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## Recommended Critical Temperatures. Part I. Aliphatic Hydrocarbons

Iwona Owczarek; Krystyna Blazej



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# Recommended Critical Temperatures. Part I. Aliphatic Hydrocarbons

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This work deals with the critical temperature ( $T_c$ ) for saturated and unsaturated aliphatic hydrocarbons. For 175 hydrocarbons (branched alkanes, branched and unbranched alkenes, and alkynes), an existing lack of critical temperature values have been complemented. Prediction methods have been used, the usefulness of which for specific groups and subgroups of the above mentioned hydrocarbons had been previously critically evaluated. The evaluation of accuracy of the relevant aspects of these methods is given in this study. An additional result of this work is the creation of a set of recommended experimental data on critical temperatures and normal boiling points for aliphatic hydrocarbons. Such a set has been created mainly for the purpose of evaluation of prediction methods applied in this study. © 2003 American Institute of Physics.

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Key words: alkanes; alkenes; critical temperature; evaluation; normal boiling points; predicted data; recommended data.

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## 1. Introduction

The calculation of properties of pure hydrocarbons and their mixtures, essential in process designs, especially those involving high pressure vapor–liquid equilibria and thermal properties, requires the use of reliable data on critical parameters and normal boiling points. Critical properties are difficult to measure experimentally since expensive high quality equipment is required to enable the possibility of high accuracy measurements in high temperature and high pressure regions. Moreover, for compounds with numerous single bonds, the processes of thermal decomposition constitute a major obstacle to the measurement of critical properties (temperature, pressure, and density). That is why the world literature resources provide the measured critical parameters for only a limited number of compounds. In this latter case, prediction methods are the only means by which those properties may be determined. In the course of a preliminary study dealing with testing accuracy of prediction methods (based on experimental data), it has been found that most of the available methods yield satisfactory results only when applied to narrow subgroups of hydrocarbons having similar molecular structure groups.

One purpose of this work was the comparative evaluation of the accuracy and applicability of prediction methods for  $T_c$  for the aliphatic hydrocarbons. On this basis, selected methods were applied to calculation of  $T_c$  for those hydrocarbons for which there are no available experimental data in the literature.

The preliminary stages of this work were:

- Creation of a recommended experimental data base. (Table 1), of  $T_b$  and  $T_c$  values of aliphatic hydrocarbons for which a satisfactory quantity of experimental data has been found. This data base was next used for evaluation of chosen methods.
- Creation of a recommended experimental data base (Table 2), of  $T_b$  values of chosen hydrocarbons, for which the critical temperatures have been calculated.
- Comparative determination of the accuracy of individual predictive methods of calculation of critical temperature  $T_c$  values of hydrocarbons according to their different molecular structures; and the final aim is
- Application of the chosen predictive methods for determination of  $T_c$  values of hydrocarbons for which the experimental data were not available in world literature.

The experimental data were critically evaluated and statis-

tically examined with the aim of choosing the most reliable  $T_c$  and  $T_b$  values for recommended data sets, mentioned in points (a) and (b).

The evaluation of the applicability of prediction methods was effected by determining the dependence of their accuracy upon:

- a number of carbon atoms in a molecule;
- a number of substituted  $\text{CH}_3$ - and  $\text{C}_2\text{H}_5$ - groups;
- length of a side chain;
- $C_s/C_m$  ratio, where  $C_s$  is a general number of  $C$  atoms in side chains, and  $C_m$  is a number of  $C$  atoms in the main chain; and
- type of C–C bond.

This work is the first part of a general study for the determination of critical parameters of the main groups of chemical compounds for which experimental data are not available in world literature. This study will be followed by evaluation of the aforementioned predictive methods' accuracy for critical parameters of cyclic and aromatic hydrocarbons and other groups of compounds (i.e., alcohols, esters, ketones, halogenated hydrocarbons, etc.) as well as for their critical pressure.

The critical volume will not be included as it is poorly represented in most experimental data. New predictive methods, if published, will be considered as well.

## 2. Description of Selected Methods of $T_c$ Prediction

The following methods, defined by their authors' names, have been chosen as a result of a review and a critical analysis of main prediction methods of  $T_c$  available in literature: (1) Ambrose,<sup>1</sup> (2) Joback,<sup>2</sup> (3) Fedors,<sup>3</sup> (4) Jalowka–Daubert,<sup>4–6</sup> (5) Constantinou,<sup>7</sup> (6) Somayajulu,<sup>8</sup> and (7) Klincewicz.<sup>9</sup>

All methods (except Klincewicz<sup>9</sup>) employ group contribution techniques which determine correction factors for specific groups of atoms which constitute the molecule of interest. Values of these contribution factors ( $\Delta t$ ) are tabulated for every method and their sum  $\Delta T = \sum n_i \Delta t_i$  represents the final correction applied to the calculation of the critical temperature. These specific methods differ among themselves by various group definitions and values. Most of them require the knowledge of:

- group contribution models based on molecular structure,
- molecular weight, and
- normal boiling point.

The method of Constantinou<sup>7</sup> and Klincewicz<sup>9</sup> do not require the knowing of  $T_b$  values. This fact is useful for compounds with undefined  $T_b$ , i.e., for complex structure substances.

The methods investigated represent two distinctive classes:

- The first order group techniques which determine the molecule by means of simple group contribution, ne-

TABLE 1. Recommended experimental values of normal boiling points  $T_b$  and critical temperatures  $T_c$  for hydrocarbons, used in this work for testing the selected prediction methods

Formula	Name of compound	CAS RN	$T_b$ (K)	$T_c$ (K) <sup>a</sup>
Unbranched alkanes				
CH <sub>4</sub>	methane	74-82-8	111.63 <sup>11</sup>	190.55 <sup>10</sup>
C <sub>2</sub> H <sub>6</sub>	ethane	74-84-0	184.55 <sup>11</sup>	305.42 <sup>10</sup>
C <sub>3</sub> H <sub>8</sub>	propane	74-98-6	231.05 <sup>11</sup>	369.82 <sup>11</sup>
C <sub>4</sub> H <sub>10</sub>	butane	106-97-8	272.70 <sup>11</sup>	425.16 <sup>11</sup>
C <sub>5</sub> H <sub>12</sub>	pentane	109-66-0	309.21 <sup>11</sup>	469.70 <sup>11</sup>
C <sub>6</sub> H <sub>14</sub>	hexane	110-54-3	341.88 <sup>11</sup>	507.60 <sup>11</sup>
C <sub>7</sub> H <sub>16</sub>	heptane	142-82-5	371.57 <sup>10</sup>	540.30 <sup>10</sup>
C <sub>8</sub> H <sub>18</sub>	octane	111-65-9	398.82 <sup>10</sup>	568.83 <sup>11</sup>
C <sub>9</sub> H <sub>20</sub>	nonane	111-84-2	423.96 <sup>10</sup>	594.70 <sup>11</sup>
C <sub>10</sub> H <sub>22</sub>	decane	124-18-5	447.30 <sup>10</sup>	617.70 <sup>11</sup>
C <sub>11</sub> H <sub>24</sub>	undecane	1120-21-4	469.08 <sup>11</sup>	638.80 <sup>10</sup>
C <sub>12</sub> H <sub>26</sub>	dodecane	112-40-3	489.47 <sup>11</sup>	658.25 <sup>10</sup>
C <sub>13</sub> H <sub>28</sub>	tridecane	629-50-5	508.60 <sup>10</sup>	675.80 <sup>10</sup>
C <sub>14</sub> H <sub>30</sub>	tetradecane	629-59-4	526.70 <sup>11</sup>	694.15 <sup>11</sup>
C <sub>15</sub> H <sub>32</sub>	pentadecane	629-62-9	543.83 <sup>11</sup>	707.00 <sup>11</sup>
C <sub>16</sub> H <sub>34</sub>	hexadecane	544-76-3	560.01 <sup>11</sup>	722.00 <sup>11</sup>
C <sub>17</sub> H <sub>36</sub>	heptadecane	629-78-7	574.25 <sup>10</sup>	736.00 <sup>11</sup>
C <sub>18</sub> H <sub>38</sub>	octadecane	593-45-3	590.22 <sup>11</sup>	745.80 <sup>11</sup>
C <sub>19</sub> H <sub>40</sub>	nonadecane	629-92-5	603.00 <sup>11</sup>	755.00 <sup>11</sup>
C <sub>20</sub> H <sub>42</sub>	eicosane	112-95-8	617.00 <sup>11</sup>	768.00 <sup>11</sup>
C <sub>21</sub> H <sub>44</sub>	heneicosane	629-94-7	636.05 <sup>10</sup>	777.60 <sup>11</sup>
C <sub>22</sub> H <sub>46</sub>	docosane	629-97-0	641.80 <sup>11</sup>	785.60 <sup>11</sup>
C <sub>24</sub> H <sub>50</sub>	tetracosane	646-31-1	661.70 <sup>11</sup>	802.50 <sup>11</sup>
C <sub>25</sub> H <sub>52</sub>	pentacosane	629-99-2	676.70 <sup>11</sup>	816.90 <sup>11</sup>
C <sub>27</sub> H <sub>56</sub>	heptacosane	593-49-7	701.20 <sup>11</sup>	843.10 <sup>11</sup>
C <sub>28</sub> H <sub>58</sub>	octacosane	630-02-4	708.80 <sup>11</sup>	848.70 <sup>11</sup>
Branched alkanes				
C <sub>4</sub> H <sub>10</sub>	2-methylpropane	75-28-5	261.42 <sup>10</sup>	407.80 <sup>11</sup>
C <sub>5</sub> H <sub>12</sub>	2-methylbutane	78-78-4	301.00 <sup>10</sup>	460.40 <sup>11</sup>
C <sub>5</sub> H <sub>12</sub>	2,2-dimethylpropane	463-82-1	282.65 <sup>10</sup>	433.75 <sup>10</sup>
C <sub>6</sub> H <sub>14</sub>	2-methylpentane	107-83-5	333.41 <sup>10</sup>	497.70 <sup>11</sup>
C <sub>6</sub> H <sub>14</sub>	3-methylpentane	96-14-0	336.41 <sup>10</sup>	504.60 <sup>11</sup>
C <sub>6</sub> H <sub>14</sub>	2,2-dimethylbutane	75-83-2	322.88 <sup>10</sup>	489.00 <sup>11</sup>
C <sub>6</sub> H <sub>14</sub>	2,3-dimethylbutane	79-29-8	331.15 <sup>10</sup>	499.98 <sup>11</sup>
C <sub>7</sub> H <sub>16</sub>	2-methylhexane	591-76-4	363.15 <sup>10</sup>	530.40 <sup>11</sup>
C <sub>7</sub> H <sub>16</sub>	3-methylhexane	589-34-4	364.99 <sup>10</sup>	535.26 <sup>11</sup>
C <sub>7</sub> H <sub>16</sub>	3-ethylpentane	617-78-7	366.64 <sup>11</sup>	540.60 <sup>11</sup>
C <sub>7</sub> H <sub>16</sub>	2,2-dimethylpentane	590-35-2	352.35 <sup>10</sup>	520.50 <sup>11</sup>
C <sub>7</sub> H <sub>16</sub>	2,3-dimethylpentane	565-59-3	362.93 <sup>10</sup>	537.30 <sup>11</sup>
C <sub>7</sub> H <sub>16</sub>	2,4-dimethylpentane	108-08-7	353.66 <sup>10</sup>	519.80 <sup>11</sup>
C <sub>7</sub> H <sub>16</sub>	3,3-dimethylpentane	562-49-2	359.21 <sup>10</sup>	536.50 <sup>11</sup>
C <sub>7</sub> H <sub>16</sub>	2,2,3-trimethylbutane	464-06-2	354.00 <sup>11</sup>	531.00 <sup>11</sup>
C <sub>8</sub> H <sub>18</sub>	2-methylheptane	592-27-8	390.80 <sup>10</sup>	559.70 <sup>11</sup>
C <sub>8</sub> H <sub>18</sub>	3-methylheptane	589-81-1	392.09 <sup>11</sup>	563.60 <sup>11</sup>
C <sub>8</sub> H <sub>18</sub>	4-methylheptane	589-53-7	390.87 <sup>11</sup>	561.70 <sup>11</sup>
C <sub>8</sub> H <sub>18</sub>	3-ethylhexane	619-99-8	391.70 <sup>11</sup>	565.50 <sup>11</sup>
C <sub>8</sub> H <sub>18</sub>	2,2-dimethylhexane	590-73-8	380.00 <sup>11</sup>	549.80 <sup>11</sup>
C <sub>8</sub> H <sub>18</sub>	3,3-dimethylhexane	563-16-6	385.81 <sup>11</sup>	562.02 <sup>11</sup>
C <sub>8</sub> H <sub>18</sub>	3,4-dimethylhexane	583-48-2	390.88 <sup>10</sup>	568.85 <sup>11</sup>
C <sub>8</sub> H <sub>18</sub>	2,3-dimethylhexane	584-94-1	388.76 <sup>10</sup>	563.50 <sup>11</sup>
C <sub>8</sub> H <sub>18</sub>	2,4-dimethylhexane	589-43-5	382.58 <sup>10</sup>	553.52 <sup>11</sup>
C <sub>8</sub> H <sub>18</sub>	2,5-dimethylhexane	592-13-2	382.27 <sup>10</sup>	550.00 <sup>11</sup>
C <sub>8</sub> H <sub>18</sub>	2-methyl-3ethylpentane	609-26-7	388.80 <sup>10</sup>	567.09 <sup>11</sup>
C <sub>8</sub> H <sub>18</sub>	3-methyl-3ethylpentane	1067-08-9	391.43 <sup>10</sup>	576.58 <sup>11</sup>
C <sub>8</sub> H <sub>18</sub>	2,2,3-trimethylpentane	564-02-3	383.00 <sup>10</sup>	563.50 <sup>11</sup>
C <sub>8</sub> H <sub>18</sub>	2,2,4-trimethylpentane	540-84-1	372.38 <sup>10</sup>	543.80 <sup>11</sup>
C <sub>8</sub> H <sub>18</sub>	2,3,3-trimethylpentane	560-21-4	387.92 <sup>10</sup>	573.50 <sup>11</sup>
C <sub>8</sub> H <sub>18</sub>	2,3,4-trimethylpentane	565-75-3	386.62 <sup>10</sup>	566.41 <sup>11</sup>
C <sub>8</sub> H <sub>18</sub>	2,2,3,3-tetramethylbutane	594-82-1	379.65 <sup>10</sup>	567.80 <sup>11</sup>
C <sub>9</sub> H <sub>20</sub>	2-methyloctane	3221-61-2	416.43 <sup>11</sup>	582.87 <sup>10</sup>

TABLE 1. Recommended experimental values of normal boiling points  $T_b$  and critical temperatures  $T_c$  for hydrocarbons, used in this work for testing the selected prediction methods—Continued

Formula	Name of compound	CAS RN	$T_b$ (K)	$T_c$ (K) <sup>a</sup>
Branched alkanes				
C <sub>9</sub> H <sub>20</sub>	2,2-dimethylheptane	1071-26-7	405.99 <sup>10</sup>	576.70 <sup>11</sup>
C <sub>9</sub> H <sub>20</sub>	2,2,5-trimethylhexane	3522-94-9	397.24 <sup>10</sup>	569.80 <sup>11</sup>
C <sub>9</sub> H <sub>20</sub>	2,2,3,3-tetramethylpentane	7154-79-2	413.42 <sup>10</sup>	607.50 <sup>11</sup>
C <sub>9</sub> H <sub>20</sub>	2,2,3,4-tetramethylpentane	1186-53-4	406.16 <sup>10</sup>	592.70 <sup>11</sup>
C <sub>9</sub> H <sub>20</sub>	2,2,4,4-tetramethylpentane	1070-87-7	395.43 <sup>10</sup>	574.70 <sup>11</sup>
C <sub>9</sub> H <sub>20</sub>	2,3,3,4-tetramethylpentane	16747-38-9	414.70 <sup>10</sup>	607.70 <sup>11</sup>
C <sub>10</sub> H <sub>22</sub>	3,3,5-trimethylheptane	7154-80-5	428.85 <sup>11</sup>	609.70 <sup>11</sup>
C <sub>10</sub> H <sub>22</sub>	2,2,5,5-tetramethylhexane	1071-81-4	410.61 <sup>10</sup>	581.40 <sup>11</sup>
C <sub>10</sub> H <sub>22</sub>	2,2,3,3-tetramethylhexane	13475-81-5	433.46 <sup>10</sup>	623.00 <sup>11</sup>
Alkenes, Alkynes				
C <sub>2</sub> H <sub>2</sub>	ethyne	74-86-2	189.55 <sup>11</sup>	308.30 <sup>11</sup>
C <sub>2</sub> H <sub>4</sub>	ethylene	74-85-1	169.25 <sup>10</sup>	282.34 <sup>10</sup>
C <sub>3</sub> H <sub>4</sub>	1,2-propadiene	463-49-0	238.65 <sup>11</sup>	394.00 <sup>11</sup>
C <sub>3</sub> H <sub>4</sub>	1-propyne	74-99-7	249.92 <sup>11</sup>	402.39 <sup>11</sup>
C <sub>3</sub> H <sub>6</sub>	1-propene	115-07-1	225.45 <sup>11</sup>	364.90 <sup>11</sup>
C <sub>4</sub> H <sub>4</sub>	1-buten-3-yne	689-97-4	278.10 <sup>11</sup>	455.00 <sup>11</sup>
C <sub>4</sub> H <sub>6</sub>	1,3-butadiene	106-99-0	268.75 <sup>11</sup>	425.00 <sup>11</sup>
C <sub>4</sub> H <sub>8</sub>	<i>trans</i> -2-butene	624-64-6	274.01 <sup>10</sup>	428.60 <sup>11</sup>
C <sub>4</sub> H <sub>8</sub>	<i>cis</i> -2-butene	590-18-1	276.82 <sup>11</sup>	435.50 <sup>11</sup>
C <sub>4</sub> H <sub>8</sub>	1-butene	106-98-9	266.87 <sup>10</sup>	419.50 <sup>11</sup>
C <sub>4</sub> H <sub>8</sub>	2-methylpropene	115-11-7	266.22 <sup>10</sup>	417.90 <sup>11</sup>
C <sub>5</sub> H <sub>8</sub>	<i>trans</i> -1,3-pentadiene	2004-70-8	315.10 <sup>11</sup>	496.00 <sup>11</sup>
C <sub>5</sub> H <sub>8</sub>	1,4-pentadiene	591-93-5	299.16 <sup>10</sup>	462.00 <sup>11</sup>
C <sub>5</sub> H <sub>8</sub>	1-pentyne	627-19-0	313.33 <sup>11</sup>	493.50 <sup>11</sup>
C <sub>5</sub> H <sub>8</sub>	2-methyl-1,3-butadiene	78-79-5	307.20 <sup>11</sup>	479.20 <sup>11</sup>
C <sub>5</sub> H <sub>10</sub>	<i>cis</i> -2-pentene	627-20-3	309.78 <sup>10</sup>	475.00 <sup>11</sup>
C <sub>5</sub> H <sub>10</sub>	3-methyl-1-butene	563-45-1	293.35 <sup>10</sup>	452.10 <sup>11</sup>
C <sub>5</sub> H <sub>10</sub>	2-methyl-1-butene	563-46-2	304.30 <sup>10</sup>	465.00 <sup>11</sup>
C <sub>5</sub> H <sub>10</sub>	2-methyl,2-butene	513-35-9	311.72 <sup>11</sup>	481.00 <sup>11</sup>
C <sub>5</sub> H <sub>10</sub>	1-pentene	109-67-1	303.15 <sup>10</sup>	464.74 <sup>10</sup>
C <sub>6</sub> H <sub>12</sub>	1-hexene	592-41-6	336.64 <sup>11</sup>	504.00 <sup>11</sup>
C <sub>6</sub> H <sub>12</sub>	2-methyl-1-pentene	763-29-1	335.23 <sup>10</sup>	505.00 <sup>11*</sup>
C <sub>6</sub> H <sub>12</sub>	2-methyl-2-pentene	625-27-4	340.50 <sup>11</sup>	518.00 <sup>11*</sup>
C <sub>6</sub> H <sub>12</sub>	4-methyl-1-pentene	691-37-2	327.03 <sup>11</sup>	494.80 <sup>11*</sup>
C <sub>6</sub> H <sub>12</sub>	2,3-dimethyl-2-butene	563-79-1	346.39 <sup>10</sup>	524.00 <sup>11*</sup>
C <sub>7</sub> H <sub>12</sub>	1-heptyne	628-71-7	373.01 <sup>11</sup>	559.70 <sup>11*</sup>
C <sub>7</sub> H <sub>14</sub>	1-heptene	592-76-7	366.80 <sup>10</sup>	537.30 <sup>11</sup>
C <sub>8</sub> H <sub>14</sub>	1-octyne	629-05-0	399.28 <sup>11</sup>	586.90 <sup>11*</sup>
C <sub>8</sub> H <sub>16</sub>	1-octene	111-66-0	394.41 <sup>10</sup>	566.55 <sup>10</sup>
C <sub>9</sub> H <sub>16</sub>	1-nonyne	3452-09-3	423.16 <sup>11</sup>	598.00 <sup>10*</sup>
C <sub>9</sub> H <sub>18</sub>	1-nonene	124-11-8	420.03 <sup>11</sup>	594.00 <sup>11*</sup>
C <sub>10</sub> H <sub>20</sub>	1-decene	872-05-9	443.75 <sup>10</sup>	617.00 <sup>11</sup>
C <sub>11</sub> H <sub>22</sub>	1-undecene	821-95-4	465.86 <sup>11</sup>	637.00 <sup>11*</sup>
C <sub>12</sub> H <sub>24</sub>	1-dodecene	112-41-4	486.55 <sup>10</sup>	658.00 <sup>11</sup>
C <sub>16</sub> H <sub>32</sub>	1-hexadecene	629-73-2	558.00 <sup>11</sup>	717.00 <sup>11*</sup>
C <sub>18</sub> H <sub>36</sub>	1-octadecene	112-88-9	588.08 <sup>11</sup>	739.00 <sup>11*</sup>

<sup>a</sup>An asterisk represents secondary data for I.

TABLE 2. Recommended experimental values of normal boiling points  $T_b$  of hydrocarbons for which critical temperature values were calculated in this work; all data are extracted from experimental base of NIST-TRC <sup>a</sup>

Formula	Name of compound	CAS RN	$T_b$ (K)
Branched alkanes			
C <sub>9</sub> H <sub>20</sub>	2,3-dimethylheptane	3074-71-3	413.15
C <sub>9</sub> H <sub>20</sub>	2,4-dimethylheptane	2213-23-2	405.65
C <sub>9</sub> H <sub>20</sub>	2,5-dimethylheptane	2216-30-0	407.65
C <sub>9</sub> H <sub>20</sub>	2,6-dimethylheptane	1072-05-5	408.35
C <sub>9</sub> H <sub>20</sub>	3,3-dimethylheptane	4032-86-4	410.16
C <sub>9</sub> H <sub>20</sub>	3,4-dimethylheptane	922-28-1	413.85
C <sub>9</sub> H <sub>20</sub>	3,5-dimethylheptane	926-82-8	408.65
C <sub>9</sub> H <sub>20</sub>	3,3-diethylpentane	1067-20-5	419.32
C <sub>9</sub> H <sub>20</sub>	4,4-dimethylheptane	1068-19-5	407.50
C <sub>9</sub> H <sub>20</sub>	3-ethyl-2,3-dimethylpentane	16747-33-4	414.75
C <sub>9</sub> H <sub>20</sub>	2,2,3-trimethylhexane	16747-25-4	407.40
C <sub>9</sub> H <sub>20</sub>	2,2,4-trimethylhexane	16747-26-5	399.69
C <sub>9</sub> H <sub>20</sub>	2,3,3-trimethylhexane	16747-28-7	409.45
C <sub>9</sub> H <sub>20</sub>	2,3,4-trimethylhexane	921-47-1	412.21
C <sub>9</sub> H <sub>20</sub>	2,3,5-trimethylhexane	1069-53-0	404.52
C <sub>9</sub> H <sub>20</sub>	2,4,4-trimethylhexane	16747-30-1	403.60
C <sub>9</sub> H <sub>20</sub>	3,3,4-trimethylhexane	16747-31-2	413.57
C <sub>9</sub> H <sub>20</sub>	3-ethyl-2-methylhexane	16789-46-1	411.15
C <sub>9</sub> H <sub>20</sub>	3-ethyl-3-methylhexane	3074-76-8	413.75
C <sub>9</sub> H <sub>20</sub>	3-ethyl-4-methylhexane	3074-77-9	413.55
C <sub>9</sub> H <sub>20</sub>	4-ethyl-2-methylhexane	3074-75-7	406.95
C <sub>9</sub> H <sub>20</sub>	3-ethylheptane	15869-80-4	416.25
C <sub>9</sub> H <sub>20</sub>	4-ethylheptane	2216-32-2	414.35
C <sub>9</sub> H <sub>20</sub>	3-methyloctane	2216-33-3	417.35
C <sub>9</sub> H <sub>20</sub>	4-methyloctane	2216-34-4	415.58
C <sub>9</sub> H <sub>20</sub>	3-ethyl-2,2-dimethylpentane	16747-32-3	406.96
C <sub>9</sub> H <sub>20</sub>	2,4-dimethyl-3-ethylpentane	1068-87-7	409.81
C <sub>10</sub> H <sub>22</sub>	2,3-dimethyloctane	7146-60-3	437.80
C <sub>10</sub> H <sub>22</sub>	2,5-dimethyloctane	15869-89-3	430.15
C <sub>10</sub> H <sub>22</sub>	2,7-dimethyloctane	1072-16-8	433.15
C <sub>10</sub> H <sub>22</sub>	3,3-dimethyloctane	4110-44-5	434.35
C <sub>10</sub> H <sub>22</sub>	3,5-dimethyloctane	15869-93-9	432.65
C <sub>10</sub> H <sub>22</sub>	2,2,4-trimethylheptane	14720-74-2	422.55
C <sub>10</sub> H <sub>22</sub>	2,2,6-trimethylheptane	1190-83-6	421.15
C <sub>10</sub> H <sub>22</sub>	2,4,6-trimethylheptane	2613-61-8	419.00
C <sub>10</sub> H <sub>22</sub>	2,5,5-trimethylheptane	1189-99-7	425.95
C <sub>10</sub> H <sub>22</sub>	2,4-dimethyloctane	4032-94-4	429.05
C <sub>10</sub> H <sub>22</sub>	2,6-dimethyloctane	2051-30-1	431.65
C <sub>10</sub> H <sub>22</sub>	2-methylnonane	871-83-0	440.15
C <sub>10</sub> H <sub>22</sub>	3-ethyl-3-methylheptane	17302-01-1	437.05
C <sub>10</sub> H <sub>22</sub>	3-methylnonane	5911-04-6	440.65
C <sub>10</sub> H <sub>22</sub>	5-methylnonane	15869-85-9	438.25
C <sub>10</sub> H <sub>22</sub>	2,2,3,5-tetramethylhexane	52897-09-3	422.15
C <sub>10</sub> H <sub>22</sub>	2,3,3,4-tetramethylhexane	52897-10-6	437.74
C <sub>10</sub> H <sub>22</sub>	2,3,3,5-tetramethylhexane	52897-11-7	426.15
C <sub>10</sub> H <sub>22</sub>	2,3,4,4-tetramethylhexane	52897-12-8	434.75
C <sub>10</sub> H <sub>22</sub>	2,3,4,5-tetramethylhexane	52897-15-1	429.15
C <sub>10</sub> H <sub>22</sub>	3,3,4,4-tetramethylhexane	5171-84-6	443.15
C <sub>10</sub> H <sub>22</sub>	4-ethyl-2,2-dimethylhexane	52896-99-8	420.15
C <sub>10</sub> H <sub>22</sub>	4-methylnonane	17301-94-4	441.15
C <sub>10</sub> H <sub>22</sub>	4,5-dimethyloctane	15869-96-2	436.15
C <sub>10</sub> H <sub>22</sub>	2,2,3,3,4-pentamethylpentane	16747-44-7	439.20
C <sub>10</sub> H <sub>22</sub>	3-ethyl-2,2,4-trimethylpentane	52897-18-4	428.45
C <sub>10</sub> H <sub>22</sub>	3-ethyl-2,3,4-trimethylpentane	52897-19-5	442.59
C <sub>10</sub> H <sub>22</sub>	2,2,3,4,4-pentamethylpentane	16747-45-8	432.44
C <sub>10</sub> H <sub>22</sub>	2,4-dimethyl-3-isopropylpentane	13475-79-1	430.19
C <sub>11</sub> H <sub>24</sub>	2-methyldecane	6975-98-0	462.27
C <sub>11</sub> H <sub>24</sub>	4-methyldecane	2847-72-5	461.25
C <sub>11</sub> H <sub>24</sub>	2,2,4,6-tetramethylheptane	61868-46-0	435.05
C <sub>12</sub> H <sub>26</sub>	2,2,3,5,6-pentamethylheptane	62198-87-2	461.95
C <sub>12</sub> H <sub>26</sub>	2,2,4,6,6-pentamethylheptane	13475-82-6	450.95
C <sub>15</sub> H <sub>32</sub>	6-propyldodecane	92867-09-9	524.75
C <sub>16</sub> H <sub>34</sub>	3-methylpentadecane	2882-96-4	539.45



TABLE 2. Recommended experimental values of normal boiling points  $T_b$  of hydrocarbons for which critical temperature values were calculated in this work; all data are extracted from experimental base of NIST-TRC <sup>a</sup>—Continued

Formula	Name of compound	CAS RN	$T_b$ (K)
Alkenes, Alkynes			
C <sub>16</sub> H <sub>34</sub>	7,8-dimethyltetradecane	2801-86-7	543.15
C <sub>20</sub> H <sub>42</sub>	3-ethyloctadecane	500014-84-6	614.15
C <sub>26</sub> H <sub>54</sub>	hexacosane	630-01-3	534.15
C <sub>4</sub> H <sub>6</sub>	1-butyne	107-00-6	281.25
C <sub>4</sub> H <sub>6</sub>	2-butyne	503-17-3	300.12
C <sub>5</sub> H <sub>8</sub>	3-methyl-1,2-butadiene	598-25-4	313.95
C <sub>5</sub> H <sub>8</sub>	2,3-pentadiene	591-96-8	321.35
C <sub>5</sub> H <sub>10</sub>	<i>trans</i> -2-pentene	646-04-8	309.50
C <sub>5</sub> H <sub>6</sub>	3-penten-1-yne	2206-23-7	317.05
C <sub>6</sub> H <sub>6</sub>	1,5-hexadiyne	628-16-0	359.15
C <sub>6</sub> H <sub>10</sub>	1,5-hexadiene	592-42-7	332.55
C <sub>6</sub> H <sub>10</sub>	3-methyl-1-pentyne	922-59-8	330.85
C <sub>6</sub> H <sub>10</sub>	4-methyl-1-pentyne	7154-75-8	334.45
C <sub>6</sub> H <sub>10</sub>	2-hexyne	764-35-2	357.67
C <sub>6</sub> H <sub>10</sub>	4-methyl-2-pentyne	21020-27-9	346.28
C <sub>6</sub> H <sub>10</sub>	2,3-dimethyl-1,3-butadiene	513-81-5	343.15
C <sub>6</sub> H <sub>12</sub>	3-methyl-1-pentene	760-20-3	327.37
C <sub>6</sub> H <sub>10</sub>	3-hexyne	928-49-4	354.45
C <sub>6</sub> H <sub>12</sub>	<i>trans</i> -3-methyl-2-pentene	616-12-6	343.50
C <sub>6</sub> H <sub>12</sub>	<i>trans</i> -4-methyl-2-pentene	674-76-0	331.70
C <sub>6</sub> H <sub>12</sub>	2,3-dimethyl-1-butene	563-78-0	328.76
C <sub>6</sub> H <sub>12</sub>	2-ethyl-1-butene	760-21-4	340.65
C <sub>6</sub> H <sub>12</sub>	2-methyl-1-pentene	763-29-1	335.26
C <sub>6</sub> H <sub>12</sub>	<i>trans</i> -3-methyl-2-pentene	616-12-6	343.50
C <sub>6</sub> H <sub>12</sub>	<i>trans</i> -4-methyl-2-pentene	674-76-0	331.70
C <sub>6</sub> H <sub>12</sub>	3,3-dimethyl-1-butene	558-37-2	314.43
C <sub>6</sub> H <sub>12</sub>	<i>cis</i> -2-hexene	7688-21-3	342.01
C <sub>6</sub> H <sub>12</sub>	<i>cis</i> -3-hexene	7642-09-3	339.65
C <sub>6</sub> H <sub>12</sub>	<i>cis</i> -3-methyl-2-pentene	922-62-3	340.86
C <sub>6</sub> H <sub>12</sub>	<i>cis</i> -4-methyl-2-pentene	691-38-3	329.45
C <sub>6</sub> H <sub>12</sub>	<i>trans</i> -2-hexene	4050-45-7	340.24
C <sub>6</sub> H <sub>12</sub>	3-methyl-2-pentene	922-61-2	340.65
C <sub>7</sub> H <sub>14</sub>	2,3,3-trimethyl-1-butene	594-56-9	350.85
C <sub>6</sub> H <sub>12</sub>	<i>trans</i> -3-hexene	13269-52-8	340.30
C <sub>7</sub> H <sub>12</sub>	5-methyl-1-hexyne	2203-80-7	364.65
C <sub>7</sub> H <sub>12</sub>	3-ethyl-1-pentyne	21020-26-8	360.15
C <sub>7</sub> H <sub>12</sub>	4,4-dimethyl-1-pentyne	13361-63-2	349.23
C <sub>7</sub> H <sub>12</sub>	2,4-dimethyl-1,3-pentadiene	1000-86-8	366.90
C <sub>7</sub> H <sub>12</sub>	4-methyl-2-hexyne	20198-49-6	372.69
C <sub>7</sub> H <sub>12</sub>	4-methyl-2-hexyne	53566-37-3	375.61
C <sub>7</sub> H <sub>12</sub>	2-methyl-1,5-hexadiene	4049-81-4	362.00
C <sub>7</sub> H <sub>12</sub>	4,4-dimethyl-2-pentyne	999-78-0	356.15
C <sub>7</sub> H <sub>12</sub>	3-heptyne	2586-89-2	380.31
C <sub>7</sub> H <sub>12</sub>	2-methyl-3-hexyne	36566-80-0	368.35
C <sub>7</sub> H <sub>12</sub>	1,2-heptadiene	2384-90-9	376.90
C <sub>7</sub> H <sub>12</sub>	1,5-heptadiene	1541-23-7	366.85
C <sub>7</sub> H <sub>14</sub>	2,3-dimethyl-1-pentene	3404-72-6	357.50
C <sub>7</sub> H <sub>14</sub>	2,3-dimethyl-2-pentene	10574-37-5	370.55
C <sub>7</sub> H <sub>14</sub>	2,4-dimethyl-1-pentene	2213-32-3	354.73
C <sub>7</sub> H <sub>14</sub>	2-methyl-1-hexene	6094-02-6	364.65
C <sub>7</sub> H <sub>14</sub>	<i>trans</i> -2-methyl-3-hexene	692-24-0	359.02
C <sub>7</sub> H <sub>14</sub>	<i>trans</i> -3-methyl-3-hexene	3899-36-3	366.67
C <sub>7</sub> H <sub>14</sub>	2-ethyl-1-pentene	3404-71-5	365.55
C <sub>7</sub> H <sub>14</sub>	2-ethyl-3-methyl-1-butene	7357-93-9	362.05
C <sub>7</sub> H <sub>14</sub>	3,3-dimethyl-1-pentene	3404-73-7	350.69
C <sub>7</sub> H <sub>14</sub>	3,4-dimethyl-1-pentene	7385-78-6	353.93
C <sub>7</sub> H <sub>14</sub>	3-ethyl-1-pentene	4038-04-4	357.28
C <sub>7</sub> H <sub>14</sub>	2-methyl-1-hexene	3404-61-3	357.09
C <sub>7</sub> H <sub>14</sub>	4,4-dimethyl-1-pentene	762-62-9	345.35
C <sub>7</sub> H <sub>14</sub>	4-methyl-1-hexene	3769-23-1	359.97
C <sub>7</sub> H <sub>14</sub>	5-methyl-1-hexene	3524-73-0	358.65
C <sub>7</sub> H <sub>14</sub>	<i>cis</i> -2-heptene	6443-92-1	371.56

TABLE 2. Recommended experimental values of normal boiling points  $T_b$  of hydrocarbons for which critical temperature values were calculated in this work; all data are extracted from experimental base of NIST-TRC<sup>a</sup>—Continued

Formula	Name of compound	CAS RN	$T_b$ (K)
C <sub>7</sub> H <sub>14</sub>	<i>cis</i> -2-methyl-2-hexene	15840-60-5	359.80
C <sub>7</sub> H <sub>14</sub>	<i>cis</i> -3-heptene	7642-10-6	368.90
C <sub>7</sub> H <sub>14</sub>	<i>cis</i> -3-methyl-2-hexene	10574-36-4	370.41
C <sub>7</sub> H <sub>14</sub>	<i>cis</i> -3-methyl-3-hexene	4914-89-0	368.47
C <sub>7</sub> H <sub>14</sub>	<i>trans</i> -4,4-dimethyl-2-pentene	690-08-4	349.89
C <sub>7</sub> H <sub>14</sub>	<i>cis</i> -4,4-dimethyl-2-pentene	762-63-0	353.15
C <sub>7</sub> H <sub>14</sub>	<i>trans</i> -2-heptene	14686-13-6	371.06
C <sub>7</sub> H <sub>14</sub>	<i>cis</i> -4-methyl-2-hexene	3683-19-0	359.50
C <sub>7</sub> H <sub>14</sub>	<i>trans</i> -3,4-dimethyl-2-pentene	4914-92-5	364.75
C <sub>7</sub> H <sub>14</sub>	<i>trans</i> -3-heptene	14686-14-7	368.81
C <sub>7</sub> H <sub>14</sub>	<i>trans</i> -3-methyl-2-hexene	20710-38-7	368.38
C <sub>7</sub> H <sub>14</sub>	<i>trans</i> -4-methyl-2-hexene	3683-22-5	360.79
C <sub>7</sub> H <sub>14</sub>	<i>trans</i> -5-methyl-2-hexene	7385-82-2	361.27
C <sub>7</sub> H <sub>14</sub>	2-methyl-2-hexene	2738-19-4	368.25
C <sub>8</sub> H <sub>16</sub>	2-methyl-1-heptene	15870-10-7	392.37
C <sub>8</sub> H <sub>14</sub>	2-octyne	2809-67-8	411.24
C <sub>8</sub> H <sub>14</sub>	2,5-dimethyl-2,4-hexadiene	764-13-6	407.65
C <sub>8</sub> H <sub>14</sub>	2,5-dimethyl-1,5-hexadiene	627-58-7	387.45
C <sub>8</sub> H <sub>14</sub>	<i>trans</i> -2-ethyl-3-methyl-1,3-pentadiene	32388-99-1	381.15
C <sub>8</sub> H <sub>16</sub>	3-methyl-1-heptene	4810-09-7	384.15
C <sub>8</sub> H <sub>16</sub>	4-methyl-1-heptene	13151-05-8	385.65
C <sub>8</sub> H <sub>16</sub>	6-methyl-1-heptene	5026-76-6	386.35
C <sub>8</sub> H <sub>16</sub>	2,3-dimethyl-1-hexene	16746-86-4	383.69
C <sub>8</sub> H <sub>16</sub>	2,3-dimethyl-2-hexene	7145-20-2	395.00
C <sub>8</sub> H <sub>16</sub>	2-methyl-2-heptene	627-97-4	395.77
C <sub>8</sub> H <sub>16</sub>	5-methyl-1-heptene	13151-04-7	386.15
C <sub>8</sub> H <sub>16</sub>	2-ethyl-1-hexene	1632-16-2	391.85
C <sub>8</sub> H <sub>16</sub>	2,3,3-trimethyl-1-pentene	560-23-6	381.46
C <sub>8</sub> H <sub>16</sub>	2,2-dimethyl- <i>cis</i> -hexene	690-92-6	378.95
C <sub>8</sub> H <sub>16</sub>	2-ethyl-4-methyl-1-pentene	3404-80-6	380.65
C <sub>8</sub> H <sub>16</sub>	<i>trans</i> -2-methyl-3-heptene	692-96-6	387.13
C <sub>8</sub> H <sub>16</sub>	3-methyl-3-heptene	7300-03-0	394.35
C <sub>8</sub> H <sub>16</sub>	<i>trans</i> -2,2-dimethyl-3-hexene	690-93-7	374.05
C <sub>8</sub> H <sub>16</sub>	2,4-dimethyl- <i>trans</i> -3-hexene	61847-78-7	380.75
C <sub>8</sub> H <sub>16</sub>	2,4-dimethyl- <i>cis</i> -3-hexene	37549-89-6	382.15
C <sub>8</sub> H <sub>16</sub>	3-methyl-2-heptene	3404-75-9	394.65
C <sub>8</sub> H <sub>16</sub>	<i>trans</i> -3,4-dimethyl-3-hexene	19550-88-0	387.95
C <sub>8</sub> H <sub>16</sub>	5,5-dimethyl-1-hexene	7116-86-1	376.25
C <sub>8</sub> H <sub>16</sub>	5-methyl-1-heptene	500007-01-2	386.65
C <sub>9</sub> H <sub>16</sub>	2,3,3,4-tetramethyl-1,4-pentadiene	500015-77-0	400.85
C <sub>9</sub> H <sub>18</sub>	2-methyl-1-octene	4588-18-5	418.00
C <sub>9</sub> H <sub>18</sub>	2,3,3,4-tetramethyl-1-pentene	20442-63-1	406.35
C <sub>9</sub> H <sub>18</sub>	2,4-dimethyl-3-ethyl-2-pentene	500001-23-0	403.12
C <sub>9</sub> H <sub>18</sub>	3-ethyl-4,4-dimethyl-2-pentene	53907-59-8	407.18
C <sub>10</sub> H <sub>18</sub>	3-decyne	2384-85-2	448.65
C <sub>10</sub> H <sub>20</sub>	2-methyl-2-nonene	2129-95-5	444.15
C <sub>10</sub> H <sub>20</sub>	3-methyl-3-nonene	53966-53-3	434.15
C <sub>10</sub> H <sub>20</sub>	3,4,5,5-tetramethyl-2-hexene	39083-38-0	425.15
C <sub>10</sub> H <sub>20</sub>	2,2,4,4-tetramethyl-3-methylene	5857-68-1	423.45
C <sub>10</sub> H <sub>20</sub>	<i>trans</i> -2,2,5,5-tetramethyl-3-hexene	692-48-8	398.25

<sup>a</sup>See NIST-TRC.<sup>10</sup>



glecting the next-nearest neighbors effects. The methods of Ambrose,<sup>1</sup> Joback,<sup>2</sup> Fedors,<sup>3</sup> and Somayajulu<sup>8</sup> belong to this class.

- (2) The second order group techniques, which additionally take into consideration the influence of first and second-level neighbors of a considered group. The methods of Jalowka–Daubert<sup>4–6</sup> and Constantinou<sup>7</sup> methods belong to this class.

In the short description of investigated methods provided below the following symbols are used:  $T_c$ =critical temperature (K);  $T_b$ =normal boiling point (K);  $\Delta t$ =contributions of single atoms or groups of atoms (tabulated)<sup>1–8</sup> composing a molecule;  $M$ =molecular weight; and  $n_i$ =number of occurrences of group  $i$ .

### 2.1. Ambrose's Method

Critical temperature is calculated as<sup>1</sup>

$$T_c = T_b \left[ 1 + \left( 1.242 + \sum n_i \Delta t_i \right)^{-1} \right],$$

where 1.242 is a dimensionless regression constant.

The value  $\Delta T = \sum n_i \Delta t_i$  is evaluated by summing contributions  $\Delta t_i$  for atoms or groups of atoms. The normal boiling point,  $T_b$ , is required. The branching is taken into consideration here by the correction factor name delta Platt number, used only for branched alkanes.<sup>1</sup> The delta Platt number is evaluated on the basis of branch structure and included in  $\Delta T$  calculation as  $n_i$  factor multiplied by specific Platt correction factor  $\Delta t_i$ , tabulated together with  $\Delta t$  values.

### 2.2. Joback's Method

This is Joback's modification<sup>2</sup> of Lydersen's<sup>19</sup> method. Proposed formula for critical temperature is defined as

$$T_c = T_b [0.584 + 0.965 \times \Delta T - (\Delta T)^2]^{-1},$$

where 0.584 and 0.965 are dimensionless regression constants.  $\Delta T$  is evaluated by summing contributions  $\Delta t_i$  for atoms or groups of atoms.

### 2.3. Fedors' Method

The author claims it to be less accurate than the methods of Ambrose<sup>1</sup> and Joback<sup>2</sup> but it has the advantage of not requiring the normal boiling temperature in the calculation of  $T_c$ . The Fedors' equation may be written for  $T_c$  as<sup>3</sup>

$$T_c = 535 \log \sum n_i \Delta t_i,$$

where 535 is a dimensionless regression constant. Summation of group increments  $\sum \Delta t$  is performed as in the methods previously described.

### 2.4. Jalowka–Daubert's Method

This method employs normal boiling point and contribution increments  $\Delta t$ .<sup>4,5</sup> Every type of compound is represented by number of various groups describing in detail its molecular structure.

Jalowka and Daubert introduced second order groups, taking into account next-nearest neighbors effects. The central carbon atom of the group listed first is followed by a bond which indicates the ligands it is bonded to. All monovalent ligands are then listed followed by any other polyvalent ligands. A *cis* correction group, treated as  $\Delta t$  element, is introduced to take care of isomerisation in alkene compounds. The functional form of proposed model for  $T_c$  is expressed as

$$T_c = 1.806 T_b \times \sum n_i \Delta t_i,$$

where 1.806 is a dimensionless regression constant.

### 2.5. Constantinou's Method

This is the newest contribution method.<sup>7</sup> Estimation of critical parameters is performed at two levels: the basic level uses contributions from first-order groups while the next higher level uses a small set of second-order groups having the first-order groups as building blocks. This method provides both first-order group contributions and more accurate second-order prediction for determination of  $\Delta T$ . Conjugation operators have been introduced in this method. It means that the molecular structure of a compound is viewed as a hybrid of a number of conjugate forms (alternative formal arrangements of valence electrons) and the property of a compound is a linear combination of this conjugate form contribution. Proposed correlation can be expressed as

$$f(T_c) = \sum_i N_i C_i + W \sum_j M_j D_j,$$

where  $f(T_c) = \exp(T_c/t_{co})$ , where  $t_{co}$  is an universal constant, equal to 181.128 K, and  $T_c$  is estimated critical temperature of a compound,  $C_i$ =the contribution of the first-order group of type  $i$  which occurs  $N_i$  times in a compound;  $D_j$ =the contribution of the second-order group of type  $j$  that occurs  $M_j$  times in a compound; and  $W$ =constant assigned to unity in the second level estimation, where both first- and second-order group contributions are involved and 0 is the basic level, where only the contributions of first-order groups are employed.

### 2.6. Somayajulu's Method

This method<sup>8</sup> comprises procedures provided by the method developed by Kreglewski<sup>20</sup> for the calculation of critical constants of homologous series of compounds. The proposed formula for  $T_c$  calculation is expressed as

$$T_c = \frac{T_b}{G_i} + T_b,$$

$$G_i = a_i + b_i \Delta T, \quad \Delta T = \sum n_i \Delta t_i,$$

where  $a_i = 1.242$  and  $b_i = 0.138$  constants, recorded in Somayajulu,<sup>8</sup>  $\Delta T$  is obtained by summation of the relevant group contribution indices  $\Delta t_i$ , listed in Somayajulu,<sup>8</sup> and  $\Delta t_i$  is temperature index of chosen group  $X$ , where  $X = \Delta t(x)/\Delta t(-\text{CH}_3)$ . The gauche position factor (taking into consideration the degree of branching) for branched alkanes was introduced in this method as an element of  $\Delta t$  tabulated values.

### 2.7. Klincewicz's Method

This is a simple relation<sup>9</sup> which involves only normal point  $T_b$  and molecular weight  $M$ , which was selected for testing, owing to its probable usefulness for hydrocarbons of undefined chemical structure

$$T_c = 50.2 - 0.16M + 1.41T_b,$$

where 50.2, 0.16, and 1.41 are dimensionless regression constants

### 2.8. Experimental Base of the Predictive Methods

Ambrose<sup>1</sup> and Joback<sup>2</sup> claim that a comparison made between experimental and estimated values for 400 organic and inorganic compounds yielded an average absolute percent error = 0.7 and 0.8, respectively. That wide spectrum of compounds includes among others: 117 aliphatic, 44 cyclic, and 31 aromatic hydrocarbons.

Daubert<sup>4</sup> tested his method on the base of experimental  $T_c$  data for 186 hydrocarbons: including undefined number of alkanes, alkenes, alkynes, cycloalkanes, cycloalkenes, and aromatics. The final form of equation for  $T_c$  results from the analysis of 12 regressing models.

Constantinou<sup>7</sup> claims his method was developed on the basis of 285 experimental  $T_c$  values for organic and inorganic compounds. The main source of mentioned data was the DIPPR data bank, while Somayajulu<sup>8</sup> tested the accuracy of his method on 574 compounds including 129 hydrocarbons of different type.

## 3. Recommended Experimental Data on Normal Boiling Points and Critical Temperatures

### 3.1. Criterion and Procedure for Selection of Experimental Data

The database of the recommended normal boiling point  $T_b$  and critical temperature  $T_c$  values for aliphatic hydrocarbons is based on all available experimental data extracted from the data banks in the frame of: Thermodynamics Research Center (NIST-TRC)<sup>10</sup> and Thermodynamics Data Center (TDC)<sup>11</sup> with the newest publications on  $T_c$ —as in numerous studies.<sup>6,8,12–15,17,18</sup>

Availability of data references allowed us to judge whether specific data are the primary data, that is values were derived

from the original observation, and let us know which method and equipment was used in the considered experiment. The short description, attached to every experimental result, permitted us to know if the measurement was a principal objective of the experiment, as well as to know the final purity of the substance sample used. Moreover the measurement error has been allocated for each experimental value collected in data banks.<sup>10,11</sup> That information allowed us to form verified “subsets,” concerning one property for one substance and containing reliable experimental data extracted from mentioned data banks. Any outliers were eliminated from every subset. The secondary data on  $T_b$  were rejected. The accepted data were then examined for their precision and accuracy as stated by the author. For individual cases of single or double data the selection of the reliable  $T_b$  values was additionally guided by auxiliary information seen as citation in the newest literature or comparison with data from auxiliary sources.<sup>13,15</sup> In these instances, the recommended values are those from a single investigation and occur only in Table 2.

The same selection has been performed for  $T_c$  with particular importance placed on the sample purity. In the case of  $T_c$  selection some secondary data have been accepted for substances poorly represented in measurement. It concerns 11 *n*-alkenes, containing more than six C atoms, for which no information about the experiment was available. Their  $T_c$  values listed in Sec. 3.2 have been accepted on the basis of recommendation in both data banks.<sup>10,11</sup> Discrepancies among remaining data values forming every subset did not exceed 0.5 and 2 K for  $T_b$  and  $T_c$ , respectively.<sup>16</sup>

#### 3.1.1. Statistical Analysis of Selected Data

The reliable values of  $T_b$  and  $T_c$  were selected as the closest to the weighted mean of all measured data included in individual subsets. This was feasible because each experimental value had its measurement error used subsequently for determination of weights of experimental values.

### 3.2. Recommended Experimental Data on Critical Temperatures and Normal Boiling Points for Aliphatic Hydrocarbons

Data banks included about 20–25 data values for  $T_b$  and about eight data values for  $T_c$  for every substance allocated in Table 1. Critical analysis of mentioned above data reduced those numbers to: 8, 4, and 2, respectively. The accepted secondary data for  $T_c$ , are denoted by asterisks in Table 1. The 104 hydrocarbons mentioned in point 1(a) were used for evaluating the critical temperature prediction methods. Their names together with recommended experimental data on  $T_b$  and  $T_c$  are listed in Table 1.

Table 2 represents the substances with less investigated properties, so the number of experimental  $T_b$  data amounts to about 3 reliable values per substance. Table 2 also provides the names and recommended  $T_b$  values for another chosen

TABLE 3. Deviations  $E$  (%) of predicted critical temperatures from recommended experimental values for tested methods

Name of compound	$E$ (%)						
	Author's name of method						
	Ambrose	Joback	Fedors	Daubert	Constantinou	Klincewicz	Somayajulu
Unbranched alkanes							
methane							+1.10
ethane	+0.24	−1.00	−2.97	−0.65	+0.00	+0.07	+0.22
propane	+0.18	−0.42	+0.10	−0.65	−5.76	−0.26	+0.19
butane	−0.11	−0.30	+0.24	−0.56	+0.48	+0.06	−0.12
pentane	−0.09	−0.06	+0.33	−0.19	+1.30	+1.05	−0.09
hexane	−0.12	+0.01	+0.27	+0.05	−1.77	−2.13	−0.11
heptane	−0.09	+0.05	+0.21	+0.23	+1.77	+3.28	−0.08
octane	−0.03	+0.05	+0.18	+0.34	+1.60	+3.28	+0.00
nonane	−0.04	−0.06	+0.09	+0.25	+1.27	+5.48	−0.02
decane	+0.02	−0.13	+0.06	+0.11	+0.97	+6.58	+0.03
undecane	−0.00	−0.27	+0.02	−0.19	+0.63	+7.44	+0.11
dodecane	+0.02	−0.33	−0.04	−0.52	+0.29	+8.33	+0.01
tridecane	−0.03	−0.54	−0.03	−1.05	+0.02	+9.09	+0.15
tetradecane	−0.27	−0.87	−0.28	−1.80	−0.49	+9.59	−0.19
pentadecane	+0.11	−0.56	+0.05	−1.99	−0.42	+10.72	+0.15
hexadecane	+0.04	−0.56	+0.03	−2.71	−0.76	+11.30	+0.00
heptadecane	+0.50	−0.21	−1.63	−3.93	−0.49	+12.43	+0.50
octadecane	+0.45	−0.23	+0.39	−3.78	−0.79	+12.93	+0.45
nonadecane	+0.39	−0.20	+0.53	−4.70	−0.87	+13.41	+0.49
eicosane	+0.61	+0.14	+0.68	−5.33	−0.92	+14.15	+0.63
heneicosane	+1.54	+1.26	+0.65	−4.81	−1.13	+15.86	+1.55
docosane	+0.79	+0.73	+0.96	−6.99	−1.14	+15.25	+0.79
tetracosane	−0.56	+1.13	+1.28	−9.44	−1.04	+15.76	+0.56
pentacosane	+0.49	+1.46	+0.62	−10.16	−1.84	+16.03	+0.49
octacosane	−0.12	+2.41	−0.14	−13.74	−3.00	+16.23	−0.12
heptacosane	−0.09	+1.86	−0.42	−12.43	−3.17	+15.99	−0.09
Branched alkanes							
2-methylpropane	−0.22	+0.55	+0.33	+0.17	−4.69	+0.37	+0.11
2-methylbutane	−0.13	+0.14	−0.66	−0.03	+2.16	+0.58	−0.18
2,2-dimethylpropane	+1.13	+1.68	+3.78	+0.52	+0.44	+0.79	+0.15
2-methylpentane	+0.08	+0.35	−0.05	+0.27	−0.17	+1.81	+0.16
3-methylpentane	−0.05	−0.15	−1.44	−0.85	−0.24	+1.24	+0.11
2,2-dimethylbutane	−0.09	+0.61	+0.48	−0.04	−0.72	+0.57	+0.01
2,3-dimethylbutane	−0.38	+0.02	−1.26	+0.21	−5.15	+0.66	−0.12
2-methylhexane	+0.11	+0.40	+0.17	+0.44	+0.57	+2.99	+0.18
3-methylhexane	+0.02	−0.02	−0.75	+0.13	+0.59	+2.53	+0.31
3-ethylpentane	−0.17	−0.56	−1.73	−0.31	−0.40	+1.94	+0.02
2,2-dimethylpentane	+0.12	+0.86	+1.05	+0.30	+0.71	+2.01	+0.18
2,3-dimethylpentane	+0.07	−0.19	−1.71	+0.22	−0.15	+1.58	−0.01
2,4-dimethylpentane	+0.08	+0.54	+0.16	+0.37	+0.86	+2.49	+0.25
3,3-dimethylpentane	−0.23	−0.23	−1.93	−0.37	−1.33	+0.79	−0.03
2,2,3-trimethylbutane	−0.02	+0.13	−3.02	+0.03	+0.93	+0.40	+0.01
2-methylheptane	+0.16	+0.40	+0.24	+0.55	+0.77	+4.17	+0.26
3-methylheptane	+0.07	+0.00	−0.49	+0.23	+0.80	+3.74	+0.19
4-methylheptane	+0.11	+0.04	−0.14	+0.19	+1.16	+3.80	+0.23
3-ethylhexane	−0.04	−0.41	−0.80	−0.21	+1.63	+3.31	+0.14
2,2-dimethylhexane	+0.15	+0.85	+1.17	+0.39	+1.15	+3.25	+0.21
3,3-dimethylhexane	−0.13	+0.18	−1.01	+0.09	−0.28	+2.47	+0.14
3,4-dimethylhexane	+0.07	−0.47	−0.24	+0.05	−1.92	+2.63	+0.01
2,3-dimethylhexane	−0.16	−0.07	+0.70	+0.32	−0.99	+2.94	+0.03
2,4-dimethylhexane	+0.01	+0.11	−0.35	+0.11	+0.79	+3.22	+0.21
2,5-dimethylhexane	+0.24	+0.66	+0.28	+0.64	+1.42	+3.79	+0.38
2-methyl-3-ethylpentane	−0.14	−0.69	+0.06	−0.29	−1.61	+2.32	+0.21
3-methyl-3-ethylpentane	−0.30	−0.93	−3.51	−0.68	−2.79	+1.25	+0.01
2,2,3-trimethylpentane	−0.56	−0.03	−2.96	+0.04	−2.44	+1.49	+0.03
2,2,4-trimethylpentane	−0.17	−0.70	+0.53	+0.10	−0.66	+2.41	−0.01
2,3,3-trimethylpentane	−0.02	−0.53	−4.66	−0.16	−4.15	+0.92	−0.04
2,3,4-trimethylpentane	+0.03	−0.37	+1.31	+0.23	−3.42	+1.88	−0.35
2,2,3,3-tetramethylbutane	+0.05	−0.06	−4.56	−0.22	−4.70	−0.11	−0.42
2-methyloctane	−0.02	+0.15	+0.04	+0.34	+0.53	+5.09	+0.39

TABLE 3. Deviations  $E$  (%) of predicted critical temperatures from recommended experimental values for tested methods—Continued

Name of compound	$E$ (%)						
	Author's name of method						
	Ambrose	Joback	Fedors	Daubert	Constantinou <sup>a</sup>	Klincewicz	Somayajulu
2,2-dimethylheptane	−0.05	+0.54	+0.92	+0.03	+0.97	+4.18	+0.02
2,2,5-trimethylhexane	−0.12	+0.65	+0.97	+0.08	+0.13	+3.64	−0.01
2,2,3,3-tetramethylpentane	+0.33	−0.41	−6.15	−0.01	−6.12	+0.81	+0.01
2,2,3,4-tetramethylpentane	−0.11	−0.44	−2.00	−0.11	−4.15	+1.63	−0.45
2,2,4,4-tetramethylpentane	−0.51	+0.73	−0.76	+0.10	−0.73	+2.19	−0.41
2,3,3,4-tetramethylpentane	+0.13	−0.85	−6.88	−0.03	−6.52	+1.10	−0.09
3,3,5-trimethylheptane	−0.23	−0.43	−1.67	−0.48	−1.23	+3.67	+0.04
2,2,5,5-tetramethylhexane	+0.24	+1.35	+2.40	+0.19	+2.43	+4.26	+0.34
2,2,3,3-tetramethylhexane	+0.55	−0.14	−4.42	+0.12	−4.40	+2.47	+0.26
Alkenes, Alkynes							
ethyne	+8.06	+4.28	−3.88	−0.51	—	+1.62	+0.7
ethylene	+0.83	−0.91	−4.70	+0.24	—	+0.76	+0.20
1,2-propadiene	−0.20	−0.02	−15.01	+0.09	—	−7.86	+0.06
1-propyne	+4.76	+3.20	+3.84	+0.82	−0.00*	−1.60	+0.09
1-propene	+0.22	−0.29	−0.41	−0.44	−0.74	−7.00	+0.02
1-buten-3-yne	+0.70	+0.02	+1.03	−2.95	+0.70	−4.67	−3.60
1,3-butadiene	+0.56	+0.63	−2.22	+0.13	−1.74	−7.06	+0.78
<i>trans</i> -2-butene	+0.58	+0.96	+0.46	−0.00	+0.26*	−0.24	+0.70
<i>cis</i> -2-butene	−0.01	+0.36	−1.28	−0.10	−1.34	−0.80	+0.24
1-butene	+0.08	+0.02	+0.31	−0.55	+0.02*	−0.48	−0.70
2-methylpropene	+0.23	+1.00	+0.17	−0.77	−0.72	−0.30	+0.04
<i>trans</i> -1,3-pentadiene	−1.79	−1.00	−5.11	−0.02	−3.46	−2.50	−1.33
1,4-pentadiene	+0.07	+0.46	+0.11	−0.36	+2.09	−0.20	−0.24
1-pentyne	+0.14	−0.08	+1.96	+0.75	+2.22	−2.50	−3.31
2-methyl-1,3-butadiene	−0.89	+0.26	−3.88	−1.16	−1.23	−1.40	−1.22
<i>cis</i> -2-pentene	−0.17	+0.43	−0.06	−0.05	+1.17	+0.11	+0.02
3-methyl-1-butene	−0.19	+1.94	+0.62	+0.06	+0.08*	+0.56	+3.78
2-methyl-1-butene	+0.21	+1.18	+0.01	−0.33	+1.01	+0.65	+0.55
2-methyl-2-butene	−0.76	+0.61	−1.65	−1.30	−0.59	−0.52	−0.66
1-pentene	−0.09	+0.11	+0.48	−0.42	+0.43	+0.37	−0.26
1-hexene	−0.14	+0.18	+0.25	−0.15	+1.06	+1.46	−0.28
2-methyl-1-pentene	−0.74	+0.28	+2.35	−1.10	+0.16*	+0.87	−0.44
2-methyl-2-pentene	−1.72	−0.31	−1.44	−2.16	+0.08*	−0.22	−1.19
4-methyl-1-pentene	−1.19	−0.01	−0.28	−0.52	−1.26	+0.60	−0.54
2,3-dimethyl-2-butene	−1.16	+0.98	−2.86	−1.50	+0.11*	+0.22	−1.08
1-heptyne	−0.16	+0.03	+1.02	−2.04	+1.73	+0.18	−2.90
1-heptene	−0.10	+0.25	+0.17	+0.08	+1.21	+2.67	−0.22
1-octyne	−0.27	−0.03	+0.74	−1.89	+1.34	+1.46	−2.73
1-octene	−0.07	+0.22	+0.07	+0.19	+1.08	+3.83	−0.18
1-nonyne	+1.74	+1.94	+2.75	+0.16	+3.19	+4.84	−0.52
1-nonene	+0.10	+0.30	+0.12	+0.34	+0.84	+5.10	−0.00
1-decene	+0.19	+0.26	+0.13	+0.30	+1.26	+6.23	+0.10
1-undecene	+0.11	+0.05	−0.02	−0.00	+0.79	+7.12	+0.03
1-dodecene	+0.06	−0.15	−0.13	−0.39	−0.01*	+7.96	−0.01
1-hexadecene	+0.71	+0.10	+0.46	−1.85	−0.14*	+11.7	+0.65
1-octadecene	+1.22	+0.60	+1.05	−2.81	−0.02*	+13.5	+1.17

<sup>a</sup>An asterisk indicates alkenes, represented in the second order group contributions in Constantinou<sup>7</sup> method.

TABLE 4. Unbranched alkanes—absolute percent error for tested methods for different chain lengths

Chain length	Ambrose	Joback	Fedors	Daubert	Constantinou	Klincewicz	Somayajulu
C <sub>1</sub> –C <sub>10</sub>	0.10	0.23	0.19	0.34	1.15	2.53	0.22
C <sub>11</sub> –C <sub>20</sub>	0.23	0.42	0.33	2.30	0.53	10.57	0.23
C <sub>21</sub> –C <sub>28</sub>	0.60	1.28	0.68	8.98	1.75	15.59	0.60

TABLE 5. Branched alkanes—the dependence of the absolute percent error of the tested methods upon the number of C atoms in a molecule

Number of C atoms	Ambrose	Joback	Fedors	Daubert	Constantinou	Klincewicz	Somayajulu
4	0.22	0.55	0.33	0.17	4.69	0.37	0.11
5	0.63	0.91	2.22	0.28	1.30	0.69	0.17
6	0.15	0.28	0.81	0.34	1.57	1.07	0.12
7	0.10	0.37	1.32	0.27	0.70	1.84	0.13
8	0.15	0.38	1.34	0.29	1.80	2.56	0.18
9	0.18	0.52	2.50	0.57	2.72	2.64	0.20
10	0.34	0.60	2.80	0.20	2.66	3.40	0.18

175 hydrocarbons, mentioned in point 1(b) for which experimental values of  $T_c$  were not available in literature and were calculated in this work.

#### 4. Testing Calculations

Calculations, performed for evaluation of the accuracy of seven predictive methods, were conducted for 104 hydrocarbons including branched and unbranched alkanes, alkenes, and alkynes.

The chosen prediction methods employ 10–100 specific contribution groups together with attributed temperature correction factors  $\Delta t_i$ . For each hydrocarbon and for each method all contribution groups forming the molecule were specified and their sum ( $\Delta n_i \Delta t_i$ ) yield values of final correction factor  $\Delta T$  used for prediction of critical temperature  $T_{cp}$ .

Deviations of calculated critical temperatures  $T_{cp}$  values from recommended experimental values of  $T_c$  are shown in Table 3. They were calculated according to

$$E = [(T_c - T_{cp})/T_c] \cdot 100,$$

where  $T_c$  are the experimental recommended value of  $T_c$ , and  $T_{cp}$  value of critical temperature obtained from prediction method. Error  $E$  values are listed with accuracy of 0.01%.

### 5. Results of Tests and Conclusions

#### 5.1. Alkanes

##### 5.1.1. Unbranched Alkanes

Deviations of the calculated  $T_c$  values from the experimental values for the hydrocarbons ( $C_1$ – $C_{28}$ ) (Tables 3 and 4) increase with the chain length. In the range  $C_1$ – $C_{10}$  the methods of Somayajulu,<sup>8</sup> Ambrose,<sup>1</sup> Fedors,<sup>3</sup> and Joback<sup>2</sup>

give the deviations below 0.3%. A sudden increase in the error is observed for  $C_{21}$ – $C_{28}$  hydrocarbons (Table 4). In this range only two methods—Somayajulu<sup>8</sup> and Ambrose<sup>1</sup>—yield error level less than 0.7%. These two methods, yielding an average error less than 0.4% in the whole testing range, are recommended for chains longer than  $C_{20}$ . For unbranched alkanes up to  $C_{20}$  there is a rare need to employ any prediction method, since experimental data on  $T_c$  for this group are mostly available.

##### 5.1.2. Branched Alkanes

The influence of the chain length as well as of the number and position of substituted groups on the method's errors were examined. All results of the investigation are presented in the tables below. Deviations for branched alkanes with  $CH_3$ – and  $C_2H_5$ – groups are presented in Tables 3, 5, 6, and 7. Most of the methods yield the local maximum error in the  $C_5$  region while the local minimum occurs in the  $C_9$ – $C_{10}$  region. This minimum may be related to the decreasing influence of groups on the longer chain of bigger molecule.

It has been stated that there is no influence of the position of the side chain on the value of deviation. The dependence of error on the number of substituted  $CH_3$ – groups was investigated. The results are presented in Table 6. The considerable increase in error along with the increase of the number of substituted  $CH_3$ – groups was observed only for the methods of Constantinou<sup>7</sup> and Fedors.<sup>3</sup> All the other methods appeared not to be sensitive to that fact. The fluctuation of error value due to the length of single side chain (from  $C_1$  to  $C_4$ ) does not allow any special distinction of any one of the methods tested. That is why the deviation values due to the  $C_s/C_m$  ratio were investigated, where  $C_m$  is the number of C atoms in a main chain and  $C_s$  is the number of all C atoms in side chains. The results are presented in Table 7. The accuracy of the Joback<sup>2</sup> method is strongly sensitive to the

TABLE 6. Branched alkanes—the dependence of the absolute percent error of tested methods upon the number of substituted  $CH_3$ – groups to main chain

Number of substituted $CH_3$ groups	Ambrose	Joback	Fedors	Daubert	Constantinou	Klincewicz	Somayajulu
1	0.10	0.26	0.57	0.31	0.82	2.63	0.19
2	0.20	1.43	1.14	0.26	1.07	2.18	0.13
3	0.16	0.38	2.13	0.13	1.83	2.02	0.16
4	0.27	0.53	3.84	0.09	4.12	1.75	0.25



TABLE 7. Dependence of absolute percent errors of tested methods upon the  $C_s/C_m$  ratio

$C_s/C_m$ ratio	Ambrose	Joback	Daubert	Somayajulu
0.14	0.11	0.15	0.22	0.23
0.16	0.07	0.21	0.28	0.25
0.20	0.07	0.25	0.56	0.14
0.33	0.14	0.41	0.25	0.15
0.41	0.14	0.46	0.33	0.10
0.50	0.20	0.43	0.13	0.08
0.66	0.35	0.70	0.25	0.16
0.80	0.27	0.58	0.06	0.23

$C_s/C_m$  ratio. The method of Daubert<sup>4–6</sup> yields significant fluctuation with  $C_s/C_m$ , while for the Somayajulu<sup>8</sup> and Ambrose<sup>1</sup> methods, the accuracies do not depend on the mentioned ratio and yield constant and low error level:  $-0.08$ – $0.25$  for Somayajulu<sup>8</sup> and  $-0.05$ – $0.35$  for Ambrose.<sup>1</sup>

Thus these two methods are mainly recommended for calculation of critical temperatures for branched alkanes. Both of them take the branching into consideration employing Platt number<sup>1</sup> and gauche position.<sup>8</sup> In this work the method of Somayajulu<sup>8</sup> was employed for calculation of missing values of critical temperatures of branched alkanes.

The methods of Ambrose,<sup>1</sup> Joback,<sup>2</sup> Daubert,<sup>4–6</sup> and Somayajulu,<sup>8</sup> examined for branched alkanes, were considered in Table 7. Values of  $C_s/C_m$  in this table reflect the branching extent of the tested groups of hydrocarbons.

## 5.2. Alkenes, Alkynes

The results of examining the various prediction methods (Table 3) proved that no particular method may be generally recommended for all alkenes and alkynes of the range  $C_2$ – $C_{18}$  due to significant fluctuation of errors for individual methods and types of compounds. For instance, the error increases three times in the case of substitution of the double bond by the triple one (i.e., subgroup 2—Table 8).

This test group of hydrocarbons was split into four “subgroups”:

- one double bond in a plain chain,
- one triple bond in a plain chain,
- one double bond in a branched chain, and
- two double bonds in a branched or plain chain.

The authors recommend the method of Constantinou<sup>7</sup> (yielding significant accuracy with deviations less than 0.3%) for branched alkenes, but only in cases of hydrocarbons represented in the second order group contribution of

the mentioned method (see data with \* in Table 3). In other cases the following methods are recommended for following subgroups of hydrocarbons: (a) Somayajulu<sup>8</sup> and Ambrose;<sup>1</sup> (b) Daubert<sup>4–6</sup> and Joback;<sup>2</sup> (c) Ambrose,<sup>1</sup> Joback,<sup>2</sup> and Constantinou<sup>7</sup> (in case of first and second order groups); and (d) Daubert<sup>4–6</sup> and Joback.<sup>2</sup>

Two methods provide corrections for *cis* (Daubert<sup>4–6</sup>) and *trans* (Somayajulu<sup>8</sup>) types of bond. It was observed that the accuracy of the method of Daubert<sup>4–6</sup> in the *cis* cases for subgroup (a) is significantly worse than those of Somayajulu<sup>8</sup> and Ambrose.<sup>1</sup>

## 6. Prediction of Critical Temperatures

The aliphatic hydrocarbons for which experimental critical temperature data were not accessible in literature but experimental data of normal boiling points were available, were chosen for the prediction of  $T_c$ .

Critical temperatures were predicted by means of chosen methods corresponding to conclusions given in Secs. 5.1 and 5.2. The method of Somayajulu<sup>8</sup> was chosen for branched alkanes as the most accurate and not sensitive to branching. The calculated values of  $T_c$  are listed in Table 9.

Unlike alkanes, no particular method could be applied for all alkenes, due to significant fluctuation of errors for individual cases (i.e., particular method and particular hydrocarbon). Every case—substance—was considered separately. The methods of Constantinou,<sup>7</sup> Joback,<sup>2</sup> Daubert,<sup>4–6</sup> and Somayajulu<sup>8</sup> were used in every individual case due to conclusions in Sec. 5.2. The calculated values of critical temperatures  $T_{cp}$  of alkenes are listed in Table 10.

The expected percent error, noted in captions of Tables 9 and 10, result from the analysis of the accuracy of applied predictive methods.

## 7. Results

The main result of this work is the set of critical temperatures for 175 aliphatic hydrocarbons for which experimental critical data were not available in literature (Table 9 and Table 10). In addition, other tabulated results are:

- recommended experimental data on critical temperatures of 104 aliphatic hydrocarbons, used for testing purposes (Table 1) and
- recommended experimental data on normal boiling points of 279 aliphatic hydrocarbons (Tables 1 and 2).

TABLE 8. Alkenes, alkynes—absolute percent errors for groups of hydrocarbons with different structures [cases (a), (b), (c), (d)]

Subgroup	Ambrose	Joback	Fedors	Daubert	Constantinou	Klincewicz	Somayajulu
a	0.29	0.32	0.63	0.49	0.69	4.32	0.29
b	2.24	1.36	2.16	1.30	1.53	2.41	1.97
c	0.78	0.78	1.16	0.96	0.50	0.86	1.03
d	0.59	0.40	5.27	0.35	2.11	3.80	0.61



TABLE 9. Branched alkanes—calculated values of critical temperatures ( $T_{cp}$ ) obtained by the Somayajulu<sup>8</sup> method. Expected absolute percent error for all  $T_{cp}$ —less than 0.25%. Values of critical temperature using Ambrose<sup>1</sup> method  $T_{cp}$  are given in last column for comparison purposes

CAS RN	Formula	Name	$T_{cp}$ (K) Somayajulu <sup>a</sup>	$T_{cp}$ (K) Ambrose <sup>b</sup>
3074-71-3	C <sub>9</sub> H <sub>20</sub>	2,3-dimethylheptane	588.16	588.81
2213-23-2	C <sub>9</sub> H <sub>20</sub>	2,4-dimethylheptane	577.48	576.45
2216-30-0	C <sub>9</sub> H <sub>20</sub>	2,5-dimethylheptane	580.33	579.29
1072-05-5	C <sub>9</sub> H <sub>20</sub>	2,6-dimethylheptane	579.35	578.64
4032-86-4	C <sub>9</sub> H <sub>20</sub>	3,3-dimethylheptane	588.07	587.11
922-28-1	C <sub>9</sub> H <sub>20</sub>	3,4-dimethylheptane	591.20	591.54
926-82-8	C <sub>9</sub> H <sub>20</sub>	3,5-dimethylheptane	583.77	582.40
1067-20-5	C <sub>9</sub> H <sub>20</sub>	3,3-dimethylpentane	605.60	603.88
1068-19-5	C <sub>9</sub> H <sub>20</sub>	4,4-dimethylheptane	584.26	583.30
16747-33-4	C <sub>9</sub> H <sub>20</sub>	3-ethyl-2,3-dimethylpentane	603.01	598.92
16747-25-4	C <sub>9</sub> H <sub>20</sub>	2,2,3-trimethylhexane	587.87	588.31
16747-26-5	C <sub>9</sub> H <sub>20</sub>	2,2,4-trimethylhexane	574.64	575.38
16747-28-7	C <sub>9</sub> H <sub>20</sub>	2,3,3-trimethylhexane	593.04	593.14
921-47-1	C <sub>9</sub> H <sub>20</sub>	2,3,4-trimethylhexane	592.56	594.36
1069-53-0	C <sub>9</sub> H <sub>20</sub>	2,3,5-trimethylhexane	579.43	579.71
16747-30-1	C <sub>9</sub> H <sub>20</sub>	2,4,4-trimethylhexane	582.49	581.01
16747-31-2	C <sub>9</sub> H <sub>20</sub>	3,3,4-trimethylhexane	598.91	597.11
16789-46-1	C <sub>9</sub> H <sub>20</sub>	3-ethyl-2-methylhexane	587.34	585.96
3074-76-8	C <sub>9</sub> H <sub>20</sub>	3-ethyl-3-methylhexane	595.36	594.03
3074-77-9	C <sub>9</sub> H <sub>20</sub>	3-ethyl-4-methylhexane	592.86	591.12
3074-75-7	C <sub>9</sub> H <sub>20</sub>	4-ethyl-2-methylhexane	581.34	579.97
15869-80-4	C <sub>9</sub> H <sub>20</sub>	3-ethylheptane	591.03	590.05
2216-32-2	C <sub>9</sub> H <sub>20</sub>	4-ethylheptane	588.33	587.36
2216-33-3	C <sub>9</sub> H <sub>20</sub>	3-methyloctane	590.61	589.95
2216-34-4	C <sub>9</sub> H <sub>20</sub>	4-methyloctane	588.11	587.45
16747-32-3	C <sub>9</sub> H <sub>20</sub>	3-ethyl-2,2-dimethylpentane	589.44	587.67
1068-87-7	C <sub>9</sub> H <sub>20</sub>	2,4-dimethyl-3-ethylpentane	589.11	590.90
7146-60-3	C <sub>10</sub> H <sub>22</sub>	2,3-dimethyloctane	613.01	613.62
15869-89-3	C <sub>10</sub> H <sub>22</sub>	2,5-dimethyloctane	602.29	601.32
1072-16-8	C <sub>10</sub> H <sub>22</sub>	2,7-dimethyloctane	604.63	603.95
4110-44-5	C <sub>10</sub> H <sub>22</sub>	3,3-dimethyloctane	612.11	611.20
15869-93-9	C <sub>10</sub> H <sub>22</sub>	3,5-dimethyloctane	605.80	604.81
14720-74-2	C <sub>10</sub> H <sub>22</sub>	2,2,4-trimethylheptane	596.97	596.01
1190-83-6	C <sub>10</sub> H <sub>22</sub>	2,2,6-trimethylheptane	593.06	592.42
2613-61-8	C <sub>10</sub> H <sub>22</sub>	2,4,6-trimethylheptane	589.97	588.64
1189-99-7	C <sub>10</sub> H <sub>22</sub>	2,5,5-trimethylheptane	603.77	602.47
4032-94-4	C <sub>10</sub> H <sub>22</sub>	2,4-dimethyloctane	600.75	599.78
2051-30-1	C <sub>10</sub> H <sub>22</sub>	2,6-dimethyloctane	604.40	603.42
871-83-0	C <sub>10</sub> H <sub>22</sub>	2-methylnonane	611.15	610.82
17302-02-2	C <sub>10</sub> H <sub>22</sub>	3-ethyl-3-methylheptane	617.93	616.68
5911-04-6	C <sub>10</sub> H <sub>22</sub>	3-methylnonane	614.09	613.47
15869-85-9	C <sub>10</sub> H <sub>22</sub>	5-methylnonane	610.33	609.71
52987-09-3	C <sub>10</sub> H <sub>22</sub>	2,2,3,5-tetramethylhexane	601.99	602.02
52897-10-6	C <sub>10</sub> H <sub>22</sub>	2,3,3,4-tetramethylhexane	630.93	631.86
52897-11-7	C <sub>10</sub> H <sub>22</sub>	2,3,3,5-tetramethylhexane	609.82	609.52
52897-12-8	C <sub>10</sub> H <sub>22</sub>	2,3,4,4-tetramethylhexane	624.35	625.60
52897-15-1	C <sub>10</sub> H <sub>22</sub>	2,3,4,5-tetramethylhexane	609.80	611.15
5171-84-6	C <sub>10</sub> H <sub>22</sub>	3,3,4,4-tetramethylhexane	643.63	644.77
52896-99-8	C <sub>10</sub> H <sub>22</sub>	4-ethyl-2,2-dimethylhexane	595.55	594.27
17301-94-4	C <sub>10</sub> H <sub>22</sub>	4-methylnonane	614.37	613.74
15869-96-2	C <sub>10</sub> H <sub>22</sub>	4,5-dimethyloctane	612.62	612.94
16747-44-7	C <sub>10</sub> H <sub>22</sub>	2,2,3,3,4-pentamethylpentane	639.78	640.85
52897-18-4	C <sub>10</sub> H <sub>22</sub>	3-ethyl-2,2,4-trimethylpentane	613.11	614.65
52897-19-5	C <sub>10</sub> H <sub>22</sub>	3-ethyl-2,3,4-trimethylpentane	637.92	638.86
16747-45-8	C <sub>10</sub> H <sub>22</sub>	2,2,3,4,4-pentamethylpentane	625.15	626.88
13475-79-1	C <sub>10</sub> H <sub>22</sub>	2,4-dimethyl-3-isopropylpentane	611.28	612.63
6975-98-0	C <sub>11</sub> H <sub>24</sub>	2-methyldecane	632.73	632.41
2847-72-5	C <sub>11</sub> H <sub>24</sub>	4-methyldecane	633.05	632.46
61868-46-0	C <sub>11</sub> H <sub>24</sub>	2,2,4,6-tetramethylheptane	608.20	606.94
61198-87-2	C <sub>12</sub> H <sub>26</sub>	2,2,3,5,6-pentamethylheptane	639.45	644.25
13475-82-6	C <sub>12</sub> H <sub>26</sub>	2,2,4,6,6-pentamethylheptane	626.12	624.93
92867-09-9	C <sub>15</sub> H <sub>32</sub>	6-propyldodecane	689.64	688.73
2882-96-4	C <sub>16</sub> H <sub>34</sub>	3-methylpentadecane	699.30	698.86
2801-86-7	C <sub>16</sub> H <sub>34</sub>	7,8-dimethyltetradecane	707.76	707.99
500014-84-6	C <sub>20</sub> H <sub>42</sub>	3-ethyloctadecane	771.64	771.10
630-01-3	C <sub>26</sub> H <sub>54</sub>	hexacosane	644.74	644.74

<sup>a</sup>Reference 8.

<sup>b</sup>Reference 1.

TABLE 10. Alkenes and alkynes—calculated values of critical temperatures ( $T_{cp}$ ) predicted using the selected methods specified below. Expected percent error for all  $T_{cp}$ —(from 0.29% to 1.3%),  $E$ —expected percent errors for individual cases. Numbers attributed to methods: (1) Constantinou,<sup>7</sup> (2) Joback,<sup>2</sup> (3) Somayajulu,<sup>8</sup> (4) Daubert<sup>4-6</sup>

CAS RN	Formula	Name	$T_{cp}$ (K)	$E$ (%)	Method
107-00-6	C <sub>4</sub> H <sub>6</sub>	1-butyne	442.35	1.30	4
503-17-3	C <sub>4</sub> H <sub>6</sub>	2-butyne	486.11	1.30	4
598-25-4	C <sub>5</sub> H <sub>8</sub>	3-methyl-1,2-butadiene	495.95	0.40	2
591-96-8	C <sub>5</sub> H <sub>8</sub>	2,3-pentadiene	505.73	0.40	2
646-04-8	C <sub>5</sub> H <sub>10</sub>	<i>trans</i> -2-pentene	476.87	0.29	3
2206-23-7	C <sub>5</sub> H <sub>6</sub>	3-penten-1-yne	489.82	1.30	4
628-16-0	C <sub>6</sub> H <sub>6</sub>	1,5-hexadiyne	547.30	1.30	4
592-42-7	C <sub>6</sub> H <sub>10</sub>	1,5-hexadiene	504.05	0.40	2
922-59-8	C <sub>6</sub> H <sub>10</sub>	3-methyl-1-pentyne	498.38	1.30	4
7154-75-8	C <sub>6</sub> H <sub>10</sub>	4-methyl-1-pentyne	504.80	1.30	4
764-35-2	C <sub>6</sub> H <sub>10</sub>	2-hexyne	550.18	1.40	4
21020-27-9	C <sub>6</sub> H <sub>10</sub>	4-methyl-2-pentyne	535.93	1.30	4
513-81-5	C <sub>6</sub> H <sub>10</sub>	2,3-dimethyl-1,3-butadiene	527.84	0.40	2
760-20-3	C <sub>6</sub> H <sub>12</sub>	3-methyl-1-pentene	496.57	0.50	1
928-49-4	C <sub>6</sub> H <sub>10</sub>	3-hexyne	544.37	1.30	4
616-12-6	C <sub>6</sub> H <sub>12</sub>	<i>trans</i> -3-methyl-2-pentene	518.44	0.50	1
674-76-0	C <sub>6</sub> H <sub>12</sub>	<i>trans</i> -4-methyl-2-pentene	507.25	0.50	1
563-78-0	C <sub>6</sub> H <sub>12</sub>	2,3-dimethyl-1-butene	497.32	0.50	1
760-21-4	C <sub>6</sub> H <sub>12</sub>	2-ethyl-1-butene	505.84	0.50	1
763-29-1	C <sub>6</sub> H <sub>12</sub>	2-methyl-1-pentene	511.55	0.50	1
616-12-6	C <sub>6</sub> H <sub>12</sub>	<i>trans</i> -3-methyl-2-pentene	518.44	0.50	1
674-76-0	C <sub>6</sub> H <sub>12</sub>	<i>trans</i> -4-methyl-2-pentene	507.25	0.50	1
558-37-2	C <sub>6</sub> H <sub>12</sub>	3,3-dimethyl-1-butene	489.67	0.50	1
7688-21-3	C <sub>6</sub> H <sub>12</sub>	<i>cis</i> -2-hexene	511.76	0.29	3
7642-09-3	C <sub>6</sub> H <sub>12</sub>	<i>cis</i> -3-hexene	508.23	0.29	3
922-62-3	C <sub>6</sub> H <sub>12</sub>	<i>cis</i> -3-methyl-2-pentene	516.90	0.78	2
691-38-3	C <sub>6</sub> H <sub>12</sub>	<i>cis</i> -4-methyl-2-pentene	507.25	0.50	1
4050-45-7	C <sub>6</sub> H <sub>12</sub>	<i>trans</i> -2-hexene	511.46	0.29	3
922-61-2	C <sub>6</sub> H <sub>12</sub>	3-methyl-2-pentene	518.61	0.50	1
594-56-9	C <sub>7</sub> H <sub>14</sub>	2,3,3-trimethyl-1-butene	520.67	0.50	1
13269-52-8	C <sub>6</sub> H <sub>12</sub>	<i>trans</i> -3-hexene	511.55	0.29	3
2203-80-7	C <sub>7</sub> H <sub>12</sub>	5-methyl-1-hexyne	539.50	1.30	4
21020-26-8	C <sub>7</sub> H <sub>12</sub>	3-ethyl-1-pentyne	531.37	1.30	4
13361-63-2	C <sub>7</sub> H <sub>12</sub>	4,4-dimethyl-1-pentyne	540.26	1.30	4
1000-86-8	C <sub>7</sub> H <sub>12</sub>	2,4-dimethyl-1,3-pentadiene	553.67	0.40	2
20198-49-6	C <sub>7</sub> H <sub>12</sub>	4-methyl-2-hexyne	563.70	1.30	4
53566-37-3	C <sub>7</sub> H <sub>12</sub>	5-methyl-2-hexyne	568.97	1.30	4
4049-81-4	C <sub>7</sub> H <sub>12</sub>	2-methyl-1,5-hexadiene	540.45	0.40	2
999-78-0	C <sub>7</sub> H <sub>12</sub>	4,4-dimethyl-2-pentyne	542.72	1.30	4
2586-89-2	C <sub>7</sub> H <sub>12</sub>	3-heptyne	571.14	1.30	4
36566-80-0	C <sub>7</sub> H <sub>12</sub>	2-methyl-3-hexyne	555.86	1.30	4
2384-90-9	C <sub>7</sub> H <sub>12</sub>	1,2-heptadiene	564.71	0.40	2
1541-23-7	C <sub>7</sub> H <sub>12</sub>	1,5-heptadiene	545.95	0.40	2
3404-72-6	C <sub>7</sub> H <sub>14</sub>	2,3-dimethyl-1-pentene	530.27	0.50	1
10574-37-5	C <sub>7</sub> H <sub>14</sub>	2,3-dimethyl-2-pentene	556.53	0.50	1
2213-32-3	C <sub>7</sub> H <sub>14</sub>	2,4-dimethyl-1-pentene	528.92	0.50	1
6094-02-6	C <sub>7</sub> H <sub>14</sub>	2-methyl-1-hexene	539.04	0.78	2
692-24-0	C <sub>7</sub> H <sub>14</sub>	<i>trans</i> -2-methyl-3-hexene	537.05	0.50	1
3899-36-3	C <sub>7</sub> H <sub>14</sub>	<i>trans</i> -3-methyl-3-hexene	542.13	0.50	1
3404-71-5	C <sub>7</sub> H <sub>14</sub>	2-ethyl-1-pentene	536.10	0.50	1
7357-93-9	C <sub>7</sub> H <sub>14</sub>	2-ethyl-3-methyl-1-butene	539.60	0.78	2
3404-73-7	C <sub>7</sub> H <sub>14</sub>	3,3-dimethyl-1-pentene	527.83	0.78	2
7385-78-6	C <sub>7</sub> H <sub>14</sub>	3,4-dimethyl-1-pentene	531.40	0.50	1
4038-04-4	C <sub>7</sub> H <sub>14</sub>	3-ethyl-1-pentene	533.35	0.50	1
3404-61-3	C <sub>7</sub> H <sub>14</sub>	3-methyl-1-hexene	533.35	0.50	1
762-62-9	C <sub>7</sub> H <sub>14</sub>	4,4-dimethyl-1-pentene	517.04	0.50	1
3769-23-1	C <sub>7</sub> H <sub>14</sub>	4-methyl-1-hexene	532.03	0.50	1
3524-73-0	C <sub>7</sub> H <sub>14</sub>	5-methyl-1-hexene	526.83	0.50	1
6443-92-1	C <sub>7</sub> H <sub>14</sub>	<i>cis</i> -2-heptene	544.15	0.29	3
15840-60-5	C <sub>7</sub> H <sub>14</sub>	<i>cis</i> -2-methyl-2-hexene	528.36	0.50	1
7642-10-6	C <sub>7</sub> H <sub>14</sub>	<i>cis</i> -3-heptene	544.01	0.50	1
10574-36-4	C <sub>7</sub> H <sub>14</sub>	<i>cis</i> -3-methyl-2-hexene	546.97	0.50	1

TABLE 10. Alkenes and alkynes—calculated values of critical temperatures ( $T_{cp}$ ) predicted using the selected methods specified below. Expected percent error for all  $T_{cp}$ —(from 0.29% to 1.3%),  $E$ —expected percent errors for individual cases. Numbers attributed to methods: (1) Constantinou,<sup>7</sup> (2) Joback,<sup>2</sup> (3) Somayajulu,<sup>8</sup> (4) Daubert<sup>4–6</sup>—Continued

CAS RN	Formula	Name	$T_{cp}$ (K)	$E$ (%)	Method
4914-89-0	C <sub>7</sub> H <sub>14</sub>	<i>cis</i> -3-methyl-3-hexene	542.13	0.50	1
690-08-4	C <sub>7</sub> H <sub>14</sub>	<i>trans</i> -4,4-dimethyl-2-pentene	528.16	0.50	1
762-63-0	C <sub>7</sub> H <sub>14</sub>	<i>cis</i> -4,4-dimethyl-2-pentene	529.42	0.50	1
14686-13-6	C <sub>7</sub> H <sub>14</sub>	<i>trans</i> -2-heptene	545.66	0.29	3
3683-19-0	C <sub>7</sub> H <sub>14</sub>	<i>cis</i> -4-methyl-2-hexene	538.58	0.50	1
4914-92-5	C <sub>7</sub> H <sub>14</sub>	<i>trans</i> -3,4-dimethyl-2-pentene	536.65	0.50	1
14486-14-7	C <sub>7</sub> H <sub>14</sub>	<i>trans</i> -3-heptene	542.35	0.29	3
20710-38-7	C <sub>7</sub> H <sub>14</sub>	<i>trans</i> -3-methyl-2-hexene	546.97	0.50	1
3683-22-5	C <sub>7</sub> H <sub>14</sub>	<i>trans</i> -4-methyl-2-hexene	538.58	0.50	1
7385-82-2	C <sub>7</sub> H <sub>14</sub>	<i>trans</i> -5-methyl-2-hexene	532.26	0.50	1
2738-19-4	C <sub>7</sub> H <sub>14</sub>	2-methyl-2-hexene	546.97	0.50	1
15870-10-7	C <sub>8</sub> H <sub>16</sub>	2-methyl-1-heptene	568.42	0.78	2
2809-6708	C <sub>8</sub> H <sub>14</sub>	2-octyne	607.98	1.36	2
764-13-6	C <sub>8</sub> H <sub>14</sub>	2,5-dimethyl-2,4-hexadiene	604.15	0.40	2
627-58-7	C <sub>8</sub> H <sub>14</sub>	2,5-dimethyl-1,5-hexadiene	570.17	0.40	2
32388-99-1	C <sub>8</sub> H <sub>14</sub>	<i>trans</i> -2-ethyl-3-methyl-1,3-pentadiene	562.87	0.40	2
4810-09-7	C <sub>8</sub> H <sub>16</sub>	3-methyl-1-heptene	557.26	0.78	2
13151-05-8	C <sub>8</sub> H <sub>16</sub>	4-methyl-1-heptene	559.43	0.78	2
5026-76-6	C <sub>8</sub> H <sub>16</sub>	6-methyl-1-heptene	560.45	0.78	2
16746-86-4	C <sub>8</sub> H <sub>16</sub>	2,3-dimethyl-1-hexene	561.30	0.50	1
7145-20-2	C <sub>8</sub> H <sub>16</sub>	2,3-dimethyl-2-hexene	577.78	0.78	2
627-97-4	C <sub>8</sub> H <sub>16</sub>	2-methyl-2-heptene	575.25	0.78	2
13151-04-7	C <sub>8</sub> H <sub>16</sub>	5-methyl-1-heptene	562.79	0.50	1
1632-16-2	C <sub>8</sub> H <sub>16</sub>	2-ethyl-1-hexene	566.23	0.50	1
560-23-6	C <sub>8</sub> H <sub>16</sub>	2,3,3-trimethyl-1-pentene	565.71	0.50	1
690-92-6	C <sub>8</sub> H <sub>16</sub>	2,2-dimethyl- <i>cis</i> -hexene	556.11	0.50	1
3404-80-6	C <sub>8</sub> H <sub>16</sub>	2-ethyl-4-methyl-1-pentene	555.82	0.50	1
692-96-6	C <sub>8</sub> H <sub>16</sub>	<i>trans</i> -2-methyl-3-heptene	562.85	0.50	1
7300-03-0	C <sub>8</sub> H <sub>16</sub>	3-methyl-3-heptene	571.35	0.50	1
690-93-7	C <sub>8</sub> H <sub>16</sub>	<i>trans</i> -2,2-dimethyl-3-hexene	551.74	0.50	1
61847-78-7	C <sub>8</sub> H <sub>16</sub>	2,4-dimethyl- <i>trans</i> -3-hexene	557.98	0.50	1
37549-89-6	C <sub>8</sub> H <sub>16</sub>	2,4-dimethyl- <i>cis</i> -3-hexene	557.98	0.50	1
3404-75-9	C <sub>8</sub> H <sub>16</sub>	3-methyl-2-heptene	579.26	0.50	1
19550-88-0	C <sub>8</sub> H <sub>16</sub>	<i>trans</i> -3,4-dimethyl-3-hexene	567.47	0.78	2
7116-86-1	C <sub>8</sub> H <sub>16</sub>	5,5-dimethyl-1-hexene	550.39	0.50	1
500007-01-2	C <sub>8</sub> H <sub>16</sub>	5-methyl-1-heptene	562.79	0.50	1
500015-77-0	C <sub>9</sub> H <sub>16</sub>	2,3,3,4-tetramethyl-1,4-pentadiene	591.77	0.40	2
4588-18-5	C <sub>9</sub> H <sub>18</sub>	2-methyl-1-octene	595.74	0.50	1
20442-63-1	C <sub>9</sub> H <sub>18</sub>	2,3,3,4-tetramethyl-1-pentene	595.02	0.78	2
500001-23-0	C <sub>9</sub> H <sub>18</sub>	2,4-dimethyl-3-ethyl-2-pentene	582.56	0.78	2
53907-59-8	C <sub>9</sub> H <sub>18</sub>	3-ethyl-4,4-dimethyl-2-pentene	593.64	0.78	2
2384-85-2	C <sub>10</sub> H <sub>18</sub>	3-decyne	637.92	1.30	4
2129-95-5	C <sub>10</sub> H <sub>20</sub>	2-methyl-2-nonene	624.81	0.50	1
53966-53-3	C <sub>10</sub> H <sub>20</sub>	2-methyl-3-nonene	615.54	0.50	1
39083-38-0	C <sub>10</sub> H <sub>20</sub>	3,4,5,5-tetramethyl-2-hexene	597.48	0.50	1
5857-68-1	C <sub>10</sub> H <sub>20</sub>	2,2,4,4-tetramethyl-3-methylene	612.46	0.50	1
692-48-8	C <sub>10</sub> H <sub>20</sub>	<i>trans</i> -2,2,5,5-tetramethyl-3-hexene	578.73	0.78	2

A further result is the determination of the accuracy of particular prediction methods for specific subgroups of aliphatic hydrocarbons.

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