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Recommended Critical Temperatures. Part II. Aromatic and Cyclic Hydrocarbons

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This study presents 41 recommended experimental and 52 calculated values of critical temperatures of aromatic and cyclic hydrocarbons. Additionally this work includes 93 recommended normal boiling point temperatures for these two groups of compounds. This is Part II in a series dealing with recommended critical data for organic compounds; Part I dealt with aliphatic hydrocarbons. For 33 aromatic and 19 cyclic compounds there is a significant lack of critical temperature values. Values have been provided by means of prediction methods and previously critically evaluated values, based on a recommended experimental database. One reason for the creation of this database was for the purpose of evaluation the accuracy of prediction methods applied in this study. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1647147]

Key words: aromatic hydrocarbons; critical temperature; cyclic hydrocarbons; evaluation; normal boiling point; predicted data; recommended data.

Contents

1. Introduction

Critical parameters, especially critical temperatures (T_c) are those, which are basic for determination industrially important properties. Critical properties (temperature, pressure, and density) are difficult to measure experimentally since expensive high quality equipment is required for high accuracy measurements in high temperature and high pressure regions. Moreover, the processes of thermal decomposition constitute a major obstacle to the measurement of critical properties. As a result, experimental data on T_c values, especially for ring compounds, are poorly represented in world literature. There are relatively few experimental T_c data available for aromatic and cyclic hydrocarbons and some of these data, especially for terphenyls and cyclic hydrocarbons, may be unreliable. In this latter case, prediction methods are the only means by which these properties may be determined.

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The main purpose of this work was the creation of a data base for recommended experimentally based T_c values for aromatic and cyclic hydrocarbons, as well as filling gaps in the data base in T_c values, as far as possible, by means of predictive methods. These methods had been previously comparatively evaluated with regard to the accuracy and applicability for special subgroups of mentioned hydrocarbons.

The set of recommended experimental values of normal boiling point temperatures (T_b) for aromatic and cyclic hydrocarbons is an additional result of this work, as the prediction methods for T_c require reliable and accurate T_b values.

The preliminary stages of this work were:

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

The experimental data were critically evaluated and statistically 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:

(1) a number of alkyl groups, substituted to ring and
(2) a number of rings, constituting the molecule

This work is the second 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 other groups of compounds (including alcohols, esters, ketones, and halogenated hydrocarbons) as well as for their critical pressure.

The critical volume will not be included in this study as there is insufficient experimental data. New predictive methods for the critical properties, if published, will be considered.

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

Formula	Name of compound	CAS RN	T_b (K)	T_c (K)
	Aromatic hydrocarbons			
C_6H_6	benzene	71-43-2	353.23[1]	562.16[1]
C_7H_8	toluene	108-88-3	383.73[1]	591.80[1]
C_8H_{10}	o-xylene	95-47-6	417.58[1]	630.33[1]
C_8H_{10}	m-xylene	108-38-3	412.25[1]	617.05[1]
C_8H_{10}	p-xylene	106-42-3	411.35[1]	616.20[1]
C_8H_{10}	ethylbenzene	100-41-4	409.35[1]	617.15[2]
C_9H_{10}	indan	496-11-7	449.65[1]	684.9[2]
C_9H_{12}	isopropylbenzene	98-82-8	425.54[1]	631.05[1]
C_9H_{12}	1,2,3-trimethylbenzene	526-73-8	449.23[1]	664.5[2]
C_9H_{12}	1,2,4-trimethylbenzene	95-63-6	442.5[1]	649.09[1]
C_9H_{12}	1,3,5-trimethylbenzene	108-67-8	437.87[1]	637.29[1]
C_9H_{12}	propylbenzene	103-65-1	432.46[1]	638.24[1]
$C_{10}H_8$	naphthalene	91-20-3	491.11[1]	748.35[1]
$C_{10}H_{12}$	1,2,3,4-tetrahydronaphthalene	119-64-2	478.75[1]	719.5[2]
$C_{10}H_{14}$	1,2,4,5-tetramethylbenzene	95-93-2	469.15[1]	675.65[1]
$C_{10}H_{14}$	4-isopropyltoluene	99-87-6	450.38[1]	651.8[2]
$C_{10}H_{14}$	isobutylbenzene	538-93-2	445.91[1]	650.00[1]
$C_{10}H_{14}$	butylbenzene	104-51-8	456.42[1]	660.45[1]
$C_{10}H_{14}$	p-diethylbenzene	105-05-5	456.9[1]	657.89[1]
$C_{11}H_{10}$	1-methylnaphthalene	90-12-0	517.95[1]	772.15[1]
$C_{11}H_{10}$	2-methylnaphthalene	91-57-6	514.3[1]	761.15[1]
$C_{12}H_{10}$	biphenyl	92-52-4	528.15[1]	773[2]
$C_{12}H_{18}$	hexamethylbenzene	87-85-4	536.85[1]	758.0[2]
$C_{13}H_{12}$	benzylbenzene	101-81-5	537.42[1]	760.[2]
$C_{14}H_{10}$	phenanthrene	85-01-8	613.15[1]	869.[2]
$C_{18}H_{14}$	1,2-diphenylbenzene	84-15-1	605.[1]	857.[2]
$C_{18}H_{14}$	1,3-diphenylbenzene	92-06-8	636.00[1]	883.[2]
$C_{18}H_{14}$	1,4-diphenylbenzene	92-94-4	649.[1]	908.[2]
	Cyclic hydrocarbons			
C_3H_6	cyclopropane	75-19-4	240.25[1]	397.8[1]
C_5H_{10}	cyclopentane	287-92-3	322.41[1]	511.55[1]
C_6H_{10}	cyclohexene	110-83-8	356.15[1]	560.40[1]
C_6H_{12}	methylcyclopentane	96-37-7	344.97[1]	532.70[1]
C_6H_{12}	cyclohexane	110-82-7	353.90[1]	553.45[1]
C_7H_{14}	methylcyclohexane	108-87-2	374.07[1]	572.2[1]
C_7H_{14}	cycloheptane	291-64-5	391.25[1]	604.2[2]
C_7H_{14}	ethylcyclopentane	1640-89-7	376.62[1]	569.5[2]
C_8H_{16}	*trans*-1,4-dimethylcyclohexane	2207-04-7	392.48[1]	587.70[1]
C_8H_{16}	cyclooctane	292-64-8	423.85[1]	647.20[2]
C_9H_{18}	1,*cis*-3,*trans*-5-trimethylcyclohexane	1795-26-2	413.70[1]	602.20[1]
$C_{10}H_{18}$	*cis*-decalin	493-01-6	467.75[1]	703.6[2]
$C_{10}H_{18}$	*trans*-decalin	493-02-7	458.65[1]	687.[2]

2. Recommended Experimental Data on Normal Boiling Points and Critical Temperatures

2.1. The Criterion and the Procedure for Selection of Experimental Data

The database of the recommended normal boiling point T_b and critical temperature T_c values for aromatic and cyclic hydrocarbons is based on all available experimental data extracted from two data banks: Thermodynamics Research Center (NIST-TRC)[1] and Thermodynamics Data Center (TDC)[2] as well as the more recent publications on T_c as contained in numerous studies.[3-6]

TABLE 2. Recommended experimental values of normal boiling points T_b of aromatic and cyclic hydrocarbons for which critical temperature values were calculated in this work. All data are extracted from experimental base of NIST-TRC[1]

Formula	Name of compound	CAS RN	T_b (K)
	Aromatic hydrocarbons		
C_8H_8	styrene	100-42-5	418.29
C_9H_{10}	m-vinyltoluene	100-80-1	442.65[a]
C_9H_{10}	p-vinyltoluene	622-97-9	444.95
C_9H_{10}	isopropenylbenzene	98-83-9	438.65
C_9H_{12}	o-ethyltoluene	611-14-3	438.3
C_9H_{12}	m-ethyltoluene	620-14-4	434.45
C_9H_{12}	p-ethyltoluene	622-96-8	435.15
$C_{10}H_{12}$	4-phenyl-1-butene	768-56-9	450.15
$C_{10}H_{12}$	o-isopropenyltoluene	7399-49-7	445.35
$C_{10}H_{12}$	p-isopropenyltoluene	1195-32-0	450.85
$C_{10}H_{12}$	4-allyltoluene	3333-13-9	456.06
$C_{10}H_{14}$	1,2,3,5-tetramethylbenzene	527-53-7	471.25
$C_{10}H_{14}$	m-diethylbenzene	141-93-5	454.77
$C_{10}H_{14}$	1-ethyl-3,4-dimethylbenzene	934-80-5	462.7
$C_{10}H_{14}$	1-methyl-4-propylbenzene	1074-55-1	456.65
$C_{10}H_{14}$	2-isopropyltoluene	527-84-4	451.28
$C_{10}H_{14}$	3-isopropyltoluene	535-77-3	448.35
$C_{10}H_{14}$	sec-butylbenzene	135-98-8	446.45
$C_{10}H_{14}$	tert-butylbenzene	98-06-6	442.27
$C_{10}H_{14}$	o-diethylbenzene	135-01-3	454.35
$C_{11}H_{16}$	pentamethylbenzene	700-12-9	505.15
$C_{11}H_{16}$	pentylbenzene	538-68-1	477.40
$C_{11}H_{16}$	1-methyl-3-tert-butylbenzene	1075-38-3	462.44[a]
$C_{11}H_{16}$	tert-pentylbenzene	2049-95-8	459.15
$C_{12}H_{12}$	1,6-dimethylnaphthalene	575-43-9	537.15
$C_{12}H_{12}$	2,3-dimethylnaphthalene	581-40-8	541.15
$C_{12}H_{12}$	2,6-dimethylnaphthalene	581-42-0	535.15
$C_{12}H_{18}$	hexylbenzene	1077-16-3	498.15
$C_{13}H_{10}$	9H-fluorene	86-73-7	569.55
$C_{13}H_{20}$	heptylbenzene	1078-71-3	515.15
$C_{14}H_{10}$	anthracene	120-12-7	613.05
$C_{14}H_{22}$	octylbenzene	2189-60-8	537.65
$C_{18}H_{30}$	2-phenyldodecane	2719-61-1	575.65[a]
	Cyclic hydrocarbons		
C_5H_6	1,3-cyclopentadiene	542-92-7	313.15
C_5H_{10}	1-methylcyclobutane	598-61-8	310.25
C_5H_{10}	ethylcyclopropane	1191-96-4	309.35
C_5H_{10}	trans-1,2-dimethylcyclopropane	2402-06-4	301.35
C_6H_{10}	methylenecyclopentane	1528-30-9	351.65
C_6H_{10}	ethylidenecyclobutane	1528-21-8	353.41[a]
C_6H_{10}	1-methylcyclopentene	693-89-0	348.75
C_6H_{10}	2-cyclopropylpropene	4663-22-3	343.56
C_6H_{10}	3-methylcyclopentene	1120-62-3	338.35[a]
C_6H_{12}	1-ethyl-1-methylcyclopropane	53778-43-1	329.94
C_6H_{12}	cis-1-methyl-2-ethylcyclopropane	19781-68-1	338.55
C_7H_{12}	methylenecyclohexane	1192-37-6	378.15[a]
C_8H_{16}	1,1-dimethylcyclohexane	590-66-9	392.69
C_8H_{16}	1,1,2-trimethylcyclopentane	4259-00-1	386.88
C_8H_{16}	1,1,3-trimethylcyclopentane	4516-69-2	378.04
C_8H_{16}	ethylcyclohexane	1678-91-7	404.95
C_9H_{18}	n-propylcyclohexane	1678-92-8	429.85
C_9H_{18}	isopropulcyclohexane	696-29-7	427.71
C_9H_{18}	1,cis-3,cis-5-trimethylcyclohexane	1795-27-3	411.15

[a]Values from a single investigation.

The data references, attached to every experiment result 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 experiment. The short description, attached to every experimental result, permitted us to know if the measurement was a principal objective of experiment, as well as to know the purity of substance sample used. Moreover the measurement error has been allocated for each experimental value collected in data banks.[1,2]

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 outlying data points were eliminated from every subset. 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, such as a citation in the more recent literature or comparison with data from auxiliary sources.[7,8] In these instances, the recommended values, denoted with asterisks, are those from a single investigation and occur only in Table 2. Secondary data, that is values which were not derived from the original observation on T_b, have been rejected.

The same selection has been performed for T_c with particular attention paid to the sample purity.

Discrepancies, among the remaining data values forming every subset, did not exceed 0.5 K and 1.5 K for T_b and T_c, respectively

2.1.1. Statistical Analysis of Selected Data

The reliable values of T_b and T_c selected were those 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.

2.2. Recommended Experimental Data on Critical Temperatures and Normal Boiling Points for Aromatic and Cyclic Hydrocarbons

Data banks[1,2] include about 10–15 data values for T_b and about six data values for T_c per substance allocated in Table 1. Critical analysis of this data reduced those numbers to: 4–6 for T_b and 4 for T_c. The experimental T_b and T_c values of 28 aromatic and 11 cyclic hydrocarbons, mentioned in point 1(a) were used for evaluation of the critical temperature prediction methods. Their names together with the 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 on average to about three reliable values per substance. This table provides the names and recommended T_b values for chosen 33 aromatic and 19 cyclic hydrocarbons, mentioned in point 1(b) for which experimental values of T_c were not available in literature and were calculated in this work.

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

Name of compound	E (%) Name of method						
	Ambrose	Joback	Fedors	Daubert	Constantinou	Somayajulu	Klincewicz
	Aromatic hydrocarbons Normal alkylbenzenes						
benzene	+0.01	−0.11	−0.59	−0.35	+0.17	−0.00	−4.69
toluene	+0.11	+0.34	−1.27	−0.49	+0.73	+0.29	−2.58
ethylbenzene	−0.10	+0.28	−1.45	+0.08	+0.47	+0.05	−1.09
propylbenzene	−0.12	+0.24	−1.31	+0.19	−0.21	−0.04	+0.39
butylbenzene	−0.20	+0.18	−1.63	−0.01	−0.15	−0.07	+1.79
	Other alkylbenzenes						
o-xylene	−0.06	+0.00	−0.67	+0.04	−0.98	+0.16	−1.33
m-xylene	+0.12	+0.85	−1.61	−0.16	+1.14	+0.31	−0.41
p-xylene	+0.08	+0.82	−1.47	−0.56	+1.28	+0.75	−0.44
1,2,3-trimethylbenzene	−0.11	−0.27	−0.44	+0.59	−2.44	−0.28	−0.02
1,2,4-trimethylbenzene	+0.12	+0.56	−0.57	−0.03	−0.12	+0.35	+0.89
1,3,5-trimethylbenzene	+0.31	+1.35	−1.46	−0.52	+1.72	+0.52	+1.74
1,2,4,5-tetramethylbenzene	+0.13	+0.26	−0.37	+0.35	−0.89	+0.02	+2.15
hexamethylbenzene	−0.12	−1.55	−0.46	+2.31	−6.86	−0.10	+3.05
p-diethylbenzene	−0.12	+0.54	−1.38	+0.27	+0.82	+0.41	+2.28
isopropylbenzene	−0.00	+0.06	−1.29	0.14	−0.09	−0.20	−0.00
isobutylbenzene	−0.34	+0.21	−1.02	−0.35	+0.15	−0.52	+1.14
4-isopropyltoluene	−0.04	+0.80	−1.43	−0.37	+0.32	+0.19	+1.83
	Polyphenyls						
biphenyl	+0.13	+0.69	−8.28	+2.04	−1.61	+0.25	−0.35
benzylbenzene	+1.64	+2.15	−4.84	+0.93	−3.23	+1.76	+2.76
1,2-diphenylbenzene	−2.10	−2.00	−5.73	−1.12	−0.49	+1.30	+1.09
1,3-diphenylbenzene	−0.12	−0.01	−9.47	+1.51	−3.42	+2.80	+3.07
1,4-diphenylbenzene	−0.88	−0.78	−11.96	+1.30	−6.08	+2.38	+2.25
	Condensed polycyclic						
indan	−0.85	−1.10	−5.29	+0.28	−0.20	+0.66	−2.86
naphthalene	−0.01	−1.46	−9.67	−0.09	−1.24	−0.00	−3.49
1,2,3,4-tetrahydronaphthalene	−1.00	−0.92	−6.48	+1.21	+2.66	+0.42	−2.14
1-methylnaphthalene	−0.32	−1.54	−14.85	−0.31	−1.36	−0.15	−1.86
2-methylnaphthalene	+0.40	−0.82	−9.13	+0.26	−1.17	+0.57	−1.12
phenanthrene	−2.15	+0.94	−13.30	+4.31	−5.11	+3.71	+1.95
	Cyclic hydrocarbons Unsubstituted cyclics						
cyclopropane	+0.34	−1.32	−2.54	+0.01	−4.49	+0.47	−2.41
cyclopentane	+0.28	+2.98	−0.56	−1.35	−0.14	+0.46	−3.51
cyclohexene	−0.17	+0.04	−1.20	−0.58	+0.18	−0.02	−3.78
cyclohexane	−0.17	+0.18	−0.42	+0.02	+0.86	+0.03	−3.20
cycloheptane	−0.65	+0.14	−4.25	−1.17	+0.02	−0.44	−2.99
cyclooctane	−1.13	+0.02	−6.83	−1.96	−3.35	−0.90	−2.68
	Substituted cyclics						
methylcyclohexane	−0.67	+0.30	−0.40	+0.73	+0.63	−0.40	−1.79
ethylcyclopentane	−0.35	+0.36	−1.54	−0.09	−0.99	−0.12	−0.70
methylcyclopentane	+0.34	+0.91	−0.32	+0.16	+0.12	+0.60	−1.53
trans-1,4-dimethylcyclohexane	−0.92	+0.46	−0.08	+0.87	+0.69	−0.61	−0.35
1,cis-3,trans-5-trimethylcyclohexane	−0.23	+1.44	+0.19	+2.55	+0.71	+0.13	+1.85
cis-decalin	−0.64	−1.34	−6.48	+0.87	−6.56	−2.24	−2.27
trans-decalin	−0.22	−0.93	−4.22	+0.91	−4.31	−1.83	−1.78

TABLE 4. The dependence of absolute percent errors of the tested methods upon the number of CH_3 groups substituted to benzene ring

Number of CH_3 groups	Ambrose	Joback	Fedors	Daubert	Constantinou	Somayajulu	Klincewicz
0	0.01	0.11	0.59	0.35	0.17	0.00	4.69
1	0.11	0.34	1.27	0.49	0.73	0.29	2.58
2	0.09	0.56	1.25	0.25	1.13	0.41	0.73
3	0.18	0.73	0.82	0.38	1.43	0.38	0.88
4	0.38	0.40	1.17	0.27	0.46	0.24	1.84
6	0.12	1.55	0.46	2.31	6.86	0.10	3.05

The accuracy of a given value is defined by the number of digits after the decimal point in the numeric value.

3. List of Selected Methods of T_c Prediction

The following methods, defined by the names of one of the authors, 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,[9] (2) Joback,[10] (3) Fedors,[11] (4) Jalowka-Daubert,[3,12,13] (5) Constantinou,[14] (6) Somayajulu,[4] and (7) Klincewicz.[15]

All tested methods, except that of Klincewicz,[15] employ group contribution techniques which determine correction factors for specific groups of atoms which constitute the molecule of interest. Values of these contribution factors are tabulated for every method and their sum 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:

(1) group contribution models based on molecular structure,
(2) molecular weight, and
(3) normal boiling point.

The method of Constantinou[14] and Klincewicz[15] do not require the knowledge of T_b values. This fact is useful for compounds with undefined T_b, i.e., for complex structure substances. The investigated methods represent two distinctive classes:[16]

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

glecting the next-nearest neighbors effects. The methods of Ambrose,[9] Joback,[10] Fedors,[11] and Somayajulu[4] 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[3,12,13] and Constantinou[14] belong to this class.

A more detailed description of these methods was presented in Part I of this series.[17]

4. Testing Calculations

Calculations, performed for evaluation of the accuracy of the seven predictive methods, were conducted for 13 cyclic and 28 aromatic hydrocarbons including: normal alkylbenzenes, other alkylbenzenes, polyphenyls, and condensed polycyclics.

The chosen prediction methods employ 10–100 specific contribution groups together with attributed temperature correction factors. For each hydrocarbon and for each method, all contribution groups forming the molecule were specified and their sum yielded values of the final correction factor used for prediction of the critical temperature T_{cp}. Deviations of the calculated critical temperatures values T_{cp} from the recommended experimental values of T_c are shown in Table 3. They were calculated according to

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

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

TABLE 5. The dependence of absolute percent errors of the tested methods upon the number of overall number of C atoms substituted to benzene ring

Number of C atoms	Ambrose	Joback	Fedors	Daubert	Constantinou	Somayajulu	Klincewicz
0	0.01	0.11	0.59	0.35	0.17	0.00	4.69
1	0.11	0.34	1.27	0.49	0.73	0.29	2.58
2	0.10	0.42	1.35	0.16	0.80	0.23	0.91
3	1.08	1.50	1.25	1.22	1.50	1.05	1.40
4	0.38	0.40	1.17	0.27	0.47	0.24	1.84
6	0.12	1.55	0.46	2.31	6.86	0.10	3.05

TABLE 6. Average absolute percent error for tested methods for different groups of aromatics

Group	Ambrose	Joback	Fedors	Daubert	Constantinou	Somayajulu	Klincewicz
Normal alkylbenzenes	0.11	0.23	1.25	0.22	0.35	0.09	2.11
Other alkylbenzenes	0.13	0.61	1.01	0.47	1.40	0.32	1.27
Polyphenyls	0.81	0.93	5.47	0.84	2.23	1.41	1.53
Condensed polycyclics	0.79	1.13	9.78	1.07	1.95	0.91	2.24

5. Results of Tests and Conclusions

5.1. Aromatic Hydrocarbons

The influence of the number and position of ring and alkyl substituted groups on the accuracy of selected methods were examined. The length of alkyl groups, and the overall number of substituted C atoms was considered too. All results of the investigation are presented in the tables below.

It has been stated that there is no general influence of the number and the length of the substituted alkyl groups on the method's error (Tables 4 and 5). However the slight increasing effect of substituted groups position: *ortho, meta, para* has been observed (refer to Table 3).

Deviations of calculated T_c value from experimental data vary significantly among particular subgroups. As shown in Table 6 all the methods yield higher deviations for polyphenyls and condensed aromatics. Generally the methods of Ambrose[9] and Somayajulu[4] yield the lowest deviations, average less than 0.81% and 1.41%, respectively, for all subgroups and are recommended by authors as the most reliable for T_c calculation for aromatics. Nevertheless every subgroup, and even every compound should be considered individually, as strong fluctuation of methods' accuracy was observed among particular subgroups and particular compounds [i.e., recommended the Somayajulu[4] method for condensed polycyclic, (except for phenanthrene) yields for the remaining compounds of this group an average deviation 0.36%, while for phenanthrene this error increases to 3.71%]. This may result from the fact, that each method takes into account different nuances of complex and varied structure of the ring compounds, i.e., the method of Somayajulu[4] takes the condensed aromatic ring into consideration by employing benzene atom contribution and common "fused atoms" contribution, while the method of Ambrose[9] employs correction factor for all C_4H_4 groups fused as in naphthalene. The latter way is more accurate.

The preliminary results of attempts of extrapolation of T_c prediction towards heavy condensed ring compounds point to the possibility of occurrence of high errors.

5.2. Cyclic Hydrocarbons

An extensive examination of the selected methods was not possible as there are relatively few experimental data available for cyclic hydrocarbons. The examinations of selected methods have been performed for two subgroups of substances: substituted and unsubstituted cyclic hydrocarbons. Results for individual compounds are shown in Table 3 and absolute percent errors for two main mentioned subgroups are presented in Table 7. The method of Ambrose[9] and Somayajulu[4] are generally recommended for cyclic hydrocarbons, yielding the constant error level less than 0.85%. As shown in Table 7 the method of Joback[10] yields average lower deviation for the second subgroup than the method of Somayajulu,[8] but relatively high in individual cases. As well as in the case of the aromatic hydrocarbons, cyclic compounds should be considered individually: (1) the method of Constantinou[14] provides the most accurate correction factor for five- and seven-membered cyclic ring, (2) the method of Fedors[11] does not take into consideration more than six-membered cyclic ring, and (3) the method of Somayajulu[4] is more reliable than other ones in cases of double bond in cyclic ring.

It was noticed that the specific treatment of a cyclic ring in the method of Ambrose[9] has proved to be the most effective in giving the smallest deviations in the case of a saturated ring. Thus, this method is employed for calculation T_c values of most cyclic hydrocarbons (Table 8).

6. Prediction of Critical Temperatures

Using the conclusions from the analysis of the results of examination (Secs. 4 and 5), the proper prediction methods have been applied for calculation of critical temperatures for particular aromatic and cyclic hydrocarbons. The critical temperature data base for the hydrocarbons was enriched by the calculated critical temperatures for 52 compounds, for which experimental T_c data were not available in the literature, but reliable boiling point temperatures were available.

TABLE 7. Absolute percent error for tested methods for two subgroups of cyclic hydrocarbons

Group	Ambrose	Joback	Fedors	Daubert	Constantinou	Somayajulu	Klincewicz
Unsubstituted	0.51	0.93	2.92	0.90	1.77	0.46	2.96
Substituted	0.48	0.82	1.89	0.88	2.00	0.85	1.47

TABLE 8. Aromatic and cyclic hydrocarbons—calculated values of critical temperatures T_{cp} predicted using the selected methods specified below. Expected percent error for all T_{cp}—(from 0.02% to 0.85%)

CAS RN	Formula	Name	T_{cp} (K)	E^a (%)	Method[b]
		Aromatic hydrocarbons			
100-42-5	C_8H_8	styrene	635.47	0.13	1
100-80-1	C_9H_{10}	m-vinyltoluene	654.35	0.31	2
622-97-9	C_9H_{10}	p-vinyltoluene	662.73	0.27	3
98-83-9	C_9H_{10}	isopropenylbenzene	651.17	0.13	1
611-14-3	C_9H_{12}	o-ethyltoluene	647.92	0.16	2
620-14-4	C_9H_{12}	m-ethyltoluene	638.04	0.32	2
622-96-8	C_9H_{12}	p-ethyltoluene	641.89	0.32	2
768-56-9	$C_{10}H_{12}$	4-phenyl-1-butene	654.64	0.52	2
7399-49-7	$C_{10}H_{12}$	o-isopropenyltoluene	643.99	0.13	1
1195-32-0	$C_{10}H_{12}$	p-isopropenyltoluene	652.84	0.13	1
3333-13-9	$C_{10}H_{12}$	4-allyltoluene	663.23	0.41	2
527-53-7	$C_{10}H_{14}$	1,2,3,5-tetramethylbenzene	678.81	0.02	2
135-01-3	$C_{10}H_{14}$	o-diethylbenzene	657.00	0.13	1
141-93-5	$C_{10}H_{14}$	m-diethylbenzene	654.06	0.13	1
934-80-5	$C_{10}H_{14}$	1-ethyl-3,4-dimethylbenzene	667.75	0.32	2
1074-55-1	$C_{10}H_{14}$	1-methyl-4-propylbenzene	656.76	0.13	1
527-84-4	$C_{10}H_{14}$	o-isopropyltoluene	655.65	0.32	2
535-77-3	$C_{10}H_{14}$	m-isopropyltoluene	647.66	0.32	2
135-98-8	$C_{10}H_{14}$	sec-butylbenzene	648.56	0.13	1
98-06-6	$C_{10}H_{14}$	tert-butylbenzene	649.71	0.13	1
700-12-9	$C_{11}H_{16}$	pentamethylbenzene	714.9	0.02	2
538-68-1	$C_{11}H_{16}$	pentylbenzene	677.92	0.09	2
1075-38-3	$C_{11}H_{16}$	1-methyl-3-tert-butylbenzene	660.19	0.32	2
2049-95-8	$C_{11}H_{16}$	tert-pentylbenzene	661.42	0.13	1
575-43-9	$C_{12}H_{12}$	1,6-dimethylnaphthalene	778.46	0.79	1
581-40-8	$C_{12}H_{12}$	2,3-dimethylnaphthalene	790.35	0.36	2
581-42-0	$C_{12}H_{12}$	2,6-dimethylnaphthalene	780.03	0.36	2
1077-16-3	$C_{12}H_{18}$	Hexylbenzene	695.92	0.09	2
86-73-7	$C_{13}H_{10}$	9H-fluorene	825.15	0.81	1
1078-71-3	$C_{13}H_{20}$	heptylbenzene	709.05	0.09	2
120-12-7	$C_{14}H_{10}$	anthracene	900.87	0.79	1
2189-60-8	$C_{14}H_{22}$	octylbenzene	730.03	0.07	2
2719-61-1	$C_{18}H_{30}$	2-phenyldodecane	748.73	0.07	2
		Cyclic hydrocarbons			
542-92-7	C_5H_6	1,3-cyclopentadiene	505.03	0.48	1
598-61-8	C_5H_{10}	1-methylcyclobutane	488.04	0.48	1
1191-96-4	C_5H_{10}	ethylcyclopropane	481.88	0.48	1
2402-06-4	C_5H_{10}	trans-1,2-dimethylcyclopropane	468.95	0.48	1
1528-30-9	C_6H_{10}	methylenecyclopentane	547.63	0.85	2
1528-21-8	C_6H_{10}	ethylidenecyclobutane	546.21	0.48	1
693-89-0	C_6H_{10}	1-methylcyclopentene	543.09	0.85	2
4663-22-3	C_6H_{10}	2-cyclopropylpropene	534.00	0.48	1
1120-62-3	C_6H_{10}	3-methylcyclopentene	526.89	0.85	2
53778-43-1	C_6H_{12}	1-ethyl-1-methylcyclopropane	507.90	0.48	1
19781-68-1	C_6H_{12}	cis-1-methyl-2-ethylcyclopropane	513.42	0.48	1
1192-37-6	C_7H_{12}	methylenecyclohexane	575.31	0.48	1
590-66-9	C_8H_{16}	1,1-dimethylcyclohexane	590.42	0.48	1
4259-00-1	C_8H_{16}	1,1,2-trimethylcyclopentane	576.62	0.48	1
4516-69-2	C_8H_{16}	1,1,3-trimethylcyclopentane	563.44	0.48	1
1678-91-7	C_8H_{16}	ethylcyclohexane	601.24	0.48	1
1678-92-8	C_9H_{18}	n-propylcyclohexane	625.15	0.48	1
696-29-7	C_9H_{18}	isopropulcyclohexane	625.91	0.48	1
1795-27-3	C_9H_{18}	1,cis-3,cis-5-trimethylcyclohexane	599.24	0.85	2

[a]Expected percent errors for individual cases.
[b]Numbers attributed to methods: (1) Ambrose,[9] (2) Somayajulu,[4] (3) Daubert.[3,12,13]

Except for the general recommendation of the methods of Ambrose[9] and Somayajulu[8] for cyclic and aromatic hydrocarbons, every compound was considered individually. The calculation was guided additionally by the fact that the three methods of (1) Ambrose,[9] (2) Daubert,[3,12,13] and (3) Somayajulu[4] provide corrections for *ortho* substitution, and only the method of Somayajulu[8] provides *meta* correction. The results, together with expected deviations, are included in Table 8. The expected deviations for every substance have been assumed based on its subgroup average deviation (Tables 5 and 6), unless the deviation of the model compound of similar molecular structure has been found in Table 3.

7. Results

The main result of this work is the set of critical temperatures for 52 aromatic and cyclic hydrocarbons for which experimental critical data were not available in the literature (Table 7). The other results of this work are the sets of:

(1) recommended experimental data on critical temperatures of 41 aromatic and cyclic hydrocarbons, used for testing purposes (Table 1) and

(2) recommended experimental data on normal boiling points of 93 aromatic and cyclic hydrocarbons (Tables 1 and 2).

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

9. References

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