Reliability Analysis of Group-Contribution Methods in Predicting Critical Temperatures of Organic Compounds

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This article examines four group-contribution methods (Joback–Reid, Constantinou–Gani, Wilson–Jasperson, and Marrero–Pardillo) with respect to their abilities for calculating critical temperatures (T_c) of organic compounds on the basis of the parameters published in the original papers. To have a reliable data set for this examination, all experimental data of T_c collected in the SOURCE data system at the Thermodynamics Research Center (TRC) were evaluated. This data system contains more than 1900 T_c data points for about 630 organic compounds from which we compiled a selected T_c data set involving 510 compounds with uncertainty less than or equal to 5 K. Upon reviewing the normal boiling point (NBP) values for the same 510 compounds, we selected a NBP data set including 448 compounds with uncertainty less than or equal to 3 K for use in the T_c calculations. We then compared the selected T_c values with the values calculated by the four group-contribution methods on the basis of either selected or estimated NBP data. Particularly, we selected 71 compounds that were not included in the development of the parameters for the four models, and we used them to examine the predictive abilities of the models. The deviations of the calculated T_c data were categorized by compound types.

Introduction

Critical temperature (T_c) is one of the fundamental physicochemical properties frequently used in various industrial and scientific applications. However, up-to-date information stored in the TRC SOURCE data system[1,2] indicates that critical temperatures have been measured for only about 630 organic compounds. SOURCE has been developed at the Thermodynamics Research Center (TRC) with the aim of collecting all formally published experimental physicochemical property data.

Experimental T_c data of organic compounds are so limited due to the fact that many compounds become unstable during the measurements near or even far from the vicinity of the critical point. Accordingly, estimation methods play a key role for obtaining critical property data. The most prevalent technology adapted in estimating critical-property data in various applications including chemical-process design is the group-contribution method. In this paper we shall examine the reliability of group-contribution methods in predicting critical temperatures of various classes of organic compounds.

Upon the basis of our review of the current state of physicochemical property estimation, reports are scarce in providing evaluations on the predictive ability of models. Some major problems of model evaluation are summarized below:

(1) The purpose of developing a model should be to predict the physicochemical properties when no experimental data exist. However, there is little research conducted on model capability in predicting the properties of compounds that were not used in parameter optimizations of the model.

(2) The data sets used for testing model abilities are too small to be conclusive. Some studies examined models using a data set that is not much greater or even smaller than that used in determining the parameters of models.[3] Generally, there is lack of clarification about how many compounds in a testing set were used in model development.

(3) Some calculated data that are not related to the prediction ability of models are included in evaluations. For example, some models have special parameters for methanol,[4,5] and these parameters cannot be used to calculate T_c data of any other compounds. As a result, the deviations for methanol obtained from the models can be very close or equal to zero. Obviously, including such kind of data can make the models look better than they really are.

To establish a reliable data set for this study, we evaluated all experimental data of T_c and a portion of the normal boiling point (NBP) data stored in the TRC SOURCE data system, which currently contains more than 1900 data points of critical temperature for 630 organic compounds published from 1822 to the present.

This work is a part of an ongoing project, the TRC Integrated Information System (TIIS), which consists of evaluated property data, models, and knowledge. Models for other properties are being or will be evaluated and integrated into TIIS. It also relates to another project currently taking place, Data Quality Assurance (DQA) for the TRC Source Data system.[6] Generally, there is a 2 to 5% deviation range in a large experimental database without critical reviews. Under the DQA project, a systematic examination is being carried out periodically on all experimental values in the data system on the basis of thermodynamics theories and models. As a result, a list of anomalous values is carefully reviewed against original articles and other reliable data sources. In assisting this process, a reliable model can be a powerful tool to identify and verify anomalous values if the model is capable of producing reliable predictions and never ridiculous values. For example, data calculated from models are used as a range reference, and any data that are far from these of reliable models are to be examined.

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Over the years, a variety of models have been developed to calculate critical properties of organic compounds: Lydersen (1955),[7] Ambrose (1978, 1980),[8,9] Joback and Reid (JR, 1984, 1987),[10,11] Constantinou and Gani (CG, 1994),[12] Wilson and Jasperson (WJ, 1996),[13,15] Marrero and Pardillo (MP, 1999),[5] and Marrero and Gani (2001).[14] Among them, four group-contribution methods were selected in this study: JR, CG, WJ, and MP, considering their representation of four distinctive types of models as well as our preference for newly developed models. Introductions and discussions on the four methods can be found in *The Properties of Gases and Liquids* (2001).[15] JR can be considered as a pure group-contribution method, in that it uses 41 functional groups and no corrections related to substructures or interactions among the groups. In nature, WJ is an atom-contribution method, which permits its calculation power spanning all organic compounds as well as inorganic compounds. For common organic compounds it needs only 10 atomic parameters to form its major part as the first level. Its second level consists of 11 corrections for special functional groups or substructures, which contribute some improvement to the model's capability. MP, described as a "group-interaction-contribution-method", incorporates the elements of the group scheme and the substructure scheme. Each MP group is constructed by connecting two commonly used functional groups via a chemical bond. MP provided 167 such groups for computing critical properties, normal boiling points, and melting points. CG is a relatively complex method consisting of contributions at two levels. The first level consists of 78 functional groups, while the second level refers to a variety of corrections for different substructures.

Method

Data Set. More than 1900 measured T_c data for 630 organic compounds in the TRC SOURCE data system were evaluated. As a result, a set of selected data of 510 compounds was formed. This data set was also partly the result of an exchange of information with the IUPAC Commission I.2 on Thermodynamics, whose results have been published in a series of review articles on critical properties since 1995.[16]

Since most of the models, such as JR, WJ, and MP, use NBP values for T_c calculations, we prepared a data set with selected NBP values for 448 compounds by the same procedures designed for T_c data. The two sets of selected data (T_c and NBP) form an essential foundation for this study.

In generating the selected data set, there are two distinct cases that need to be handled. One is that there are many duplicate measurements (in so-called multiple data points in the paper) for a particular compound, and another is that there are few measurements. The following principles were adopted in dealing with different cases.

(1) For compounds with multiple data points, a weighted-average method[6] was used to process selected values. The method is based on several weight factors, among which, besides a primary weight factor (numerical uncertainty), some additional weight factors (year of publication, sample purity, and experimental objective) are also contributing factors in calculating a weighted-average value. The factors are adopted in consideration of possible major problems involving greater deviations, missing uncertainty values, and incorrectly assigned uncertainties, presented in a noncritically evaluated data set.

(2) For compounds with only single or few experimental values, inspection was performed through (a) a thermody-

namics relationship such as the ratio of T_c and NBP, (b) values of similar compounds, (c) comparison of the values with those from group-contribution methods, or (d) comparison of other well-characterized sources.

(3) Original articles related to questionable data were reviewed.

A general assessment was made of the uncertainties of the selected T_c and NBP, in which the compounds with T_c uncertainties greater than 5 K or with NBP uncertainties greater than 3 K were excluded. For the T_c data, uncertainties of 86% of the selected compounds are less than or equal to 2 K, while, for the NBP data, uncertainties of 88% of the selected compounds are less than or equal to 1 K. According to our calculation, the average uncertainty of the selected NBP data is about 0.76 K, and it is 1.2 K for the selected T_c data. In generating selected NBP values, both experimental NBP and vapor pressure data in TRC SOURCE were used, and the selected NBP values of over 90% of the compounds were generated from two or more experimental data.

Model Examination. A comparison of models can be conducted on the basis of the same or different conditions, which would yield a significant difference on the compared results. A comparison based on the same conditions means parameters of all involved models are processed from the same data set and even the same processing method; otherwise, the comparison is based on different conditions. More specifically, although models may be similar in nature, one model can provide much better results compared to another simply because of the model parameters. In generating model parameters, the quantity and quality of experimental data play a decisive role in ensuring the quality of parameters. From a different-condition comparison, no complete conclusion can be drawn with respect to a model's functionality. Both comparisons are indispensable because the same-condition comparison reveals in nature the advantage or disadvantage of a model, while the different-condition comparison indicates which model is more applicable on the basis of available parameters. This study was based on the different-condition comparison, and the parameters used in these models were basically from the original papers.

In the evaluation process, some methods were adopted for investigating the characteristics of each group-contribution method. First, for the three methods (JR, WJ, and MP) that need NBP data in the T_c calculation, we utilized two sets of the NBP values, the selected NBP values and the estimated NBP values, to examine the models. Second, we made two types of comparisons on the models. One showed the general calculation capability of the models in calculating T_c values on the basis of either the selected or the estimated NBP data. Another probed the predictive ability of the models by comparing with a data set of 75 compounds, all of which were initially published in the literature after the JR, CG, and WJ models had been reported. The MP model, though published more recently, utilized data exclusively from Reid et al. (1987).[17] Third, some compounds were excluded from the testing data set due to the fact that there were special parameters assigned to them in the models. In this study, fourteen compounds, CH_3F, CH_3CHO, CH_3Cl, CH_3CN, CH_3NH_2, CH_3NO_2, CH_3OH, CH_3SH, CH_3CCH, C_2H_2, C_2H_4, C_2H_6, $HCOOH$, and CH_3COOH, were not included in the testing data set for the MP method, while, for the CG method, C_2H_6 was not included. In an attempt to make a fair comparison between the CG method and others, CG's calculations were only compared with those of the others when the estimated NBP

Table 1. Classes of Compounds, Number (*n*) of Compounds of Each Class, and Average Absolute Deviations (AAD/K) of Estimated NBP by JR, CG, and MP

compound class	JR		CG		MP	
	n	AAD/K	*n*	AAD/K	*n*	AAD/K
alkanes (including cycloalkanes)	70	10.0	69	5.5	67	5.0
alkenes (including cycloalkenes)	49	13.0	47	6.0	46	5.9
alkynes	2	17.6	1	8.6		
halogen containing	71	18.8	66	26.2	68	10.3
alcohols	67	15.3	67	10.4	66	10.7
ethers	31	9.4	27	15.6	30	4.2
ketones	31	6.4	30	9.8	30	2.9
aldehydes	8	9.5	8	10.3	7	2.8
acids	12	11.2	12	1.2	11	9.4
esters	30	9.2	30	9.3	26	2.8
amines	23	22.4	20	12.1	20	5.9
heterocyclic nitrogen containing	10	9.1	9	15.2	10	3.2
nitriles	8	8.1	5	5.4	7	2.3
−S−, −SH containing	11	13.0	7	12.9	7	1.2
halogen−oxygen containing	25	20.0	18	40.2	21	14.0
total	448	13.4	416	13.0	418	6.9

values were used, because CG does not require NBP data as input.

All of the compounds used in the study were classified into 15 groups: (1) alkanes and cycloalkanes, (2) alkenes and cycloalkenes, (3) alkynes, (4) halogen-containing compounds, (5) alcohols, (6) ethers, (7) ketones, (8) aldehydes, (9) acids, (10) esters, (11) amines, (12) heterocyclic nitrogen-containing compounds, (13) nitriles, (14) −S− and −SH, and (15) halogen−oxygen-containing compounds. The general classification is made unsophisticated to simplify variety examinations on the models, taking into account the fact that many compounds contain more than one functional group. It is worth noting that the halogen−oxygen-containing compounds were distinguished from other types given the fact that both kinds of elements have a significant impact on the thermodynamic properties of organic compounds. Considering that some models produce larger deviations for halogen-containing compounds, we analyzed this class of compounds in light of the number of halogen atoms per molecule. A comparison of the calculated T_c values between cyclic and noncyclic compounds was also provided.

An average absolute deviation (AAD) between the calculated and the selected data was defined as a criterion for model evaluations. The AAD can be expressed as

For NBP

$$AAD = \{\sum |NBP_i(calc) - NBP_i(recommend.)|\}/n \quad (1)$$

For Tc

$$AAD = \{\sum |T_{ci}(calc) - T_{ci}(recommend.)|\}/n \quad (2)$$

Here, *n* is the number of total compounds and *i* indicates the *i*-th compound. The sum is from 1 to *n*.

Procedure. An automated computing procedure for the four group-contribution methods was established in this work. More than 14 000 chemical structures are stored in two forms in TRC SOURCE: structure image and connectivity table. The Chemical Abstract Service Registry Number (CASRN) was utilized to identify compounds in the testing data sets and then to search for the corresponding connectivity tables from the data system. In the following, the captured connectivity table was transformed into an adjacency matrix.[18] The ring types and number presented in each structure are recognized. Particular groups were formed on the basis of the group definitions of each model, and their type and numbers are accounted

Table 2. Ranges of Absolute Deviations (dev/K) of Estimated NBP Data by JR, CG, and MP and Number of Compounds in Each Deviation Range

dev/K	JR	CG	MP
dev ≤ 2	68	87	111
2 < dev ≤ 5	76	91	119
5 < dev ≤ 10	90	88	97
10 < dev ≤ 20	112	89	71
20 < dev ≤ 30	58	18	8
dev > 30	44	43	12
total	448	416	418

for as well. It is worthwhile to note that the whole process involves some sophisticated algorithms in fragmenting, in analyzing a variety of structures and substructures, and in constructing the concrete groups specified in each model. In the end, T_c values were calculated by associating the retrieved parameters and the analyzed groups.

Calculation Results

Normal Boiling Point (NBP). The accuracy of estimated NBP data has a significant impact on that of the T_c values calculated through group-contribution methods when no experimental NBP data are available. Thus, we examined the JR, CG, and MP methods with respect to their abilities in calculating NBP. WJ is incapable of generating NBP data, though it uses NBP data as an input argument.

Table 1 shows the distributions of average absolute deviation (AAD/K) of the NBP data calculated by JR, CG, and MP, involving 15 compound classes. In reading the table, the features of the above models were obtained as follows: (1) Among the three models, MP produced the most accurate result overall, with an AAD of 6.9 K covering 418 compounds. (2) JR covered a wider range of compounds compared with those of the other two models. (3) CG produced good NBP values for alkanes, alkenes, and acids. Nevertheless, CG's AAD is not much better than that of JR. A further study shows that halogen and halogen−oxygen-containing compounds caused the higher AAD of CG.

An analysis was made in Table 2 of exploring the functionality of the three models with respect to different deviation ranges and the number of compounds within each range. From Table 2 it can be calculated that the probabilities of generating a deviation of less than or equal to 10 K of NBP data by the JR, CG, and MP methods are 0.52, 0.64, and 0.78, respectively.

Table 3. Ranges of Deviations (dev/K) of the T_c Calculated by JR, WJ, MP, and CG (Based on the Selected and Estimated NBP) and Number of Compounds in Each Range[a]

dev/K	A			B			C
	JR	WJ	MP	JR	WJ	MP	CG
dev ≤ 2	133	132	180	49	51	92	96
2 < dev ≤ 5	129	110	125	56	95	133	94
5 < dev ≤ 10	89	123	52	77	114	106	114
10 < dev ≤ 20	66	68	38	140	152	98	74
20 < dev ≤ 30	16	13	12	79	42	26	27
dev > 30	15	2	11	109	24	23	69
total number	448	448	418	510	478	478	474
AAD, K	6.9	5.9	5.2	21.1	11.5	9.4	17.1
max dev, K	56.4	31.0	48.8				

[a] Note: For A, T_c was calculated with the selected NBP. For B, it was calculated with the estimated NBP. For C, no NBP data were used in CG.

Table 4. Ranges of Deviations (dev/K) of the T_c Predicted by JR, WJ, CG, and MP for the Compounds with Experimental Data Reported between 1996 and 2001, and Number of Compounds in Each Range (Based on the Selected and Estimated NBP)

dev/K	A			B			C
	JR	WJ	MP	JR	WJ	MP	CG
dev ≤ 2	7	9	0	11	3	5	8
2 < dev ≤ 5	11	6	10	7	17	9	8
5 < dev ≤ 10	12	19	6	8	7	12	10
10 < dev ≤ 20	4	4	3	17	26	22	14
20 < dev ≤ 30	2	5	3	8	6	9	6
dev > 30	7	0	5	20	5	7	22
total number	43	43	37	71	64	64	68
AAD/K	12.0	8.0	11.0	24.3	13.0	15.7	32.1

[a] Note: For A, T_c was calculated with the selected NBP. For B, it was calculated with the estimated NBP. For C, no NBP data were used in CG.

Critical Temperature (T_c). NBP values are required to calculate T_c values in most group-contribution methods. The NBP values obtained from MP were adopted in the WJ method under consideration because it does not have the function to calculate NBP and, in general, MP generates the most accurate NBP data. Consequently, the calculated T_c results from both WJ and MP covered the same set of compounds where the estimated NBP data were adopted. Of four models, only CG does not require NBP in T_c calculations.

Tables 3 and 4, analogous to Table 2, present the analysis on T_c values in regard to different deviation ranges and compound coverage within each range. There are two categories labeled "selected NBP" and " estimated NBP" in each table. For each given deviation range, the corresponding compound coverage of the models is listed. At the bottom of the tables are statistical data on the total number of compounds, and the average absolute deviation calculated by each model.

Although the same strategy was employed in the analysis depicted in Tables 3 and 4, they differ in their testing purpose. Table 3 focuses on the overall computing functionalities of the models, while Table 4 attempts to probe their predictive abilities by comparing the calculated T_c values with the experimental T_c values of over 71 compounds reported between 1996 and 2001.

Table 5 presents calculated values for cyclic and noncyclic compounds. Apparently, there is an insignificant difference in the distribution of average absolute deviation (AAD) for cyclic and noncyclic compounds, especially for the data calculated with the selected NBP. Hence, no further analysis of the AAD distribution between the cyclic and noncyclic compounds was performed.

Tables 6 and 7 present the AAD distributions of the calculated T_c data for 15 compound classes using either the selected or the estimated NBP data. A comparison of both tables confirms the key role that NBP data play. In Table 6, where the selected NBP data were used, the accuracies of the JR, WJ, and MP models were reasonably good. On the contrary, Table 7 shows that the deviations became much larger by using the estimated NBP data. Note that in Table 6 the AAD values are 6.9 K (JR), 5.9 K (WJ), and 5.2 K (MP), while in Table 7 the AAD values are 21.2 K (JR), 11.5 K (WJ), and 9.4 K (MP), respectively. These data show that the corresponding increases in deviation are 200% (JR), 95% (WJ), and 81% (MP), when using the estimated NBP instead of the selected NBP.

Considering large deviations of T_c values for the halogen-containing compounds when the estimated NBP data were used, we carried out more analyses on them, results of which are given in Tables 8 and 9. It can be seen from Table 8 that large deviations occur for compounds containing more than two halogen atoms.

The relationships between number of carbon atoms and the AAD values of alkane, alkene, and alkyne-chain compounds are summarized in Table 10. It is interesting to see that the deviations obtained from the JR, CG, and MP methods do not correspond to the changes in carbon atom numbers. Unlike them, deviations from WJ become larger in accordance with an increase of carbon atom number.

As we discussed so far, all tests on the four models were carried out with a different number of compounds due to each model's distinct availability and applicability. Nevertheless, it is interesting to compare the four models by using the same number of compounds. Therefore, 400 compounds, which are applicable for all four models, were used for this comparison. The calculated average deviations of T_c are 7.1, 5.8, 15.4, and 5.3 K for JR, WJ, CG, and MP, respectively (for JR, WJ, and MP, selected NBP data were used).

In the Supporting Information we present the values of selected T_c and NBP, as well as calculated values by JR, WJ, and MP for 448 compounds for which there are reliable NBP data.

Table 5. Number (n) of Cyclic and Noncyclic Compounds and Their Average Absolute Deviations (AAD/K) of the T_c Values Calculated by JR, WJ, MP, and CG

compound	NBP	JR		WJ		MP		CG[a]	
		n	AAD/K	n	AAD/K	n	AAD/K	n	AAD/K
noncyclic	selected	332	7.4	332	5.6	312	5.7		
cyclic	selected	116	5.6	1166.6	106	3.9			
noncyclic	estimated	68	22.5	346	10.7	346	8.5	347	16.4
cyclic	estimated	142	17.8	132	13.5	132	11.6	127	19.0

[a] No NBP data used in CG.

Table 6. Classes of Compounds, Number (n) of Compounds of Each Class, and Average Absolute Deviations (AAD/K) of the T_c Values Calculated by JR, WJ, and MP on the Basis of the Selected NBP Values

	JR		WJ		MP	
compound class	n	AAD/K	n	AAD/K	n	AAD/K
alkanes (including cycloalkanes)	70	2.6	70	7.2	69	1.8
alkenes (including cycloalkenes)	49	4.3	49	4.2	45	2.7
alkynes	2	13.0	2	10.0		
halogen containing	71	5.3	71	5.1	68	3.5
alcohols	67	18.3	67	7.9	66	14.9
ethers	31	3.9	31	5.5	30	2.2
ketones	31	8.1	31	4.1	29	5.8
aldehydes	8	12.5	8	9.7	7	5.6
acids	12	8.7	12	6.9	11	7.5
esters	30	3.2	30	3.7	26	2.4
amines	23	4.3	23	5.3	20	3.7
heterocyclic nitrogen containing	10	2.4	10	3.9	10	1.0
nitriles	8	7.7	8	7.3	7	7.6
$-S-$, $-SH$ containing	11	4.9	11	6.3	7	0.4
halogen$-$oxygen containing	25	6.5	25	5.5	21	6.4
summary	448	6.9	448	5.9	418	5.2

Table 7. Classes of Compounds, Number (n) of Compounds of Each Class, and Average Absolute Deviations (AAD/K) of the T_c Data Calculated by JR, WJ, MP, and CG on the Basis of the Estimated NBP Values

	JR		WJ		MP		CG[a]	
compound class	n	AAD/K	n	AAD/K	n	AAD/K	n	AAD/K
alkanes (including cycloalkanes)	71	16.6	70	12.9	70	7.2	70	7.3
alkenes (including cycloalkenes)	49	22.0	46	11.7	46	8.8	47	8.8
alkynes	2	42.8	1	0.0				
halogen containing	107	26.9	103	14.4	103	14.8	101	32.9
alcohols	75	16.8	74	13.4	74	8.4	75	11.1
ethers	31	15.7	30	9.1	30	6.0	27	18.6
ketones	40	11.8	39	3.5	39	4.2	39	5.2
aldehydes	9	27.2	8	8.8	8	3.0	9	7.3
acids	12	19.7	11	11.4	11	10.7	12	7.0
esters	33	13.2	29	6.1	29	5.0	33	12.8
amines	23	34.2	20	10.6	20	8.8	20	18.9
heterocyclic nitrogen containing	10	15.7	10	8.4	10	4.8	9	25.5
nitriles	8	8.7	7	5.4	7	5.7	5	2.8
$-S-$, $-SH$ containing	11	20.4	7	4.1	7	1.7	7	15.4
halogen$-$oxygen containing	29	41.7	24	18.4	24	21.6	19	53.3
summary	510	21.2	478	11.5	478	9.4	474	17.1

[a] No NBP data used in CG.

Table 8. Number (m) of Halogen Atoms in Each Compound, Number (n) of Compounds, and Average Absolute Deviations (AAD/K) of the T_c Calculated by JR, WJ, MP, and CG on the Basis of the Estimated NBP Values

	JR		WJ		MP		CG[a]	
m	n	AAD/K	n	AAD/K	n	AAD/K	n	AAD/K
0	374	18.0	351	10.2	351	6.9	354	10.6
1 or 2	42	19.8	40	9.4	40	11.2	40	12.6
3 or 4	40	36.4	37	22.4	37	23.3	35	52.4
5 or 6	24	37.0	23	15.3	23	15.9	21	43.7
>6	30	30.6	27	13.6	27	13.7	24	45.0

[a] No NBP data used in CG.

Table 9. T_c Deviation Ranges (dev/K) of Halogen-Containing Compounds Calculated by JR, WJ, MP, and CG on the Basis of the Selected and Estimated NBP[a]

	A			B			C
dev/K	JR	WJ	MP	JR	WJ	MP	CG
dev $\leq$ 2	17	19	38	14	10	8	21
2 < dev $\leq$ 5	26	24	23	11	20	20	8
5 < dev $\leq$ 10	20	17	4	9	12	17	17
10 < dev $\leq$ 20	7	10	1	19	35	30	14
20 < dev $\leq$ 30	0	1	0	17	15	20	5
dev > 30	1	0	2	37	11	8	36
total	71	71	68	10	103	103	101
AAD/K	5.3	5.1	3.5	26.9	14.4	14.8	32.9

[a] Note: For A, T_c was calculated with the selected NBP. For B, it was calculated with the estimated NBP. For C, no NBP data were used in CG.

Discussion

Obviously, the reliability of the data set used to examine the models plays a very important role in generating the rational report on test results. Therefore, we have taken extra care in studying and determining uncertainties of NBP and T_c values, and on the basis of this information, the selected data sets were formed in the investigation. Among the selected data, the NBP values with uncertainty larger than 3 K and T_c data with uncertainty larger than 5 K were excluded. Specifically, there is only a small portion of compounds that have larger uncertainties in our selected NBP and T_c data sets. The average uncertainty of the selected NBP is 0.76 K; its impact on the uncertainty of the calculated T_c should be small. For the selected T_c, the average uncertainty is 1.2 K, which is only a small proportion of the average deviations of T_c calculated by the four models, and should not cause a significant uncertainty on the result of this evaluation. Having excluded the compounds with large uncertainty, there is no evidence to indicate the existence of a relationship between the uncertainties of the selected Tc data and the deviations of T_c calculated by the models.

Table 10. Number (m) of Carbon Atoms of Noncyclic Alkane, Alkene, and Alkyne Compounds, Number (n) of Compounds for Each Given m, and Average Absolute Deviations (AAD/K) of the T_c Calculated by JR, WJ, MP, and CG[a]

		A			B			C
		JR	WJ	MP	JR	WJ	MP	CG
m	n	AAD/K	AAD/K	AAD/K	AAD/K	AAD/K	AAD/K	AAD/K
3	3	4.1[b]	2.8[b]	1.0	45.4[b]	8.8	7.7	13.8
4	7	2.3	1.2	1.6	34.3	7.0	8.1	5.9
5	6	4.2	2.8	2.7	21.1	3.5	6.5	5.7
6	6	1.1	4.4	1.2	7.4	4.6	2.5	3.6
7	10	1.7	6.3	1.5	9.5	8.5	2.8	4.6
8	18	2.1	7.9	1.7	12.5	11.8	3.0	5.1
9	9	3.0	12.3	1.3	15.6	15.3	4.4	6.0
10	5	2.7	11.2	1.1	20.8	13.2	6.3	6.3

[a] Note: For A, T_c was calculated with the selected NBP. For B, it was calculated with the estimated NBP. For C, no NBP data were used in CG. [b] Four compounds were used in these calculations.

This study shows that when reliable NBP data are available, JR, WJ, and MP can produce reasonably good T_c values for most kinds of compounds studied here, except for certain compounds that are very branched or contain multiple functional groups; see the Supporting Information. Particularly, JR and MP are quite reliable for alkanes, alkenes, ethers, esters, and so forth.

The method of JR (Joback and Reid) demonstrated a satisfactory result when the selected NBP values were used. Nevertheless, it produced the largest deviations in both T_c and NBP calculations. The larger deviations from JR may partially relate to the smaller experimental data set from which the model was developed in the early 1980s. Moreover, when the NBP values that were estimated by JR itself were used, the average deviation of calculated T_c values increased greatly compared to those using the selected NBP data. Considering that the MP method generates more accurate NBP values, it is interesting to know the deviation of T_c calculated by JR with the NBP values estimated by MP. In conducting such a test, an average deviation of 10.7 K was yielded by JR for 478 compounds. This deviation is even smaller than that generated by WJ (11.5 K). The test shows that with a reliable NBP the JR model is able to perform reasonably well.

On the whole, CG performed slightly better than JR in NBP and T_c calculations. It should be noted that CG does not need NBP data in T_c calculations. This gives CG the advantage over the other models in terms of availability and reliability of NBP data. Another advantage of the CG method is its ability to handle alkane and alkene classes, as shown in Table 7. In handling alkanes, for correcting group interactions, the CG method specifies five substructures [$CH(CH_3)_2$, $C(CH_3)_3$, $CH(CH_3)CH(CH_3)$, $CH(CH_3)C$-$(CH_3)_2$, and $C(CH_3)_2C(CH_3)_2$] in addition to four functional groups (CH_3, CH_2, CH, C). Predictably, a group-based model such as JR and an atom-based model such as WJ cannot produce results as accurate as those of the CG method for the branched hydrocarbons.

Tables 7 and 8 indicate that for compounds without halogens CG is able to yield more accurate values compared with those of JR, or similar results to those of WJ, while CG is somewhat not adequate for handling halogen-containing compounds. Table 8 also shows that CG is basically consistent with the other models when the halogen number is 1 or 2, but its deviations become much larger when there are multiple halogen atoms in a com-

pound. A further analysis of halogen compounds was summarized in Table 9 concerning deviation ranges and compound distributions. It can be seen from Table 9 that, on one hand, for CG there are 21 compounds with deviations less than or equal to 2 K, which means that CG can calculate T_c with smaller deviations for a larger group of compounds than those of the other three models in using estimated NBP. On the other hand, under CG there are 36 compounds with deviations greater than 30 K, which is much worse than those of WJ and MP.

Simplicity is a feature unique to the WJ model, which needs only 10 atomic parameters and 11 groups' parameters for organic compounds. Compared with the other three models, WJ yielded surprisingly good results in T_c calculations. Another favorable feature is that when the selected NBP data are used, this model produced fewer very large deviations than those of other methods, as shown in Tables 3 and 4. This implies that WJ has a smaller tendency to produce absurd values if reliable NBP data are available. More importantly, WJ is able to deliver the best predictive T_c values, illustrated in Table 4.

The employment of a few well-processed parameters may be a key factor to the above striking features of the WJ model. This methodology allows the parameters to be generated on the basis of a very representative data set with a variety of different chemical structures, which guarantees that the parameters are applicable to many different compounds. In multiple-group models, each parameter might be processed from just one or two compounds due to lack of experimental data. In such cases, the models can provide, as expected, excellent results for the compounds that participated in parameter fittings, but, otherwise, may produce large deviations for compounds not included.

Despite the WJ method's advantages in reliability, generality, and simplicity, it is limited in predicting T_c values with high accuracy. Lack of parameters describing the characteristics of chemical structure might be an understandable reason for the performance of WJ. Consequently, all compounds covered by WJ have the same group-contribution value if their atom types and numbers are the same, and their differences in T_c values depend completely on their NBP values. A good example was WJ's application to isomers, as illustrated in the Supporting Information and Table 10. Generally, WJ produced fewer good data as well as fewer bad data compared to the cases of the other models, illustrated in Tables 3 and 4. Most deviations obtained from WJ were moderate.

MP scores the highest among the four models in terms of the reliability in calculating T_c and NBP data. But results from Table 4 regarding predictive ability show that the MP method demonstrates no advantage over the WJ method. This behavior may reveal a reliability problem of the MP parameters that were processed from scant experimental data. On the basis of our estimation, the generation of 167 MP group parameters may only involve around 400 compounds, for which there were experimental data. For example, in the MP model, certain groups, such as CH_2-CH_2 and CH_2-CH_3, could be processed respectively on the basis of as many as 200 to 300 compounds. On the other hand, many groups, such as C-$COOH$ and C-CH=, might be processed on the basis of only one or two compounds.

This study indicates, similarly as previous works did, that the quality of NBP data has a significant impact on the quality of calculated T_c. This factor should be carefully considered if estimated NBP values have to be used for predicting T_c. Generally, the NBP data calculated by MP

are more reliable than those of JR and CG. If the NBP data estimated by MP are used to calculate T_c, the average deviations for 478 compounds are 10.7 K (JR), 11.5 K (WJ), and 9.4 K (MP), compared with the deviations of T_c obtained with selected NBP (6.9 K, JR; 5.9 K, WJ; 5.2 K, MP), and the increases in deviation are 3.8 K (55%), 5.9 K (95%), and 3.6 K (62%) for JR, WJ and MP, respectively. It is interesting to note that three models used the same estimated NBP data, but their increases in deviation are quite different. This may suggest that WJ is more sensitive to (or dependent on) the quality of NBP.

Conclusion

On the basis of our selected T_c data set of 510 compounds, an investigation was made of analyzing the abilities in calculating and predicting critical temperature (T_c) of the JR, WJ, CG, and MP models with the published parameters. This examination concludes as follows: (1) The JR method generates reasonably good T_c values when employing reliable NBP data, yet it produces much larger deviations when self-given NBP data are used. (2) The CG model is the favorable choice in dealing with alkanes and alkenes; however, it tends to produce large deviations for compounds containing multiple halogen atoms. (3) The WJ model displays three strong points. It is simple, reliable, and applicable to all the organic (as well as inorganic) compounds. (4) The MP model shows an overall strength in T_c calculations in this examination. However, with 167 groups the MP model displays a predictive ability for T_c values of new structures no better than that of the WJ method.

Acknowledgment

Supporting Information Available:

The selected T_c (K) and NBP (K) values and calculated values (K) by JR, WJ, and MP on the basis of the selected NBP for the 448 compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Wilhoit, R. C.; Marsh, K. N. Automation of Numerical Data Compilations. *J. Chem. Inf. Comput. Sci.* **1989**, *29*, 17−22.

(2) Frenkel, M.; Dong, Q.; Wilhoit, R. C.; Hall, K. R. TRC SOURCE Database: A Unique Tool for Automatic Production of Data Compilations. *Int. J. Thermophys.* **2001**, *22*, 215−226.

(3) Kijevcanin, M. Lj.; Grozdanic, D. K. A Critical Review of Relations for Predicting the Critical Temperature of Organic Compounds. *Hem. Ind.* **1997**, *51*, 1−12, in Serbian.

(4) Somayajulu, G. R. Estimation Procedures for Critical Constants. *J. Chem. Eng. Data* **1989**, *34*, 106−120.

(5) Marrero-Morejon, J.; Pardillo-Fontdevila, E. Estimation of Pure Compound Properties Using Group-Interaction Contributions. *AIChE J.* **1999**, *45*, 615−621.

(6) Dong, Q.; Yan, X.; Wilhoit, R. C.; Hong, X.; Chirico, R. D.; Diky, V. V.; Frenkel, M. Data Quality Assurance for Thermophysical Property Databases−Applications to the TRC SOURCE Data System. *J. Chem. Inf. Comput. Sci.* **2002**, *42*, 473−480.

(7) Lydersen, A. L. Estimation of Critical Properties of Organic Compounds. Coll. Eng. University Wisconsin; *Engineering Experimental Station Report 3*; Madison, WI, 1955.

(8) Ambrose, D. Correlation and Estimation of Vapor-Liquid Critical Properties: I. Critical Temperatures of Organic Compounds. *NPL Rep. Chem. 92*; Nat. Physical Lab.: Teddington, U.K., 1978.

(9) Ambrose, D. Correlation and Estimation of Vapor-Liquid Critical Properties: II. Critical Pressures and Critical Volume. *NPL Rep. Chem. 107*; Nat. Physical Lab.: Teddington, U.K., 1980.

(10) Joback, K. J. A Unified Approach to Physical Property Estimation Using Multivariate Statistical Techniques. M.S. Thesis, Chem. Eng., Massachusetts Institute of Technology, Cambridge, MA, 1984.

(11) Joback, K. G.; Reid, R. C. Estimation of Pure-Component Properties from Group-Contributions. *Chem. Eng. Commun.* **1987**, *57*, 233−243.

(12) Constantinou, L.; Gani, R. New Group-Contribution Method for Estimating Properties of Pure Compounds. *AIChE J.* **1994**, *40*, 1697−1710.

(13) Wilson, G. M.; Jasperson, L. V. Critical Constants T_c, P$_c$, Estimation Based on Zero, First, Second-Order Methods. AIChE Meeting, New Orleans, LA, 1996.

(14) Marrero, L.; Gani, R. *Fluid Phase Equilib.* **2001**, *183− 184*, 183−208.

(15) Poling, B. E.; Prausnitz, J. M.; O'Connell, J. P. *The properties of Gases and Liquids*, 5th ed.; McGraw-Hill: New York, 2001.

(16) Ambrose, D.; Young, C. L.; Tsonopoulos, C.; Gude, M.; Teja, A. S.; Daubert, T. E.; Kudchadker, A. P. A series of contributions by the critical properties group of the IUPAC Commission I.2 on Thermodynamics, Subcommittee on Thermodynamic Data, Reviews 1−8, in *J. Chem. Eng. Data*. Review 1, **1995**, *40*, 345−357; Review 2, **1995**, *40*, 531−546; Review 3, **1995**, *40*, 547−558; Review 4, **1995**, *40*, 1025−1036; Review 5, **1996**, *41*, 365−372; Review 6, **1996**, *41*, 645−656; Review 7, **2001**, *46*, 457−479; Review 8, **2001**, *46*, 480−485.

(17) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The properties of Gases and Liquids*, 4th ed.; McGraw-Hill: New York, 1987.

(18) King, R. B. *Chemical Applications of Topology and Graph Theory*; Elsevier Science Publishing Company Inc.: Amsterdam, 1983.