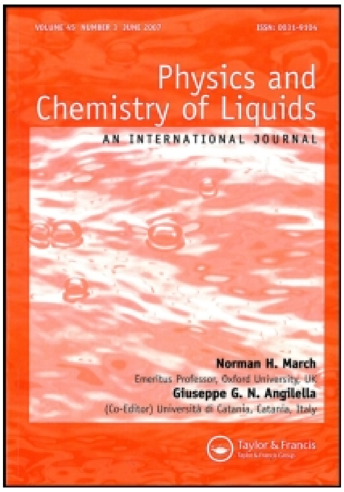

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Critical temperatures of organic compounds from their boiling points

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Critical temperatures of organic compounds from their boiling points

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A simple relation between critical temperature (T_c) and boiling point (T_b) is shown to be valid for many organic series. The relation is as follows: $1/T_c = \alpha/T_b + \beta$, where α and β are constants. It has been applied to a total of 24 homologous series and the results for T_c are quite accurate, the average percent error over all the compounds is 0.20%. Predictions are made for critical temperature and boiling point of certain compounds.

Keywords: critical temperature; boiling point; aliphatic series; aromatic series

1. Introduction

The knowledge of critical constants is of fundamental importance for a variety of applications, for example in the application of equations of state or corresponding-states methods. With their help, thermodynamic and volumetric properties and phase conditions can be predicted. Critical properties are required for predicting the vapour pressure or the effect of temperature and pressure on density, on thermal properties, and on transport properties. Van der Waals constants a and b can also be calculated from the critical constants [1]. Critical properties are also involved in the design and operation of many processes which routinely handle fluids at elevated temperatures and pressures. For example, in the supercritical fluid extraction process.

There are difficulties in the accurate experimental measurement of critical constants. For example, the sample has to be of high purity because it is known that critical properties are highly sensitive to even small amount of impurities. Furthermore, the experimental determination of critical constants becomes more difficult as one goes to heavier molecules because thermal decomposition sets in before T_c is reached.

Empirical or semiempirical methods serve to predict the critical constants of organic substances and if the predictions are of high quality for most of the molecules in a homologous series they can also serve to provide an indication of the accuracy of the predicted property of the remaining molecules. Over the years, there have been many attempts to predict the critical temperature of substances. The early work has been summarised by Kobe and Lynn [2] and by Partington [3]. The book by Reid, Prausnitz and Poling [4] gives developments up to the 1980s. The proposed methods for organic compounds can be broadly divided in five categories:

(1) Group contribution methods [5–19]. Most of the methods in this category require T_b. There are two subgroups: (a) The first order group techniques which determine

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the molecule by means of simple group contribution, neglecting the next-nearest neighbours effects. (b) The second order group techniques, which additionally take into consideration the influence of first and second-level neighbours of a considered group.

(2) Correlations with the number of carbon atoms (n) or molecular weight [20–28] or the number of links per molecule [29].
(3) Correlation with T_b alone [30] or with T_b and n.
(4) Equation of state correlations [31].
(5) Zenkevich [32] has recently proposed a new method. He connects T_c of a homologue having n carbon atoms with T_c of the preceding member by a linear relation:

$$T_c(n) = aT_c(n-1) + b, \tag{1}$$

where a and b are constants. He has also proposed similar relations for various other properties.

Throughout this article all temperatures will be expressed in K.

2. Linear relation for different series

The author had proposed [30] the following simple equation in 1953 for predicting T_c from T_b for alkanes:

$$1/T_c = \alpha/T_b + \beta, \tag{2}$$

where α and β are constants. Subsequently, this equation was applied by Ambrose, Cox and Townsend [33] to 15 n- and *iso*-paraffins and they found that it accurately represents the T_c values of these substances, the differences between T_c(Calcd) and T_c(obs.) being on average only about 0.1% of T_c.

To make the reciprocals in Equation (2) sizable we shall write it as follows

$$1000/T_c = 1000A/T_b + B, \tag{3}$$

where A and B are constants.

In 1953, critical temperatures for only some of the other organic series were known. During the last 50 years critical temperatures of a great many organic compounds have been measured. In the present article, we wish to show that the above relation gives fairly accurate values for the critical temperatures of organic compounds of a large number of homologous series.

Owczarek and Blazej [34] have compiled of a set of recommended experimental data on critical temperatures and normal boiling points for aliphatic hydrocarbons. These authors have then used these data to compare seven of the proposed methods. These methods, which are all group contribution methods, are due to Ambrose [5], Joback [7], Fedors [6], Jalowka–Daubert [10–12], Constantinou [17], Somayajulu [14], and Klincewicz [8]. We have extracted data for T_b and T_c for many organic homologous series from Owczarek and Blazej [34] and Lide [35] and these data were used to examine the applicability of Equation (3). Though in many cases data have been taken from Lide's [35] compilation,

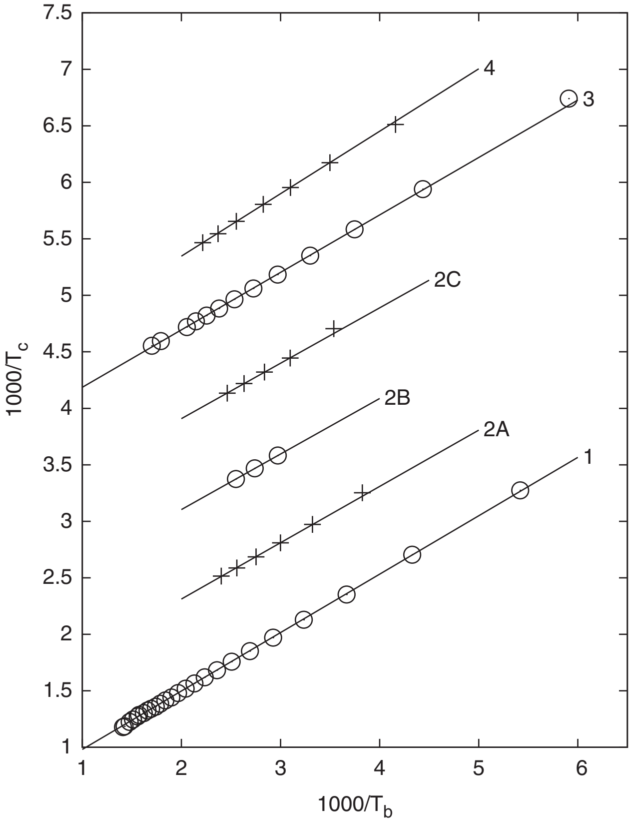

Figure 1. $1000/T_c$ *vs.* $1000/T_b$ for group numbers 1–4. To avoid overlapping and to accomodate several series in one diagram, series numbers 2–4 have been moved up by amounts (in the ordinate units) given in parenthesis. The labels are as follows. 1: Alkanes, branched alkanes 2A: 2-methylpropane (0.8), 2B: 3-methylpentane (1.6), 2C: 2,2-dimethylpropane (2.4), 3: alkenes (3.2), 4: cycloalkanes (4.0).

when discussing individual compounds we would frequently refer to the original source from which Lide has taken the data.

3. Results and discussion

In Figures 1–6, we show the plots of $1000/T_c$ *versus* $1000/T_b$ for 16 groups of compounds as follows:

Figure 1. 1: Alkanes, 2: branched alkanes, 3: alkenes and 4: cycloalkanes.
Figure 2. 5: alkanols.
Figure 3. 6: alkyl-benzenes.
Figure 4. 7: alkanones (ketones).
Figure 5. 8: alkanals, 9: ethers, 10: alkanoic acids. 11: acetates and 12: alkylamines.
Figure 6. 13: alkylnitriles, 14: alkylthiols, 15: chloroalkanes and 16: perfluoroalkanes.

It has been known that the first member of a homologous series often does not obey the regularity of later members [23–28,36,37]. Several of the existing correlations often

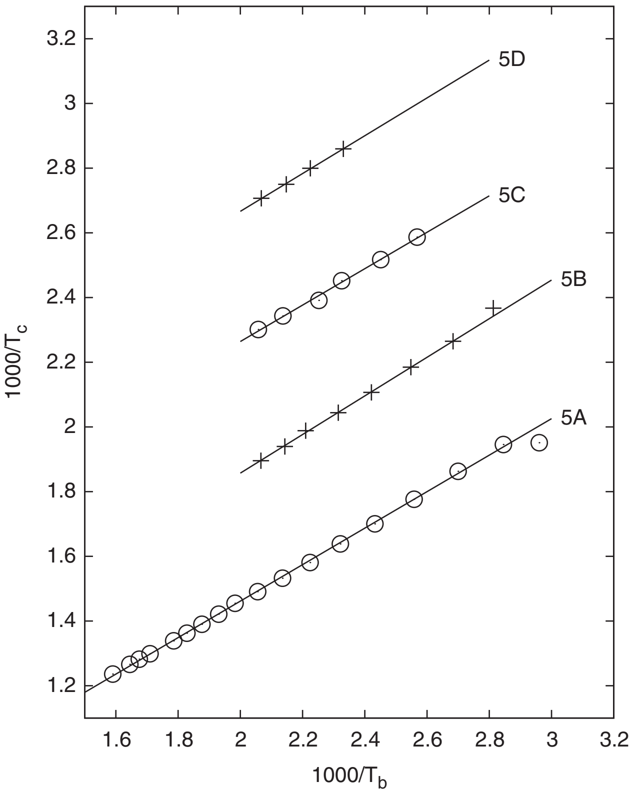

Figure 2. $1000/T_c$ *vs.* $1000/T_b$ for Alkanols. To avoid overlapping and to accomodate several series in one diagram, series numbers 5B–5D have been moved up by amounts (in the ordinate units) given in parenthesis. The labels are as follows. 5A: methanol, 5B: 2-propanol (0.4), 5C: 3-pentanol (0.8), 5D: 4-heptanol (1.2).

exclude the first member. A general inspection of the six figures shows that this is also true for some of the series here. In one case (alkanoic acids), the first three members do not follow the straight line. Excluding these cases the rest of the data for each series were treated by the method of least squares to obtain the parameters *A* and *B*. The values thus obtained are given in Table 1.

Table 2 presents a detailed numerical comparison between the experimental and calculated values together with the percent errors. For certain molecules for which either the boiling point or the critical temperature was not known, such boiling point or critical temperature has been predicted and such values are labelled with an asterisk. We discuss each series in the following. Sub-series have been identified by the leading member of the series. We then discuss each series individually.

1: Alkanes. Except for methane, there is good agreement between the calculated and experimental values. The average percent error by our method, excluding methane, is 0.22%. It may be compared with the average percent errors as found for some other methods for these compounds which are as follows (in parenthesis): Ambrose (0.29%), Joback (0.46%), Fedors (0.51%), Jalowka–Daubert (2.63%), Constantinou (1.12%), Klincewicz (8.46%), Somayajulu (0.30%). These averages were calculated from the results

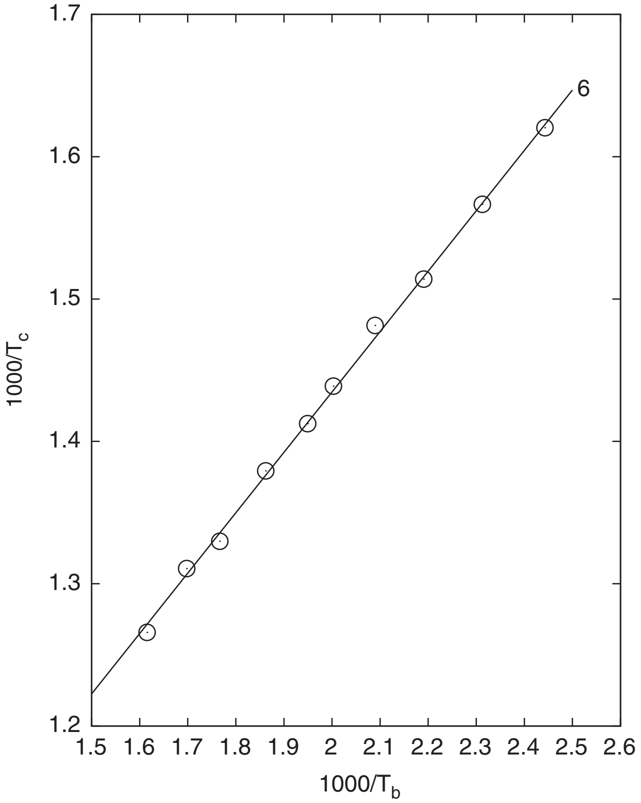

Figure 3. $1000/T_c$ *vs.* $1000/T_b$ for group number 6: alkyl-benzenes.

given by Owczarek and Blazej [34]. Thus, it is seen that our method gives the least error. A close inspection of the percent errors by our method (Table 2) shows that two of the compounds heneicosane ($C_{21}H_{44}$) and tricosane ($C_{23}H_{48}$) have rather large errors as compared to others. Beyond $C_{10}H_{22}$ the uncertainties in T_c values get progressively larger as one goes to heavier compounds, as these compounds are unstable before T_c is reached. Ambrose and Tsonopoulos [38] give the uncertainty in T_c values of these two compounds as $\pm 8\,\mathrm{K}$, which may account for the relatively large errors for these compounds.

2: Branched alkanes.

2A: 2-Methylpropane. Except for the first member, the errors are quite small.

2B: 3-Methylpentane. Data for only three members are available and the errors are negligible.

2C: 2,2-Dimethylpropane. Here again the first member is an exception, otherwise the percent errors are quite small.

3: Alkenes. The first member is an exception, otherwise the errors are quite small except for 1-octadecene. The data for this compound are from Owczarek and Blazej [34] who give their source being reference [39]. This reference is, however, not available to us, so we do not know the uncertainty in the T_c of this compound.

4: Cycloalkanes. Here also the first member is an exception, otherwise the percent errors are quite small.

5: Alkanols.

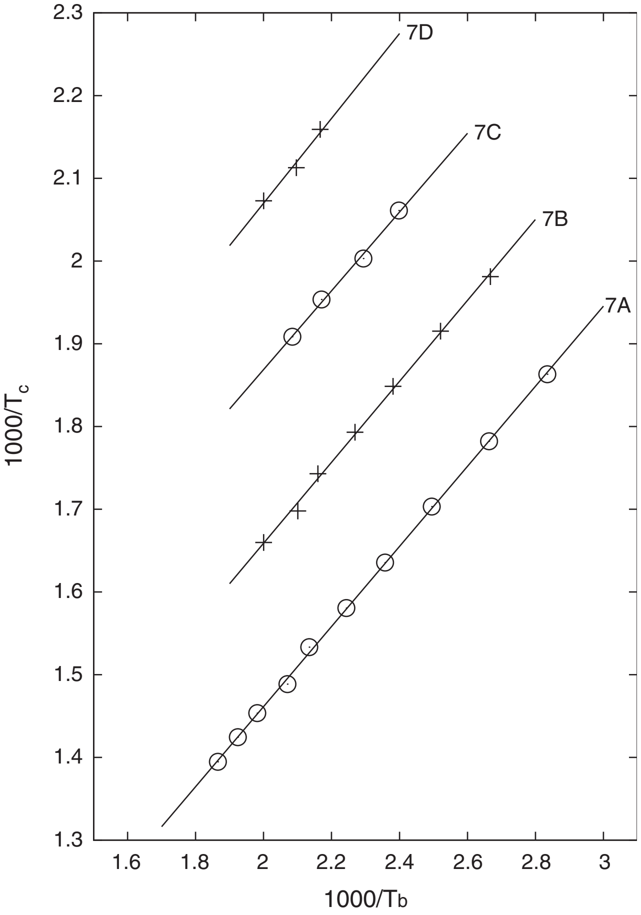

Figure 4. $1000/T_c$ *vs.* $1000/T_b$ for group number 7: alkanones. To avoid overlapping and to accomodate several series in one diagram, series numbers 7B–7D have been moved up by amounts (in the ordinate units) given in parenthesis. The labels are as follows. 7A: 2-propanone, 7B: 3-pentanone (0.2), 7C: 4-heptanone (0.4), 7D: 5-nonanone (0.6).

5A: Methanol. Except for the first member, the errors in all cases are below 0.5%.

5B: 2-Propanol. The pattern of results is quite similar to that for the Methanol group.

5C: 3-Pentanol. The error for 3-octanol is much larger than for all other alkanols except the first member. This raises the question of the accuracy of T_b and T_c of this compound. Gude and Teja [40] give the uncertainty in the T_c as ±0.5 K, but the uncertainty in T_b is not known.

5D: 4-Heptanol. The errors are negligible.

6: Alkylbenzenes. The first member is seen to be not an exception. For three of the compounds, pentylbenzene, decylbenzene and tridecylbenzene the percent errors are a little on the larger side. Nikitin *et al.* [41] estimate the uncertainty in T_c for compounds heavier than butylbenzene to be from ±7 to ±8 K. This easily accounts for the larger errors.

7: Alkanones (Ketones).

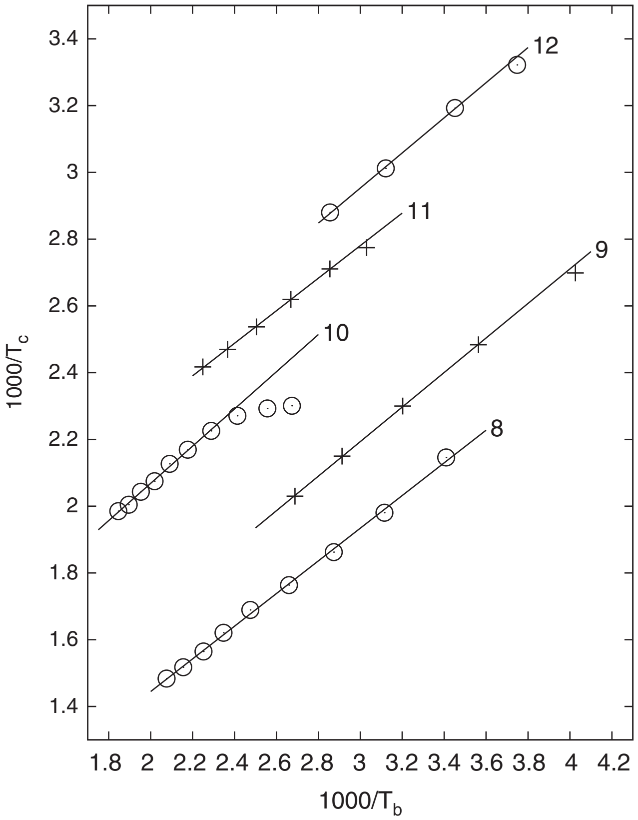

Figure 5. $1000/T_c$ *vs.* $1000/T_b$ for group numbers 8–12. To avoid overlapping and to accomodate several series in one diagram, series numbers 9–12 have been moved up by amounts (in the ordinate units) given in parenthesis. The labels are as follows. 8: alkanals, 9: ethers (0.2), 10: alkanoic acids (0.6) 11: alkyl acetates (0.8), and 12: alkylamines (1.0).

7A: 2-Propanone. Here also the first member is not an exception. The percent errors for 2-nonanone and 2-decanone are much larger than the rest of the group. Kudchadker *et al.* [42] estimate the uncertainty in the T_c of 2-nonanone to be ±0.5 K and that of 2-decanone to be ±1 K. These uncertainties can only partially account for the errors in these compounds. We do not know the uncertainties in the boiling points of these compounds.

7B: 3-Pentanone. The errors are small except that for 3-decanone. Kudchadker *et al.* [42] estimate the uncertainty in the T_c of this compound to be ±1 K. The calculated value of T_c suggests a total uncertainty in T_b and T_c to be about 3.

7C: 4-Heptanone. The errors are small.

7D: 5-Nonanone. Because data for so few compounds of 5-nonanone and 6-undecanone types were available, we have combined 5-nonanone and 6-undecanone groups together. The errors are reasonable.

8: Alkanals. The experimental T_c values given by Lide [35] are from Kudchadker *et al.* [42]. These authors estimate the uncertainties in the experimental values to be about ±2 K. If we assume the uncertainties in experimental values of T_b to be about ±1 K, this can easily

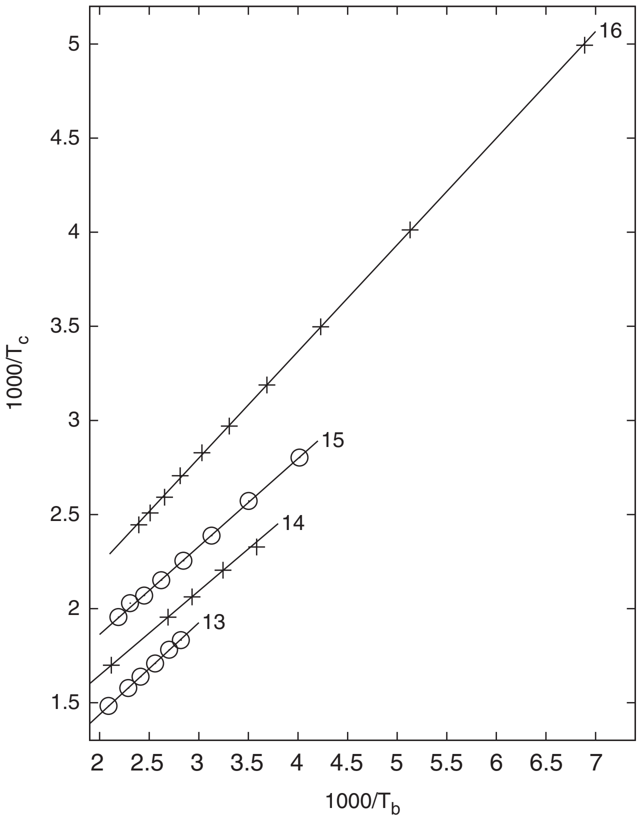

Figure 6. $1000/T_c$ *vs.* $1000/T_b$ for group numbers 13–16. To avoid overlapping and to accomodate several series in one diagram, series numbers 14–16 have been moved up by amounts (in the ordinate units) given in parenthesis. The labels are as follows. 13: alkylnitriles, 14: alkylthiols (0.2), 15: chloroalkanes (0.4), and 16: perfluoroalkanes (0.6).

lead to about 0.5% uncertainty in the calculated value if the errors are in opposite directions. Bearing this in mind, the percent errors for alkanals are in line with other series.

9: Ethers. The first member is an exception, otherwise the percent errors are quite small.

10: Alkanoic acids. This series is rather different from others in that the first three members of this series do not fall on the linear relation obeyed by the other members of the series. The departure is rather regular. The first member shows the largest error, the second less, and the third least. The errors for higher compounds are small. Interestingly enough, while the critical temperatures of compounds higher than decanoic acid are known, the boiling points seem not to be known. At least in Lide's [35] compilation, which is quite comprehensive and up to date, these are not listed. We have predicted the boiling points of these compounds. The uncertainties in these values, of course, depend on the uncertainty in the T_c of the corresponding compound.

11: Alkyl acetates. The first member is an exception, otherwise the percent errors are quite small.

12: Alkylamines. Here also the first member is an exception, otherwise the percent errors are small.

Table 1. Values of the constants *A* and *B* in Equation (3) and the average percent errors for the various groups. Values of *A* and *B* are given to a greater number of significant figures than is warranted by experimental data. This has been done merely to preserve consistency with the original data.

Group	Name	A	B	Average percent error
1	Alkanes	0.5169526	0.4636376	0.22
2	Branched alkanes			
2A	2-Methylpropane	0.4983529	0.5148676	0.12
2B	3-Methylpentane	0.4913189	0.5215551	0.02
2C	2,2-Dimethylpropane	0.4904538	0.5273498	0.08
3	Alkenes	0.5083661	0.4782388	0.24
4	Cycloalkanes	0.5528384	0.2405996	0.14
5	Alkanols			
5A	Methanol	0.5639873	0.3336600	0.25
5B	2-Propanol	0.5970890	0.2628420	0.12
5C	3-Pentanol	0.5630524	0.3377034	0.32
5D	4-Heptanol	0.5846012	0.2972209	0.09
6	Alkylbenzenes	0.4243016	0.5860827	0.27
7	Alkanones			
7A	2-Propanone	0.4860883	0.4890435	0.16
7B	3-Pentanone	0.4891153	0.4806674	0.26
7C	4-Heptanone	0.4760469	0.5167753	0.19
7D	5-Nonanone	0.5126447	0.4446994	0.33
8	Alkanals	0.4891321	0.4666619	0.21
9	Ethers	0.5176184	0.4405678	0.10
10	Alkanoic acids	0.5572453	0.3540011	0.26
11	Alkyl acetates	0.4877434	0.5173494	0.10
12	Alkylamines	0.5260090	0.3750923	0.16
13	Alkylnitriles	0.4882635	0.4609079	0.11
14	Alkylthiols	0.4472919	0.5516050	0.05
15	Chloroalkanes	0.4677549	0.5267047	0.17
16	Perfluoroalkanes	0.5666965	0.4998266	0.33
1 + 2 + 3	Alkanes + Branched alkanes + Alkenes	0.5174243	0.4595265	0.36

13: Alkylnitriles. The first member is not an exception and the percent errors are quite small.

14: Alkylthiols. Here also the first member is an exception, otherwise the percent errors are negligible.

15: Chloroalkanes. The first member is in line with others, but 1-chloroheptane shows a very large error. The experimental value of T_c for this compound is due to Morton *et al.* [43] who estimate its uncertainty to be ±6 K. This would, for the most part, explain the error.

16: Perfluoroalkanes. In this series the first member is not an exception. Three compounds, perfluoroheptane, perfluorononane and perfluorodecane show rather large errors as compared to others in the series. We believe part of these errors is due to uncertainties in T_c.

The average percent error, excluding the percent errors in parenthesis, for each series is shown in the last column of Table 1. The overall average percent error is 0.20%. Our method gives results of high accuracy, probably the highest amongst all other

Table 2. Experimental values of T_b and T_c together with calculated values of T_c and the corresponding percent errors. For certain molecules for which either the boiling point or the critical temperature was not known, such boiling point or critical temperature has been predicted and such values are labelled with an asterisk. All temperatures are in K.

Group	Formula	Name	T_b obs.	T_c obs.	T_c calcd.	Percent error
1	Alkanes					
	CH_4	Methane	111.63	190.55	196.29	(3.01)
	C_2H_6	Ethane	184.55	305.42	306.30	0.29
	C_3H_8	Propane	231.05	369.82	370.23	0.11
	C_4H_{10}	Butane	272.70	425.16	423.85	−0.31
	C_5H_{12}	Pentane	309.21	469.70	468.28	−0.30
	C_6H_{14}	Hexane	341.88	507.60	506.14	−0.29
	C_7H_{16}	Heptane	371.57	540.30	539.11	−0.22
	C_8H_{18}	Octane	398.82	568.83	568.23	−0.11
	C_9H_{20}	Nonane	423.96	594.70	594.18	−0.09
	$C_{10}H_{22}$	Decane	447.30	617.70	617.53	−0.03
	$C_{11}H_{24}$	Undecane	469.08	638.80	638.69	−0.02
	$C_{12}H_{26}$	Dodecane	489.47	658.25	657.99	−0.04
	$C_{13}H_{28}$	Tridecane	508.60	675.80	675.65	−0.02
	$C_{14}H_{30}$	Tetradecane	526.70	694.15	691.98	−0.31
	$C_{15}H_{32}$	Pentadecane	543.83	707.00	707.11	0.01
	$C_{16}H_{34}$	Hexadecane	560.01	722.00	721.11	−0.12
	$C_{17}H_{36}$	Heptadecane	574.25	736.00	733.21	−0.38
	$C_{18}H_{38}$	Octadecane	590.22	745.80	746.55	0.10
	$C_{19}H_{40}$	Nonadecane	603.00	755.00	757.04	0.27
	$C_{20}H_{42}$	Eicosane	617.00	768.00	768.35	0.05
	$C_{21}H_{44}$	Heneicosane	636.05	777.60	783.46	0.75
	$C_{22}H_{46}$	Docosane	641.80	785.60	787.95	0.30
	$C_{23}H_{48}$	Tricosane	653.00	790.00	796.63	0.84
	$C_{24}H_{50}$	Tetracosane	661.70	802.50	803.29	0.10
	$C_{25}H_{52}$	Pentacosane	676.70	816.90	814.62	−0.28
2	Branched alkanes					
2A	2-Methylpropane					
	C_4H_{10}	2-Methylpropane	261.42	407.80	413.02	(1.28)
	C_5H_{12}	2-Methylbutane	301.00	460.40	460.72	0.07
	C_6H_{14}	2-Methylpentane	333.41	497.70	497.62	−0.02
	C_7H_{16}	2-Methylhexane	363.15	530.40	529.89	−0.10
	C_8H_{18}	2-Methylheptane	390.80	559.70	558.63	−0.19
	C_9H_{20}	2-Methyloctane	416.43	582.87	584.25	0.24
	$C_{10}H_{22}$	2-Methylnonane	440.20		607.2*	
2B	3-Methylpentane					
	C_6H_{14}	3-Methylpentane	336.41	504.60	504.53	−0.01
	C_7H_{16}	3-Methylhexane	364.99	535.26	535.43	0.03
	C_8H_{18}	3-Methylheptane	392.09	563.60	563.50	−0.02
2C	2,2-Dimethylpropane					
	C_5H_{12}	2,2-Dimethylpropane	282.65	433.75	441.98	(1.90)
	C_8H_{18}	2,2-Dimethylhexane	380.00	549.80	550.05	0.05
	C_6H_{14}	2,2-Dimethylbutane	322.88	489.00	488.68	−0.07
	C_7H_{16}	2,2-Dimethylpentane	352.35	520.50	521.02	0.10
	C_9H_{20}	2,2-Dimethylheptane	405.99	576.70	576.24	−0.08
3	Alkenes					
	C_2H_4	Ethylene	169.25	282.34	287.20	(1.72)

(*continued*)

Table 2. Continued.

Group	Formula	Name	T_b obs.	T_c obs.	T_c calcd.	Percent error
	C_3H_6	1-Propene	225.45	364.90	365.88	0.27
	C_4H_8	1-Butene	266.87	419.50	419.61	0.03
	C_5H_{10}	1-Pentene	303.15	464.74	464.00	−0.16
	C_6H_{12}	1-Hexene	336.64	504.00	502.93	−0.21
	C_7H_{14}	1-Heptene	366.80	537.30	536.43	−0.16
	C_8H_{16}	1-Octene	394.41	566.55	565.88	−0.12
	C_9H_{18}	1-Nonene	420.03	594.00	592.22	−0.30
	$C_{10}H_{20}$	1-Decene	443.75	617.00	615.82	−0.19
	$C_{11}H_{22}$	1-Undecene	465.86	637.00	637.15	0.02
	$C_{12}H_{24}$	1-Dodecene	486.55	658.00	656.57	−0.22
	$C_{16}H_{32}$	1-Hexadecene	558.00	717.00	719.79	0.39
	$C_{18}H_{36}$	1-Octadecene	588.08	739.00	744.77	0.78
4	Cycloalkanes					
	C_3H_6	Cyclopropane	240.34	398.00	393.57	(−1.11)
	C_4H_8	Cyclobutane	285.80	460.00	459.78	−0.05
	C_5H_{10}	Cyclopentane	322.50	511.70	511.55	−0.03
	C_6H_{12}	Cyclohexane	353.88	553.80	554.69	0.16
	C_7H_{14}	Cycloheptane	391.60	604.20	605.20	0.17
	C_8H_{16}	Cyclooctane	422.00	647.20	644.89	−0.36
	C_9H_{18}	Cyclononane	451.60	682.00	682.70	0.10
	$C_{10}H_{20}$	Cyclodecane	474.10		710.9*	
5	Alkanols					
5A	Methanol					
	CH_4O	Methanol	337.80	512.50	499.19	(−2.60)
	C_2H_6O	Ethanol	351.44	514.00	515.88	0.37
	C_3H_8O	1-Propanol	370.40	536.80	538.70	0.35
	$C_4H_{10}O$	1-Butanol	390.88	563.00	562.90	−0.02
	$C_5H_{12}O$	1-Pentanol	411.13	588.10	586.35	−0.30
	$C_6H_{14}O$	1-Hexanol	430.80	610.30	608.71	−0.26
	$C_7H_{16}O$	1-Heptanol	449.60	632.60	629.69	−0.46
	$C_8H_{18}O$	1-Octanol	468.31	652.50	650.21	−0.35
	$C_9H_{20}O$	1-Nonanol	486.52	670.70	669.84	−0.13
	$C_{10}H_{22}O$	1-Decanol	504.30	687.30	688.70	0.20
	$C_{11}H_{24}O$	1-Undecanol	518.00	703.60	703.02	−0.08
	$C_{12}H_{26}O$	1-Dodecanol	533.00	719.40	718.50	−0.13
	$C_{13}H_{28}O$	1-Tridecanol	547.00	734.00	732.75	−0.17
	$C_{14}H_{30}O$	1-Tetradecanol	560.00	747.00	745.83	−0.16
	$C_{16}H_{34}O$	1-Hexadecanol	585.00	770.00	770.57	0.07
	$C_{17}H_{36}O$	1-Heptadecanol	597.00	780.00	782.25	0.29
	$C_{18}H_{38}O$	1-Octadecanol	608.00	790.00	792.85	0.36
	$C_{20}H_{42}O$	1-Eicosanol	629.00	809.00	812.81	0.47
5B	2-Propanol					
	C_3H_8O	2-Propanol	355.50	508.30	514.82	(1.28)
	$C_4H_{10}O$	2-Butanol	372.66	536.20	536.17	−0.01
	$C_5H_{12}O$	2-Pentanol	392.50	560.30	560.51	0.04
	$C_6H_{14}O$	2-Hexanol	413.00	585.90	585.28	−0.11
	$C_7H_{16}O$	2-Heptanol	432.00	608.30	607.91	−0.06
	$C_8H_{18}O$	2-Octanol	452.50	629.60	631.96	0.38
	$C_9H_{20}O$	2-Nonanol	466.70	649.60	648.41	−0.18
	$C_{10}H_{22}O$	2-Decanol	484.00	668.60	668.23	−0.06

(*continued*)

Table 2. Continued.

Group	Formula	Name	T_b obs.	T_c obs.	T_c calcd.	Percent error
5C	3-Pentanol					
	$C_5H_{12}O$	3-Pentanol	389.40	559.60	560.65	0.19
	$C_6H_{14}O$	3-Hexanol	408.00	582.40	582.16	−0.04
	$C_7H_{16}O$	3-Heptanol	430.00	605.40	607.12	0.28
	$C_8H_{18}O$	3-Octanol	444.00	628.50	622.73	−0.92
	$C_9H_{20}O$	3-Nonanol	468.00	648.00	649.01	0.16
	$C_{10}H_{22}O$	3-Decanol	486.00	666.10	668.34	0.34
5D	4-Heptanol					
	$C_7H_{16}O$	4-Heptanol	429.00	602.60	602.44	−0.03
	$C_8H_{18}O$	4-Octanol	449.50	625.10	625.87	0.12
	$C_9H_{20}O$	4-Nonanol	465.70	645.10	644.11	−0.15
	$C_{10}H_{22}O$	4-Decanol	483.70	663.70	664.09	0.06
6	Alkyl-benzenes					
	C_7H_8	Toluene	383.78	591.80	591.13	−0.11
	C_8H_{10}	Ethylbenzene	409.34	617.15	616.28	−0.14
	C_9H_{12}	Propylbenzene	432.39	638.35	638.01	−0.05
	$C_{10}H_{14}$	Butylbenzene	456.46	660.50	659.79	−0.11
	$C_{11}H_{16}$	Pentylbenzene	478.60	675.00	679.06	0.60
	$C_{12}H_{18}$	Hexylbenzene	499.30	695.00	696.44	0.21
	$C_{13}H_{20}$	Heptylbenzene	513.00	708.00	707.62	−0.05
	$C_{14}H_{22}$	Octylbenzene	537.00	725.00	726.63	0.22
	$C_{16}H_{26}$	Decylbenzene	566.00	752.00	748.65	−0.45
	$C_{17}H_{28}$	Undecylbenzene	589.00	763.00	765.43	0.32
	$C_{19}H_{32}$	Tridecylbenzene	619.00	790.00	786.44	−0.45
7	Alkanones					
7A	2-Propanone					
	C_3H_6O	2-Propanone	329.20	508.10	508.75	0.13
	C_4H_8O	2-Butanone	352.74	536.70	535.60	−0.21
	$C_5H_{10}O$	2-Pentanone	375.41	561.10	560.58	−0.09
	$C_6H_{12}O$	2-Hexanone	400.80	587.10	587.60	0.09
	$C_7H_{14}O$	2-Heptanone	424.20	611.40	611.64	0.04
	$C_8H_{16}O$	2-Octanone	445.70	632.70	633.05	0.05
	$C_9H_{18}O$	2-Nonanone	468.50	652.20	655.06	0.44
	$C_{10}H_{20}O$	2-Decanone	483.00	671.80	668.70	−0.46
	$C_{11}H_{22}O$	2-Undecanone	504.70	688.00	688.63	0.09
	$C_{12}H_{24}O$	2-Dodecanone	519.70	702.00	702.07	0.01
	$C_{13}H_{26}O$	2-Tridecanone	536.00	717.00	716.37	−0.09
	$C_{14}H_{28}O$	2-Tetradecanone	549.5*	728.00		
7B	3-Pentanone					
	$C_5H_{10}O$	3-Pentanone	374.90	561.40	560.12	−0.23
	$C_6H_{12}O$	3-Hexanone	396.70	583.00	583.56	0.10
	$C_7H_{14}O$	3-Heptanone	420.00	606.60	607.82	0.20
	$C_8H_{16}O$	3-Octanone	440.70	627.70	628.72	0.16
	$C_9H_{18}O$	3-Nonanone	463.00	648.10	650.59	0.38
	$C_{10}H_{20}O$	3-Decanone	476.00	667.60	663.03	−0.68
	$C_{11}H_{22}O$	3-Undecanone	500.00	685.00	685.45	0.07
	$C_{12}H_{24}O$	3-Dodecanone	517.1*	701.00		
	$C_{13}H_{26}O$	3-Tridecanone	534.0*	716.00		
	$C_{14}H_{28}O$	3-Tetradecanone	546.6*	727.00		

(*continued*)

Table 2. Continued.

Group	Formula	Name	T_b obs.	T_c obs.	T_c calcd.	Percent error
7C	4-Heptanone					
	$C_7H_{14}O$	4-Heptanone	417.00	602.00	603.00	0.17
	$C_8H_{16}O$	4-Octanone	436.00	623.80	621.65	−0.34
	$C_9H_{18}O$	4-Nonanone	460.70	643.70	645.12	0.22
	$C_{10}H_{20}O$	4-Decanone	479.70	662.90	662.62	−0.04
	$C_{11}H_{22}O$	4-Undecanone	500.2*	681.00		
	$C_{12}H_{24}O$	4-Dodecanone	518.6*	697.00		
	$C_{13}H_{26}O$	4-Tridecanone	536.3*	712.00		
	$C_{14}H_{28}O$	4-Tetradecanone	551.9*	725.00		
7D	5-Nonanone					
	$C_9H_{18}O$	5-Nonanone	461.60	641.40	642.97	0.24
	$C_{10}H_{20}O$	5-Decanone	477.00	661.00	658.14	−0.43
	$C_{11}H_{22}O$	5-Undecanone	500.00	679.00	680.28	0.19
	$C_{12}H_{24}O$	5-Dodecanone	515.7*	695.00		
	$C_{13}H_{26}O$	5-Tridecanone	531.9*	710.00		
	$C_{11}H_{22}O$	6-Undecanone	501.00	678.00	681.23	0.48
	$C_{12}H_{24}O$	6-Dodecanone	514.6*	694.00		
	$C_{13}H_{26}O$	6-Tridecanone	530.8*	709.00		
8	Alkanals					
	C_3H_6O	Propanal	321.00	505.00	495.06	(−1.97)
	C_4H_8O	Butanal	348.00	537.00	527.96	(−1.68)
	$C_5H_{10}O$	Pentanal	376.00	567.00	560.96	(−1.07)
	$C_6H_{12}O$	Hexanal	404.00	592.00	592.89	0.15
	$C_7H_{14}O$	Heptanal	426.00	617.00	617.25	0.04
	$C_8H_{16}O$	Octanal	444.00	639.00	636.72	−0.36
	$C_9H_{18}O$	Nonanal	464.00	659.00	657.90	−0.17
	$C_{10}H_{20}O$	Decanal	481.70	674.00	676.25	0.33
9	Ethers					
	C_2H_6O	Dimethyl ether	248.40	400.20	396.14	(−1.02)
	C_3H_8O	Ethyl methyl ether	280.60	437.90	437.59	−0.07
	$C_4H_{10}O$	Methyl propyl ether	312.30	476.20	476.64	0.09
	$C_5H_{12}O$	butyl methyl ether	343.31	512.78	513.27	0.10
	$C_6H_{14}O$	Methyl pentyl ether	372.00	546.50	545.85	−0.12
10	Alkanoic acids					
	CH_2O_2	Formic acid	374.00	588.00	542.31	(−7.77)
	$C_2H_4O_2$	Acetic acid	391.10	590.70	562.17	(−4.83)
	$C_3H_6O_2$	Propanoic acid	414.30	598.50	588.57	(−1.66)
	$C_4H_8O_2$	Butanoic acid	436.90	615.20	613.70	−0.24
	$C_5H_{10}O_2$	Pentanoic acid	459.30	637.20	638.06	0.14
	$C_6H_{12}O_2$	Hexanoic acid	478.40	655.00	658.41	0.52
	$C_7H_{14}O_2$	Heptanoic acid	495.40	678.00	676.21	−0.26
	$C_8H_{16}O_2$	Octanoic acid	512.00	693.00	693.30	0.04
	$C_9H_{18}O_2$	Nonanoic acid	527.70	712.00	709.22	−0.39
	$C_{10}H_{20}O_2$	Decanoic acid	541.90	722.00	723.42	0.20
	$C_{11}H_{22}O_2$	Undecanoic acid	546.5*	728.00		
	$C_{12}H_{24}O_2$	Dodecanoic acid	561.8*	743.00		
	$C_{14}H_{28}O_2$	Tetradecanoic acid	582.5*	763.00		
	$C_{15}H_{30}O_2$	Pentadecanoic acid	597.3*	777.00		
	$C_{16}H_{32}O_2$	Hexadecanoic acid	605.8*	785.00		
	$C_{17}H_{34}O_2$	Heptadecanoic acid	613.3*	792.00		

(*continued*)

Table 2. Continued.

Group	Formula	Name	T_b obs.	T_c obs.	T_c calcd.	Percent error
	$C_{18}H_{36}O_2$	Octadecanoic acid	625.2*	803.00		
	$C_{20}H_{40}O_2$	Eicosanoic acid	643.8*	820.00		
	$C_{22}H_{44}O_2$	Docosanoic acid	662.8*	837.00		
11	Alkyl acetates					
	$C_3H_6O_2$	Methyl-acetate	330.02	506.50	501.19	(−1.05)
	$C_4H_8O_2$	Ethyl-acetate	350.26	523.30	523.60	0.06
	$C_5H_{10}O_2$	Propyl-acetate	374.69	549.70	549.73	0.01
	$C_6H_{12}O_2$	Butyl-acetate	399.30	575.60	575.09	−0.09
	$C_7H_{14}O_2$	Pentyl-acetate	422.40	599.00	598.07	−0.16
	$C_8H_{16}O_2$	Hexyl-acetate	444.70	618.40	619.52	0.18
12	Alkylamines					
	CH_5N	Methylamine	266.83	430.70	426.18	(−1.05)
	C_2H_7N	Ethylamine	289.70	456.00	456.46	0.10
	C_3H_9N	Propylamine	320.37	497.00	495.79	−0.24
	$C_4H_{11}N$	Butylamine	350.15	531.90	532.67	0.14
	$C_6H_{15}N$	Hexylamine	402.00		594.0*	
13	Alkylnitriles					
	C_2H_3N	Acetonitrile	354.80	545.60	544.34	−0.23
	C_3H_5N	Propanenitrile	370.29	561.30	561.95	0.12
	C_4H_7N	Butanenitrile	390.80	585.40	584.69	−0.12
	C_5H_9N	Pentanenitrile	414.50	610.30	610.18	−0.02
	$C_6H_{11}N$	Hexanenitrile	436.80	633.80	633.42	−0.06
	$C_8H_{15}N$	Octanenitrile	478.40	674.40	674.98	0.09
14	Alkylthiols					
	CH_4S	Methanethiol	279.10	470.00	464.20	(−1.23)
	C_2H_6S	Ethanethiol	308.20	499.00	499.27	0.05
	C_3H_8S	1-Propanethiol	341.00	537.00	536.68	−0.06
	$C_4H_{10}S$	1-Butanethiol	371.70	570.00	569.81	−0.03
	$C_8H_{18}S$	1-Octanethiol	472.30	667.00	667.26	0.04
15	Chloroalkanes					
	CH_3Cl	Chloromethane	249.06	416.25	415.84	−0.10
	C_2H_5Cl	Chloroethane	285.50	460.40	461.88	0.32
	C_3H_7Cl	1-Chloropropane	319.70	503.00	502.56	−0.09
	C_4H_9Cl	1-Chlorobutane	351.60	539.20	538.48	−0.13
	$C_5H_{11}Cl$	1-Chloropentane	381.60	571.20	570.62	−0.10
	$C_6H_{13}Cl$	1-Chlorohexane	408.30	599.00	597.97	−0.17
	$C_7H_{15}Cl$	1-Chloroheptane	433.60	614.00	622.87	(1.44)
	$C_8H_{17}Cl$	1-Chlorooctane	456.70	643.00	644.78	0.28
16	Perfluoroalkanes					
	CF_4	Tetrafluoromethane	145.20	227.60	227.13	−0.20
	C_2F_6	Hexafluoroethane	195.10	293.00	293.73	0.25
	C_3F_8	Perfluoropropane	236.60	345.10	345.42	0.09
	C_4F_{10}	Perfluorobutane	271.30	386.40	386.30	−0.03
	C_5F_{12}	Perfluoropentane	302.40	420.59	421.26	0.16
	C_6F_{14}	Perfluorohexane	329.80	448.77	450.83	0.46
	C_7F_{16}	Perfluoroheptane	355.70	474.80	477.78	0.63
	C_8F_{18}	Perfluorooctane	379.10	502.00	501.34	−0.13
	C_9F_{20}	Perfluorononane	398.50	524.00	520.32	−0.70
	$C_{10}F_{22}$	Perfluorodecane	417.40	542.00	538.36	−0.67

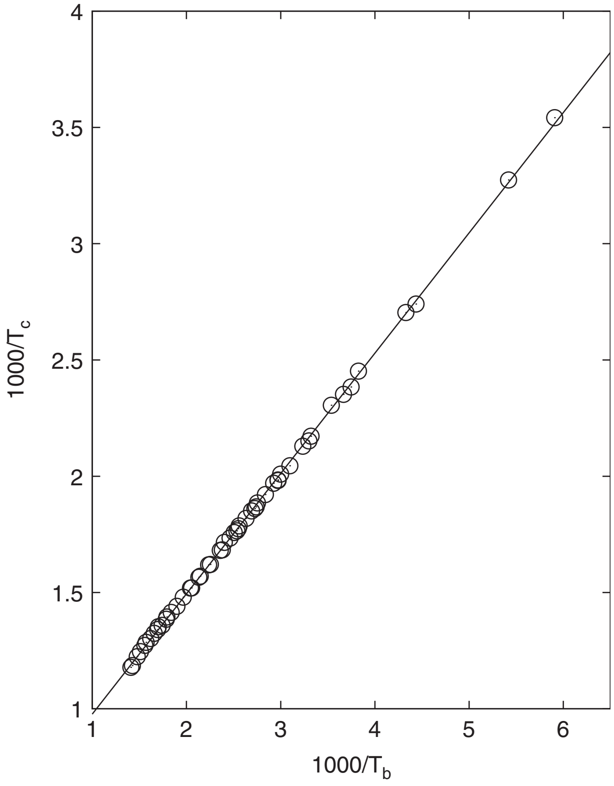

Figure 7. $1000/T_c$ *vs.* $1000/T_b$ for alkanes, branched alkanes and alkenes all taken together.

methods which are available. It has the simplicity of requiring only the boiling point of a compound, though of course it has the limitation that T_b and T_c should be known for at least two members of the same series. To a certain extent this limitation can be reduced if we combine together similar homologous series. We illustrate this method by taking together all members of series numbers 1, 2 and 3, that is, alkanes, branched alkanes and alkenes. In Figure 7, we show the result. It will be noticed that it still gives a fairly good straight line, but the errors are a little higher, the average percent error is now 0.36%, as compared to 0.20%, when the various series are considered separately. These errors have been calculated excluding the compounds whose errors are shown in parenthesis in Table 2.

Most of the group contribution methods require a knowledge of the boiling points and sometimes their use requires a large number of data for various types of groups, for example, Somayajulu's method [15] has no less than 144 types of groups for organic compounds.

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