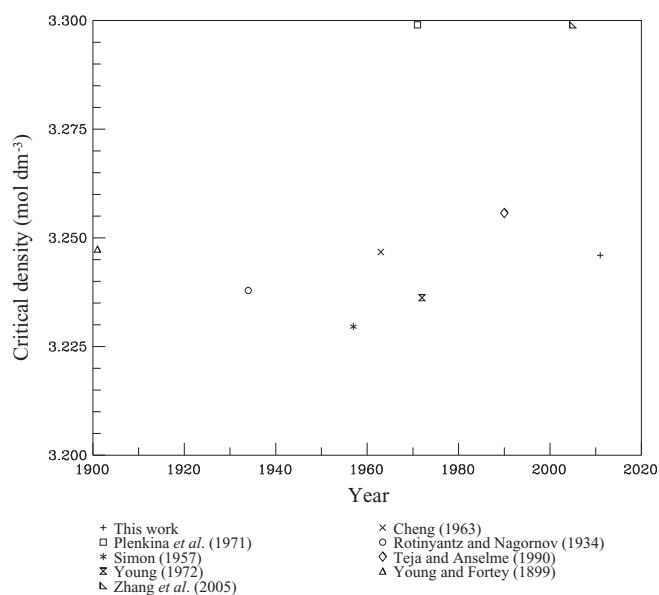


FIG. 3. Reported critical densities of cyclohexane as a function of the year published.

equation of state reported here as a calculated point at the critical temperature and density.

The triple point of a fluid defines the lowest temperature at which most substances can remain in the liquid state. There are a large number of triple-point temperatures reported by various authors. As carefully evaluated, the triple-point temperature is  $(279.86 \pm 0.06)$  K.<sup>13</sup> The triple-point pressure was calculated to be 5.3487 kPa from the final equation of state. There is only one data point published, which is  $(5.331\ 56 \pm 0.053)$  kPa.<sup>14</sup> Other fundamental constants are given in Table 2.

TABLE 2. Physical constants and characteristic properties of cyclohexane

Symbol	Quantity	Value
$R$	Molar gas constant <sup>38</sup>	$8.314\ 4621\ \text{J mol}^{-1}\ \text{K}^{-1}$
$M$	Molar mass	$84.159\ 48\ \text{g mol}^{-1}$
$T_c$	Critical temperature	553.6 K
$p_c$	Critical pressure	4080.5 kPa
$\rho_c$	Critical density	$3.224\ \text{mol dm}^{-3}$
$T_{tp}$	Triple-point temperature	279.86 K
$p_{tp}$	Triple-point pressure	5.3487 kPa
$\rho_{tpv}$	Vapor density at the triple point	$2.31 \times 10^{-3}\ \text{mol dm}^{-3}$
$\rho_{tpl}$	Liquid density at the triple point	$9.3991\ \text{mol dm}^{-3}$
$T_{nbp}$	Normal boiling-point temperature	353.865 K
$\rho_{nbpv}$	Vapor density at the normal boiling point	$0.0358\ \text{mol dm}^{-3}$
$\rho_{nbpl}$	Liquid density at the normal boiling point	$8.549\ \text{mol dm}^{-3}$
$\omega$	Acentric factor	0.2096
$T_0$	Reference temperature for ideal-gas properties	300 K
$p_0$	Reference pressure for ideal-gas properties	1.0 kPa
$h_0^0$	Reference ideal-gas enthalpy at $T_0$	$23\ 949.010\ 00\ \text{J mol}^{-1}$
$s_0^0$	Reference ideal-gas entropy at $T_0$ and $p_0$	$104.292\ 6004\ \text{J mol}^{-1}\ \text{K}^{-1}$

### 3. Experimental Data

The experimental data for cyclohexane are summarized in Table 3; the data used in the fit are shown in parentheses. The temperatures for all experimental data are converted to ITS-90. Figures 4 and 5 show the experimental  $p\rho T$  and caloric data as a function of temperature and pressure, which indicate that the properties in the liquid region are

sufficient, but properties in the vapor region should be further investigated.

Most of the data reported here were obtained from either the work of Penoncello *et al.*<sup>5</sup> or the ThermoData Engine<sup>48</sup> of the Thermodynamics Research Center (TRC) of NIST. Data sets with only one to four data points are combined and labeled as "TRC" in the figures, except those that are important to the development of the equation of state.

TABLE 3. Summary of experimental data for cyclohexane

Author	Total points (Used)	$T$ (K)	$p$ (MPa)	AAD <sup>a</sup> (%)	Bias <sup>a</sup> (%)
<b>Ideal gas heat capacity, <math>c_p^0</math></b>					
Montgomery and de Vries (1942) <sup>39</sup>	3	370–410		0.301	0.035
Aston <i>et al.</i> (1943) <sup>40</sup>	3	370–410		0.164	0.164
Brickwedde <i>et al.</i> (1946) <sup>41</sup>	14	298–1500		1.270	–1.270
Spitzer and Pitzer (1946) <sup>42</sup>	8	384–544		0.322	–0.174
Beckett <i>et al.</i> (1947) <sup>43</sup>	14 (14)	298–1500		0.062	–0.056
Dorofeeva <i>et al.</i> (1986) <sup>44</sup>	16	100–1500		2.569	0.896
<b>Vapor pressure, <math>p_\sigma</math></b>					
Young and Fortey (1899) <sup>15</sup>	58	268–553	0.003–4.03	0.826	–0.826
Young (1910) <sup>16</sup>	29	273–550	0.004–3.89	0.661	–0.661
Rotinyantz and Nagornov (1934) <sup>17</sup>	7	296–553	0.012–4.11	0.490	0.486
Nagai and Isii (1935) <sup>45</sup>	6	283–303	0.006–0.016	0.543	–0.495
Scatchard <i>et al.</i> (1939) <sup>46</sup>	6	303–353	0.016–0.099	0.168	0.168
Scatchard <i>et al.</i> (1939) <sup>47</sup>	5	303–343	0.016–0.072	0.078	–0.031
Aston <i>et al.</i> (1943) <sup>40</sup>	5	279–294	0.005–0.011	1.485	1.485
Willingham <i>et al.</i> (1945) <sup>49</sup>	16	293–355	0.01–0.104	0.062	–0.046
Brown and Ewald (1950) <sup>50</sup>	6	303–354	0.016–0.101	0.085	0.085
Brown (1952) <sup>51</sup>	6	303–354	0.016–0.101	0.087	0.087
Glaser and Ruland (1957) <sup>21</sup>	19	354–552	0.101–4.05	2.182	–1.917
Kumarkrishna Rao <i>et al.</i> (1957) <sup>52</sup>	26	354–487	0.101–1.72	1.120	0.809
Myers (1957) <sup>53</sup>	6	354	0.101	0.110	–0.029
Reamer and Sage (1957) <sup>54</sup>	26	311–511	0.024–2.41	3.120	3.005
Reamer <i>et al.</i> (1958) <sup>23</sup>	18	294–444	0.011–0.827	0.467	–0.416
Azimi-Pour (1960) <sup>55</sup>	8	283–313	0.006–0.024	0.532	–0.111
Krichevskii and Sorina (1960) <sup>25</sup>	14	473–533	1.34–3.17	0.625	0.365
Scatchard and Satkiewicz (1964) <sup>56</sup>	5	278–338	0.005–0.061	0.053	0.005
Marinichev and Susarev (1965) <sup>57</sup>	13	316–354	0.027–0.101	0.452	–0.243
Marinichev and Susarev (1965) <sup>58</sup>	8	308–354	0.02–0.101	1.076	–0.963
Cruikshank and Cutler (1967) <sup>59</sup>	36	298–348	0.013–0.085	0.365	0.365
Rozhnov (1967) <sup>60</sup>	8	298	0.013	0.058	–0.027
Rivenq (1969) <sup>61</sup>	14	303–413	0.016–0.45	0.610	0.610
Jain and Yadav (1971) <sup>62</sup>	5	315–354	0.027–0.101	0.694	0.492
Lenoir <i>et al.</i> (1971) <sup>63</sup>	8	298–328	0.013–0.044	1.568	0.478
Li <i>et al.</i> (1973) <sup>64</sup>	8	435–537	0.689–3.45	0.194	0.194
Jain and Yadav (1974) <sup>65</sup>	6	279–298	0.005–0.013	0.722	0.311
Konakbaeva <i>et al.</i> (1974) <sup>66</sup>	10	303–323	0.016–0.037	0.090	0.016
Bittrich <i>et al.</i> (1975) <sup>67</sup>	8	314–354	0.027–0.101	0.837	0.756
Aim (1978) <sup>68</sup>	10	280–297	0.005–0.012	0.084	–0.084
Hugill and McGlashan (1978) <sup>12</sup>	12 (1)	451–553	0.937–4.07	0.061	0.004
Diaz Pena <i>et al.</i> (1980) <sup>69</sup>	8	313–348	0.025–0.085	0.084	–0.084
Malanowski and Raetzsch (1981) <sup>70</sup>	5	308–348	0.02–0.085	0.015	0.015
Palczewska-Tulinska <i>et al.</i> (1983) <sup>71</sup>	9	300–353	0.014–0.098	0.128	0.128
Weclawski (1983) <sup>72</sup>	7	298–348	0.013–0.085	0.104	0.104
Weclawski and Bylicki (1983) <sup>73</sup>	15	298–349	0.013–0.086	0.028	0.005
Ksiazczak (1986) <sup>74</sup>	60	293–330	0.01–0.046	0.058	–0.040
Ksiazczak (1986) <sup>75</sup>	42	287–327	0.008–0.042	0.077	–0.070
Ksiazczak and Kosinski (1988) <sup>76</sup>	24	293–343	0.01–0.072	0.055	–0.053
Ksiazczak and Kosinski (1988) <sup>77</sup>	20	287–316	0.008–0.028	0.071	–0.044
Wu and Sandler (1988) <sup>78</sup>	7	308–340	0.02–0.066	0.101	0.032
Kaiser <i>et al.</i> (1992) <sup>79</sup>	6	323–343	0.036–0.073	0.585	0.585
Pividal <i>et al.</i> (1992) <sup>80</sup>	12	313–350	0.024–0.09	0.063	0.008
Reich and Sanhueza (1992) <sup>81</sup>	20	299–358	0.013–0.115	0.152	–0.152
Lee and Holder (1993) <sup>82</sup>	9	360–470	0.118–1.28	0.577	–0.570
Negadi <i>et al.</i> (1993) <sup>83</sup>	8	283–373	0.006–0.174	0.227	–0.097

TABLE 3. Summary of experimental data for cyclohexane—Continued

Author	Total points (Used)	$T$ (K)	$p$ (MPa)	AAD <sup>a</sup> (%)	Bias <sup>a</sup> (%)
Wisniewska <i>et al.</i> (1993) <sup>84</sup>	7	373–433	0.176–0.673	0.093	0.093
Krishnaiah <i>et al.</i> (1994) <sup>85</sup>	17	304–354	0.016–0.101	0.169	–0.166
Diogo <i>et al.</i> (1995) <sup>86</sup>	29	313–336	0.024–0.056	0.379	–0.344
Blanco <i>et al.</i> (1997) <sup>87</sup>	11	349–363	0.087–0.132	0.217	0.039
Dahmani <i>et al.</i> (1997) <sup>88</sup>	11	273–363	0.004–0.132	0.175	–0.050
Dahmani <i>et al.</i> (1997) <sup>89</sup>	5	303–343	0.016–0.072	0.119	–0.067
Segovia <i>et al.</i> (1998) <sup>90</sup>	5	313	0.025	0.037	0.003
Del Rio <i>et al.</i> (1999) <sup>91</sup>	6	298–318	0.013–0.03	0.320	–0.111
Ewing and Sanchez Ochoa (2000) <sup>92</sup>	66 (12)	281–552	0.006–3.99	0.004	–0.001
Segura <i>et al.</i> (2000) <sup>93</sup>	18	316–354	0.028–0.101	0.076	–0.044
Joseph <i>et al.</i> (2001) <sup>94</sup>	5	318–354	0.03–0.101	0.108	0.096
Lubomska <i>et al.</i> (2002) <sup>95</sup>	19	302–340	0.016–0.066	0.184	–0.178
Antosik <i>et al.</i> (2004) <sup>96</sup>	16	303–348	0.016–0.085	0.106	–0.106
Garriga <i>et al.</i> (2004) <sup>97</sup>	9	283–323	0.006–0.036	0.056	–0.055
Steyer and Sundmacher (2004) <sup>98</sup>	9	308–354	0.02–0.102	0.732	–0.732
Hidouche and Dahmani (2006) <sup>99</sup>	12	325–354	0.038–0.102	0.277	0.047
Negadi <i>et al.</i> (2007) <sup>100</sup>	12	263–363	0.002–0.132	0.200	–0.031
Sapei <i>et al.</i> (2007) <sup>101</sup>	10	318–353	0.031–0.1	0.521	0.521
Uno <i>et al.</i> (2007) <sup>102</sup>	5	334–353	0.053–0.099	0.182	–0.172
Uno <i>et al.</i> (2007) <sup>103</sup>	5	326–351	0.04–0.093	0.366	0.366
Mejia <i>et al.</i> (2008) <sup>104</sup>	14	303–354	0.016–0.102	0.089	0.076
Gierycz <i>et al.</i> (2009) <sup>105</sup>	103	295–353	0.011–0.1	0.453	–0.403
Marrufo <i>et al.</i> (2009) <sup>106</sup>	31	313–354	0.025–0.101	0.332	0.332
Khimeche <i>et al.</i> (2010) <sup>107</sup>	10	273–363	0.004–0.132	0.178	–0.072
<b>Saturated liquid density, <math>\rho'</math></b>					
Fortey (1898) <sup>108</sup>	6	273–298		0.887	–0.887
Young and Fortey (1899) <sup>15</sup>	29	303–552		0.418	0.391
Young (1910) <sup>16</sup>	32	273–552		0.403	0.375
Drapier (1911) <sup>109</sup>	5	280–308		0.072	–0.072
Jaeger (1917) <sup>110</sup>	7	282–353		0.346	0.206
Smyth and Stoops (1929) <sup>111</sup>	7	283–343		0.035	–0.035
Azim (1933) <sup>112</sup>	5	293–333		0.272	–0.013
Rotinyantz and Nagornov (1934) <sup>17</sup>	6	280–351		0.117	–0.117
Massart (1936) <sup>113</sup>	5	288–352		0.032	0.022
Vogel (1938) <sup>114</sup>	7	293–318		0.053	–0.027
Friend and Hargreaves (1944) <sup>115</sup>	5	284–349		0.085	–0.027
Friend and Hargreaves (1944) <sup>116</sup>	5	284–349		0.085	–0.027
Kuss (1955) <sup>117</sup>	8	293–353		0.014	0.001
Reamer <i>et al.</i> (1958) <sup>23</sup>	5	311–444		0.261	–0.261
Golubev and Frolova (1959) <sup>118</sup>	14	293–354		0.096	–0.053
Nikolaev <i>et al.</i> (1966) <sup>119</sup>	11	283–333		0.016	0.002
Prengle <i>et al.</i> (1967) <sup>120</sup>	6	301–343		0.016	–0.007
Findenegg (1970) <sup>121</sup>	16	280–333		0.015	–0.015
Rastorguev <i>et al.</i> (1975) <sup>122</sup>	7	298–348		0.526	0.526
Kurumov <i>et al.</i> (1977) <sup>123</sup>	13	280–349		0.016	–0.016
Hoepfner <i>et al.</i> (1979) <sup>124</sup>	7	279–333		0.094	0.094
Dymond and Young (1981) <sup>125</sup>	8	283–393		0.016	–0.007
Malanowski and Raetzsch (1981) <sup>70</sup>	5	308–348		0.115	–0.075
Marsh (1987) <sup>126</sup>	7	293–323		0.001	–0.000
Sun <i>et al.</i> (1988) <sup>127</sup>	12	282–336		0.014	0.008
Toscani <i>et al.</i> (1990) <sup>128</sup>	10	292–343		0.086	0.083
Banipal <i>et al.</i> (1991) <sup>129</sup>	7	303–333		0.024	–0.024
Cueto <i>et al.</i> (1991) <sup>130</sup>	7	283–313		0.073	–0.071
Papanastasiou and Ziogas (1991) <sup>131</sup>	5	288–308		0.050	–0.050
Qin <i>et al.</i> (1992) <sup>132</sup>	5	293		0.013	0.013
Beg <i>et al.</i> (1993) <sup>133</sup>	10	298–473		0.026	–0.019
Beg <i>et al.</i> (1994) <sup>134</sup>	5	298–353		0.013	–0.000
Beg <i>et al.</i> (1995) <sup>135</sup>	5	298–353		0.013	–0.000
Padua <i>et al.</i> (1996) <sup>136</sup>	5	298–348		0.037	0.004
Dahmani <i>et al.</i> (1997) <sup>88</sup>	11	273–363		0.530	0.530
Dahmani <i>et al.</i> (1997) <sup>89</sup>	5	303–343		0.553	0.553
Gomez-Diaz <i>et al.</i> (2001) <sup>137</sup>	6	298–323		0.302	–0.302
Hirokyu (2002) <sup>138</sup>	4	283–328		0.007	–0.007
George and Sastry (2003) <sup>139</sup>	4	298–313		0.034	–0.029
Rodriguez <i>et al.</i> (2003) <sup>140</sup>	4	293–313		0.018	–0.018

TABLE 3. Summary of experimental data for cyclohexane—Continued

Author	Total points (Used)	$T$ (K)	$p$ (MPa)	AAD <sup>a</sup> (%)	Bias <sup>a</sup> (%)
Ma <i>et al.</i> (2004) <sup>141</sup>	5	323–413		0.305	0.261
Yang <i>et al.</i> (2004) <sup>142</sup>	5	298–333		0.006	–0.001
Yang <i>et al.</i> (2007) <sup>143</sup>	4	303–333		0.005	0.001
Awwad and Abu-Daibes (2008) <sup>144</sup>	4	298–323		0.025	–0.018
Fang <i>et al.</i> (2008) <sup>145</sup>	5	288–308		0.004	0.004
Silva <i>et al.</i> (2009) <sup>146</sup>	5	283–323		0.006	0.003
Domanska and Zawadzki (2010) <sup>147</sup>	5	298–338		0.004	–0.004
Khimeche <i>et al.</i> (2010) <sup>107</sup>	9	273–353		0.524	0.524
Zhou <i>et al.</i> (2010) <sup>148</sup>	5	293–313		0.014	0.014
<b>Saturated vapor density, <math>\rho''</math></b>					
Young and Fortey (1899) <sup>15</sup>	35	363–552		0.857	–0.697
Young (1910) <sup>16</sup>	24 (1)	353–552		0.868	–0.868
Kozicki and Sage (1961) <sup>149</sup>	11	311–428		0.584	0.584
Nagarajan and Robinson (1987) <sup>150</sup>	1	344		39.956	39.956
Shibata and Sandler (1989) <sup>151</sup>	2	366–411		24.128	20.907
<b>Enthalpy of vaporization, <math>h_{\text{vap}}</math></b>					
Kozicki and Sage (1961) <sup>149</sup>	11	311–428		0.552	–0.552
Graue <i>et al.</i> (1966) <sup>152</sup>	22	278–533		1.584	–1.584
Svoboda <i>et al.</i> (1973) <sup>153</sup>	5	313–354		0.266	0.266
Majer <i>et al.</i> (1979) <sup>154</sup>	6	298–353		0.225	0.221
<b>Saturation heat capacity, <math>c_{\sigma}</math></b>					
Parks <i>et al.</i> (1930) <sup>155</sup>	5	283–299		1.402	–1.402
Paramo <i>et al.</i> (2002) <sup>156</sup>	7 (3)	288–348		0.240	–0.240
<b>Liquid phase <math>p\rho T</math></b>					
Reamer and Sage (1957) <sup>54</sup>	230	311–511	0.367–68.9	0.202	0.048
Golubev and Vagina (1959) <sup>157</sup>	90	294–548	0.392–53.5	0.353	0.179
Khodzhaev <i>et al.</i> (1968) <sup>158</sup>	14	333–353	9.81–68.6	1.202	–1.202
Kuss and Taslimi (1970) <sup>159</sup>	6	313–353	39.2–118	0.163	–0.163
Golik <i>et al.</i> (1972) <sup>160</sup>	30	303–393	50.7–253	0.667	–0.626
Apaev and Kerimov (1974) <sup>161</sup>	101	283–553	2.06–68.7	0.155	0.135
Burkat and Richard (1975) <sup>162</sup>	20	293–298	1–10	0.025	–0.025
Grigor'ev <i>et al.</i> (1975) <sup>163</sup>	40 (16)	498–548	2.06–79.1	0.056	–0.039
Rastorguev <i>et al.</i> (1975) <sup>122</sup>	59	298–423	0.145–80.4	3.737	3.713
Kurumov <i>et al.</i> (1977) <sup>123</sup>	30	283–298	1.22–32.4	0.024	–0.024
Isdale <i>et al.</i> (1979) <sup>164</sup>	6	298–348	10–100	0.057	–0.007
Jonas <i>et al.</i> (1980) <sup>165</sup>	40	313–383	5–214	0.079	0.025
Holzapfel <i>et al.</i> (1986) <sup>166</sup>	5	293	1–10	0.011	–0.011
Voss and Sloan (1989) <sup>167</sup>	24	326–450	0.4–10.4	0.455	0.455
Toscani <i>et al.</i> (1990) <sup>128</sup>	55	308–343	4.56–102	0.089	–0.035
Tanaka <i>et al.</i> (1991) <sup>168</sup>	23	298–348	6.2–100	0.058	–0.058
Wang and Shi (1995) <sup>169</sup>	28	288–318	5–19.5	0.032	0.006
Padua <i>et al.</i> (1996) <sup>136</sup>	20	298–348	5.1–38	0.035	–0.010
Ma <i>et al.</i> (2004) <sup>141</sup>	10	323–413	0.25–6.1	0.156	0.038
Amorim <i>et al.</i> (2007) <sup>170</sup>	54	318–413	6.89–62.1	0.065	0.061
Zhou <i>et al.</i> (2010) <sup>148</sup>	25	293–313	5–40	0.027	0.026
Sommer <i>et al.</i> (2011) <sup>3</sup>	164 (59)	293–473	0.01–30	0.004	–0.000
<b>Vapor phase <math>p\rho T</math></b>					
Lambert <i>et al.</i> (1949) <sup>171</sup>	12	324–404	0.038–0.1	0.131	–0.042
Waelbroeck (1955) <sup>172</sup>	9	315–348	0.027–0.085	0.162	0.162
Bottomley and Remington (1958) <sup>173</sup>	4	295–308	0.011–0.02	0.038	0.034
Golubev and Vagina (1959) <sup>157</sup>	40	556–576	3.09–53	1.701	–1.006
Hajjar <i>et al.</i> (1969) <sup>174</sup>	11	317–473	0.028–0.1	0.113	–0.004
Koehler and Sens (1969) <sup>175</sup>	8	304–344	0.017–0.074	0.052	0.052
Powell (1969) <sup>176</sup>	5	365–475	0.1	0.063	–0.063
Apaev and Kerimov (1974) <sup>161</sup>	39	523–748	2.06–68.7	0.611	–0.231
Kerns <i>et al.</i> (1974) <sup>177</sup>	10	423–523	0.1–0.5	1.155	0.897
Grigor'ev <i>et al.</i> (1975) <sup>163</sup>	79 (21)	573–698	5.25–70.1	0.167	–0.127
Rastorguev <i>et al.</i> (1975) <sup>122</sup>	70	298–473	0.001–0.807	6.750	6.750
Belousova and Sulimova (1976) <sup>178</sup>	7	433–493	0.1	0.049	0.049
Al-Bizreh and Wormald (1978) <sup>179</sup>	8	323–393	0.036–0.1	0.034	0.034
Barkan (1983) <sup>180</sup>	32	300–600	0.014–0.1	0.052	0.050
Bich <i>et al.</i> (1984) <sup>181</sup>	12	373–623	0.1	0.016	–0.007
Beg <i>et al.</i> (1994) <sup>134</sup>	6	373–473	0.101	0.018	–0.003
Beg <i>et al.</i> (1995) <sup>135</sup>	6	373–473	0.101	0.358	0.347



TABLE 3. Summary of experimental data for cyclohexane—Continued

Author	Total points (Used)	$T$ (K)	$p$ (MPa)	AAD <sup>a</sup> (%)	Bias <sup>a</sup> (%)
<b>Second virial coefficient, <math>B</math></b>					
Lambert <i>et al.</i> (1949) <sup>171</sup>	12	324–404		45.315	5.385
Waelbroeck (1955) <sup>172</sup>	9	315–348		75.744	–75.744
Bottomley and Remington (1958) <sup>173</sup>	4	295–308		52.711	–52.543
Bottomley and Coopes (1962) <sup>182</sup>	3	308–343		9.852	–9.678
Hajjar <i>et al.</i> (1969) <sup>174</sup>	11	317–473		30.114	16.373
Koehler and Sens (1969) <sup>175</sup>	8	304–344		35.281	–35.281
Powell (1969) <sup>176</sup>	5	365–475		19.766	19.766
Kerns <i>et al.</i> (1974) <sup>177</sup>	5	423–523		59.226	59.226
Belousova and Sulimova (1976) <sup>178</sup>	7	433–493		17.403	–17.403
Al-Bizreh and Wormald (1978) <sup>179</sup>	8	323–393		13.466	–13.466
Barkan (1983) <sup>180</sup>	32 (1)	300–600		20.018	–19.403
Bich <i>et al.</i> (1984) <sup>181</sup>	11 (3)	373–623		7.385	4.275
<b>Third virial coefficient, <math>C</math></b>					
Kerns <i>et al.</i> (1974) <sup>177</sup>	5	423–523		298.437	–218.437
<b>Isobaric heat capacity, <math>c_p</math></b>					
Aston <i>et al.</i> (1943) <sup>40</sup>	7	280–295	0.101	0.746	0.746
Ruehrwein and Huffman (1943) <sup>183</sup>	10	280–301	0.101	0.063	–0.063
Spitzer and Pitzer (1946) <sup>42</sup>	8	384–544	0.03–0.101	0.404	–0.247
Moelwyn-Hughes and Thorpe (1964) <sup>184</sup>	4	298–328	0.101	0.408	–0.408
Safir <i>et al.</i> (1975) <sup>185</sup>	135 (10)	295–570	0.5–50	1.580	1.548
Safir and Grigor'ev (1976) <sup>186</sup>	92	418–675	0.5–4	0.108	–0.108
San Jose <i>et al.</i> (1976) <sup>187</sup>	47	398–523	0.5–4	0.164	0.164
D'Arcy <i>et al.</i> (1977) <sup>188</sup>	3	298	0.101	0.133	–0.133
Safir (1978) <sup>189</sup>	20	299–312	0.101	0.690	–0.690
Sun <i>et al.</i> (1987) <sup>190</sup>	88	288–323	0.1–85	0.778	–0.146
Pardo <i>et al.</i> (2001) <sup>191</sup>	3	288–308	0.101	0.690	–0.690
Nan and Tan (2004) <sup>192</sup>	19	284–340	0.101	1.067	1.067
<b>Sound speed, <math>w</math></b>					
Khodzhaev <i>et al.</i> (1968) <sup>158</sup>	14	333–353	9.81–68.6	0.941	0.373
Sun <i>et al.</i> (1987) <sup>190</sup>	80 (12)	288–323	5–85	0.035	0.031
Takagi <i>et al.</i> (2002) <sup>193</sup>	48	283–333	0.7–20	0.260	–0.260
Nikolaev <i>et al.</i> (1966) <sup>119</sup>	11	283–333	Saturated	0.365	–0.299
Durov and Artikov (1985) <sup>194</sup>	8	283–313	Saturated	1.942	1.481
Lavrent'ev and Yakovlev (1985) <sup>195</sup>	19	293–536	Saturated	6.989	–6.521
Sun <i>et al.</i> (1987) <sup>190</sup>	8	288–323	Saturated	0.057	0.057
Takagi <i>et al.</i> (2002) <sup>193</sup>	7	283–333	Saturated	0.153	–0.153
Rodriguez <i>et al.</i> (2003) <sup>140</sup>	4 (2)	293–313	Saturated	0.047	–0.047

<sup>a</sup>For the second and third virial coefficients, the AAD stands for average absolute difference, and the Bias stands for average difference. The units for AAD and Bias of  $B$  and  $C$  are  $\text{cm}^3 \text{mol}^{-1}$  and  $\text{cm}^6 \text{mol}^{-2}$ , respectively. For other properties, the AAD stands for absolute average deviation, and the Bias stands for average deviation. Detailed definitions are given in Sec. 5.

## 4. Equation of State

The equation of state developed in this work is formulated with the Helmholtz energy as the fundamental property and with temperature and density as independent variables:

$$f(T, \rho) = f^0(T, \rho) + f^r(T, \rho), \quad (1)$$

where  $f$  is the Helmholtz energy,  $f^0(T, \rho)$  is the ideal-gas Helmholtz energy and  $f^r(T, \rho)$  is the residual Helmholtz energy. Modern equations of state are often formulated in this way, because all other thermodynamic properties can be calculated through the derivatives of the Helmholtz energy.<sup>6,8</sup> The dimensionless reduced Helmholtz energy  $\phi$  becomes

$$\frac{f(T, \rho)}{RT} = \frac{f^0(T, \rho)}{RT} + \frac{f^r(T, \rho)}{RT} = \phi^0(\tau, \delta) + \phi^r(\tau, \delta), \quad (2)$$

where the inverse reduced temperature is  $\tau = T_c/T$  and the reduced density is  $\delta = \rho/\rho_c$ .

### 4.1. Ideal-gas Helmholtz energy

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

$$\begin{aligned} \phi^0(\tau, \delta) = & \frac{h_0^0 \tau}{RT_c} - \frac{s_0^0}{R} - 1 + \ln \frac{\delta \tau_0}{\delta_0 \tau} - \frac{\tau}{R} \int_{\tau_0}^{\tau} \frac{c_p^0}{\tau^2} d\tau \\ & + \frac{1}{R} \int_{\tau_0}^{\tau} \frac{c_p^0}{\tau} d\tau, \end{aligned} \quad (3)$$

where  $c_p^0$  is the ideal-gas heat capacity,  $\tau_0 = T_c/T_0$ ,  $\delta_0 = \rho_0/\rho_c$ ,  $\rho_0$  is the ideal-gas density, which can be calculated by the ideal-gas equation of state ( $\rho_0 = p_0/RT_0$ ),  $T_0$  and  $p_0$  are

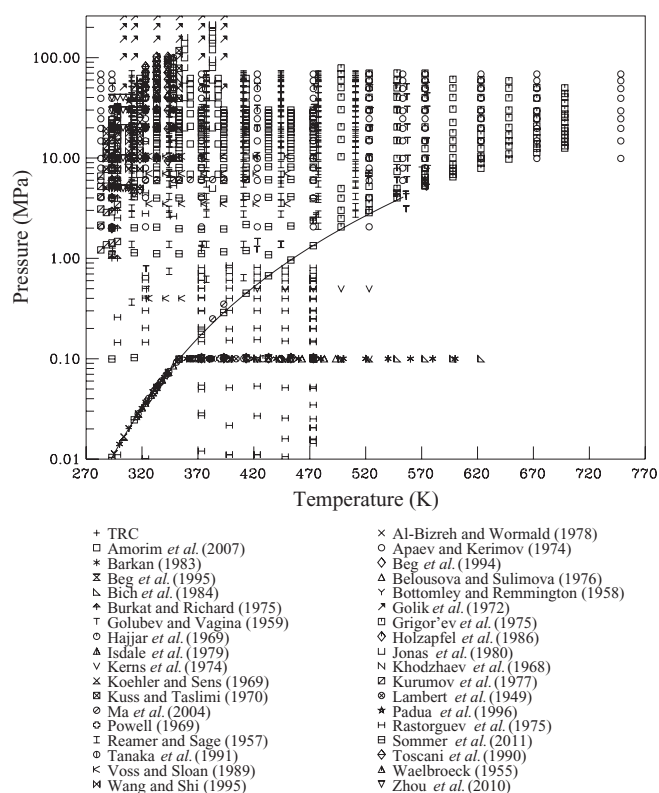


FIG. 4. Experimental  $p\rho T$  data as a function of temperature and pressure.

arbitrary constants,  $h_0^0$  is the enthalpy at  $(T_0, \rho_0)$ , and  $s_0^0$  is the entropy at  $(T_0, \rho_0)$ . As shown in the above equations, the ideal-gas heat capacity  $c_p^0$  is used to calculate the ideal-gas Helmholtz energy. The ideal-gas heat capacity  $c_p^0$  can be obtained by

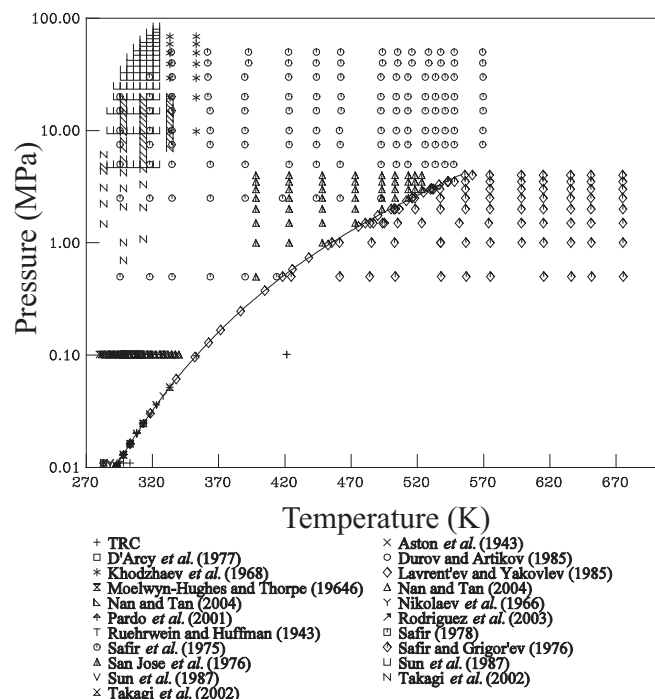


FIG. 5. Experimental calorific data as a function of temperature and pressure.

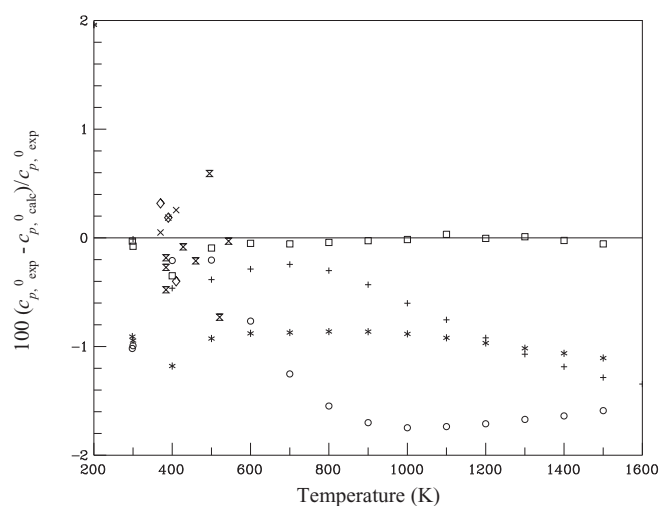


FIG. 6. Comparisons of ideal-gas heat capacities calculated with Eq. (4) to experimental and theoretical data as a function of temperature.

statistical methods or by correlating experimental data. In general, all fluids can be fitted to the same functional form,<sup>8</sup>

$$\frac{c_p^0}{R} = c_0 + \sum_{k=1}^4 v_k \left(\frac{u_k}{T}\right)^2 \frac{\exp(u_k/T)}{(\exp(u_k/T) - 1)^2}, \quad (4)$$

where  $R = 8.3144621 \text{ J mol}^{-1} \text{ K}^{-1}$  is the molar gas constant.<sup>38</sup> Parameters for cyclohexane are  $c_0 = 4$ ,  $u_1 = 773 \text{ K}$ ,  $u_2 = 941 \text{ K}$ ,  $u_3 = 2185 \text{ K}$ ,  $u_4 = 4495 \text{ K}$ ,  $v_1 = 0.83775$ ,  $v_2 = 16.036$ ,  $v_3 = 24.636$ , and  $v_4 = 7.1715$ , which were obtained by fitting to the data reported by Beckett *et al.*<sup>43</sup> Comparisons of ideal-gas heat capacities calculated with Eq. (4) to experimental and theoretical data as a function of temperature are shown in Fig. 6.

The ideal-gas Helmholtz energy equation, derived from Eqs. (3) and (4) with the application of a reference state of zero enthalpy and entropy for the saturated liquid at the normal boiling point,<sup>9</sup> is

$$\phi^0 = a_1 + a_2 \tau + \ln \delta + (c_0 - 1) \ln \tau + \sum_{k=1}^4 v_k \ln[1 - \exp(-u_k \tau / T_c)], \quad (5)$$

where  $a_1 = 0.9891140602$  and  $a_2 = 1.6359660572$ . The ideal-gas reference state points are  $T_0 = 300 \text{ K}$ ,  $p_0 = 1 \text{ kPa}$ ,  $h_0^0 = 23949.01000 \text{ J mol}^{-1}$ , and  $s_0^0 = 104.2926004 \text{ J mol}^{-1} \text{ K}^{-1}$ . Other reference states can also be used. The values of the other coefficients in Eq. (5) are the same as those used in Eq. (4).

## 4.2. Residual Helmholtz energy

Unlike the ideal-gas Helmholtz energy equation, the residual Helmholtz energy equation is fitted to large numbers of multi-property experimental data, such as  $p\rho T$ , heat capacity, sound speed, vapor pressure, saturated-liquid density, and

saturated-vapor density. Table 3 summarizes the available experimental data for cyclohexane. The final data used in the fitting of the equation of state are shown in parentheses.

In this work, the nonlinear fitting algorithm used to optimize the residual Helmholtz energy equation was based on the Levenberg-Marquardt method.<sup>196</sup> The fitting algorithm minimizes the function

$$S = \sum W_p \left[ \frac{(p_{\text{exp}} - p_{\text{calc}})}{\rho_{\text{exp}}} \left( \frac{\partial p}{\partial p} \right) \right]^2 + \sum W_w \left[ \frac{(w_{\text{exp}} - w_{\text{calc}})}{w_{\text{exp}}} \right]^2 + \sum W_{c_p} \left[ \frac{(c_{p,\text{exp}} - c_{p,\text{calc}})}{c_{p,\text{exp}}} \right]^2 + \dots, \quad (6)$$

where  $W$  specifies the weight assigned to a particular property. A different weight  $W$  was assigned to each data point used in the fitting process. The quality of the resulting equation of state is determined through comparisons of calculated deviations of all data points and the total deviations of specific data sets. The final weight on a data point should reflect the approximate uncertainty. In general, data points with uncertainties less than 0.01% are given a weight of 1000, those with uncertainties less than 0.1% are given weights of 10 to 100, those with uncertainties of 0.1%–0.2% are given weights of 1–10, and those with higher uncertainties are given weights of 0.01–0.1. The process of fitting the equation of state requires finding a balance between the weights and the deviations of reliable data.

There are some criteria for the equation of state to conform to expected behavior at experimentally accessible states and at high temperatures and pressures. The values of  $t_i$  in the equation given below should be greater than zero, and  $d_i$  and  $l_i$  should be integers greater than zero. The temperature exponent  $t_i$  on the density exponent  $d_i = 4$  is fixed exactly to 1 for the equation of state to have proper extrapolation behavior at high densities and temperatures<sup>196</sup>—Sec. 6 shows that the extrapolation behavior of the equation of state is reasonable at extremely high pressures and densities.

The residual Helmholtz energy equation  $\phi^r(\tau, \delta)$  was developed with the fitting methods of Lemmon and Jacobsen;<sup>196</sup> the equation is constrained by various criteria explained in that work and in Ref. 4. The form of  $\phi^r(\tau, \delta)$  is as follows with the coefficients and exponents given in Table 4:

$$\phi^r(\tau, \delta) = \sum_{i=1}^5 n_i \delta^{d_i} \tau^{t_i} + \sum_{i=6}^{10} n_i \delta^{d_i} \tau^{t_i} \exp(-\delta^{l_i}) + \sum_{i=11}^{20} n_i \delta^{d_i} \tau^{t_i} \exp(-\eta_i(\delta - \varepsilon_i)^2 - \beta_i(\tau - \gamma_i)^2). \quad (7)$$

## 5. Comparisons with Experimental Data

The accuracy of the equation of state was determined by statistical comparisons of property values calculated with the

TABLE 4. The coefficients and exponents of the residual Helmholtz energy

$i$	$n_i$	$t_i$	$d_i$	$l_i$
1	0.05483581	1	4	–
2	1.607734	0.37	1	–
3	–2.375928	0.79	1	–
4	–0.5137709	1.075	2	–
5	0.1858417	0.37	3	–
6	–0.9007515	2.4	1	2
7	–0.5628776	2.5	3	2
8	0.2903717	0.5	2	1
9	–0.3279141	3	2	2
10	–0.03177644	1.06	7	1
11	0.8668676	1.6	1	–
12	–0.1962725	0.37	1	–
13	–0.1425992	1.33	3	–
14	0.004197016	2.5	3	–
15	0.1776584	0.9	2	–
16	–0.04433903	0.5	2	–
17	–0.03861246	0.73	3	–
18	0.07399692	0.2	2	–
19	0.02036006	1.5	3	–
20	0.00272825	1.5	2	–
$i$	$\eta_i$	$\beta_i$	$\gamma_i$	$\varepsilon_i$
11	0.99	0.38	0.65	0.73
12	1.43	4.2	0.63	0.75
13	0.97	1.2	1.14	0.48
14	1.93	0.9	0.09	2.32
15	0.92	1.2	0.56	0.2
16	1.27	2.6	0.4	1.33
17	0.87	5.3	1.01	0.68
18	0.82	4.4	0.45	1.11
19	1.4	4.2	0.85	1.47
20	3	25	0.86	0.99

equation of state to experimental data. The statistics used in the comparisons are the absolute average deviation (AAD) and the Bias. The percent deviation between the experimental data and the values calculated with the equation of state for any property,  $X$ , is defined as

$$\% \Delta X = 100 \left( \frac{X_{\text{exp}} - X_{\text{calc}}}{X_{\text{exp}}} \right). \quad (8)$$

With this definition, the AAD and Bias are defined as

$$\text{AAD} = \frac{1}{N_{\text{exp}}} \sum_{i=1}^{N_{\text{exp}}} |\% \Delta X_i|, \quad (9)$$

and

$$\text{Bias} = \frac{1}{N_{\text{exp}}} \sum_{i=1}^{N_{\text{exp}}} (\% \Delta X_i), \quad (10)$$

where  $N_{\text{exp}}$  is the number of data points. The AAD and Bias are listed in the last two columns of Table 3.

### 5.1. Comparisons with saturation thermal data

Table 3 summaries the experimental vapor pressure data for cyclohexane. Figures 7 and 8 compare vapor pressures  $p_{\text{G}}$

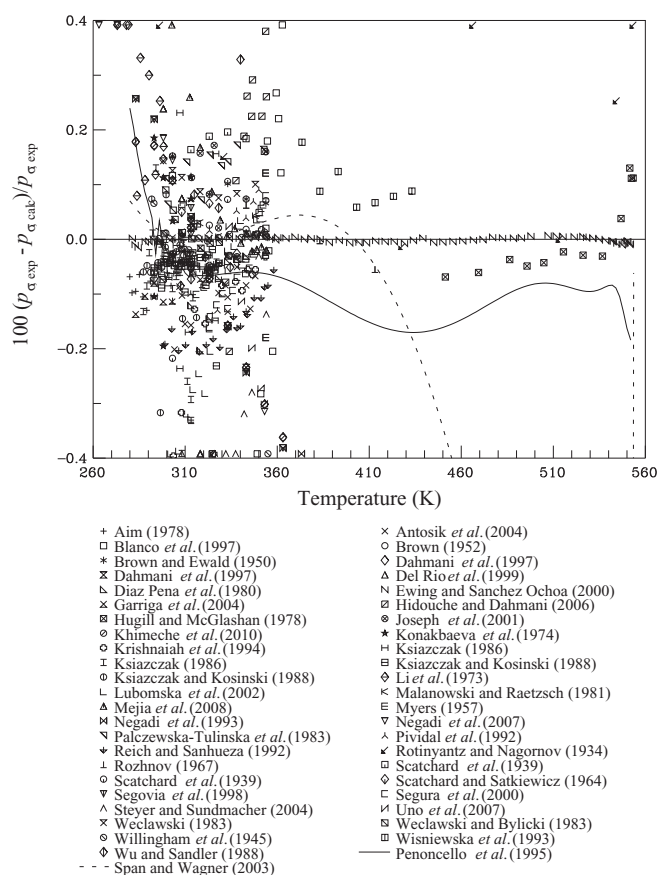


Fig. 7. Comparisons of vapor pressures calculated with the equation of state to experimental data as a function of temperature (the y-axis range is  $\pm 0.4\%$ ).

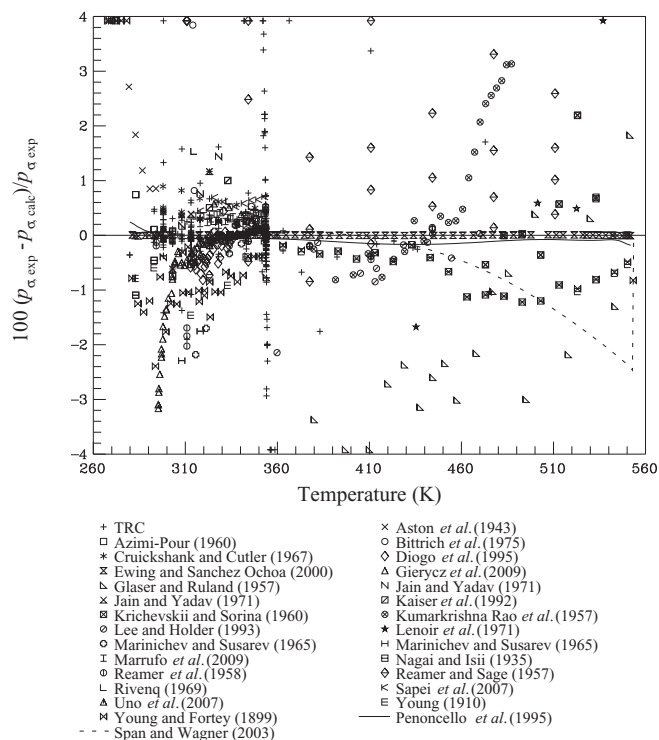


Fig. 8. Comparisons of vapor pressures calculated with the equation of state to experimental data as a function of temperature (the y-axis range is  $\pm 4\%$ ).

calculated with the equation of state to experimental data as a function of temperature. Values calculated from the equations of state by Span and Wagner<sup>4</sup> and Penoncello *et al.*<sup>5</sup> are also compared with the new equation of state in the figures. The equation of state represents most vapor pressures generally within 0.2%. Above 350 K, the amount of experimental data substantially decreases. However, the accurate data of Ewing and Sanchez Ochoa<sup>92</sup> were published in 2000, which were not available during the development of the equation of Penoncello *et al.*<sup>5</sup> The uncertainties of the data of Ewing and Sanchez Ochoa<sup>92</sup> are estimated to be 0.02%. 12 out of 60 of the data by Ewing and Sanchez Ochoa<sup>92</sup> were used in fitting the equation, and are represented to within 0.01%. The limited number of fitted data was chosen to increase the speed of the fitting program. There are many experimental data below 350 K, and the equation passes through the center. The equations by Span and Wagner<sup>4</sup> and Penoncello *et al.*<sup>5</sup> show opposite trends at low temperatures below 290 K, and both show a downward trend at high temperatures.

The experimental saturated liquid density data of cyclohexane are summarized in Table 3. Comparisons of saturated liquid densities  $\rho'$  calculated with the equation of state to experimental data as a function of temperature  $T$  are presented in Fig. 9. There are many experimental saturated liquid densities below 350 K, with the equation passing through the

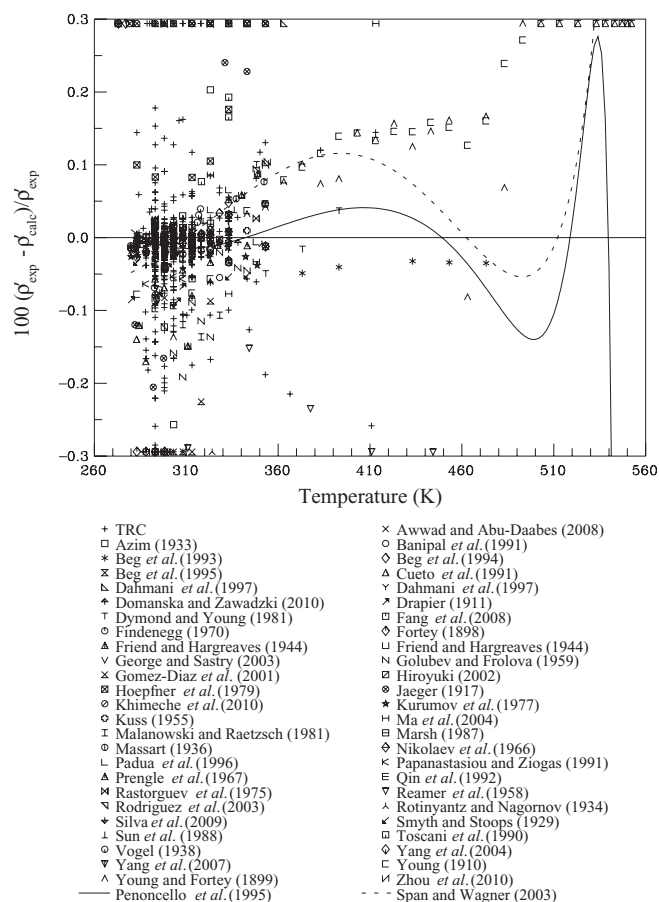


Fig. 9. Comparisons of saturated liquid densities calculated with the equation of state to experimental data as a function of temperature.

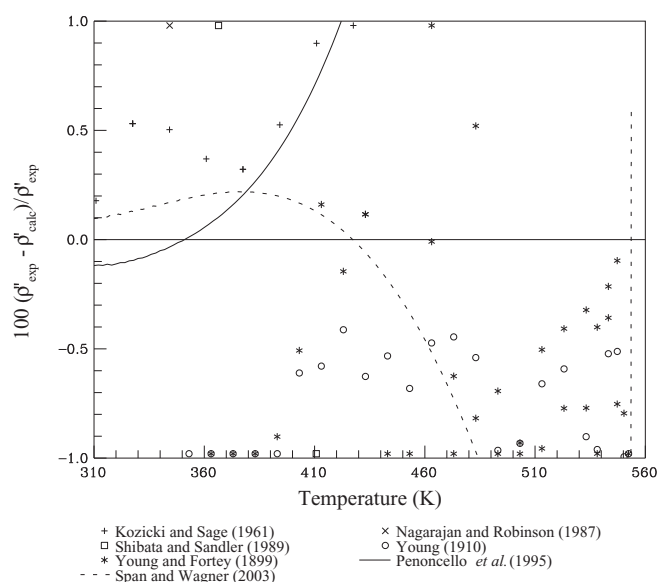


FIG. 10. Comparisons of saturated vapor densities calculated with the equation of state to experimental data as a function of temperature.

center, representing most of the data within 0.05%. However, the data are limited at higher temperature, with no reliable data. The data obtained by Young and Fortey<sup>15</sup> and Young,<sup>16</sup> measured over a hundred years ago, show deviations of 0.15%. No data were used during the fitting of the equation of state at higher temperatures. The equation represents the data generally within 0.02% below 350 K, and 0.15% at higher temperatures. The uncertainty in saturated liquid density is estimated to be 0.02% below 500 K due to the highly accurate  $p\rho T$  data<sup>3</sup> that were used in the fit.

The experimental saturated vapor density data of cyclohexane are summarized in Table 3. As the data are limited and scattered, none of the data were used in the fit. Comparisons of saturated vapor densities  $\rho^v$  calculated with the equation of state to experimental data as a function of temperature  $T$  are given in Fig. 10. The equation represents the data generally within 1.0%. The data reported by Kozicki and Sage,<sup>149</sup> Young and Fortey,<sup>15</sup> and Young<sup>16</sup> show opposite trends at low temperatures.

## 5.2. Comparisons with $p\rho T$ data and virial coefficients

The experimental  $p\rho T$  data are summarized in Table 3 and shown in Fig. 4. Comparisons of densities calculated with the equation of state to experimental data and values generated from the equations of state by Span and Wagner<sup>4</sup> and Penoncello *et al.*<sup>5</sup> are shown in Fig. 11 as a function of pressure; the deviations are shown in groups containing data within 20 K intervals. The deviations between the new equation and the old equations<sup>4,5</sup> are generally within 0.1% except in the critical region and the high-pressure

region. In the compressed liquid region, the high-accuracy data by Sommer *et al.*<sup>3</sup> were used in fitting the equation of state, and the equation represents the data within 0.02% with an AAD of 0.009% and a Bias of 0.006%. The data obtained by Grigor'ev *et al.*<sup>163</sup> were used in the fitting process in the supercritical region, and the new equation represents the data generally within 0.2%. For the vapor-phase region, no density data were employed, however, second virial coefficients and some constraints for the equation of state were used to achieve proper behavior.

The published second and third virial coefficients are summarized in Table 3. Figure 12 presents comparisons of second virial coefficients  $B$  calculated with the equation of state to experimental data as a function of temperature. The values calculated with the equations of state by Span and Wagner<sup>4</sup> and Penoncello *et al.*<sup>5</sup> show an opposite trend at low temperatures. The data reported by Bich *et al.*<sup>181</sup> deviate from the data reported by Barkan.<sup>180</sup> The equation of state represents second virial coefficients generally within  $10 \text{ cm}^3 \text{ mol}^{-1}$  above 500 K, and  $30 \text{ cm}^3 \text{ mol}^{-1}$  at lower temperatures. Only one data set for the third virial coefficient for cyclohexane was published, and they are very limited and scattered; comparisons are not shown in the form of a diagram here. Figure 13, in which the y intercept (zero density) represents the second virial coefficient at a given temperature and the third virial coefficient is the slope of each line at zero density, shows that the behavior of the second and third virial coefficients as well as the shape of the equation of state are reasonable.

## 5.3. Comparisons with caloric data

The limited caloric data for cyclohexane are summarized in Table 3 and shown in Fig. 5. Comparisons of isobaric heat capacities  $c_p$  calculated with the equation of state to experimental data are shown in Fig. 14. The equation represents isobaric heat capacities generally within 2%. The data reported by Safir and Grigor'ev<sup>186</sup> show an upward trend, and the data of Sun *et al.*<sup>190</sup> show a downward trend. The data by Safir *et al.*<sup>185</sup> and San Jose *et al.*<sup>187</sup> as well as Safir and Grigor'ev<sup>186</sup> overlap with each other very well. As shown in Fig. 14, the heat capacity behavior of the new equation is similar to the Span and Wagner<sup>4</sup> equation, but with improvements compared to the equation of Penoncello *et al.*<sup>5</sup>

Figure 15 shows comparisons of sound speeds  $w$  calculated with the equation of state to experimental data. The equation represents the experimental data generally within 0.5%. The experimental sound-speed data are very scattered, except the data reported by Sun *et al.*<sup>190</sup> and Takagi *et al.*<sup>193</sup> The experimental data above 350 K are very limited; only data reported by Lavrent'ev and Yakovlev<sup>195</sup> were found. Figure 15 also shows that the equation of this work is improved compared to the equations developed by Penoncello *et al.*<sup>5</sup> and Span and Wagner.<sup>4</sup>

Figure 16 shows comparisons of enthalpies of vaporization,  $h_{\text{vap}}$ , and saturation heat capacities,  $c_{\sigma}$ , calculated with the equation of state to experimental data as a function of

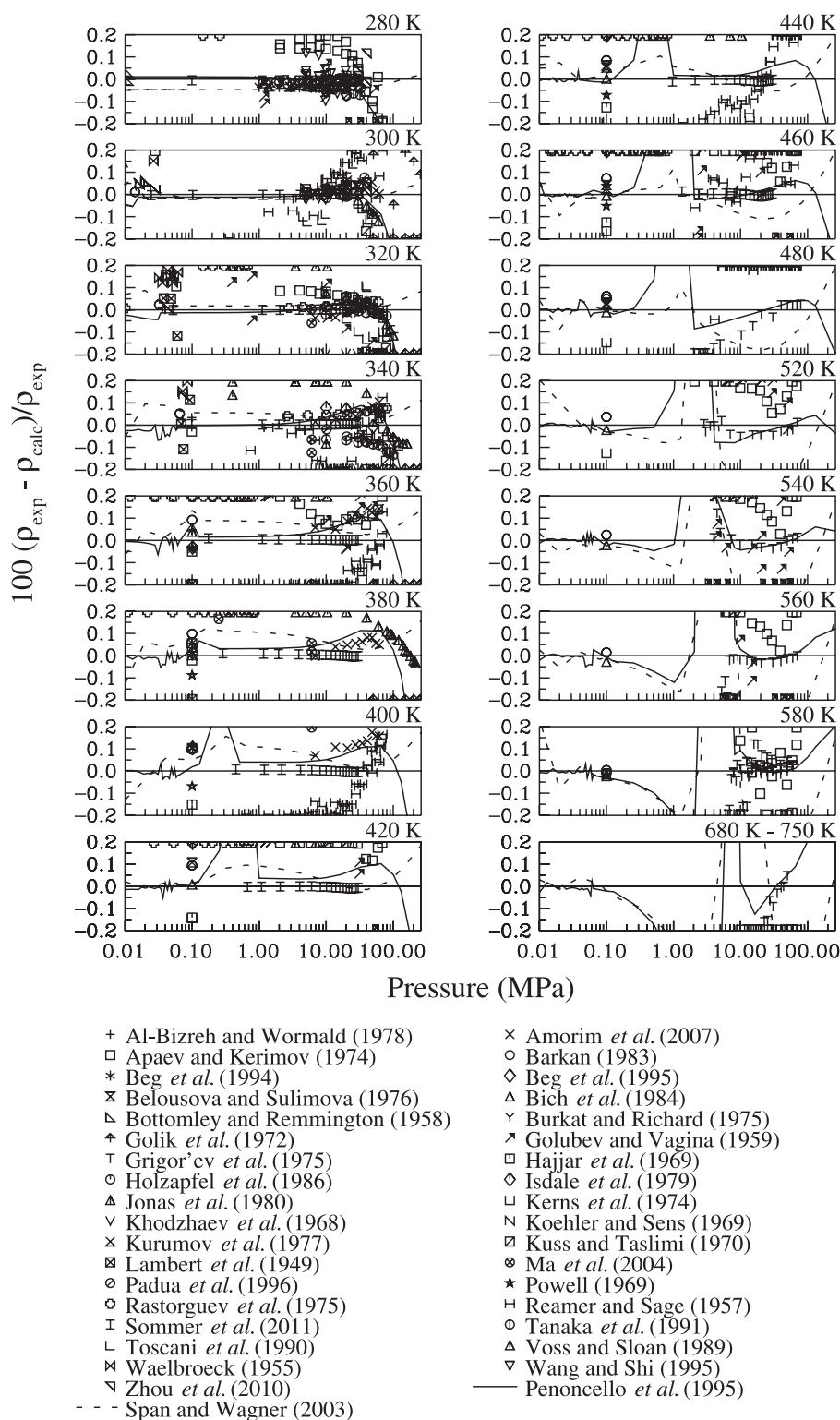


Fig. 11. Comparisons of densities calculated with the equation of state to experimental data as a function of pressure.

temperature. At temperatures below 400 K, the equation of this work represents most data within 1%, however, additional measurements are needed at higher temperatures to verify calculations from the equation of state. The figure also compares the equations developed by Penoncello *et al.*<sup>5</sup> and Span and Wagner<sup>4</sup> to the new equation.

## 6. Extrapolation Behavior of the Equation of State

The equation of state should have reasonable extrapolation behavior, and a plot of constant property lines on various thermodynamic coordinates is useful in assessing the

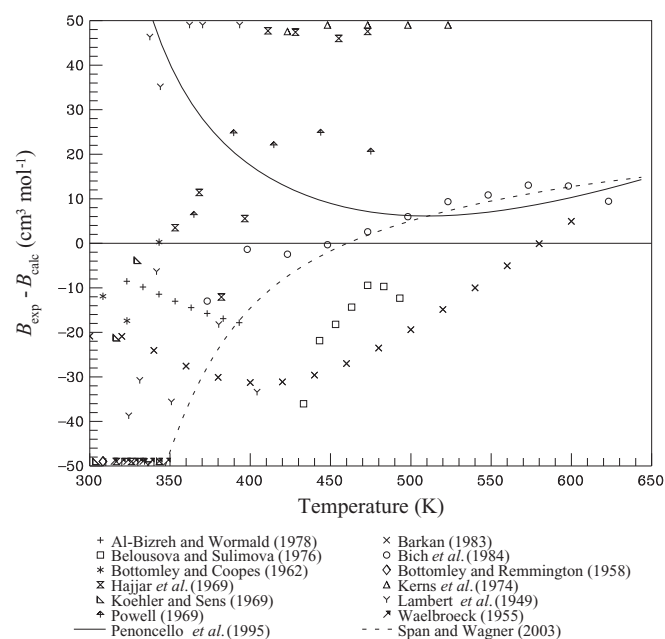


FIG. 12. Comparisons of second virial coefficients calculated with the equation of state to experimental data as a function of temperature.

behavior. The equation developed in this work was used to plot isochoric heat capacity, isobaric heat capacity, sound speed, and density versus temperature, as well as pressure versus density and characteristic (ideal) curves of the equation of state. In these figures, the behavior of the equation at extreme conditions is also shown to verify the mathematical stability of the equation, even though cyclohexane would decompose long before the extreme temperatures are reached.

Figure 17 shows a diagram for isochoric heat capacity  $c_v$  versus temperature  $T$ . There is an upward trend around the critical point, and the value of the isochoric heat capacity

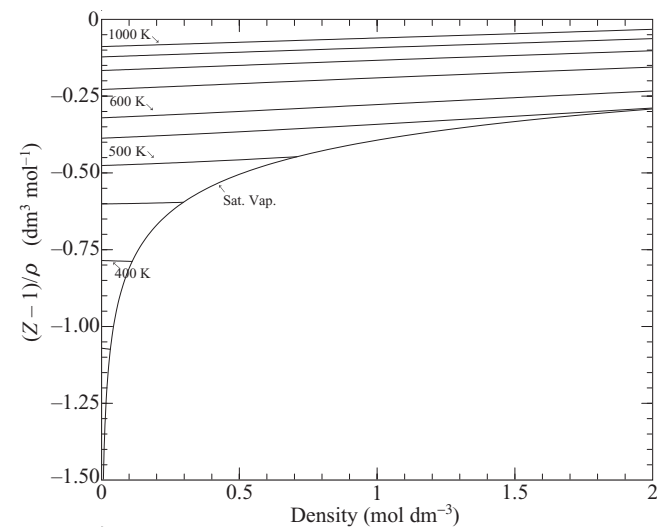


FIG. 13. Calculations of  $(Z-1)/\rho$  along isotherms versus density. Isotherms are shown at temperatures of (350, 400, 450, 500, 550, 600, 700, 800, 900, and 1000) K.

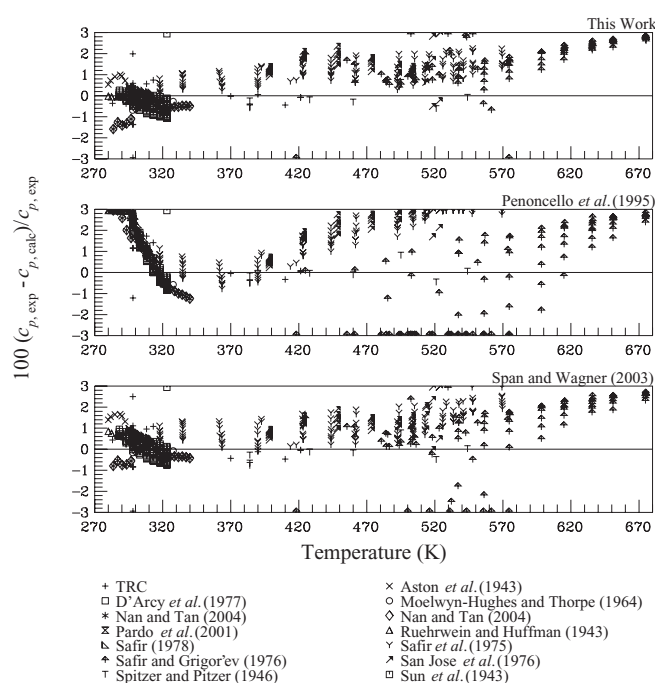


FIG. 14. Comparisons of isobaric heat capacities calculated with the equation of state to experimental data as a function of temperature.

achieves a local maximum at the critical point. Figure 18 is a diagram for isobaric heat capacity  $c_p$  versus temperature  $T$ . Both figures indicate that the equation of state behavior is appropriate within the range of validity, and that the extrapolation behavior is reasonable at higher temperatures and pressures. In addition, these figures show that there is a reasonable upward trend in the liquid region at low temperatures below the triple-point temperature, as expected.<sup>9</sup>

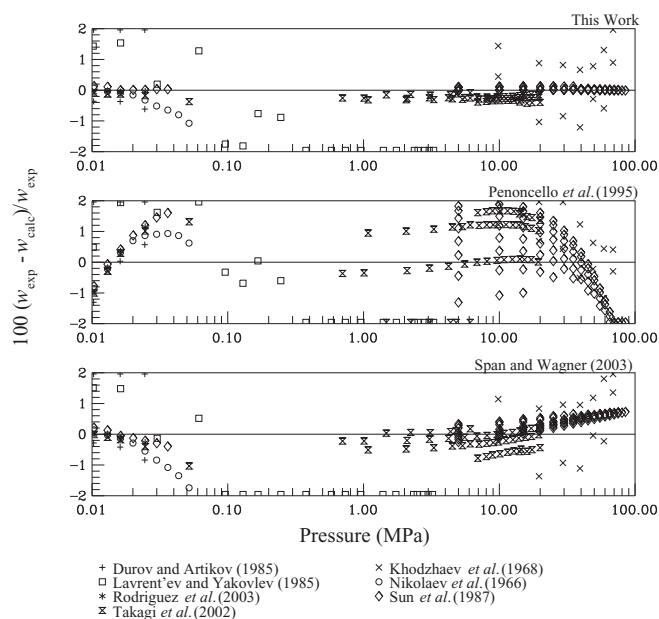


FIG. 15. Comparisons of sound speeds calculated with the equation of state to experimental data as a function of temperature.

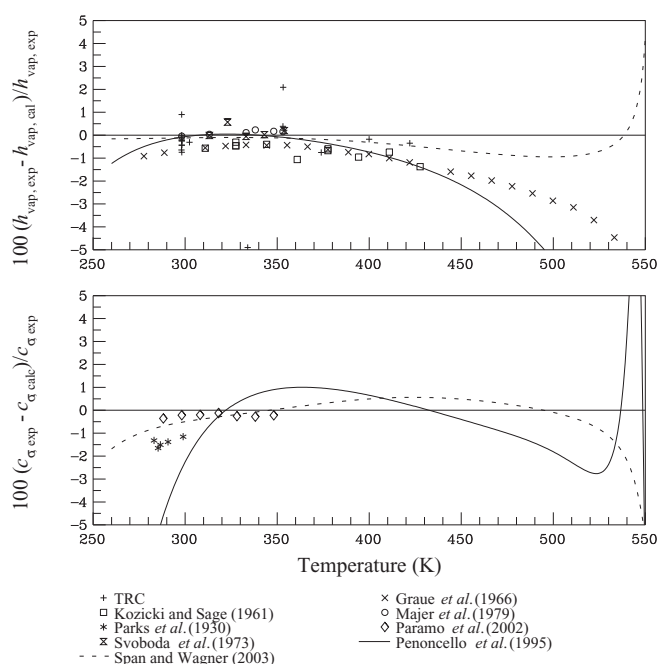


Fig. 16. Comparisons of enthalpies of vaporization,  $h_{\text{vap}}$ , and saturation heat capacities,  $c_g$ , calculated with the equation of state to experimental data as a function of temperature.

Figure 19 shows sound speed  $w$  versus temperature  $T$ . The figure also shows that the extrapolation behavior to high temperatures and pressures is reasonable, aside from a slight abnormality at the highest pressure (1000 MPa).

Figures 20 and 21 show the density behavior along isobars. The rectilinear diameter is shown in Fig. 21, and is straight, as it should be, clear up to the critical point.

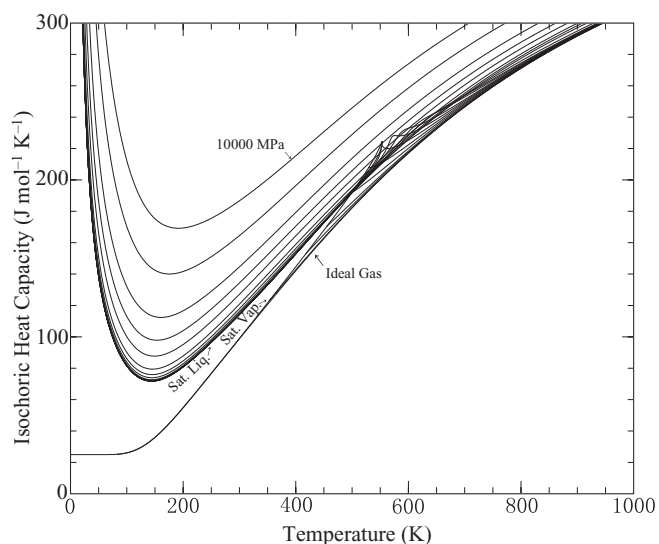


Fig. 17. Isochoric heat capacity  $c_v$  versus temperature. Isobars are shown at pressures of (0, 0.1, 0.5, 1, 2, 3, 4, 5, 6, 8, 10, 20, 50, 100, 200, 500, 1000, 2000, 5000, and 10 000) MPa.

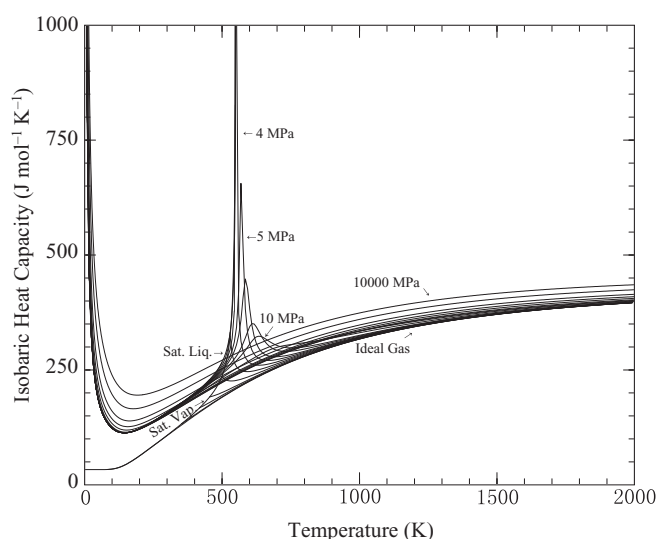


Fig. 18. Isobaric heat capacity  $c_p$  versus temperature. Isobars are shown at pressures of (0, 0.1, 0.5, 1, 2, 3, 4, 5, 6, 8, 10, 20, 50, 100, 200, 500, 1000, 2000, 5000, and 10 000) MPa.

Figure 22 shows the isothermal behavior of the equation of state at extreme conditions of temperature and pressure. The figure indicates that the extrapolation behavior to extremely high pressures, densities, and temperatures is reasonable. As explained by Lemmon and Jacobsen,<sup>196</sup> the smooth behavior comes from the term with  $t_i = 1$  and  $d_i = 4$ .

Figure 23 shows the characteristic (ideal) curves of the equation of state as a function of reduced temperature  $T/T_c$  and reduced pressure  $p/p_c$ . Figure 23 is used to assess the behavior of the equation of state in regions without available experimental data.<sup>8,9,196</sup> The characteristic curves include the Boyle curve, the Joule-Thomson inversion curve, the Joule inversion

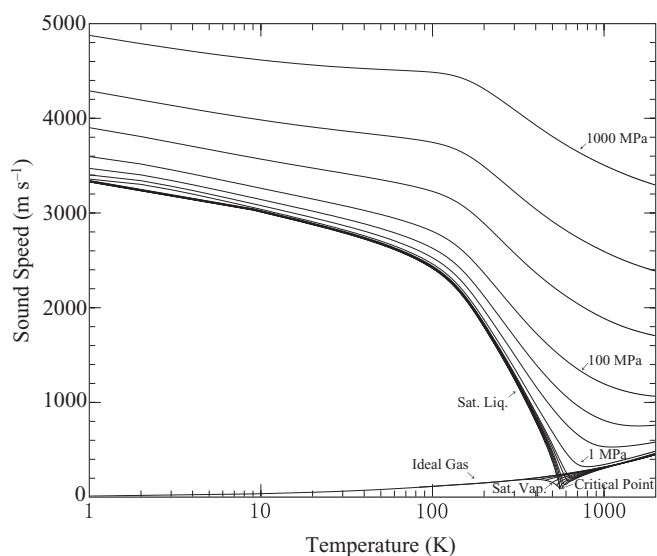


Fig. 19. Sound speed versus temperature. Isobars are shown at pressures of (0, 0.1, 0.5, 1, 2, 3, 4, 5, 6, 8, 10, 20, 50, 100, 200, 500, and 1000) MPa.



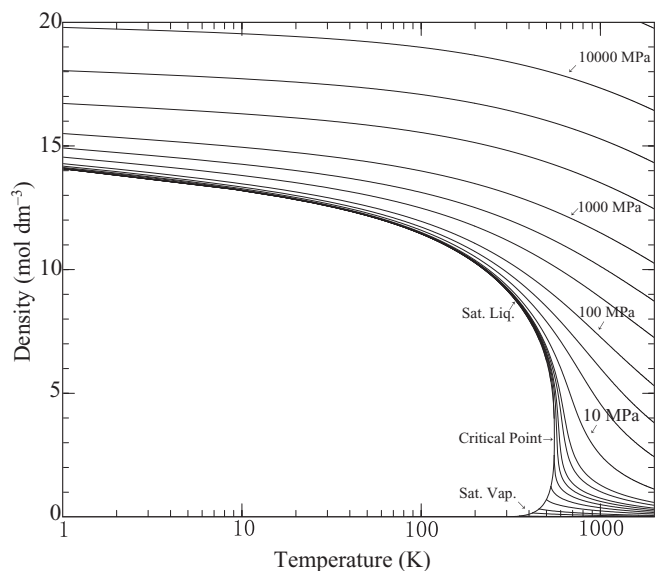


FIG. 20. Isobaric behavior of the equation of state for cyclohexane. Isobars are shown at pressures of (0, 0.1, 0.5, 1, 2, 3, 4, 5, 6, 8, 10, 20, 50, 100, 200, 500, 1000, 2000, 5000, and 10 000) MPa.

curve, and the ideal curve. The Boyle curve is given by

$$\left(\frac{\partial Z}{\partial v}\right)_T = 0. \quad (11)$$

The Joule-Thomson inversion curve is given by

$$\left(\frac{\partial Z}{\partial T}\right)_p = 0. \quad (12)$$

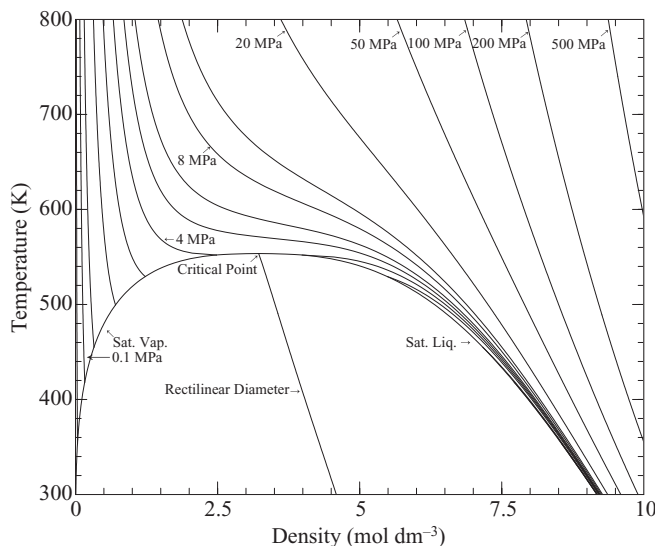


FIG. 21. Isobaric behavior of the equation of state for cyclohexane at temperatures above 300 K. Isobars are shown at pressures of (0, 0.1, 0.5, 1, 2, 3, 4, 5, 6, 8, 10, 20, 50, 100, 200, and 500) MPa. The rectilinear diameter is shown in the diagram.

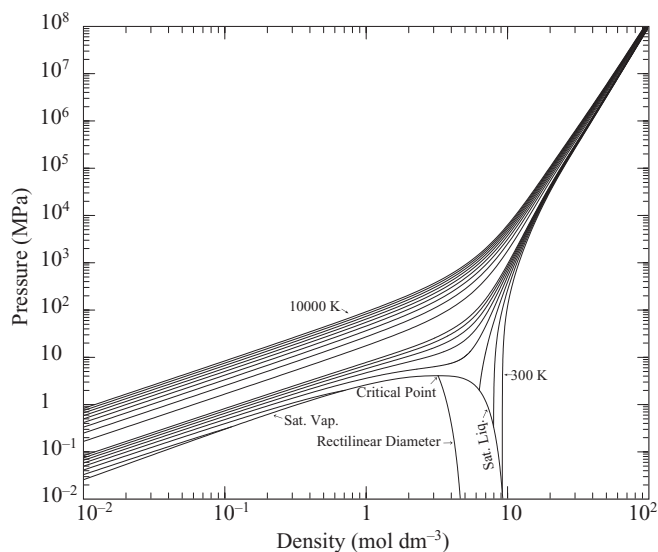


FIG. 22. Isothermal behavior of the equation of state at extreme conditions of temperature and pressure. Isotherms are shown at temperatures of (300, 400, 500, 600, 700, 800, 900, 1000, 2000, 3000, 4000, 5000, 6000, 7000, 8000, 9000, and 10 000) K. The rectilinear diameter is shown in the diagram.

The Joule inversion curve is given by

$$\left(\frac{\partial Z}{\partial T}\right)_v = 0. \quad (13)$$

The ideal curve is given by

$$Z = \frac{p}{\rho RT} = 1. \quad (14)$$

Overall, these plots indicate that the equation of state behavior is appropriate within the valid range, and that the extrapolation behavior is reasonable at higher temperatures and pressures.

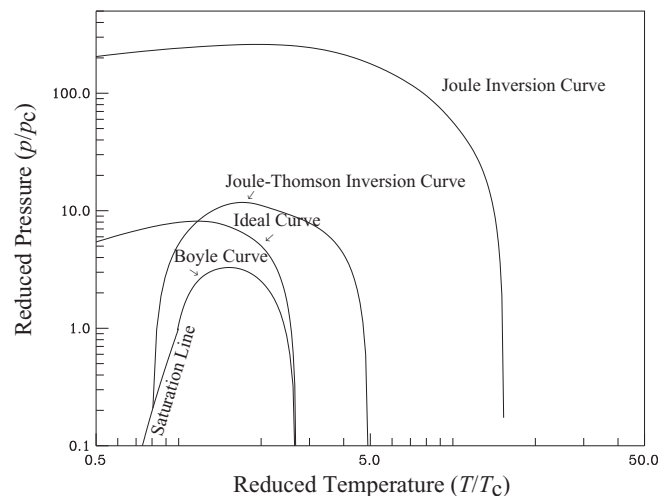


FIG. 23. Characteristic (ideal) curves of the equation of state as a function of reduced temperature  $T/T_c$  and reduced pressure  $p/p_c$ .

TABLE 5. Sample state points for algorithm verification of equation implementation

Temperature (K)	Density (mol dm <sup>-3</sup> )	Pressure (MPa)	Isochoric heat capacity (J mol <sup>-1</sup> K <sup>-1</sup> )	Isobaric heat capacity (J mol <sup>-1</sup> K <sup>-1</sup> )	Speed of sound (m s <sup>-1</sup> )	Enthalpy (J mol <sup>-1</sup> )	Entropy (J mol <sup>-1</sup> K <sup>-1</sup> )
300.0	9.4	24.173 705	115.286 00	154.769 56	1383.387 8	-8400.083 4	-28.889 069
500.0	6.5	3.924 6630	192.520 56	255.570 87	434.130 64	31 070.127	70.891 447
500.0	0.7	1.998 1172	191.964 46	235.522 81	155.348 00	52 757.706	122.926 57
600.0	3.5	6.822 5506	232.792 22	388.551 85	150.533 18	70 150.132	143.423 23
553.6	3.3	4.080 5433	224.195 55	199 224.62	87.913 911	58 532.604	123.598 10
353.864 939 <sup>a</sup>	8.548 785 1	0.101 325	134.616 30	179.072 23	994.058 62	0	0
353.864 939 <sup>b</sup>	0.035 779 032	0.101 325	123.430 50	133.358 95	186.913 49	29 991.286	84.753 484

<sup>a</sup>Saturated liquid.<sup>b</sup>Saturated vapor.

## 7. Conclusions

A new equation of state for cyclohexane has been developed for the need of scientific research and engineering applications. The uncertainties of the equation of state in density for the equation of state are 0.1% (liquid and vapor) up to 500 K and 0.2% above 500 K, with higher uncertainties approaching the critical region. Between 283 K and 473 K with pressures less than 30 MPa, the uncertainty is as low as 0.03% in density in the liquid phase. The uncertainties in the speed of sound are 0.2% between 283 K and 323 K in the liquid, and 1% elsewhere. Other uncertainties are 0.05% in vapor pressure and 2% in heat capacities.

The equation of state of this work is valid from the triple-point temperature,  $T_{tp} = 279.86$  K, to 700 K, with pressures up to 250 MPa, and densities up to 10.3 mol dm<sup>-3</sup>. As analyzed in this article, the equation of state obtains a good balance between behavior at normal conditions and extrapolation behavior compared to the old equations developed by Penoncello *et al.*<sup>5</sup> and Span and Wagner.<sup>4</sup> The extrapolation behavior of the equation of state is reasonable, and the equation can be extrapolated up to the dissociation limit of the fluid, with pressures up to 500 MPa.

Gas-phase  $pVT$  data above 500 K should be further measured to develop a reference equation of state. There is a need for further measurement of caloric properties of cyclohexane, including sound speed and heat capacity. Calculated values of properties from the equation of state of this work are given in Table 5 to aid in computer implementation.

## Acknowledgments

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